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Mechanical Properties of Carbon Nanotubes Composites

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A critical review of theoretical models aiming to explain the physical properties of composites based on polymeric matrices reinforced with carbon nanotubes is presented. Attention is paid to descriptions based on molecular dynamics, continuum mechanics, and finite element analysis. It is shown that both the continuum mechanics approximation and the finite size element analyses fail to describe composites with very thin interfaces, while the performances of molecular dynamics simulations are still restricted by computer's performances. The limitations of the continuum mechanics approximation are analyzed in detail.

Keywords: Nanocomposites, carbon nanotubes, modeling, mechanical properties, finite size element, dynamical modeling.

1. INTRODUCTION

The outstanding properties of single walled carbon nanotubes,[1–10] including elastic modules larger than 1 TPa,[1, 5–7] elastic strain up to 5%,[1] breaking strain up to 20%, strength ranging from 40 to 640 GPa,[2] high thermal stability, good thermal conductivity and high electrical conductivity,[10] explain the attention paid to such nanomaterials. While the mechanical properties of nanotubes at nanometer size are impressing, the bulk (macroscopic) features are usually modest.[2] The reduced density of multiwalled carbon nanotubes (about 2160 kg/m^3 (Ref. 3)) justifies the interest for space applications.

By measuring the amplitude of the vibration of carbon nanotubes, their Young modulus was estimated to be about 1 TPa.[4–9] Nevertheless, the errors of this measurement are large and it was argued that this value is an overestimation of the Young modulus of carbon nanotubes.[6] Atomic Force Microscopy measurements of the deflection force of a SWNT bundle resulted in an estimated Young modulus of about 810 ± 410 GPa[6] for individual nanotubes and of 1.28 ± 0.59 TPa for six MWNT.

This article includes a critical analysis of some recent models proposed to explain the mechanical properties of composites based on carbon nanotubes, developed either within the molecular dynamics framework or within the continuum mechanics approximation. From a rigorous point of view, the projection of the quantum features of a composite at macroscopic scale requires various multiscale materials modeling approaches. While the fundamental level is associated to the quantum features of the condensed matter, the next step is represented by classical molecular dynamics models that disregard quantum principles. Several empirical approaches are frequently used to insert quantum mechanics features within molecular dynamics models. A typical example exists in the introduction of atomic potentials and quasi-classical bond representations in molecular dynamics simulations. Such approaches are dominating the analysis of the mechanical properties of carbon nanotubes and composites based on carbon nanotubes. Monte Carlo simulations are also used extensively to analyze the mechanical properties of such materials. In the case of composite materials based on carbon nanotubes, the simulation of mechanical properties has to be carried out further, by introducing statistical mechanics concepts and testing the results for self-consistence.

The emphasis on theoretical approaches based on molecular dynamics simulations reflects the general opinion that such models are restricted solely by the limited capacity and reduced speed of actual computers. Nevertheless, in the case of the composites based on polymeric matrices reinforced with carbon nanotubes, the chain like structure of macromolecules complicates the modeling of their mechanical properties. The beauty of this approach is its direct connection with the interactions between atoms and molecules. The contributions of both bonding and non-bonding interactions may be accurately introduced and modeled to obtain the best fit between theory and experiment.

The continuum approximation offers a simplified picture for the description of the mechanical properties. In nanocomposites, this approximation is extremely rough, especially if the nanometer size confinement or interfaces triggers quantum effects. Such effects are washed out by the continuous approximations and, therefore, the case in which the quantum effects (triggered by nanometer sized confinement) are projected onto the macroscopic features of the composite cannot be accurately described by models developed within this approximation. At the extreme theoretical limit, the continuous approximation disregards the molecular structure of the materials. Hence, it is not capable to furnish direct information regarding the effect of atomic interactions and interfaces on the mechanical properties of a bulk sample. Nevertheless, the simplicity of the approaches (developed within the continuum mechanics) explains their frequent use in the analysis of atomic force microscopy (AFM) data on carbon nanotubes and composites based on carbon nanotubes, and in some cases, the analysis of Raman or Fourier Transform Infrared (FTIR) spectra of carbon nanotubes and polymeric matrices reinforced with carbon nanotubes.

The finite element does not have this direct connection to the interactions between atoms. Nevertheless, its simplicity and the reduced computational time are the main arguments for its use. The finite element approximation fails to predict accurately the physical properties of composites with sharp and narrow interfaces. The rapid change in the physical properties of the composite along the interface requires the decrease of the finite element cell size to the point where the computational time and the errors implied by the simplicity of the model are too important to be neglected.

In a composite material, the load applied to the polymeric matrix is transferred to filler; this justifies the huge number of papers focused on the mechanical properties of carbon nanotubes and on carbon nanotubes reinforced polymers. In such materials, the role of the polymer-carbon nanotube interface is extremely important. Experimental data indicate that the load transfer from the polymeric matrix to the nanotube is controlled by the physical properties of the polymer.[2] Detailed studies revealed a decrease in the free volume of the polymer after the intercalation of carbon nanotubes, associated with a significant enhancement of mechanical properties. The nanocomposites obtained by dispersing carbon nanotubes in polyvinylacetate[2] showed an increase of the modulus up to 6.9 GPa (from 2.3 GPa), of the strength by about one order of magnitude (to 57 GPa from 6.29 GPa) and of the toughness (energy absorbed per unit volume to break) from 1.41 × 10^4 J/m^3 to 39 × 10^4 J/m^3. The relationship between the hydrophobicity of the polymeric matrix and load transfer in carbon nanotube reinforced composites was reported; the best load transfer was obtained by using hydrophobic polymeric matrices.[2] Nanoidentation studies of composites based on carbon nanotubes confirmed[3] the enhancement of the mechanical properties of polymeric matrices due to the dispersion of carbon nanotubes. Although there is a strong correlation between mechanical properties and electrical properties, both in carbon nanotubes,[10] as well as in composites based in carbon nanotubes,[11] such aspects are beyond the objectives of this paper.

2. THE STRUCTURE OF CARBON NANOTUBES

Four main types of carbon nanotubes have been obtained; singled walled carbon nanotubes, multiwalled carbon nanotubes, coiled multiwalled carbon nanotubes and ropes of carbon nanotubes. Some important structural characteristics of carbon nanotubes will be discussed within the next subsections.

