Study and prediction of the mechanical performance of a nanotube-reinforced composite

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\begin{abstract}
Carbon nanotubes (CNTs) have been regarded as ideal reinforcements for high-performance composites. A key factor for the reinforcement efficiency is the interface bonding between the CNTs and the matrix. This paper presents a new constitutive model to predict the mechanical performance of composites made with CNTs. The model takes into account explicitly the performance of the interface between the matrix and the CNTs. The formulation developed is based in the mixing theory. It divides the composite in matrix and reinforcement elements. On the other hand, the main task of the reinforcement is to improve the matrix properties.

In case of considering an iso-strain hypothesis, the properties of the composite depend on the properties of its constituents. In case of interface damage, it also becomes non-linear the law defined to couple the interface with the CNTs. After describing the formulation, it is validated studying the elastic response of several composites made with different types of CNTs reinforcements. The non-linear behavior provided by the formulation is also studied. In both cases the numerical results are compared with experimental data showing good agreement.
\end{abstract}

\section{1. Introduction}

Composites are materials made of at least two different components. Most composites consist in a matrix containing reinforcement elements [1]. The main function of matrix is to give cohesion, support the reinforcement and transfer the external actions to the reinforcements. On the other hand, the main task of the reinforcement is to improve the matrix properties.

In case of using fibers or nanotubes as reinforcement, the performance of the composite depends on the achievement of four main characteristics:

- **Aspect ratio of the fibers**: The fiber aspect ratio is a dimensionless geometric measurement that results from dividing the length of the reinforcement by its diameter. This parameter is important because the stress distribution in the reinforcement depends on it [2]. In fibers with high aspect ratios the fiber end effect is less important. The reinforcement is considered to behave as a long fiber when its aspect ratio is larger than 1000.

- **Dispersion of fibers in the composite**: A uniform distribution of reinforcement in the composite is fundamental to ensure that it is completely surrounded by matrix. This is necessary to obtain an effective stress transfer. A good dispersion of the reinforcement in the composite also helps to have a more uniform stress distribution in it, reducing the regions susceptible having stress concentrations.

- **Fiber alignment**: It has been shown that the difference between random distribution and perfect alignment may represent a factor of five in the composite Young’s modulus [3]. Fiber alignment also affects the isotropy of the composite, as perfect alignments increase its anisotropy.

- **Load transmission from the matrix to the fiber**: The last and probably most important factor is the interfacial tension between matrix and reinforcement. In general, the loads in a composite structure are introduced through the matrix and are transferred to the reinforcement through the interface [2]. Therefore, the interface can be defined as the region surrounding the reinforcement where this stress transfer takes place. The properties of the composite depend on the properties of this region, and on its ability to transfer the load efficiently.

The external load applied to a composite is shared disproportionately by the different components, as their elastic properties are different. In case of considering an iso-strain hypothesis [4]...
the stresses on the reinforcement will be larger than in the matrix, as the reinforcement is stiffer than the matrix. This unequal stress distribution generates shear stresses between both materials in a region that can be usually called the interface. The load transfer from the matrix to the reinforcement is produced in this region. Shear stresses in the interface increase proportionally to the external load until a critical value, beyond which the interface breaks. This critical value is known as interfacial shear strength (IFSS) and it limits the stress transfer capacity.

Since their discovery by Iijima in 1991 [5], carbon nanotubes (CNTs) are considered a new generation of reinforcements [6]. Their “nano” size structure makes them potentially free of defects, which gives them with excellent physical properties [7,8]. A nanotube is a tubular cylinder formed by sp2 bonds between the carbon atoms along its length. There are two main nanotube types: single wall nanotubes (SWCNT), which are made of a single wall tube with an outer diameter in the order of 1 nm; and multiwall nanotubes (MWCNT), which consist in several concentric walls, one inside the other, separated by a distance of 0.34 nm [5]. The diameters range of MWCNT varies from 2 to 100 nm. MWCNT can have lengths up to 100 μm.

Carbon nanotubes can be obtained by several procedures. The first method used was the arc-discharge [9], which consists in generating an arc discharge between two graphite electrodes in an inert gas atmosphere at low pressure. The continuous electric discharge sublimates the carbon atoms of the electrodes and forms a plasma around them. This method produces free defect nanotubes along their length. The length of these nanotubes can reach 50 μm. Another procedure is the laser ablation. This consists in vaporizing the graphite by radiation with a laser pulse, in an inert gas atmosphere, inside a high temperature reactor. The nanotubes are formed when the graphite vapor touches the cold walls of the reactor. Finally, the most common procedure used for commercial production of carbon nanotubes is the deposition of Catalytic Vapor Phase (also named, Chemical Vapor Deposition – CVD). This procedure allows producing large amounts of nanotubes at a low cost. This method produces nanotubes with defects on its surface. This method can provide oriented nanotubes if there is plasma during their growth. Nanotubes obtained by arc-discharge have Young modulus values in the order of 1 TPA, and ultimate tensile stresses of 3.6 GPa. Later on, new procedures made by Cadeck et al. [14,15] using the arc-discharge process has to be selected taking into account that it must not affect the properties of the composite components.

