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MODELLING THE ELASTIC BEHAVIOUR OF CARBON NANOTUBE-REINFORCED COMPOSITES.

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Introduction

Carbon nanotubes (CNTs), since their discovery by Lijima in 1991[1], are considered a new generation of reinforcement [2]. Their "nano" size structure makes them potentially free of defects, which provides them with excellent physical properties [3,4]. There are two main nanotube types: single wall nanotubes (SWNT), which are made of a single wall tube; and multiwall nanotubes (MWNT), which consist in several concentric walls, one inside the other.

In a composite, one the 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 then are transferred to the reinforcement through the interface [5]. 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 its ability to transfer the load efficiently.

This work proposes a new formulation to predict the mechanical properties of nanotube-reinforced composites. The formulation is based in the mixing theory [6]. It obtains the properties of the composite from the mechanical performance of its constitutive materials: matrix, carbon-nanotube and the interface that bonds both of them.

Description of constitutive model

The theory presented obtains the mechanical performance of the composite from the behaviour of the composite constituents, each one simulated with its own constitutive equation [7]. As it is written, the theory can be understood as a constitutive equation manager. The new constitutive model has been 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 interface zone [8]. The interface corresponds to the matrix surrounding the CNTs. It is considered as an independent component, with its own constitutive law. The function of the interface material in the model is to define the capacity of the matrix to transfer the loads to the reinforcement.

Although the phenomenological performance of the composite completely justifies the definition of an interface material; this is also justified by experimental measurements made to CNTs reinforced composites. Differential Scanning Calorimetry (DSC) measurements, carried out in composites with semi-crystalline polymer as matrix material, show a linear increase of crystalline matrix as the nanotube volume fraction increases. This result suggests that each nanotube has a crystalline coating [9]. This phenomenon can be also seen in Scanning Electron Microscope (SEM) images such the ones shown in Figure 1. Such images revealed that the structures protruding from the fracture surface seemed to have larger diameters than the original MWCNTs used in the sample preparation [10].

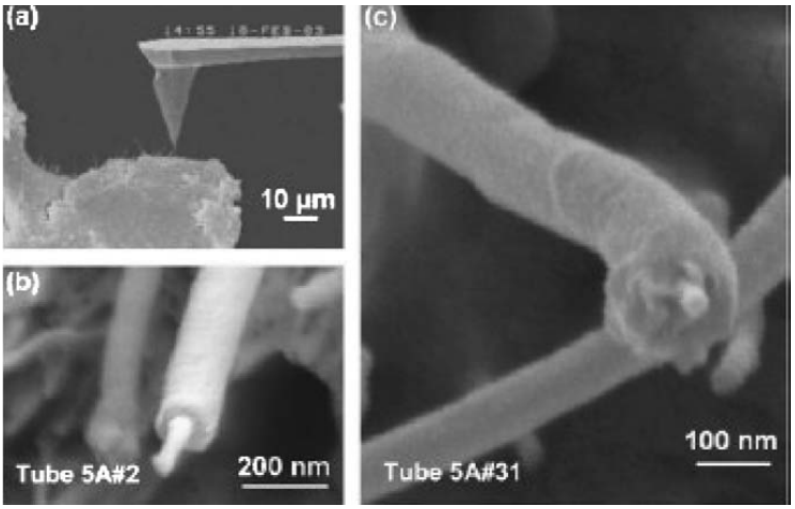

Figure 1: SEM image of nanomanipulation and fracture surface of composites [10].

A general description of the proposed procedure to simulate CNTs reinforced composites is showing in figure 2. This figure shows that the composite is divided in several layers, in this case, each one containing nanotubes with a different orientation. The layers, in general, can be formed with others component materials and also, different theories can be used for the layers [11]. All layers are coupled together using the parallel mixing theory. This division into layers allow taking into account the different orientations that may have the nanotubes in the composite. On the other hand, this gives the possibility to form composite with different sort of layers.