2.1. Single Walled Carbon Nanotubes (SWNTs)

SWNTs are characterized by the chiral vector $\mathbf{C_h}$ (defined by $\mathbf{C_h} = \mathbf{na_1} + \mathbf{ma_2}$), and by the wrapping angle ϕ formed between $\mathbf{C_h}$ and the Armchair line (see Fig. 1). The vector $\mathbf{a_1}$ lies along the zigzag direction and the vector $\mathbf{a_2}$ is a reflection of $\mathbf{a_1}$ over the Armchair direction.[10] The values of n and m determine the chirality (twist) of the nanotube. Carbon nanotubes are classified depending on their chirality and wrapping angle.

1. The Armchair nanotube is defined by $\phi = 0°$; the translation indices are (n, n).

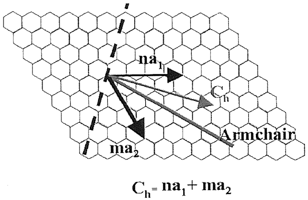

Figure 1. The definition of the chiral vector.

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2. The Zigzag nanotube is defined by $\phi = 30°$; the translation indices are $(n, 0)$.
3. The Chiral nanotube is characterized by $0° < \phi < 30°$; the translation indices are (n, m).

The chirality affects the size, the lattice structure, the density, and the electric and thermal conductance of the nanotube. The diameter of the single walled carbon nanotube D is expressed by:

$$D = \frac{\sqrt{3}}{\pi} d_0 \sqrt{m^2 + n^2 - mn} \tag{1}$$

where d_0 is the distance between neighboring carbon atoms in the graphite sheet (0.142 nm).

2.2. Multiwalled Carbon Nanotubes (MWNTs)

There are three types of MWNTs. The most frequent structure consists of a collection of concentric tubes coaxially stacked together. The second structure is represented by a collection of coaxial prisms stacked together. These MWNTs are frequently defined as multilayered carbon nanotubes (MLNTs). It is also possible to obtain a structure that presents several walls, by rolling a single graphite sheet in a multi layer carbon nanotube (scroll). For most MWNTs, the interlayer spacing is about 0.34 nm, connected with the graphite crystal.

2.3. Coiled Multiwalled Carbon Nanotubes

These carbon nanotubes are no more one-dimensional systems. They are very long (of about 10^2 microns and more), and have the tendency to form a random coil, similar to the macromolecular chain. The theory predicts that the stress transfer is improved by increasing the length of the carbon nanotube. Some preliminary results indicate an improvement in the stress transfer in composite based on coiled multiwalled nanotubes in comparison with the data obtained in the case of short (bamboo) nanotubes. Some authors assigned this behavior to a mechanical interlocking mechanism.[8]

2.4. Carbon Nanotube Ropes (CNR)

Carbon nanotube ropes are clusters of tightly connected single-walled carbon nanotube (bundles of nanotubes) held together by relatively strong adhesion forces. It is speculated that, in such ropes, the Van der Waals interaction between non-bonding carbon atoms has a major contribution to the adhesion between the single-walled carbon nanotubes. Frequently, the ropes are entangled each with other. The cross section of a single-walled carbon nanotube rope may be schematically represented by a central nanotube surrounded by six carbon nanotubes, almost equally spaced. The resulting structure, reminiscent to a honeycomb structure,[12] has outstanding mechanical properties.

3. THE PHYSICAL PROPERTIES OF CARBON NANOTUBES

The physical properties of carbon nanotubes cannot be easily assessed due to their reduced size. In certain cases, numerical estimations of their mechanical features based on various models have been reported. The mechanical properties of carbon nanotube ropes, single-walled nanotubes, multiwalled nanotubes and nanotube ropes have been estimated from indirect measurements, followed by detailed analyses based on various theoretical approaches. Atomic Force Microscopy provides a simple and direct way to test the mechanical properties of carbon nanotubes, but the macroscopic significance of such measurements is still under debate, as in most cases, the number of experiments did not reach the required statistical relevance. That explains the wide range of values for the Young modulus of multiwalled carbon nanotubes (from 270 GPa to about 950 GPa).[9] The mechanical properties of SWNT have been simulated within various approaches. Attention has been paid to the outstanding values estimated for the tensile modulus and strength, and to the effect of chirality on mechanical properties.

Under the effect of external stresses, the carbon nanotubes are subjected to various deformations such as bending, buckling, torsion, rolling, breading and vibrations (oscillations), characterized by different frequencies (see Fig. 2). In certain cases, these deformations are non-linear. The defect generation under stress is another important feature of carbon nanotubes. It was reported that the armchair nanotubes could release the excess strain when subjected to uniaxial tensile stress via a Stone-Wales defect, i.e., through the nucleation of a dislocation loop in the hexagonal network of the graphite sheet. The Stone-Wales defect is one of the most important defects produced in NT. It is obtained by rotating the C-C bond in the hexagonal network by 90^0, resulting in the creation of a dipole.[13] The formation energy of a Stone-Wales defect in a nanotube, E_{SW}^{NT}, is:[13]

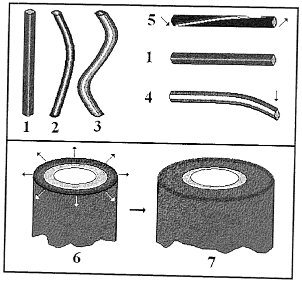

Figure 2. Main mechanical distortions of carbon nanotubes.

1. Carbon nanotube (not distorted).
2. Buckled carbon nanotube (mode 1).
3. Buckled carbon nanotube (mode 2).
4. Bending of the carbon nanotube.
5. Torsion mode in carbon nanotube.

6–7. Breathing mode in carbon nanotube.

$$E_{SW}^{NT} = E_{SW}^{0} + ae^{-br} + \frac{c}{r^2} \tag{2}$$

where E_{SW}^{0} is the energy required to produce a Stone-Wales defect in a flat grapheme sheet, r is the radius of the nanotube, and a, b and c were considered as fitting parameters.

The most frequently used approaches to explain the physical properties of carbon nanotubes are the molecular dynamics and the models developed within the continuum mechanics approximation. The main limits of molecular dynamics simulations will be discussed in detail within the next paragraphs.

