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Modelling of behaviour of carbon nanotube-reinforced composites

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ABSTRACT

Carbon nanotubes (CNTs) have been regarded as ideal reinforcements of high-performance composites. A key factor for the reinforcement efficiency is the interface bonding between the CNTs and the matrix. The present work presents a new constitutive model to predict the performance of composites made of CNTs that takes into account explicitly the mechanical performance of the interface between the matrix and the CNTs. The constitutive model is based in the mixing theory, which allows representing each composite component with its own constitutive law.

The new formulation divides the composite in matrix and a new element result of the coupling of CNTs with the interface material. The matrix and the CNTs-interface are related with the parallel mixing theory; this is, they are assumed to have an isostrain behaviour. On the other hand, CNTs and interface material are bonded together with a combination of parallel and serial mixing theories.

The relation defined between interface and CNTs components considers that there are two regions situated at both ends of the nanotube, where the stress of the interface and the CNTs are coincident. In these regions the load is transferred from the interface to the nanotube and has a serial performance. On the other hand, the central section of the CNTs has a parallel performance; in it CNTs are capable to develop their full strength.

When de stress in the region of ends of the nanotube reaches to the limit tension of the interface starts nonlinear behaviour. The properties of the interface zone are degraded and the region of ends of the nanotube starts to grow, in other words, is like if the nanotube is shortened. Finally, for high nonlinear behaviour the interface and CNTs are bonded together with a full serial theory, but at this point of the interface properties are highly degraded. Then, the final properties of the composite are similar to the properties of the matrix component.

The numerical results of the model presented have been compared with experimental data showing good agreement.

1. INTRODUCTION

The constitutive model is based in the mixing theory, which allows representing each composite component with its own constitutive law (Car et al. 2000). Figure 1 shows a general description of the proposed procedure to simulate CNTs reinforced composites.

In order to take into account the directionality of CNTs, the composite is divided in several layers; each one with a different orientation of CNTs.

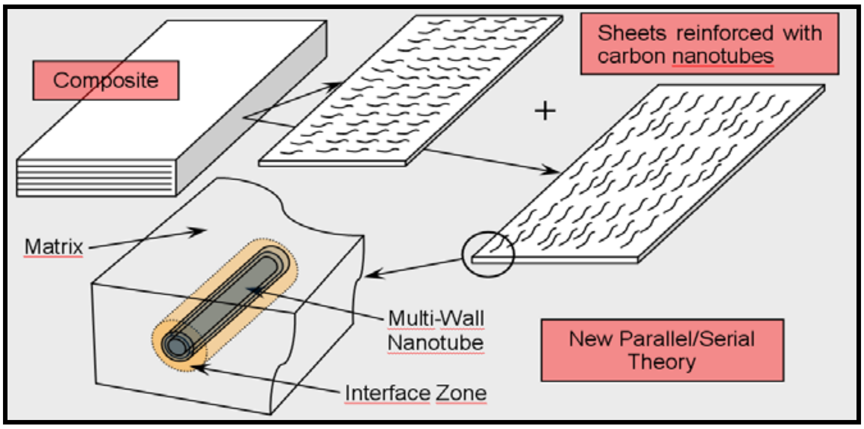

Fig. 1. Representation of formation of a reinforced composite.

2. DESCRIPTION OF CONSTITUTIVE MODEL

The different layers are coupled together with the parallel mixing theory. Therefore, the strain and stress tensor of the composite can be written as:

$$\varepsilon^{C} = \varepsilon^{L1} = \varepsilon^{L2} = \cdots = \varepsilon^{Ln} \tag{1}$$

$$\sigma^{C} = k^{L1}\sigma^{L1} + k^{L1}\sigma^{L1} + \cdots + k^{Ln}\sigma^{Ln} \tag{2}$$

Layers reinforced with CNTs have been obtained using a new mixing theory formulation, which combines the mechanical performance of the three co-existing components: matrix, CNTs and the interface region between them (Coleman et al. 2006). Therefore, with the current formulation the behaviour of the composite also depended on the constitutive model of the interface.

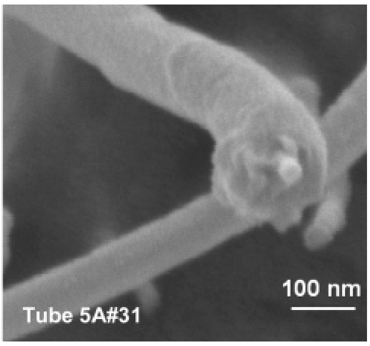

Fig. 2. Images of the fracture surface of the composite (Ding et al. 2003).