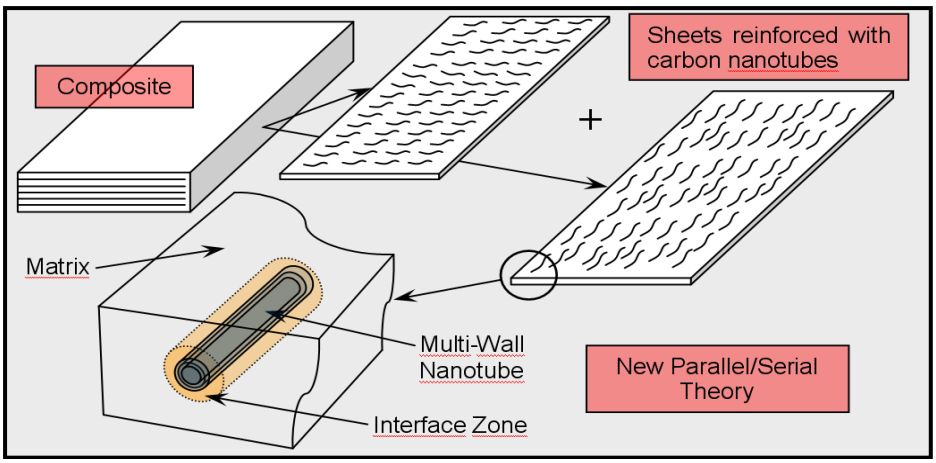

Figure 2: Representation of formation for reinforced composite.

Layers are defined by the volume content of matrix, interface and carbon nanotubes. The mechanical performance of each layer is obtained with a new mixing theory formulation, which combines the mechanical performance of the three co-existing materials.

First, the layer is split into matrix and a new material result of coupling the CNTs with the interface. The relation between the matrix and the CNTs-interface is established in terms of the parallel mixing theory; this is, they are assumed to have an iso-strain behaviour. On the other hand, CNTs and the interface zone are bonded together with a combination of parallel and serial mixing theories. In a serial behaviour all composite constituents have the same stresses.

Figure 3 shows scheme used to obtain the performance of the CNTs-interface material. This is based in the short-fibre model developed by [12]. According to this model, the load transfer from the interface to the nanotube is produced at both the ends of the reinforcement, through shear stresses. At the centre of the reinforcement there is no load transfer and, therefore, shear stresses are null. A simplified model can be defined in which the CNT-interface performance is defined with a serial

mixing theory at the ends of the reinforcement (iso-stress behaviour) and with a parallel mixing theory at the centre of it (iso-strain behaviour).

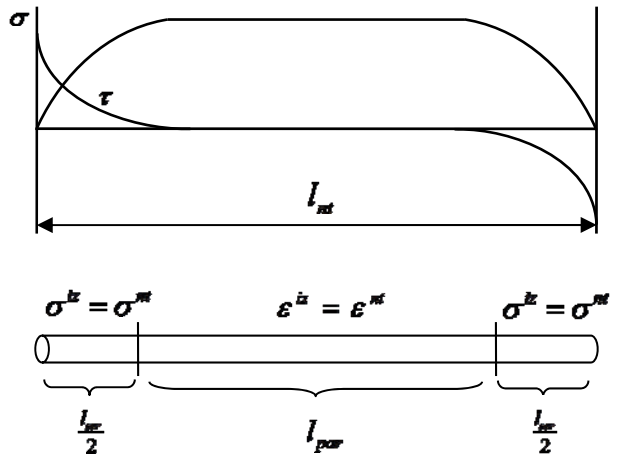

Figure 3: Different regions in the new material CNTs-interface.

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

Formulation of constitutive model

The Helmholtz free energy [13] of a material point subjected to small deformations can be described with the following thermodynamic formulation [14, 15]:

$$\Psi = \Psi(\boldsymbol{\varepsilon}; \theta, \boldsymbol{\alpha}) \tag{1}$$

where $\boldsymbol{\varepsilon}$ is the deformation tensor, θ the temperature and $\boldsymbol{\alpha} = \{\boldsymbol{\varepsilon}^p; d; \boldsymbol{s}\}$ a set of inner variables, for example: $\boldsymbol{\varepsilon}^p$ is the plastic deformation, d damage inner variable and $\boldsymbol{s}$ any other material internal variables.