4. MOLECULAR DYNAMICS SIMULATION

At the atomic scale, the carbon nanotube shows the same sp^2 bond structures and essentially the same energies as a single graphene sheet.[14] As the diameter of the carbon nanotube is increased, the strain energy increases by about 1% (Ref. 14). Hence, the ideal isolated carbon nanotube is distorted. In such a distorted structure, the possibility of sp^3 bonding between curved graphene sheets may result in a superhard carbon nanocluster.[15] The mechanical properties of carbon nanotubes have been tentatively explained by molecular dynamics simulations. Such theoretical estimations, starting from the structure of carbon nanotubes, included the contribution of chemical bonds as well as the effect of Van der Waals interactions. First principle techniques,[16–18] semi-empirical schemes[19] and empirical potential methods[20, 21] have been used to simulate the structure and the mechanical properties of carbon nanotubes. Atomistic models consider that the repulsive and attractive interactions between pair of adjacent atoms and molecules are described by Morse potential, and that the Lennard Jones potential describes non bonded Van der Waals interactions. DREIDING[22] offers an excellent framework for molecular simulations of carbon nanotubes and composites based on carbon nanotubes. For covalently bonded atoms, DREIDING provides several interactions such as two-body interactions (bond stretch), three-body interactions (bond angle bend) and four-body interactions (dihedral angle torsion and inversion). DREIDING also takes into account nonbonding interactions such as Van der Waals (dispersion) interactions, electrostatic interactions and hydrogen bonds. Odegard et al.[23] proposed a model to analyze the mechanical properties of carbon nanotubes by using molecular mechanics. The equivalent truss model used by Odegard—although more simple than DREIDING—has the advantage of a reduced number of parameters. While DREIDING has the ability to include more molecular details and interactions, it is important to mention that there is no significant difference between the capabilities of DREIDING and the molecular mechanics simulation used by Odegard et al.[23]

The most important terms that are contributing to the mechanical features of nanotubes and composites based on nanotubes are:

4.1. Bonded Interactions

The bond stretch is affecting the distance between two adjacent atoms. In the general case, it is described by a Morse potential, U_{BS}:

$$U_{BS} = E_D(e^{-(\alpha R - R_e)} - 1)^2 \tag{3}$$

where E_D is the energy required to break the bond between the two atoms, R_e represents the equilibrium distance between the 2 atoms and α is a constant that relates the "equivalent" spring constant k_e associated to the Morse potential to E_D.

$$2\alpha^2 E_D = k_e \tag{4}$$

The angle bend reflects the change in the angle between two adjacent bonds sharing a common atom. For a chain of three atoms, the corresponding energy, E_{123}, may be expressed as:

$$E_{123} = \frac{C_{123}}{2}(\cos\theta_{123} - \cos\theta_0)^2 \tag{5}$$

where θ_0 defines the equilibrium position.

Torsion interactions between two bonds, 12 and 34, connected by a common bond, 23, is generally expressed by:

$$E_{1234} = \frac{V_{12-34}}{2}[1 - \cos m(\phi - \phi_{12-34}^0)] \tag{6}$$

where V_{12-34} is the potential that describes the rotation barriers between the two bonds, m is an integer, ϕ is relative orientation of the two bonds and ϕ_{12-34}^0 is the corresponding equilibrium orientation.

4.2. Non-Bonded Interactions

It is considered that Van der Waals interactions represent the most important contribution to the stability of carbon nanotubes. This is a distance-dependent interaction between neighboring atoms, which are not connected by a chemical bond:

$$U_{NT} = 4D_{NT}\left(\frac{R_{NT}}{r_P^{12}} - \frac{R_{NT}}{r_P^{6}}\right) \tag{7}$$

where D_{NT} is the well depth, r_P is the distance between two atoms, which are sufficiently close each to other, but are not connected by covalent bonds, and R_{NT} is the Van der

Waals equilibrium separation between the pair of atoms. Van der Waals interactions are extremely important in the case of MWNT and of carbon nanotubes ropes, where carbon atoms that are not connected by covalent bonds are in close vicinity.

Molecular dynamics simulations are expected to provide a rather accurate picture of the mechanical properties of SWNT. For the case of MWNT and carbon nanotubes ropes, the number of atoms is higher and the interactions among them more complex. That would increase the simulation time and will make the prediction of the physical properties of carbon nanotubes less accurate. It is expected that the finite size analysis would give a sufficiently accurate picture of the mechanical properties of carbon nanotubes.

Xin et al.[24] used a simplified expression for the energy of carbon nanotubes, including, solely, the energy of the band electrons and the repulsion energies obtained by assuming a distance-dependent repulsive pair potential. The Van der Waals interactions were not explicitly introduced, although they may be included in calculation through the pair potential. Molecular dynamics simulations performed using the Tersoff Brenner bond order potential indicated[8] that, in multiwalled nanotubes, solely, the external wall takes the uniaxial load. Theoretical studies[25] indicated that the Young modulus of multiwalled carbon nanotubes, E_{MWNT}, decreases as the number of wall layers is increased:

$$E_{\mathrm{MWNT}} = \frac{\eta N}{N-1+\eta} E_{\mathrm{SWNT}} \tag{8}$$

where E_{SWNT} is the Young modulus of single-walled carbon nanotubes, N is the number of tube layers and η is the ratio thickness-to-interlayer.[24]

5. THE CONTINUUM APPROXIMATION

The continuum approximation is a crude approximation that allows us to make some estimation concerning the physical properties of carbon nanotubes. The carbon nanotube in the continuum approximation is imagined as a cylindrical elastic shell of a finite thickness. The small size of the carbon nanotube requires us to take into account all interactions occurring at nanometer scale. Carbon nanotubes are characterized by a high aspect ratio (length to radius ratio). The continuum approximation may be used to derive the mechanical properties of carbon nanotubes if the homogenization criterion[26, 27] $L_{\mathrm{NT}}/a > 10$ is fulfilled, and if the axial strain $\varepsilon_{\mathrm{CNT}} \cong \frac{L_{\mathrm{CNT}} - L_{\mathrm{CNT}}^{(0)}}{L_{\mathrm{CNT}}^{(0)}} \ll 1$, where $L_{NT}^{(0)}$ is the length of the carbon nanotube, L_{NT} is the length of the deformed nanotube, and a is the width of hexagonal rings. The continuum approximation describes the situation in which the wavelength of phonons is larger than the interatomic distance.[28–29] A detailed analysis of continuum and shell theories resulted in the identification of three broad classes of carbon nanotubes,[24–28] namely; thin and thick shell like structures, high aspect ratio nanotubes and nanotube beams. If the nanotube may be assimilated with a beam, and some additional requirements such as the constancy of the direction of the applied load during deformation and the invariance of the nanotube cross section along the length of the nanotube are satisfied, then the carbon nanotube is well described by the Euler problem:

$$EI\frac{d^2w(x)}{dx^2} + Pw = 0 \tag{9}$$

where $w(x)$ is the deflection, E the Young modulus of the carbon nanotube, I its inertia momentum and P the load. The general solution for the nanotube beam is:

$$w(x) = A_1 \sin\left(x\sqrt{\frac{P}{EI}}\right) + A_2\cos\left(x\sqrt{\frac{P}{EI}}\right) + A_3x + A_4 \tag{10}$$

The rough continuum approximation is rewarding with a simple and elegant solution that expresses the mechanical behavior of a SWNT subjected to a mechanical stress. AFM tests have been interpreted by assuming that the continuity approximation is fulfilled and, hence, that the solutions of the Euler problem describes their mechanical properties.

The continuum approximation is frequently used to simulate and analyze the Raman spectra of carbon nanotubes. The vibrational modes of isolated nanotubes, the breading modes of two-layers nanotubes and the modes of multiwalled carbon nanotubes were estimated from a simple analysis of the elastic displacements of carbon nanotubes atoms.[30]

The classical elastic theory assumes that the stress tensor at a given point depends linearly on the strain tensor at the same point. Sudak[1] observed that this assumption completely removes the effect of long-range interaction, as there is no internal length scale associated to the material. In a tentative to improve this situation, the non-local continuum approximation assumes that the stress at a given point is a function of all strain states of all points associated to the elastic body. Formally, the non-local continuum approach is a mean field theory. In the non-local continuum theory, the beam problem is associated to the differential equation:[1]

$$EI\frac{d^4w(x)}{dx^4} - N\frac{d^2w(x)}{dx^2} = p(x) - (e_0a)^2 \left(\frac{d^2p(x)}{dx^2} + N\frac{d^2w(x)}{dx^2}\right) \tag{11}$$

where N is the constant axial force applied to the body, $p(x)$ is the distributed lateral pressure per unit length, a is a scale factor frequently chosen to be the length of a C-C bond (1.42 A) and e_0 is a material constant.

In the absence of interlayer displacement, the MWNT may be considered formally as a SWNT. The critical axial strain for a single-walled nanotube within the non-local continuum mechanics is:[1]

$$\sigma_x^0 = \frac{I\left(\frac{m\pi}{L}\right)^2}{A\left[1+\left(\frac{m\pi e_0 a}{L}\right)^2\right]} \tag{12}$$

where A is the total cross section of the nanotube. The classical case is obtained by assuming that $e_0a = 0$. In the absence of Van der Walls interactions, the nanotubes are not coupled, and the critical axial strain is determined by the inner tube.

The difficulties of continuum mechanics in describing the physical properties of carbon nanotubes were also revealed during the study of large-scale deformations.[31–32] The basic definition of the Young modulus during an uniaxial test (see Equation (12)) has to be questioned due to the absence of the translational invariance in the radial direction.

$$E = \frac{1}{V}\frac{\partial^2 E_S}{\partial \varepsilon^2} \tag{13a}$$

where V is the volume of the nanotube, E_S the strain energy and ε is the tensile strain. This example proves the difficulties encountered in the calculation of the Young modulus and in the analysis of mechanical data on carbon nanotubes within the continuum approximation.[31]

The applicability of classical continuum mechanics for systems that are structured or confined at nanometer scale, or that present interfaces at nanometer scale, has yet to be assessed. Another hypothesis, frequently embedded in the mechanical analysis, is that the reaction of the sample to the applied stress is linear or may be described by assuming a linear superposition approximation. The effect of the rippling mode on the static deflection of multiwalled nanotube was discussed by Liu et al.[33] They concluded that the use of linear elasticity to analyze the dynamics of carbon nanotubes is a rough approximation, as the answer of nanotubes is not always linear. Non-linear carbon nanotube deformations were simulated by Pantano et al.,[34] and by Xiao and Liao at the large axial deformation limit.[35] The Young modulus of MWNT has been estimated[35] within the continuum approximation. It was found[35] that the Young modulus of MWNT decreases as the number of layers in the MWNT is increased.

Another typical example that shows the limitations of continuum models is provided by the expression of the bending stiffness, B_S (Ref. 36),

$$B_S = \frac{Eh^3}{12(1-\upsilon^2)} \tag{13b}$$

where E is the in-plane Young modulus, h is the thickness of the nanotube and υ is the Poisson ratio. The observed bending for carbon nanotubes is much lower[36] than the value predicted by the expression (13b).

6. COMPOSITES BASED ON CARBON NANOTUBES

The physical and, in particular, the mechanical properties of composites based on carbon nanotubes have been investigated in detail by several authors. The particular attention to nanocomposites obtained by reinforcing different polymeric matrices with carbon nanotubes resides in the high mechanical properties of carbon nanotubes. In certain cases, significant increases in the mechanical properties of the polymer after the dispersion of carbon nanotubes were reported. It is recognized that the improvement of the mechanical properties of polymeric matrices after the reinforcement with carbon nanotube are derived from the physical properties of the carbon nanotube-polymer interface. The role of the interface in the mechanical properties of the composites based on carbon nanotubes is not yet fully understood. Pull out experiments of carbon nanotubes from fractured samples revealed a relatively poor adhesion. The interfacial energies[6] corresponding to the covalent bonds between carbon nanotubes and polymers are frequently between 50 Jm^{-2} and 300 Jm^{-2}, while the Van der Waals interaction is much smaller (from 0.05 Jm^{-2} to 0.35 Jm^{-2}). Various approaches have been used to analyze and model the mechanical properties of carbon nanotubes.