Several studies have shown that the composite formation generates an interface zone around the carbon nanotubes. This interface has a different morphology and properties than the original matrix [14,15]. The size, shape and properties of the interface have a strong dependence on the matrix type [16] and the formation process. Pull out experimental tests indicate that the IFSS values are much higher than the theoretical ones [17], which are calculated using the shear strength of the matrix. This result suggests that the interface region around the nanotube has better properties than the rest of the matrix [18]. Some studies estimate that in this region matrix properties may improve by an order of magnitude [19]. In fracture surfaces obtained from composites with strong nanotube/matrix bonds, the interface thickness can be several times larger than the nanotube diameter [20–22]. In the case of semi-crystalline matrices, the interface zone is associated with crystal nucleation around the nanotube [22]. All manufacture procedures seek to obtain a composite with a strong bond between the nanotube and the matrix, in order to transfer effectively the loads. The IFSS defines the capacity of the bond. Values of 500 MPa have been obtained for the IFSS when obtained using a Transmission Electron Microscope (TEM). The study attributes this value to the presence of covalent bonds between the matrix and the nanotube [23]. Molecular Dynamics (MDs) simulations carried out confirm that strong bonds are obtained when these are covalent. In fact, the transfer load of the interface increases by an order of magnitude with just a 1% of covalent bonds in its surface [24]. On the other hand, the generation of many covalent bonds in the interface is detrimental to the intrinsic properties of the nanotube [24,25].

When there are no covalent bonds, the interaction between matrix and nanotube is made with Van der Waals forces. Several studies show that this union is weaker. Molecular Dynamics simulations made by [24] predicted values of the IFSS that do not exceed 2.8 MPa. Another study made by [26] predicted values up to 160 MPa. According to [27], the differences in the results depend on the polymer type and they can be in the range of 80–135 Mpa. The difference in the results, and the good values of IFSS, were attributed to the morphology and the capacity of the matrix to generate helical chains around the nanotube. On the other hand, nanotubes have a smoother outer surface and therefore, the contribution of the frictional forces to the IFSS are an order of magnitude lower [28].

Experimental results of pull-out tests show values of IFSS between 20 and 90 MPa [19,28]. Other experiments using the drag-out technique have shown values between 35 and 376 MPa [18]. The disparity of the results suggests that is not always possible to generate covalent bonds. The maximum values obtained experimentally are associated to covalent bonds and consider that the interface zone has better properties than the rest of the matrix.
Carbon nanotubes, mainly SWCNTs, tend to agglomerate. This makes it very difficult to obtain a good dispersion of those in the polymer. Besides, the smooth surface of the nanotubes leads to a possible lack of bond between the nanotube and the matrix. Currently these problems are solved with a chemical functionalization of the CNTs. The covalent functionalization can be done by modifying the carboxylic acid groups on the nanotube surface and or by direct addition of reagents. The drawback of functionalizing the nanotubes is that there is an intrinsic degradation of their properties [25]. In general, two different methods have been used for the functionalization: “grafting from” and “grafting to”.

The “grafting from” method is based on the initial immobilization of initiators on the nanotube surface, followed by an in situ polymerization of the suitable matrix for the formation of polymer molecules around the nanotube [29,30]. The advantage of this method is that it allows the formation of composites with a high density of nanotubes. The disadvantage is that this method requires strict control of the quantities and the conditions in which the polymerization reaction takes place.

The “grafting to” method makes the union of preformed polymer molecules to functional groups on the surface of the nanotube through chemical reactions [31,32]. The advantage of this method is that it can be used with commercial polymers. However, it has as a limitation that the initial union of the polymer chains inhibits the diffusion of macromolecules to the surface. Therefore, the density of functionalization is low.

The above description shows that the final properties of the composite depend on many parameters. Together with them, there are others aspects that may also condition the final properties of the composite, such as the ondulation and misalignment of the nanotubes inside the matrix. All this variability can be considered the responsibility of not having yet an accepted theory capable of describing correctly the performance of nanotube-reinforced composites. It is also the reason for the existing theories fail in their predictions. Comparisons between measured mechanical properties of nanotube-reinforced composites and those of the components are generally three times higher than measured results [21,33].

This paper proposes a new formulation to predict the mechanical properties of nanotube-reinforced composites. The formulation is based in the mixing theory, and it obtains the properties of the composite from the mechanical performance of its constitutive materials: matrix, carbon nanotubes and the interface that bonds both of them. This new formulation is capable of predicting the response of the composite fairly accurately, requiring only the calibration of the mechanical properties of the interface.

In the following is described the constitutive model developed. Afterwards, Section 3 formulates the model and Section 4 describes its performance in the non-linear range. The implementation of the proposed formulation into a finite element code is described in Section 5. The validation of the model is shown in Section 6, where the results provided by the model are compared with experimental ones. Finally in last section some conclusions are drawn from the results obtained.

2. Description of constitutive model

The constitutive model presented in the following section is based in the classical mixing theory. This theory obtains the mechanical performance of the composite from the behavior of the composite constituents, each one simulated with its own constitutive law [34]. As it is written, the theory can be understood as a constitutive equation manager. The new constitutive model is formulated with the same philosophy, which increases its versatility and simulation capability.

The model assumes that the composite is the combination of three different materials: matrix, CNTs and an interface [35]. The interface corresponds to the matrix that surrounds the CNTs. It is considered as an independent component, with its own constitutive law. The interface is used to define the capacity of the matrix to transfer the loads to the reinforcement.