The model proposed to simulate the composite material consists on a combination of the different components of the composite, using the parallel and the serial mixing theories, as has been described in previous section. The expression of the Helmholtz free energy for the composite material may be written as:

$$\Psi = k_m \Psi_m + (k_{nt} + k_{iz}) \left[\underbrace{N^{par}\left(\bar{k}_{nt}\Psi_{nt} + \bar{k}_{iz}\Psi_{iz}\right)}_{\tilde{\Psi}^{par}_{ntiz}} + \underbrace{\left(1 - N^{par}\right)\left(\bar{k}_{nt}\Psi_{nt} + \bar{k}_{iz}\Psi_{iz}\right)}_{\tilde{\Psi}^{ser}_{ntiz}} \right] \tag{2}$$

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

$$\bar{k}_{nt} = \frac{k_{nt}}{k_{nt} + k_{iz}} \qquad \bar{k}_{iz} = \frac{k_{iz}}{k_{nt} + k_{iz}} \tag{3}$$

are the volume fractions of the composite components. These must verify:

$$k_m + k_{nt} + k_{iz} = 1 \qquad \bar{k}_{nt} + \bar{k}_{iz} = 1 \tag{4}$$

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

$$\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}_m = \boldsymbol{\varepsilon}_{ntiz}^{par} = \boldsymbol{\varepsilon}_{ntiz}^{ser} \tag{5}$$

where $\boldsymbol{\varepsilon}$ and $\boldsymbol{\varepsilon}_m$ are the composite and matrix deformations, respectively; $\boldsymbol{\varepsilon}_{ntiz}^{par}$ is the deformation of a new material, result of the combination of nanotubes with the interface, that has a parallel behaviour; and $\boldsymbol{\varepsilon}_{ntiz}^{ser}$ is deformation of a nanotube-interface material that has a serial behaviour.

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

$$\mathbf{C} = \frac{\partial^2 \boldsymbol{\Psi}}{\partial \boldsymbol{\varepsilon} \otimes \partial \boldsymbol{\varepsilon}} = k_m \frac{\partial^2 \boldsymbol{\Psi}_m}{\partial \boldsymbol{\varepsilon}_m \otimes \partial \boldsymbol{\varepsilon}_m} + \frac{\partial^2 \widetilde{\boldsymbol{\Psi}}_{ntiz}^{par}}{\partial \boldsymbol{\varepsilon}_{ntiz}^{par} \otimes \partial \boldsymbol{\varepsilon}_{ntiz}^{par}} + \frac{\partial^2 \widetilde{\boldsymbol{\Psi}}_{ntiz}^{ser}}{\partial \boldsymbol{\varepsilon}_{ntiz}^{ser} \otimes \partial \boldsymbol{\varepsilon}_{ntiz}^{ser}} \tag{6}$$

A parallel behaviour means that all composite constituents have the same value for this strain component and therefore:

$$\varepsilon_{ntiz}^{par} = \varepsilon_{nt} = \varepsilon_{iz} \quad \Rightarrow \quad \frac{\partial^2 \widetilde{\Psi}_{ntiz}^{par}}{\partial \varepsilon_{ntiz}^{par} \otimes \partial \varepsilon_{ntiz}^{par}} = N^{par} \left[\bar{k}_{nt} \mathbf{C}_{nt} + \bar{k}_{iz} \mathbf{C}_{iz} \right] = N^{par} \mathbf{C}_{ntiz}^{par} \tag{7}$$