7. DYNAMICAL MOLECULAR SIMULATIONS

Dynamical molecular simulations are, at least in principle, able to provide an accurate description of the physical properties of carbon nanotubes based composites (CNBC). Brenner potential function was used to estimate the atomic stress values in carbon nanotubes, resulting in an estimation of the Young modulus (about 500 GPa, Ref. 35). The calculations indicated that the stress is tensile in the radial direction and compressive in the tangential direction. It was concluded that the (absolute) value of the tangential stress, radial stress and Young modulus increases as the radius of the nanotube is increased. DREIDING offers a more flexible approach to the problem of nanocomposites, as it implies both bonding and non-bonding interactions. The bonding interactions will contain the interactions between the atoms located on carbon nanotubes or within the atoms belonging to the polymer chain. There is no proof of a chemical bond between the polymeric chain and the carbon nanotubes, although its presence was speculated by some authors. In the absence of such a chemical bond, it is mandatory to assign the enhanced mechanical properties of CNBC to non-bonding interactions among carbon nanotubes and the polymeric matrix. The most important interactions contributing to the mechanical properties of CNBC are:

7.1. The Van der Waals Interaction

1. The Van der Waals interaction between the atoms of carbon nanotubes and the atoms of the polymeric chain $W_{\text{P-NT}}$, which is modeled by a Lennard Jones potential, U;

$$U_{\text{P-NT}} = 4D_{\text{P-CNT}}\left(\frac{R_{\text{P-NT}}}{r^{12}_{\text{P-NT}}} - \frac{R_{\text{P-NT}}}{r^{6}_{\text{P-NT}}}\right) \tag{14}$$

where $D_{\text{P-NT}}$ is the well depth, $r_{\text{P-NT}}$ is the distance between two nearest atoms, one belonging to the nanotube and the other to the polymeric matrix, and $R_{\text{P-NT}}$ is the Van der Waals equilibrium separation between the pair of atoms. This type of interaction changes the physical properties of the first polymeric layer that is coating the carbon nanotube. By increasing the loading of the polymeric matrix with carbon nanotubes, the intensity of this interaction should be enhanced. Qualitatively, this interaction would depend on the total area of carbon nanotubes exposed to the polymeric matrix. The effect is expected to be stronger in SWNT that in MWNT. At a very large concentration of carbon nanotubes due to the coalescence of nanotubes, the area exposed to polymer molecules will decrease, leading to a decrease of the Van der Waals interaction between the polymeric matrix and the nanometer sized filler.

2. Van der Waals interaction between atoms belonging to adjacent carbon nanotubes (located on carbon nanotubes), $W_{\text{NT-NT}}$ is also modeled by a Lennard Jones potential, $U_{\text{NT-NT}}$;

$$\begin{aligned} U_{\text{NT-NT}} &= 4D_{\text{NT-NT}}f^{\text{N}}_{\text{NT}}\left(\frac{R_{\text{NT-NT}}}{r^{12}_{\text{NT-NT}}} - \frac{R_{\text{NT-NT}}}{r^{6}_{\text{NT-NT}}}\right) \\ &\quad + 4D_{\text{P-CNT}}f_P f_{\text{CNT}}\left(\frac{R_{\text{P-NT}}}{r^{12}_{\text{P-NT}}} - \frac{R_{\text{P-NT}}}{r^{6}_{\text{P-NT}}}\right) \end{aligned} \tag{15}$$

where $D_{\text{NT-NT}}$ is the well depth, $r_{\text{NT-NT}}$ is the distance between two nearest atoms, both belonging to adjacent nanotubes, and $R_{\text{P-NT}}$ is the Van der Waals equilibrium separation between the pair of atoms. This interaction plays a role only if the concentration of carbon nanotubes is very large. In SWNT based composites, the contribution of this term is, in most cases, negligible, as the usual loading of the polymeric matrix with nanofiller is under 10%. The Van Der Waals interaction between two atoms not involved in a direct chemical bond is more efficient for MWNT and nanotube ropes, where two carbon atoms belonging to adjacent layers may interact through a Van der Waals interaction.

7.2. The Electrostatic Interactions

Certain polymers present charging capabilities. Electronic interactions among polymeric chain and carbon nanotube may be invoked. While such interactions are extremely weak at the meter scale, at nanometer scale, the effect of electrostatic interactions may be extremely important. As in the case of Van der Waals interactions, the electrostatic interactions E_{e_1,e_2} are also distance dependent;

$$E_{e_1,e_2} = k\frac{e_1e_2}{\varepsilon R_{12}} \tag{16}$$

where e_1 and e_2 are the charges of the two species, k is a constant, ε is the dielectric constant and R_{12} is the distance between the two species.

Another interaction that may be considered mainly if the polymeric matrix has an important electric dipole moment is the dipole-dipole interaction between the polymer chain and the carbon nanotube. As this potential depends on the distance raised to power 6, it is possible to formally include this contribution into the Van der Waals potential. Such an extended Van der Waals potential between the atoms of the polymeric chain and of the carbon nanotube is expressed by:

$$U_{\text{P-CNT}} = 4D_{\text{P-CNT}}\left(\frac{R_{\text{P-NT}}}{r^{12}_{\text{P-NT}}} - \frac{R^{*}_{\text{P-NT}}}{r^{6}_{\text{P-NT}}}\right) \tag{17}$$

where the ratio $R^{*}_{\text{P-NT}}/R_{\text{P-NT}}$ is a qualitative measure of the contribution of dipolar interactions.

In the case of polar polymeric matrices, the load applied to the polymer and transferred to the carbon nanotubes may induce a Stoner-Wales defect. Such a defect has a dipole moment that will interact with the dipole moment of the macromolecular chain. This may result in an apparent enhancement of the adhesion between the carbon nanotube and the polymeric matrix.

Odegard et al.[23] used a simplified molecular model (the so called equivalent truss model) to model the mechanical properties of nanocomposites based on SWNT. The introduction of the polymeric matrix required some additional hypothesis. Odegard et al.[23] assumed a transversely isotropic symmetry with the plane of isotropy perpendicular to the long axis of the nanotube. Hence, for a parallel collection of nanotubes dispersed in a polymeric matrix, they determined the elastic constants (transverse shear modulus, transverse bulk modulus, longitudinal shear modulus, longitudinal Young modulus and longitudinal elastic stiffness) from boundary conditions, by equating the potential energy of the truss model to the potential energy of the homogeneous effective fiber. This model predicts a linear increase of the ratio between the Young modulus of the composite and the Young modulus of the nanotube, as the volume fraction of nanotubes is increased.