Although the phenomenological performance of the composite already justifies the definition of an interface material; images obtained with Scanning Electron Microscope (SEM) of CNTs reinforced composites, such the ones shown in Fig. 1, prove its actual existence. These images reveal that the structures protruding from the fractured surface have larger diameters than the original MWCNTs used in the sample preparation [20]. The material surrounding the CNTs corresponds to the interface. The presence of an interface, as a differentiable material, is also proved by Differential Scanning Calorimetry (DSC) measurements carried out in composites with a semi-crystalline polymer as matrix. These measurements show a linear increase of crystalline matrix as the nanotube volume fraction increases, suggesting that each nanotube has a crystalline coating [36].

Once having conveyed the necessity of including the interface material in a formulation to simulate the mechanical performance of CNTs reinforced composites, in the following is described the new procedure proposed, which is summarized in Fig. 2. This figure shows that the composite is divided in several layers, each one containing carbon nanotubes with a different orientation. Layers are coupled together using the parallel mixing theory, that is, assuming that all layers have the same deformation. The new formulation developed provides the mechanical performance of each layer by combining the response of the three coexisting materials: matrix, interface and CNTs. The layer response depends on the materials and on their volumetric participation in the composite. First, the composite is split into matrix and a new material that results of coupling the CNTs with the interface. The relation between the stress of the composite and the stress of the materials is then defined in terms of the parallel mixing theory (they are assumed to have an iso-strain behavior). On the other hand, CNTs and the interface are coupled together with a combination of parallel and serial mixing theories. The serial mixing theory assumes that all components have the same stresses.

Fig. 3 shows scheme used to obtain the performance of the CNT-interfacel material. This is based in the short-fiber model developed by Jayatilaka [2]. According to this model, the load is transferred from the interface to the nanotube at the ends of the reinforcement, through shear stresses. In this region normal stresses in the fiber increase from zero to their maximum value, which is reached in the central part of the reinforcement. In this region there is not load transfer and shear stresses are null. This whole stress transfer scheme can be simplified assuming a CNT-interface performance defined by a serial mixing theory at the ends of the reinforcement and a parallel mixing theory at the center of it.

A parallel factor named $N^i$ is defined to differentiate these two regions. This parameter, multiplied by the nanotube length, provides the length of the nanotube-interface element with a parallel behavior. The length with a serial performance is defined by the complementary factor.

3. Formulation of the constitutive model

The Helmholtz free energy [37] of a material point subjected to small deformations can be described with the following thermodynamic formulation [38,39],

$$\Psi = \Psi(\varepsilon, \theta, x)$$

(1)
where $\varepsilon$ is the deformation tensor, $\theta$ a measure of temperature and $\alpha = \{\varepsilon, d, s\}$ a set of inner variables, for example: $\varepsilon$ is the plastic deformation, $d$ damage inner variable and $s$ any other material internal variables.

The model proposed to simulate the composite combines the different components using the serial and parallel mixing theories. If this combination is performed according to what has been described in previous section, the expression of the Helmholtz free energy may be written as:

$$\Psi = k_m \Psi_m + (k_{nt} + k_{iz})$$

where $\Psi_m$, $\Psi_{nt}$, and $\Psi_{iz}$ are the specific Helmholtz free energy for the matrix, the nanotube and the interface components, respectively; $k_m$, $k_{nt}$, and $k_{iz}$ are the volume fraction of each component; $N_{par}$ is the parallel factor and,

$$k_m = \frac{k_{nt}}{k_{nt} + k_{iz}}, \quad k_{nt} = \frac{k_{iz}}{k_{nt} + k_{iz}},$$

are the volume fractions of the carbon nanotubes and the interface in the new CNT-interface material. These volume fractions must verify:

$$k_m + k_{nt} + k_{iz} = 1 \quad k_{nt} + k_{iz} = 1$$

The relation among the strain tensors of the different components is:

$$\varepsilon = \varepsilon_m = \varepsilon_{nt} = \varepsilon_{iz}$$

being $\varepsilon$ and $\varepsilon_m$ the composite and matrix deformations, respectively; $\varepsilon_{nt}$ the deformation the new CNT-interface material with a parallel behavior; and $\varepsilon_{iz}$ the deformation of the CNT-interface material with a serial behavior.

The tangent constitutive tensor of the composite material may be derived from Eq. (2),

$$C = \frac{\partial^2 \Psi}{\partial \varepsilon \otimes \partial \varepsilon} = k_m \frac{\partial^2 \Psi_m}{\partial \varepsilon_m \otimes \partial \varepsilon_m} + \frac{\partial^2 \Psi_{nt}}{\partial \varepsilon_{nt} \otimes \partial \varepsilon_{nt}} + \frac{\partial^2 \Psi_{iz}}{\partial \varepsilon_{iz} \otimes \partial \varepsilon_{iz}}$$