A serial behaviour means that all composite constituents have the same value for this stress component and therefore:

$$\sigma_{ntiz}^{ser} = \sigma_{nt} = \sigma_{iz} \quad \Rightarrow \quad \varepsilon_{nt} = \mathbf{C}_{nt}^{-1} : \mathbf{C}_{ntiz}^{ser} : \varepsilon_{ntiz}^{ser} \quad ; \quad \varepsilon_{iz} = \mathbf{C}_{iz}^{-1} : \mathbf{C}_{ntiz}^{ser} : \varepsilon_{ntiz}^{ser} \tag{8}$$

$$\frac{\partial^2 \widetilde{\Psi}_{ntiz}^{ser}}{\partial \varepsilon_{ntiz}^{ser} \otimes \partial \varepsilon_{ntiz}^{ser}} = \left(1 - N^{par}\right) \left[\bar{k}_{nt} \mathbf{C}_{nt}^{-1} + \bar{k}_{iz} \mathbf{C}_{iz}^{-1} \right]^{-1} = \left(1 - N^{par}\right) \mathbf{C}_{ntiz}^{ser} \tag{9}$$

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

$$\mathbf{C} = k_m \mathbf{C}_m + \left(k_{nt} + k_{iz}\right) \left[N^{par} \mathbf{C}_{ntiz}^{par} + \left(1 - N^{par}\right) \mathbf{C}_{ntiz}^{ser} \right] \tag{10}$$

Definition of the parallel factor N^{par}

The parallel factor is defined as:

$$N^{par} := \frac{l_{par}}{l_{nt}} \quad , \quad 0 \le N^{par} \le 1 \tag{11}$$

where l_{nt} is the length of the nanotube and l_{par} is function of geometry and mechanical properties of the nanotube and the interface. The equation of tension distribution in a reinforcement considering perfect bond with the matrix is [5]:

$$\sigma_{nt}(x) = E_{nt} \left[1 - \frac{\cosh\left(\beta \left(l_{nt} - 2x\right)\right)}{\cosh\left(\beta l_{nt}\right)} \right] \varepsilon_m \qquad \beta = \sqrt{\frac{2 G_{iz}}{E_{nt} d_{nt}^2 \ln\left(1 + b/r_{nt}\right)}} \tag{12}$$

where x represents the longitudinal positions in the reinforcement, the subscript "*nt*" and "*iz*" refers to the properties of nanotube and interface zone, respectively, and b is the thickness of interface.

Considering that $l_{par} = l_{nt} - 2x$ and finding the positions "x" which verifies that the effective modulus obtained of integrate the tension distributions is equal to:

$$\overline{E}_{nt} = \frac{l_{par}}{l_{nt}} E_{ntiz}^{par} + \left(1 - \frac{l_{par}}{l_{nt}}\right) E_{ntiz}^{ser} \tag{13}$$

The parallel longitudinal can be written as:

$$l_{par} = \frac{1}{\beta} \cosh^{-1}\left[\tfrac{1}{3} \cosh(\beta l_{nt})\right] \tag{14}$$

Numerical Implementation

A numerical algorithm for the proposed model has been implemented in PLCd [16] a finite element code that works with 3D solid geometries. The algorithm developed has been implemented as a new composite equation manager in the FEM code [17]. PLCd has already implemented the constitutive laws that will be used to predict the performance of the composite components (elastoplastic, 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 [17] and [11].

Results

In the following are compared the composite stiffness predicted by the proposed formulation with experimental values obtained from the literature. Coleman et al. [18, 19] tested several composites made of the same matrix with different MWNTs. The matrix material was polyvinyl alcohol (PVA) and its Young's modulus was E_m = 1.9±0.3 [GPa]. The nanotubes used in [18] were an arc grown MWNT (Arc-MWNT), two types of catalytic MWNT from Nanocyl S.A. (CVD-1, CVD-2), a catalytic MWNT produced in Orléans (France) (CVD-3), and a double walled nanotube (Dwnt). In [19] the nanotubes used were MWNT from Nanocyl S.A. (MWNT).

The authors found that the Young's modulus of the crystalline polymer phase was E_{iz} = 46 [GPa]. The properties used for nanotubes were E_g = 1 [TPa] (graphite sheet) and its thickness t = 0.34[nm] (planar spacing). The properties used in the model for the CNT were obtained considering the one as a solid cylinder with the same external geometric [20], then $E_{nt} = 4.t/d_{nt}.E_g$. After, the E_{nt} was corrected with an efficiency factor related to fibre orientation (in this case, 0.38).