The formation of the interface is associated to the presence of CNTs in the matrix and may be enhanced by the functionalization of CNTs. The main difference between the original matrix and the interface is that the last one has a larger degree of cristallinization, which gives it improved mechanical properties (Coleman et al. 2006).

The new formulation divides the composite in matrix and a new element result of the coupling of CNTs with the interface material. The matrix and the CNTs-interface are related with the parallel mixing theory. On the other hand, CNTs and interface material are bonded together with a combination of parallel and serial mixing theories. In a serial behaviour all composite constituents have the same value for the stress component.

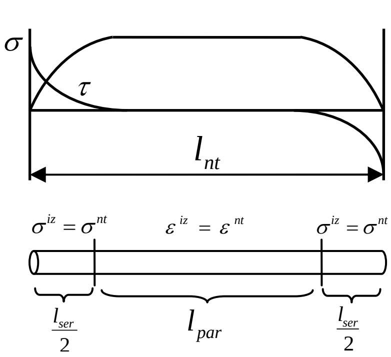

Fig. 3. Different regions in CNTs-interface.

Figure 3 shows the traction tension distribution in a short reinforcement and shear tension in interface. In the central zone, the shear stress is zero because the strain in the matrix and the reinforcement is the same. A simplified model can be obtained if it defines two regions at both ends of the nanotube. The stresses in the interface and the CNTs in this region are assumed to be equal and they have serial behaviour. The load is transferred from the interface to the nanotube in these regions. On the other hand, the central section has a parallel performance because the strains are equal. In this zone the CNTs are capable to develop their full strength.

A parallel factor named N^{par} is defined to consider these two different phenomenon. This parameter quantifies the length of the nanotube-interface element with a parallel behaviour and the length with a serial performance is the complementary. This value is calculated based on the short fiber formulation in according to Oller (2003). The b/r_{nt} is the ratio between interface thickness and nanotube radius.

$$N^{par} := \frac{l_{par}}{l_{nt}} \quad \left(0 \le N^{par} \le 1\right) \quad , \quad l_{par} = \frac{1}{\beta}\cosh^{-1}\left[\tfrac{1}{3}\cosh\left(\beta\, l_{nt}\right)\right] \quad , \quad \beta = \sqrt{\frac{2G_{iz}}{E_{nt}\, d_{nt}^2 \ln\left(1 + b/r_{nt}\right)}} \tag{3}$$

2.1 Formulation of constitutive model

The expression of the Helmholtz free energy proposed for the composite material may be described as:

$$\Psi = k_m \Psi_m + \left(k_{nt} + k_{iz}\right)\left[\underbrace{N^{par}\left(\bar{k}_{nt}\Psi_{nt} + \bar{k}_{iz}\Psi_{iz}\right)}_{\tilde{\Psi}^{par}_{ntiz}} + \underbrace{\left(1 - N^{par}\right)\left(\bar{k}_{nt}\Psi_{nt} + \bar{k}_{iz}\Psi_{iz}\right)}_{\tilde{\Psi}^{ser}_{ntiz}}\right] \tag{4}$$

where $\Psi_m, \Psi_{nt}\ y\ \Psi_{iz}$ are the specific Helmoholtz free energy for the matrix, CNTs and the interface components, respectively; $k_m, k_{nt}\ y\ k_{iz}$ are the volume fraction of each component. The tangent constitutive tensor of the composite material may be derived from (4):

$$\mathbf{C} = \frac{\partial^2 \Psi}{\partial \varepsilon \otimes \partial \varepsilon} = k_m \frac{\partial^2 \Psi_m}{\partial \varepsilon_m \otimes \partial \varepsilon_m} + \frac{\partial^2 \tilde{\Psi}^{par}_{ntiz}}{\partial \varepsilon^{par}_{ntiz} \otimes \partial \varepsilon^{par}_{ntiz}} + \frac{\partial^2 \tilde{\Psi}^{ser}_{ntiz}}{\partial \varepsilon^{ser}_{ntiz} \otimes \partial \varepsilon^{ser}_{ntiz}} \tag{5}$$