A parallel behavior means that all composite constituents have the same strain value. Therefore:

$$\varepsilon_{nt} = \varepsilon_{iz} = \varepsilon \Rightarrow \frac{\partial^2 \Psi_{nt}}{\partial \varepsilon_{nt} \otimes \partial \varepsilon_{nt}} = N_{par} [k_m C_m + k_{nt} C_{nt}]$$

$$= N_{par} C_{nt}$$

and a serial behavior means that all composite constituents have the same stress value. Thus:
\[ \sigma_{\text{mix}} = \sigma_e = \sigma_{\text{int}} \Rightarrow \varepsilon_{\text{int}} = C^{-1}_1 : \varepsilon_{\text{mix}} : \varepsilon_{\text{mix}} \]

\[
\frac{\partial^2 \phi_{\text{mix}}}{\partial \varepsilon_{\text{mix}}^2} = (1 - N\rho^{\text{par}}) \left[ k_{\text{mix}} \varepsilon_{\text{int}}^{-1} + k_{\text{mix}} \varepsilon_{\text{int}} \right]^{-1} = (1 - N\rho^{\text{par}}) \frac{\partial \phi_{\text{mix}}}{\partial \varepsilon_{\text{mix}}}
\]

Replacing Eqs. (7) and (9) in Eq. (6) it is possible to obtain a simplified expression of the tangent constitutive tensor:

\[ C = k_{\text{int}} C_{\text{am}} + (k_{\text{nt}} + k_{\text{ds}}) [N\rho^{\text{par}} C_{\text{ntiz}}^{\text{par}} + (1 - N\rho^{\text{par}}) C_{\text{ntiz}}] \]

3.1. Definition of the parallel factor

The parallel factor is defined as,

\[ N^{\text{par}} = \frac{l_{\text{par}}}{l_{\text{nt}}} \quad 0 \leq N^{\text{par}} \leq 1 \]

where \( l_{\text{nt}} \) is the length of the nanotube and \( l_{\text{par}} \) is function of geometry and mechanical properties of the nanotube and the interface. The value of this length can be obtained from the equation of tension distribution in a reinforcement considering perfect bond with the matrix, which is [2]:

\[ \sigma_{\text{nt}}(x) = \frac{1}{2G_e} \left[ \frac{1}{\cosh[^{\quad}]} \right] E_{\text{ntiz}} \]

\[ \beta = \frac{1}{E_{\text{ntiz}}} \left[ \frac{1}{\left( \cosh[^{\quad}]} \right] E_{\text{nt}} \right] \]

where \( x \) represents the longitudinal positions in the reinforcement, and the subscripts “nt” and “ntiz” refers to the properties of nanotube and interface zone, respectively. \( E \) and \( G \) are the Young’s modulus and the shear modulus, and \( b \) is the thickness material around of the CNTs associated with the interface zone.

Defining \( l_{\text{par}} = l_{\text{nt}} - 2x \), its value can be obtained by finding the position “x” for which the effective modulus obtained from the integration of the tension distribution becomes:

\[ l_{\text{par}} = \frac{1}{\beta} \cosh^{-1} \left[ \frac{1}{3} \cosh\left( \frac{2x}{l_{\text{nt}}} \right) \right] \]

3.2. Definition of the volume fraction of the interface region

Based on the results reported in [36], the interface zone can be considered the region surrounding the carbon nanotube in which an amorphous matrix becomes crystalline. The volume fraction of the interface zone can be obtained as:

\[ \chi_e = \chi_o + k_{\text{int}} \]

where \( \chi_o, \chi_e \) are the volume fractions of crystalline matrix with and without CNTs, respectively. Assuming that the interface zone is a cylinder around the CNTs, it is possible to relate the volume fraction of the interface zone with the parameter \( k_{\text{int}} \) as:

\[ k_{\text{int}} = \frac{N(\pi r^2 l_{\text{int}} - \pi r^2 l_{\text{m}})}{V} = \frac{N\pi r^2 l_{\text{int}}}{V} \left[ \left( \frac{R}{R_{\text{nt}}} \right)^2 - 1 \right] \]

where \( V \) is the total composite volume, \( r \) is the radius of interface zone and \( N \) is the total number of nanotubes in the composite.

The relation between the radius of the nanotube and the interface is obtained replacing Eq. (16) in Eq. (15):

\[ \frac{r}{R_{\text{nt}}} = \left( \frac{\chi_o}{\chi_o + \chi_{\text{miz}}} \right) + 1 \]

3.3. Constitutive model for a single material

The formulation developed require all composite components to fulfill Eq. (1). Therefore, it is possible to use any constitutive law to describe the mechanical performance of the different components. However, for the sake of simplicity, in the following are defined the three specific models that will be used for each composite component.

3.3.1. Constitutive model for matrix material

Matrix material is defined with an elastoplastic law. The specific Helmholtz free energy for this material, considering uncoupled elasticity is:

\[ \Psi(e^p, p, \theta) = \Psi^e(e^p) + \Psi^p(p) + \Psi^\theta(\theta) = \frac{1}{2} e^p : C + \Psi^p(p) + \Psi^\theta(\theta) \]

where \( \Psi^e \) is the specific elastic free energy, \( \Psi^p \) is the specific plastic free energy, \( \Psi^\theta \) is the specific temperature free energy, \( p \) is an internal variable tensor associated with plastic behavior. The total deformation of the material tensor is split into its elastic, \( e^p \) and plastic, \( \theta \) parts. This is:

\[ e = e^p + \theta \]