Molecular dynamics simulations are complicated, and require long computation times and a good knowledge of the terms that are contributing to the physical properties of composites. The main limit of the simulations for CNBC is that their starting point is the ensemble of carbon nanotube or even the isolated carbon nanotubes. For a composite material, the major contribution should come from the matrix. Some simple rules, which were observed and quantified, should be used to check the reliability of these simulations.

A self-consistency test will be the reproduction of the physical properties of the polymeric matrix by setting the carbon nanotubes concentration to zero. Other self-consistency tests may be represented by conditions to recover—at least the large-scale approximation limit as an average over the whole sample—some classical results such as the rule of phases, the filler length effect, the filler orientation effect and the filler concentration effect on the mechanical properties of the composite. At the actual stage, the molecular dynamics is not able to fulfill these tasks completely. Even more, in order to decrease the computational time and the number of parameters, some elements such as the rule of phase are introduced within the model instead of being tested.

The mechanical properties of nanocomposites subjected to uniaxial loading are defined by the rule of mixtures. Within this approach, the longitudinal elastic modulus E_{LONG} is

$$E_{\text{LONG}} = f_{\text{NT}}E^{\text{NT}}_{\text{LONG}} + f_P E^{P}_{\text{LONG}} \tag{18}$$

where $E^{\text{NT}}_{\text{LONG}}$ and E^{P}_{LONG} is the longitudinal elastic modulus for the carbon nanotube and the polymer, respectively, f_{NT} is the fraction of carbon nanotubes, f_P is the polymer fraction and $f_{\text{NT}} + f_P = 1$.

The transverse modulus of the composite, E_{TRANS}, is defined by:

$$\frac{1}{E_{\text{TRANS}}} = \frac{f_{\text{NT}}}{E^{\text{NT}}_{\text{TRANS}}} + \frac{f_P}{E^{P}_{\text{TRANS}}} \tag{18a}$$

where $E^{\text{NT}}_{\text{TRANS}}$ and E^{P}_{TRANS} are the transverse elastic modulus for the carbon nanotube and the polymer, respectively. This extreme situation defines the isobaric case, in which both the matrix and the fillers carry equal levels of stresses. For spherical fillers, this case corresponds to "no adhesion".

The ultimate tensile strength for a composite with carbon nanofibers uniaxially aligned is expressed, with an acceptable accuracy, by the rule of phases:

$$\sigma_C = f_{\text{NT}}\,\sigma_{\text{NT}} + f_P\,\sigma_P \tag{19}$$

where σ_C is the tensile strength of the composite, σ_{NT} the ultimate tensile strength of the carbon nanotube fiber and σ_P is the tensile strength within the matrix at the point at which the carbon fiber is at the ultimate stress. This expression assumes a perfect interfacial bonding between the polymeric matrix and the carbon nanotube.

7.3. The Effect of Filler Length

In classical carbon fibers reinforced composites, the effect of fiber length has been studied in detail. A critical fiber length, l_C, was found. If the length of the filler is less than the critical length, the fiber will not reach the maximum stress and, hence, the composite will fail, while the fillers will not be affected. By projecting the theory developed for carbon fibers to carbon nanotubes, the following is obtained:

$$\sigma = \begin{cases} \sigma_{\text{NT}}f_{\text{NT}}\left(1 - \dfrac{l_C}{2l}\right) + f_P\sigma_M & l > l_C \\ f_{\text{NT}}\dfrac{l}{d}\tau_{\text{INTER}} + f_P\sigma_M & l < l_C \end{cases} \tag{20}$$

where l_C is the critical length of carbon nanotube, l is the nanotube's length, σ_{NT} is the strength of carbon nanotubes, σ_P is the failure strength of the polymeric matrix and τ is the interfacial shear strength.

An important simplification in the description of the physical properties on carbon nanotubes reinforced polymer composites is related to the use of periodic boundaries. The initial density of the composite may be estimated by the rule of mixture.

Within the so-called molecular mechanics approach,[37] the strain energy for a nanotube is:

$$U = \Sigma U_{AT} + \Sigma U_B + \Sigma U_T + \Sigma U_S \tag{21}$$

where the first term represents the axial tension, the second the bending, the third the torsion and the last the shear force. The force field constants are k_r, k_θ and k_τ:

$$\begin{aligned} k_r &= \frac{EA}{L} \\ k_\omega &= \frac{EI}{L} \\ k_\tau &= \frac{GJ}{L} \end{aligned} \tag{22}$$

where A is the cross sectional area of the nanotube, L is the length of the nanotube, E is the Young modulus, G is the shear modulus and J is the polar inertia of the nanotube.

8. CONTINUUM MECHANICS AND FINITE ELEMENT ANALYSIS

Continuum mechanics is frequently used to analyze and discuss various experimental results obtained on carbon nanotubes. AFM and nanoidentations techniques are frequently analyzed using such simplified approaches. Experimental nanoidentation data[3] were analyzed by assuming that the modified Halpin-Tsai equation for randomly oriented fillers is valid for such nanocomposites:

$$E_{\text{Composite}} = \frac{1}{8}\left[\frac{3 + 6\left(\dfrac{L_{\text{NT}}}{D_{\text{NT}}}\right)\eta_L V_{\text{CNT}}}{1 - \eta_L V_{\text{NT}}} + \frac{5 + 10\eta_T V_{\text{NT}}}{1 - \eta_T V_{\text{NT}}}\right]E_{\text{Polymer}}$$

$$\eta_L = \frac{\left(\dfrac{E_{\text{NT}}}{E_{\text{Polymer}}}\right) - 1}{\left(\dfrac{E_{\text{NT}}}{E_{\text{Polymer}}}\right) + 2\left(\dfrac{L_{\text{NT}}}{D_{\text{NT}}}\right)} \cdot \qquad (23)$$

$$\eta_T = \frac{\left(\dfrac{E_{\text{NT}}}{E_{\text{Polymer}}}\right) - 1}{\left(\dfrac{E_{\text{NT}}}{E_{\text{Polymer}}}\right) + 2}$$

where E_{NT}, E_{Polymer} and $E_{\text{Composite}}$ are the Young modulus for the carbon nanotubes, polymer and composite. D_{NT} is the diameter of the carbon nanotube.