Finally, the tangent constitutive is:

$$\mathbf{C} = k_m \mathbf{C}_m + \left(k_{nt} + k_{iz}\right)\left[N^{par}\mathbf{C}^{par}_{ntiz} + \left(1 - N^{par}\right)\mathbf{C}^{ser}_{ntiz}\right] \tag{6}$$

$$\mathbf{C}^{par}_{ntiz} = \bar{k}_{nt}\mathbf{C}_{nt} + \bar{k}_{iz}\mathbf{C}_{iz} \quad \mathbf{C}^{ser}_{ntiz} = \left[\bar{k}_{nt}\mathbf{C}^{-1}_{nt} + \bar{k}_{iz}\mathbf{C}^{-1}_{iz}\right]^{-1} \quad \bar{k}_{nt} = \frac{k_{nt}}{k_{nt} + k_{iz}} \quad \bar{k}_{iz} = \frac{k_{iz}}{k_{nt} + k_{iz}} \tag{7}$$

2.2 No-elastic behaviour of the present model

There are currently different constitutive model to simulate nonlinear behaviour of materials. The model presented here can use any of such formulations (plasticity, damage, viscosity, etc.) for the simple materials. The nonlinear behaviour of the composite is coupling result of its no lineal components. The damage in the components affects the composite formulation. The interaction between simple materials depends of the actual condition of each component. The stress transfer capacity is affected by interface condition in the serial zone. The composite starts to lose stiffness when the interface initiates the damage process. The interface zone begins to break at the ends of nanotubes because the stress is the highest. This can be understood as having a shorter effective nanotube. Therefore, the length of the nanotube that behaves in parallel is reduced. The parallel length used for parallel factor definition depends on the interface damage and can be computed as:

$$l_{par} = l^{o}_{par}(1-d) \tag{8}$$

where l^{o}_{par} is the initial length of the nanotube working in parallel.

3. RESULTS

In order to validate the formulation proposed, the numerical results of the model have been compared with experimental data found in literature (Coleman et al. 2006). The mechanical properties of the MWCNT used consider that stiffness is provided by the outer wall of CNTs and that it acts as an effective solid fiber with the same diameter and length. Therefore, the simulation calculates an effective Young's modulus of the CNTs from the Young's modulus of the outer wall [1 TPa] and its thickness [0.34 nm] according to Thostenson et al. (2003).

CNTs type	D [nm]	L [μm]	L/D	b/r_{nt}	E_{eff} [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

Table 1. Relevent data for implementation of model.

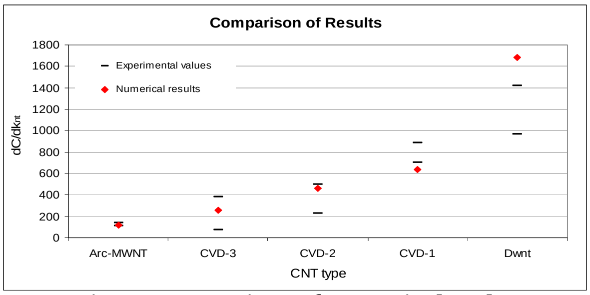

Fig. 4. Comparison of numerical and experimental results.

Table 1 shows the geometry and mechanical data of each CNT. The matrix (polyvinyl alcohol [1.9 MPa]) is the same for all composite. The Young's modulus of the interface corresponds to the one of a crystalline matrix [46 MPa].

Figure 4 shows the results of dC/dk_{nt}, that is the slope of the curves of Young's modulus

(C) divided by volume fractions of nanotubes (k_{nt}), for each kind of MWNTs. In the graphic the short lines show the range of experimental data for each CNT type.

3.1 No-elastic response comparison

The nonlinear behaviour of the numerical model has been compared with experimental data obtained from M-Rect project (see acknowledgements). The matrix used is PEEK; Young's modulus and shear modulus were measured: 3.9 [GPa] and 1.9 [GPa], respectively. The composite has a 3% weight of MWNT (Baytubes® C 70 P) but measurements with X-ray show an apparent 5% weight, this means that the nanotubes have a higher apparent diameter than the pristine one. Therefore, the b/r_{nt} is calculated assuming that 2% weight extra is the coating polymer around the nanotubes. The Young's modulus of the interface zone is estimated with the same consideration that Coleman et al. (2006) but the data used for calculate are of the paper of Díez-Pascual et al. (2010) and the Young's modulus obtained is 5 [GPa].

CNT type	D [nm]	L [mm]	L/D	b/r_{nt}	E_{eff} [Gpa]	N^{par}
MWNT	13	1	77	0,3	105	0,97

Table 2. Project data for implementation of model.

The numerical composite model is form with layers that have different orientation of CNTs. The constitutive model used for Peek material is an elasto-plastic model, for the interface zone is an explicit scalar elasto-damage and for the nanotube is an elastic model. The damage starts at the interface that works in serial with nanotubes when the shear stress exceeds 15 MPa in the interface. The damage variable on the interface controls the N^{par} factor and when the damage increases the N^{par} decreases (eq. (8)).