The local form of the Clausius–Duhem inequality for this material can be expressed as:

\[\sigma : (\dot{e}^p + \dot{\theta}) - \eta \dot{\theta} = \frac{1}{2} \eta \frac{\partial \Psi^\theta}{\partial \dot{\theta}} + \left( \frac{\partial \Psi^p}{\partial \dot{\theta}} - \frac{\partial \Psi^\theta}{\partial \dot{\theta}} \right) - \frac{1}{2} \eta \frac{\partial \Psi^p}{\partial \dot{\theta}} \geq 0 \]

\[\left( \sigma - \frac{\partial \Psi^p}{\partial \dot{\theta}} \right) : (\dot{e}^p + \dot{\theta}) + \sigma : (\dot{e}^p - \frac{\partial \Psi^p}{\partial \dot{\theta}}) \dot{p} - \frac{1}{2} q : \frac{\partial \Psi^p}{\partial \dot{\theta}} \geq 0 \]

being \( \sigma \) the stress tensor, \( \eta \) the entropy, and \( q \) the vector field of heat flow. To ensure compliance with the second thermodynamic law it must be defined,

\[\sigma = \frac{\partial \Psi^p}{\partial \dot{\theta}} \quad \eta = -\frac{\partial \Psi^\theta}{\partial \dot{\theta}} \quad p = -\frac{\partial \Psi^\theta}{\partial \dot{\theta}} \]

where \( P \) is the thermodynamic tensor associated with the internal variable tensor \( \theta \). Finally, the mechanical dissipation for a material point is,

\[\Xi_m = \Xi_p = \sigma : \dot{e}^p + P \cdot \dot{p} \geq 0 \]

3.3.2. Constitutive model for interface material

The interface region is simulated with a damage material. In this case, the expression of the Helmholtz free energy is:

\[\Psi(e, d, \theta) = \Psi^e(e, d) + \Psi^\theta(\theta) = (1 - d) \Psi^e(e) + \Psi^\theta(\theta)\]

\[= (1 - d) \frac{1}{2} e^p : C + \Psi^\theta(\theta)\]

where \( d \) is an internal variable associated with the damage. The local form of the Clausius–Duhem inequality Eq. (21) for this material can be expressed as,
\[
\sigma: \dot{\varepsilon} - \eta \dot{\varepsilon} - \left[ \frac{\partial \Psi}{\partial \varepsilon} : \dot{\varepsilon} + \frac{\partial \Psi}{\partial \dot{\varepsilon}} \dot{\varepsilon} + \frac{\partial \Psi}{\partial \theta} \dot{\theta} \right] \frac{1}{2} \mu \left( \frac{\partial \varepsilon}{\partial \varepsilon} + \frac{\partial \dot{\varepsilon}}{\partial \dot{\varepsilon}} + \frac{\partial \theta}{\partial \theta} \right) \geq 0 \quad (27)
\]

\[
\left( \sigma - \frac{\partial \Psi}{\partial \varepsilon} : \dot{\varepsilon} - \left( \eta + \frac{\partial \Psi}{\partial \dot{\varepsilon}} \right) \dot{\varepsilon} - \frac{1}{2} \mu \frac{\partial \varepsilon}{\partial \varepsilon} \geq 0 \quad (28)
\]

To ensure compliance with the second thermodynamic law it must be defined:
\[
\sigma=\frac{\partial \Psi}{\partial \varepsilon}, \eta=\frac{\partial \Psi}{\partial \dot{\varepsilon}} D=\frac{\partial \Psi}{\partial \theta} (29)
\]

being D the thermodynamic scalar associated with the internal scalar variable d. And, the mechanical dissipation for a material point is:
\[
\xi_m = \xi_d = D \cdot \dot{d} \geq 0 \quad (30)
\]

3.3.3. Constitutive model for nanotubes

Nanotubes are considered elastic. In this case the Helmholz free energy can be written as,
\[
\Psi(\varepsilon, \theta) = \Psi_0(\varepsilon) + \Psi_1(\theta) = \frac{1}{2} \varepsilon : C : \varepsilon + \Psi_1(\theta) (31)
\]

and the local form of the Clausius–Duhem inequality Eq. (21) can be expressed in this case as,
\[
\sigma: \dot{\varepsilon} - \eta \dot{\varepsilon} - \left( \frac{\partial \Psi}{\partial \varepsilon} : \dot{\varepsilon} + \frac{\partial \Psi}{\partial \dot{\varepsilon}} \dot{\varepsilon} + \frac{\partial \Psi}{\partial \theta} \dot{\theta} \right) \frac{1}{2} \mu \left( \frac{\partial \varepsilon}{\partial \varepsilon} + \frac{\partial \dot{\varepsilon}}{\partial \dot{\varepsilon}} + \frac{\partial \theta}{\partial \theta} \right) \geq 0 \quad (32)
\]

\[
\left( \sigma - \frac{\partial \Psi}{\partial \varepsilon} : \dot{\varepsilon} - \left( \eta + \frac{\partial \Psi}{\partial \dot{\varepsilon}} \right) \dot{\varepsilon} - \frac{1}{2} \mu \frac{\partial \varepsilon}{\partial \varepsilon} \geq 0 \quad (33)
\]

To ensure compliance with the second thermodynamic law,
\[
\sigma=\frac{\partial \Psi}{\partial \varepsilon}, \eta=\frac{\partial \Psi}{\partial \dot{\varepsilon}} D=\frac{\partial \Psi}{\partial \theta} (34)
\]