The most important data of the nanotubes used is presented in the following table:

Type	d_{nt} [nm]	l_{nt} [μm]	l_{nt}/d_{nt}	b/r_{nt}	E_{nt} [GPa]	N^{par}
Arc-MWNT	24	1	42	0.81	57	0.97
CVD-3	16	3.8	238	1.47	85	0.99
CVD-2	14	2.1	150	2.27	97	0.99
CVD-1	15	1.8	120	2.83	91	0.98
Dwnt	2.5	2.2	880	4.87	544	0.99
MWNT	15	1.72	115	3.3	91	0.98

Table 1: Relevant data of the nanotubes used by Coleman et al. [18, 19]

Figure 4 shows the values of dC/dk_{nt}, this is: the slope of the curves 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 [18,19] 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.

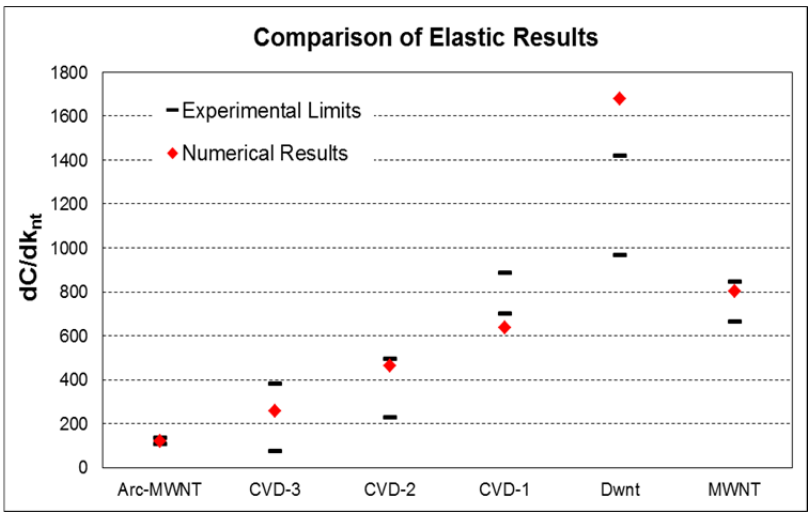

Figure 4: Comparison of numerical and experimental results.

The study of influence the angle of CNTs over the elastic properties has been done with information from the M-Rect project (see acknowledgements).

The composite used has a 3% weight of MWNT (~1.94% volume, Baytubes® C 70 P). However, measurements made with X-rays show an apparent 5% weight. This difference is obtained because the nanotubes have a higher apparent diameter than the pristine one. Therefore, the b/r_{nt} is calculated assuming that difference of 2% in weight is the result of having a coating polymer, or an interface, around the nanotubes. This interface represents approximately a 1.31% of the total composite volume. It is also necessary to know of mechanical properties of the interface zone. The Young's modulus of the interface zone is estimated with the same consideration made by Coleman et al. [18] using the data defined in the paper of Díez-Pascual et al. [21,22]. This calculation provides a Young's modulus of 5 [GPa]. The poisson's ratio was taken equal to the Peek material and the shear modulus was estimated as $G_{iz} = (E_{iz}/E_m).G_m$, then G_{iz} = 2.46 [GPa] and ν_{iz} = 0.4.

The matrix used in the composite is PEEK; which Young's modulus and shear modulus were measured and had a value of 3.9 [GPa] and 1.9 [GPa], respectively. The nanotube is considered as an orthotropic material so its mechanical properties are different along the directions of each of the axes. The properties of the CNTs used to get the effective properties were E_g = 1 [TPa], G_g = 0.44 [TPa] (the shear modulus of graphite sheet) and its thickness t = 0.34[nm] [20]. The effective shear modulus of nanotubes is $G_{nt} = [1- (1-2.t/d_{nt})^4].G_g$.

The model developed requires also some data of the nanotube geometry. The data used is shown in the table 2.