Due to the relatively reduced number of atoms and to the possibility to define an extremely small cell, the simulations of the mechanical properties of carbon nanotubes within the finite size element approximation were successful. However, such simulations failed to explain the mechanical properties of the composites based on carbon nanotubes. It is possible to conclude that the thickness of the interface between the filler and the polymeric matrix is the main source of the discrepancy between polymeric composites and nanometer sized fillers. For thin interfaces, the size of the cell required for the finite size analysis has to be drastically reduced. This will result in longer calculation times and sometimes decreases in the accuracy of final estimations. As long as the finite element analysis will be based on cells characterized by the same volume (or by cells with the volume chosen in such a way that the change in the elastic properties across the cell is small) and solely linear effects will be considered, narrow interfaces, abrupt interfaces and nonlinear interactions will make the simulation of experimental data difficult.

Such a case is represented by the study of the effect of carbon nanotubes' waviness on the mechanical features of the composite[39–40] within the finite element analysis (FEA). This study was justified, as the ropes of carbon nanotubes are not exactly one-dimensional filler. Although, in principle, by choosing an appropriate cell size, FEA should be able to describe the effect of filler in polymeric matrices, the authors forced the solution by defining a cell that for parallel solicitations that obeys the rule of phase. Although the authors proved that the cell size is not a parameter of their finite size element analysis, they did that after assuming that the cells obey the rule of phase (see Equation 19). The convergence of effective reinforcing modulus E_{ERM} for sufficiently large matrix is killing the quantum effects and filler length effect, usually associated with the confinement. This analysis shows that the finite size analysis is not able to embed directly, neither the quantum effects, nor some classical results, derived from the discrete nature of the filler. To conclude, the finite element analysis has difficulties in describing the features of composites with sharp and abrupt interfaces, as well as the contribution of nonlinear effects. The artificial explanation of the effect of carbon nanotubes on the mechanical properties of polymeric matrices is reflected by the need to define, in addition, the elastic modulus of the carbon nanotube E_{NT} another parameter E_{ERM} ($E_{\text{ERM}} < E_{\text{NT}}$) that includes the waviness contribution. This extremely ingenious construction is necessary to go beyond the limitations of the finite size element in order to describe the actual properties of composites based on carbon nanotubes. Nevertheless, the expression for the parallel model of the effective cell response, as defined by the authors, cannot be associated with carbon waviness of carbon nanotubes. For perfectly aligned, one-dimensional fillers oriented along the stress direction, the Young modulus of the composite is:

$$E_{\|} = f_{\text{NT}} E_{\text{NT}}^{1D\|} + f_p E_p^{\|} \qquad (24)$$

where $E_{\text{NT}}^{1D\|}$ is the elastic modulus of the ideal 1-dimensional carbon nanotubes, when the applied force and the deformation are measured along the carbon nanofiber direction. The waviness of the carbon nanotube will introduce a component normal to the stress direction. In the ideal case;

$$\frac{1}{E_{\perp}} = \frac{f_{\text{NT}}}{E_{\text{NT}}^{1\perp}} + \frac{f_p}{E_p^{\perp}} \qquad (25)$$

While the expected deviation from 1-dimensional filler is small for short nanotubes, it increases with the length of nanotubes and becomes important in composites based on carbon ropes. The average isotropic elastic modulus, E, may be approximately defined by;

$$E = \sqrt{\left(f_{\text{NT}} E_{\text{NT}}^{1D} + f_p E_p\right)^2 \sin^2\phi + \frac{E_p^2 (E_{\text{NT}}^{1D})^2 \cos^2\phi}{\left(f_{\text{NT}} E_{\text{NT}}^{1D} + f_p E_p\right)^2}} \qquad (26)$$

where $E_{\text{NT}}^{1D\perp}$ describes the amplitude of carbon nanotube waviness. The self-consistency of this relationship may be easily tested;

$$E\Big|_{\phi=0} = \frac{E_p E_{\text{NT}}^{1D}}{\left(f_{\text{CNT}} E_p + f_p E_{\text{NT}}^{1D}\right)} = E_{\perp} \qquad (27a)$$

$$E\Big|_{\phi=\pi/2} = \left(f_{\text{NT}} E_{\text{NT}}^{1D} + f_p E_p\right) = E_{\|} \qquad (27b)$$

The expected effect of carbon nanotubes waviness is to transfer some parallel stress into a perpendicular stress. In the absence of this component, the simulation would result in a shifted value of the Poisson coefficient. The need for a micromechanical analysis is recognized.[39] Some authors developed improved approximations[32–33, 37, 40] based on the micromechanical picture to explain the mechanical properties of the composites based on carbon nanotubes. Measurements done on PAN-single-walled carbon nanotube ropes indicated that the strength of SWNT ranges between 3.6 and 22 Gpa, and that the Young modulus is less than 20 GPa (Ref. 1). A multiple shell theory has been proposed by Ru[41–42] for composites based on MWNT. By assuming that, in a MWNT, the nanotubes are concentrically nested, Ru proved that the Van der Waals interactions between nanotubes affect the buckling behavior of axially compressed nanotubes dispersed in an elastic polymeric matrix.

The finite element was used within the continuous shell theory.[27–29] Several difficulties such as an appropriate set of mechanic constants, a correct value for the wall thickness of the shell, the introduction of an initial bending stress distributed through the thickness of the tube, strong Van der Waals interactions between surface elements of the nanotube, an interval pressure dependent on the interval distance and negligible wall to wall shear resistance have been reported.[27–29] The finite element bending simulations performed by Pantano[37] revealed that the finite element based modeling should include non-linear mechanical features. It is pointed out that both the shell theory and the finite element predictions are comparable. Accordingly, both of them are not able to describe the relationship between the buckle wavelength and the geometric characteristics of the nanotube, unless the parameter h that was supposed to be the outer wall thickness is taken to be the total tube thickness.[37] This difference between the cylinder and the tube may reflect the limits of such "classical" approximations.