3.3.4. Equivalent properties for MWCNTs

MWCNTs consist of concentric SWCNTs joined together with relatively weak van der Waals forces. For this reason, the capacity to transfer the load from the external wall to the internal walls is low. Some papers [40,41] propose to simulate the CNTs like a solid cylinder with same exterior diameter and length, but with effective properties. The effective properties are obtained assuming that the outer wall takes the total load. In this approach it is assumed that the properties of the outer wall correspond to those of a graphite sheet. The effective stiffness of the MWCNT is calculated by imposing that for a same applied force, the deformation must be the same:
\[
\tilde{E}_{nt} = \tilde{E}_{nt} \Rightarrow E_{nt} = \frac{A_{ow}}{A_{nt}} E_g \quad (35)
\]

where \(E_g\) and \(E_n\) are the Young’s modulus of the effective solid nanotube and graphite sheet, respectively, and \(A_{nt}\) and \(A_{ow}\) are the areas of the effective solid nanotube and outer wall, respectively. Eq. (35) can also be read as,
\[
E_{nt} = \left[ 1 - \left( 1 - \frac{2t}{d_{nt}} \right)^2 \right] E_g, \quad \frac{L}{d_{nt}} \leq 0.5 \quad (36)
\]

being t the thickness of one wall in the MWCNT and \(d_{nt}\) is the external diameter of the MWCNT.

Using the same procedure it is possible to obtain the shear modulus of the solid cylinder, by forcing the same twist when applying the same torque (T):
\[
\tilde{G}_{nt} = \tilde{G}_{nt} \Rightarrow G_{nt} = \frac{G_{ow}}{G_{nt}} G_g \quad (37)
\]

where \(G_{nt}\) and \(G_g\) are the shear modulus of the effective solid CNTs and graphite sheet, respectively, and \(J_{nt}\) and \(J_{ow}\) are the polar moment of inertia of the effective solid CNTs and outer wall, respectively.
\[
J_{nt} = \frac{\pi d_{nt}^4}{32}, \quad J_{ow} = \frac{\pi \left( d_{nt}^4 - (d_{nt} - 2t)^4 \right)}{32} \quad (38)
\]

Replacing the expressions of Eq. (38) in Eq. (37), the equivalent shear modulus can be written as,
\[
\tilde{G}_{nt} = \left[ 1 - \left( 1 - \frac{2t}{d_{nt}} \right)^4 \right] G_g \quad (39)
\]

Finally, it is necessary to obtain the new density of the effective solid CNTs, as the total weight of the MWCNTs cannot change in the composite when they are considered a solid cylinder.
\[
\rho_{nt} = \frac{A_{nt}}{A_{nt}} \rho_g \Rightarrow \rho_{nt} = \left[ 1 - \left( \frac{d_{nt}}{d_{nt}} \right)^2 \right] \rho_g \quad (40)
\]

being \(\rho_g\) the density of the graphite sheet (\(\rho_g = 2.25 \text{[g cm}^{-3}\text{]}\)) and \(d_{nt}\) the internal diameter of the MWCNTs.

The most common parameter used to define the amount of CNTs added to a composite is their weight fraction. However, the numerical model developed requires knowing the volume fraction. The volume fraction of CNTs in the composite is the volume that occupies a solid cylinder with the same external diameter. This parameter can be calculated with the following expression [40]
\[
\rho_{nt} = \frac{w_{nt} \rho_{nt}}{1 + \rho_{nt} \rho_{nt}} \rho_{nt} \quad (41)
\]

where \(w_{nt}\) is the weight fraction and \(\rho_{nt}\) is the density of the matrix.

4. Material non-linearity of the proposed model

In the proposed model, the composite performance is obtained from the mechanical response of its constituent materials, and each constituent is simulated with its own constitutive law. Therefore, if a constituent (i.e. the interface) is simulated with a non-linear law, the whole composite will become non-linear. As it has been already explained, with the present model it is possible to use any non-linear formulation to simulate the constituents, such as plasticity, damage, and viscosity.

Besides the non-linear performance provided by each constituent, the load transfer capacity of the interface region is also affected if the interface is damaged. This effect must be included in the formulation.

According to Fig. 3, the load is transferred from the interface to the CNTs reinforcements at their ends. Interface damage is expected to occur at the ends of the reinforcement, where there is larger stress concentrations. Assuming that the damaged region is unable to transfer loads and that the length required to transfer loads must remain constant, interface damage ends up affecting the parallel length of the nanotube, which can be calculated as:
\[
l_{par} = \ell_{par}(1 - d) \quad (42)
\]

where \(\ell_{par}\) is the initial length of the nanotube working in parallel and \(d\) is the interface damage.

The dependence of the parallel length on the interface material damage provides a non-linear response of the composite, even when matrix and the carbon nanotube reinforcement are in their linear range.
5. Numerical implementation

The proposed model has been implemented in PLCd [42], a finite element code that works with 3D solid geometries. The algorithm developed is described in Fig. 4. PLCd has already implemented the constitutive laws that will be used to predict the performance of the composite components (elasto-plastic, elasto-damage, and elastic). The formulation proposed has been written so that the constitutive laws of the constituents are seen as "black boxes", following the recommendations of [43,44].