The angle and the volume fraction of each layer that show the figure 6 is proposed to represent the angles distribution of CNTs into the composite. Figure 5 shows the numerical and experimental results of tensile test for the composite; it shows also the behaviour of serial interface in each layer. The damage onset in the layers with higher angle because the shear stresses are higher on these layers. In each layer, the constitutive behaviour changes with the N^{par} factor. Finally, when the damage variable the interface is equal to one, the behaviour between nanotube and interface is full serial; the interface is full damaged too and stress transfer to the nanotube is impossible.

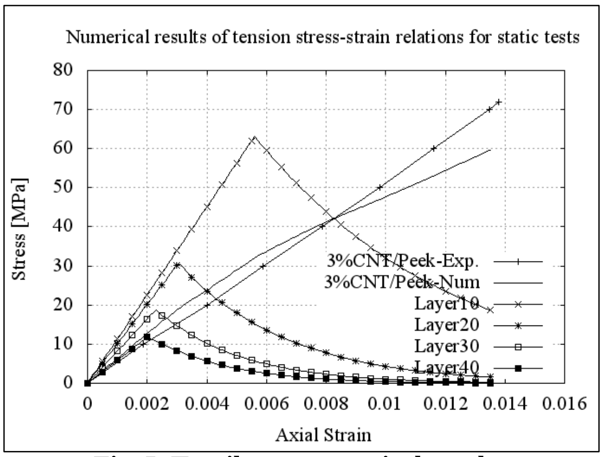

Fig. 5. Tensile test numerical results.

Therefore, the numerical curve of the composite loses stiffness when at the different layers start the damage process. At the end of the test, the stiffness of composite is equal to 96.75% (95% weight of PEEK) of the stiffness of

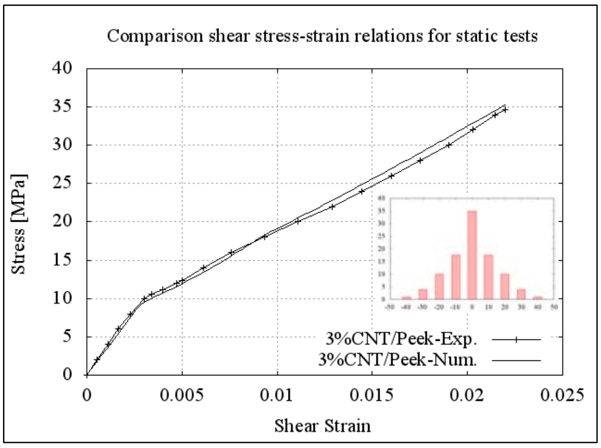

Fig. 6. Shear test results and CNT's

matrix at this stage. The matrix changes its behaviour in the composite that when is alone. This would explain the different final slopes shown in figure 5.

Figure 6 shows the numerical and experimental data for shear test. The general behaviour of layers is similar to the tensile test before. In this case, the numerical prediction curve is very good in comparison with the experimental result.

4. CONCLUSIONS

The main advantage of the model presented is that it can use any constitutive model for the component materials (CNTs, matrix, interface). On the other hand, the model considers an explicit interface zone and its influence in the behaviour of composite. The elastic properties and nonlinear behaviour estimated with the model are in good agreement with experimental values.

REFERENCES

CAR, E., OLLER, S., And OÑATE, E. (2000) An anisotropic elastoplastic constitutive model for large strain analysis of fiber reinforced composite materials, *Comput. Methods Appl. Mech. Engrg.* 185 pp. 245-277.

COLEMAN, J. N., CADEK, M., Et al. (2006) Reinforcement of polymers with nanotubes. The role of an ordered polymer interfacial region. Experiment and modeling, *Polymer* 47, pp. 8556-8561.

DÍEZ-PASCUAL, A., Et al. (2010) High performance peek/carbon nanotube composites compatibilized with polysulfones-II. Mechanical and electrical properties, *Carbon* 48, pp. 3500-3511.

DING, W., EITAN, A., Et al. (2003) Direct observation of polymer sheathing in carbon nanotube-polycarbonate composites, *Nano Letters*, Vol. 3 No. 11, pp. 1593-1597.

OLLER, S. (2003) Simulación numérica del comportamiento mecánico de los materiales compuestos, *CIMNE*, Universidad Politécnica de Cataluña.

THOSTENSON, E. T. And CHOU T. W. (2003) On the elastic properties of carbon nanotube-based composites: modelling and characterization, *J. Phys. D: Appl. Phys.* 36, pp. 573-582.

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