Type	d_{nt} [nm]	l_{nt} [μm]	l_{nt}/d_{nt}	b/r_{nt}	E_{nt} [GPa]	G_{nt} [GPa]	N^{par}
MWNT	13	1	77	0.3	105	85	0.97

Table 2: Project data for implementation of model

The final properties of the CNTs used in the model were:

$$E_1 = E_{nt} = 105\ GPa \qquad G_{12} = G_{13} = G_{nt} = 85\ GPa$$

$$\nu_{12} = \nu_{13} = \nu_{23} = \nu_{nt} = 0.2$$

Assuming that the transversal properties of nanotubes are the same that of interface zone:

$$E_2 = E_3 = E_{iz} = 5\ GPa \qquad G_{23} = G_{iz} = 2.46\ GPa$$

$$v_{21} = \frac{E_2}{E_1} v_{12} = 0.0097 \quad v_{31} = \frac{E_2}{E_1} v_{13} = 0.0097 \quad v_{32} = \frac{E_3}{E_2} v_{23} = 0.2$$

Figure 5 shows the change of elastic properties with the angle of the nanotubes, "E1" represent the Young's modulus in load direction; "E2" is the transversal Young's modulus and "G12" is the Shear modulus.

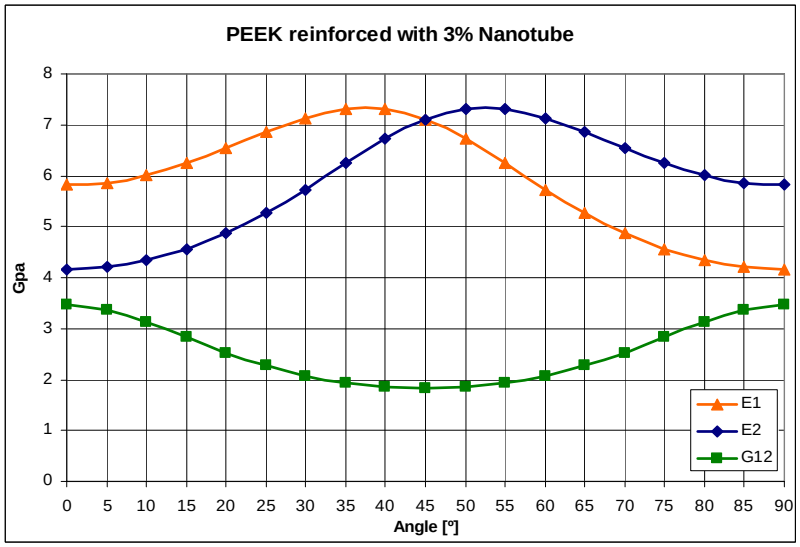

Figure 5: Elastic properties of PEEK reinforced with nanotube.

The curves shown in the figure 5 are symmetrical respect to the line of 45º, but these are different to the typical results for the matrices reinforced. In general the maximum value for the E1 is in 0º. In this case, the E1 and E2 increase until 40º, in return, the G12 decreases. This happening because the value of the G_{nt} is higher than the normal approach that it is used in fibre.

$$G_{12} = \left[\frac{1+\nu_{12}}{E_2} + \frac{1+\nu_{21}}{E_1} \right]^{-1} \qquad G_{31} = \left[\frac{1+\nu_{31}}{E_1} + \frac{1+\nu_{13}}{E_3} \right]^{-1} \qquad G_{23} = \left[\frac{1+\nu_{23}}{E_3} + \frac{1+\nu_{32}}{E_2} \right]^{-1} \tag{15}$$

Conclusions

A new formulation has been presented, which is based on the mixing theory, developed to predict the mechanical performance of composites reinforced with carbon nanotubes. The model presented has the advantage of relating the CNTs and the matrix in which they are embedded with an interface material. This makes possible to simulate composite material by using constitutive laws defined for each composite component.

It has been shown that the elastic properties estimated with the model presented are in good agreement with experimental values. The influence of the angle of nanotubes over the elastic properties was study.

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