The FEM code enters into the new formulation with the prediction of the strain of the composite material in the actual time step. Layers are assumed to have all the same strain; therefore the strain tensor of each layer is obtained rotating the composite strain to the direction in which the CNTs are oriented. In each layer, the strain of the matrix and the CNTs-interface are the same, as they work in parallel (Eq. (5)). Knowing the strains for matrix material it is possible to obtain its stresses straightforward. On the other hand, to obtain the stresses for the CNTs-interface, the constitutive laws of each one are used to calculate their stress tensor.

\[
[e]_n^{1-M} = \left[ [e]_n^{1} + \left( k_{ntiz}\Delta [e]_n^{1-M} + k_{ntiz}[e]_n^{1-M} \right) \right]_n
\]

Afterwards it is necessary to verify that the iso-stress condition is indeed fulfilled. If the residual stress is greater than the tolerance, the prediction of the interface deformation must be corrected. A Newton–Raphson scheme is adopted to do this correction. The method uses the Jacobian to update the unknown variable, in this case, the interface strain.

\[
\sigma_n^{ser} + \frac{\partial \sigma_n^{ser}}{\partial \sigma_n^{ser}} \cdot \frac{\partial \sigma_n^{ser}}{\partial \sigma_n^{ser}} \cdot \frac{\partial \sigma_n^{ser}}{\partial \sigma_n^{ser}} \cdot \frac{\partial \sigma_n^{ser}}{\partial \sigma_n^{ser}} = \left[ \frac{\partial \sigma_n^{ser}}{\partial \sigma_n^{ser}} \right]_n
\]

Finally, the strain of the interface for the next step \( n + 1 \) is estimated as,

\[
[e]_n^{1-M} = \left[ [e]_n^{1} + \left( k_{ntiz}\Delta [e]_n^{1-M} + k_{ntiz}[e]_n^{1-M} \right) \right]_n
\]

Once knowing the strains of both component materials, the constitutive law of each one is used to calculate their stress tensor. Afterwards it is necessary to verify that the iso-stress condition is indeed fulfilled.

\[
|\Delta \sigma_n^{ser}| = |\sigma_n^{ser}| - |\sigma_n^{ser}| \leq \text{tolerance}
\]

If the residual stress is greater than the tolerance, the prediction of the interface deformation must be corrected. A Newton–Raphson scheme is adopted to do this correction. The method uses the Jacobian to update the unknown variable, in this case, the interface strain.

\[
J = \frac{\sigma_n^{ser}}{\partial \sigma_n^{ser}} \cdot \frac{\partial \sigma_n^{ser}}{\partial \sigma_n^{ser}} \cdot \frac{\partial \sigma_n^{ser}}{\partial \sigma_n^{ser}} \cdot \frac{\partial \sigma_n^{ser}}{\partial \sigma_n^{ser}} = \left[ \frac{\partial \sigma_n^{ser}}{\partial \sigma_n^{ser}} \right]_n
\]

The iterative process continues until the residual stress is smaller than the required tolerance. The final stresses in the serial region (Serial Block) of the CNTs-interface are:

\[
\sigma_n^{ser} = \left[ \sigma_n^{ser}^{1-M} + \left( k_{ntiz}\Delta \sigma_n^{ser} + k_{ntiz}[\sigma_n^{ser}]^{1-M} \right) \right]_n
\]

and the final stress tensor for a specific layer is obtained as:

\[
\sigma_n^{ser}^{1-M} = \left[ \sigma_n^{ser}^{1-M} + \left( k_{ntiz}\Delta \sigma_n^{ser} + k_{ntiz}[\sigma_n^{ser}]^{1-M} \right) \right]_n
\]

6. Results

6.1. Validation of the elastic response provided by the formulation

In the following are compared the composite stiffness predicted by the proposed formulation with experimental values obtained from the literature. Coleman et al., [35,45] tested several composites made of the same matrix with different MWCNTs. The matrix material was polyvinyl alcohol (PVA) and its Young’s modulus was \( E_m = 1.9 \pm 0.3 \) (GPa).

The authors found that the Young’s modulus of the crystalline polymer phase was \( E_m = 46 \) (GPa) and the parameter \( \lambda_m^{ntz} \) was estimated following the same procedure described in Section 3.2.
The nanotubes used in [35] were arc grown MWCNT (Arc-MWCNT), two types of catalytic MWCNT from Nanocyl S.A. (CVD-1, CVD-2), a catalytic MWCNT produced in Orléans (France) (CVD-3), and a double walled nanotube (Dwnt). In [45] the nanotubes used were MWCNT from Nanocyl S.A. (MWCNT).

The maximum Young’s modulus of the CNTs is ~1 (TPa) [35], which corresponds to the stiffness of a perfect graphite sheet. This is the value used in the model validation. The equivalent stiffness of the nanotube is calculated considering a thickness of the outer layer of $t = 0.34$ (nm) [5,40].

The most important data of the nanotubes used is presented in Table 1:

A parameter missing in Table 1 is the direction distributions of the CNT. In general, obtaining this information is very complicated. To outstep this impendiment it is possible to rewrite Eq. (10) for one layer as,

$$C_{layer} = k_n C_m + k_{ntz} C_{ntz}^{eff}$$

where

$$k_{ntz} = k_n + k_{nt}$$

$$C_{ntz}^{eff} = N_{ntz}^{go} C_{ntz}^{go} + (1 - N_{ntz}^{go}) C_{ntz}^{ter}$$

Cox and Krenchel modified the rule of mixtures proposing the following equation to calculate the composite Young’s modulus,

$$E = k_n E_n + k_{nt} E_{nt}$$

where $E_n$ and $E_{nt}$ are the Young’s modulus of the matrix and effective reinforcement, respectively. The volume fraction for each component is $k$ and $\eta_o$ is a fiber orientation efficiency factor.