9. INTERFACES AND ADHESION

The improvement of the mechanical properties of polymers reinforced with carbon nanotubes was assigned to the polymer carbon nanotube interface.[39–44] Several physical properties of the polymeric matrix are also affected by carbon nanotube reinforcement. For example, the thermal stability is slightly improved, the conductivity is enhanced, and shifts in the glass and melting temperatures were reported.[39] The adhesion is not accurately defined. Some authors consider that the adhesion involves solely non-bonding interactions, while others include all contributions. The adhesion plays a major role in the physical properties of composites based on carbon nanotubes.[1, 44, 46] The interfacial strength may be measured directly by atomic force microscopy by using a nanopull-out technique.[2] Individual single-walled and multiwalled carbon nanotube bundles were detached by AFM[3] from a composite consisting of carbon nanotubes dispersed into a cured epoxy resin. Such an experiment will result in the measurement of the total adhesion, as the eventual bonding interactions between carbon nanotubes and the polymeric matrix are destroyed. The corresponding total work, W, a result of pulling out a carbon nanotube from a composite material, is assumed to be controlled by the interfacial shear stress τ. Within this approximation, the work performed to pull out a single-walled carbon nanotube with the outer radius r and the length L from the polymeric matrix is given by:[3]

$$W = \int_{x=0}^{x=L} 2\pi r(L-x)\tau dx = \pi r \tau L^2 \qquad (28)$$

From the molecular point of view, the non-bonding adhesion reflects the effect on non-bonding interactions on the interface between carbon nanotubes and the matrix. The total energy associated to this contribution has been expressed as the difference between the total energy of the composite and the sum of the nanotube and polymer energies.[17] This definition neglects the entropic effects completely.

A major point in understanding the mechanical properties of nanocomposites is associated with the adhesion between carbon nanotubes and the polymeric matrix. The most important factors contributing to the adhesion between carbon nanotubes and the polymeric matrix are:

1. The chemical (covalent) bond between carbon nanoparticles and the polymeric matrix. This has been speculated by different authors, mainly in connection to the use of sonication to disperse the carbon nanotubes within the polymeric matrix. Although covalent bonding is assumed to be a very important factor in explaining the adhesion in polymer-carbon nanotubes composites, there is no compelling experimental evidence to support it. The presence of a C-C bond between the nanotubes and the polymeric matrix has been derived from FTIR spectra of NT/polymethylmethacrylate composite,[47] while [48] Raman spectroscopy showed the absence of any covalent bond between carbon nanotubes and the polymeric matrix in the system NT/polypyrrole.
2. Electrostatic interaction. At nanometer scale, relatively low potentials are generating huge internal electric fields and some polymeric materials are known to be easily charged. The main problem is that carbon nanotubes have certain conducting properties (either semiconducting or even conducting features). As the increase in the carbon nanotube concentration is associated with an enhancement of the electric properties, it is natural to assume that, at the percolation threshold, the charge is delocalized over the whole composite. It results that, if a local ionization of the carbon nanotubes and polymer matrix is assumed to contribute to the adhesion, this contribution decays as the carbon nanotubes concentration is increased and becomes zero at carbon nanotubes concentration above the percolation threshold. The corresponding change in the energy of the composite reflects the maximum amount of energy that may be assigned to local ionization.
3. Van der Waals interaction. The contribution of Van der Waals interaction has been speculated by many authors

and discussed in detail. For such nanocomposites the volume fraction includes the contribution of Van der Waals interactions. For composite based on a (10, 10) carbon nanotube, the following is obtained:[1]

$$f_{\mathrm{CNT}} = \frac{\pi\left(R_{\mathrm{NT}} + \dfrac{\delta_{\mathrm{VW}}^{\mathrm{P-NT}}}{2}\right)^2}{S_{\mathrm{CELL}}} \tag{29}$$

where R_{NT} is the radius of the carbon nanotubes, $\delta_{\mathrm{VW}}^{\mathrm{P-NT}}$ is the Van der Waals distance and S_{CELL} is the cross section of the unit cell.

4. The simulation reported by Liao[44] indicates that the mismatch between the coefficient of thermal expansion of carbon nanotube and of polymeric matrix plays an important role in the mechanical interlocking mechanism.

5. Hydrogen bonds. Some authors use the Van der Waals like potential to derive the energy of the hydrogen bond.[6]

6. Dipole-dipole induced interactions. Such interactions are important if the polymeric matrix has an important dipole moment. The dipole-dipole interactions may be triggered by the applied load and assigned to the appearance of a dipole moment on carbon nanotubes due to Stone-Wales defects.

7. The stress induced fragmentation of carbon nanotubes in polymeric matrices.[47, 49] This contribution points toward a better adhesion between carbon nanotubes and the polymeric matrix than between the polymeric matrix and macroscopic carbon fibers. The stress transfer mechanism in carbon nanotubes has to be studied in detail in order to exploit more efficient the capabilities of nanocomposites. There is possible correlation between mechanical and electrical[48] properties of polymers filled with carbon nanotube.

10. CONCLUSIONS

The physical properties of carbon nanotubes were described with acceptable accuracy within several approximations such as molecular dynamics and continuum mechanics. Although the limitations of such models were recognized, the simplicity of the initial assumption, the reduced number of variables and the computation time are the major factors for this success. Going from isolated nanotubes to carbon nanotubes reinforced polymers, the difficulties are amplified and the predictions (simulations) based on such simplified assumptions become poorer. To balance the technical limitations (computer speed and memory capacity) with the complexity of such nanocomposites, "external" conditions are imposed. Although, in certain cases, such simulations were successful, the need to obey the rule of phase at local scale is not obvious. Nevertheless, in the case of smooth and broad interfaces, if non-linear contributions are weak, the above-mentioned approaches may result in a sounding analysis of the experimental data.

The physical properties of carbon nanotube reinforced polymers are controlled by the interface between the carbon nanotube and the polymer. Although certain models developed within the continuum mechanics approximation take into account the adhesion between the nanofiller and the matrix, further details regarding the adhesion are expected from molecular simulations. The analysis is complicated by the fact that the adhesion is not well defined at nanometer scale; it is not obvious if the covalent bond plays any role in polymeric matrices reinforced with carbon nanotubes.

To conclude, a large effort is required to improve the actual simulations of the mechanical properties of composites based on carbon nanotubes. That would provide a better understanding of molecular interactions and of adhesion, and will allow a further improvement of the mechanical properties of these composites.

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