For the present validation Eq. (57) will be modified, adapting it to the developed formulation. Therefore,

$$C_{composite} = k_n C_m + k_{nt} C_{ntz}^{eff}$$

The value of the efficiency factor related to fiber orientation was taken from literature. In composites with a random distribution, $\eta_o = 0.38$.

The value of $C_{composite}$ is calculated by multiplying the value of Young’s modulus (C) divided by volume fractions of nanotubes ($k_{nt}$), for the different composites considered. In the figure the short lines represent the limits of the range experimental results presented in [35,45] and the red points correspond to the numerical result for each CNT type, obtained with the formulation proposed in this paper.

This figure shows that the formulation is capable of predicting the elastic stiffness of the composite, as most of the values obtained are comprehended between the limits defined by the experimental tests. There is only one case in which the value obtained exceed the limits of the numerical test. This is because the effective Young’s modulus of the Dwnt is highest since its diameter is really low.

6.2. Validation of the non-linear performance of the formulation

The non-linear behavior of the numerical model has been validated comparing the results provided by the model with the experimental data obtained from the paper of Meng et al. [46]. In this paper the matrix used was Polyamide 6 (PA6) and all composites contained a 1 wt.% of MWCNTs reinforcement.

The MWCNTs used in the experimental tests were purchased from Chengdu Organic Chemistry Co. Ltd. Two different composites where manufactured with these nanotubes. One of them contains the nanotubes “as is”, without any previous treatments. These nanotubes are called U-MWCNT. The other composite uses nano-

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1 For interpretation of color in Figs. 5–8, the reader is referred to the web version of this article.
the three composite components in each layer. This table also shows some geometry information of the MWCNTs and the interface zone, as well as the initial value of $N_{\text{par}}$.

In Fig. 7 are represented the numerical and experimental results obtained for the composite made with A-MWCNTs. The mechanical properties of each composite component are those defined previously.

This figure shows an initial reduction of the composite stiffness, result of matrix yielding. Afterwards damage begins in the interface zone and, consequently, the composite continues reducing its stiffness. Interface damage leads to a reduction of the parallel length (Eq. (42)). When the interface is completely damaged, the whole CNT-interface material has a serial performance. At this stage stresses in the interface are zero, and so must be the stresses in the carbon nanotube. Therefore, the final stiffness of the composite corresponds to a material with a volumetric participation of 95.4% of PA6 matrix, and the rest of the material correspond to voids.

![Comparison of Elastic Results](image)

**Table 2**

| Composite        | $k_{nt}$ (%) | $k_{iz}$ (%) | $k_{m}$ (%) | $l_{nt}/d_{nt}$ | $b/r_{nt}$ | $N_{\text{par}}$ |
|------------------|--------------|--------------|-------------|-----------------|------------|-----------------|
| PA6/A-MWCNT      | 0.5          | 4.1          | 95.4        | 250             | 2.00       | 0.98            |
| PA6/U-MWCNT      | 0.5          | 5.3          | 94.2        | 250             | 2.35       | 0.98            |

**Fig. 5.** Comparison of numerical and experimental results [35,45].

![PA6 stress–strain relations for static tests](image)

**Fig. 7.** PA6/A-MWCNT stress–strain relations for static tests [46].

**Fig. 8.** shows the results for the composite made with U-MWCNTs. This composite is the same than the previous one (made with A-MWCNTs), with the only difference that in this case the bond between U-MWCNTs and interface zone is weaker. To take
into account this difference, the numerical model used for this composite is the same used for the previous one, varying the threshold at which damage starts in the interface. In current simulation this value is reduced to 70 (MPa).

This simulation provides a maximum stress in the composite lower than the value obtained for previous one, consequence of having a weaker interface. The simulation also shows some divergences between the numerical and the experimental values. Both graphs start to differ for a strain of 2.5% and the maximum load reached by the numerical simulation is larger than in the experimental tests. However, it has to be noted that the experimental tests provide a maximum stress lower than having just plain matrix (Fig. 6). Therefore, the differences observed in Fig. 8 may be justified.

7. Conclusions

The present paper has presented a new formulation, based on the mixing theory, capable of predicting the mechanical performance of composites reinforced with carbon nanotubes. The model presented relates the CNTs and the matrix in which they are embedded, using an interface material. This approach makes possible to consider non-linear phenomenons, such as CNT debonding, by using non-linear constitutive laws to characterize the interface material. The formulation is written in a way in which all materials can be defined with their own constitutive law, improving the versatility of the model.

It has been shown that the elastic properties estimated with the model are in good agreement with experimental values obtained from literature. Only the model of the composite made with the Dwsnt reinforcement has given results in which the composite stiffness is overestimated. This is because the Dwsnt has a very small diameter, which leads to a very high value of its equivalent Young’s modulus.

The validation of the non-linear response provided by the new formulation has been performed using the experimental data of two different composites made with MWCNTs randomly distributed. The numerical curve obtained for the A-MWCNT is in good agreement with the experimental results. On the other hand, the numerical prediction obtained for the U-MWCNTs differs from the experimental results for strains larger than 2.5%. However, it has to be said that the experimental results are lower than expected, as this composite is weaker than plain matrix.

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