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Coupled effect of CNT waviness and agglomeration: A case study of vibrational analysis of CNT/polymer skew plates

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ABSTRACT

The main contribution of this work lies in a critical comparison of different mean-field homogenization approaches for the study of carbon nanotube-reinforced polymers with waviness and agglomeration effects. In particular, this paper focuses on the consistency of predictions in terms of diagonal symmetry of the constitutive tensors and comparison against theoretical bounds. The analysis comprises general axisymmetric orientation distributions of fillers, both planar sinusoidal and helical wavy fillers, as well as different agglomeration schemes by means of a two-parameter agglomeration model. The results demonstrate that waviness and agglomeration simultaneously weaken the macroscopic stiffness of composites. The results also reveal that the widely used Mori-Tanaka method fails to simulate the coupled effect of these two phenomena and, therefore, it is necessary to apply extended approaches with consideration of ad hoc Eshelby's tensors that account for particular wavy microstructures. A case study of carbon nanotube-reinforced skew plates is finally presented to illustrate the coupled effect of waviness and agglomeration on the macroscopic vibrational behavior.

1. Introduction

Over the last decade, numerous publications have reported about the outstanding enhancements of the mechanical properties of polymeric matrices doped with small concentrations of Carbon Nanotubes (CNTs) [1,2]. Since the mechanical behavior of CNT-reinforced composites is crucially dominated by their microstructure, a reliable dimensioning has to take into consideration their properties as accurately as possible. Three major features are typically distinguished, namely filler statistical orientation distribution, waviness, and agglomeration. Firstly, fillers orientations are governed by complicated flow fields induced by the manufacturing process. Notwithstanding there exists a number of techniques of aligning CNTs (see e.g. [3–5]), most procedures lose effectiveness when embedding the nanotubes throughout the matrix material [6] and, thus, CNTs orientations are typically of statistical nature. Secondly, it has been extensively reported in the literature that due to a high aspect ratio, up to 10^6 [1], as well as a very low bending stiffness, CNTs usually exhibit a certain degree of waviness [7,8]. Finally, given the electronic configuration of the tube walls and their high specific surface area, CNTs tend to agglomerate and form bundles due to large van de Waals (vdW) attraction forces [9–11]. Although there exists a variety of techniques to improve the dispersion of fillers, including the use of dispersants or sonication, the achievement of uniform CNT dispersions is still an intricate task. On the whole, accurate homogenization approaches must allow for considering the coupled effect of waviness and agglomeration.

In order to calculate the effective material properties using microstructural data, several homogenization methods have been proposed in the literature. Since Molecular Dynamics (MD) and multi-scale finite element simulations [12–15] are limited to systems with a small number of atoms due to computational limitations, approaches based on the mean-field homogenization theory have drawn considerable attention. In particular, a large number of recent works in the realm of CNT nanocomposites have been undertaken using the Extended Rule of Mixtures (EROM) [16–18] and the Mori-Tanaka (MT) method [19–21]. The EROM is based upon a modification of the classical Voigt (VT) and Reuss (RS) bounds by the so-called efficiency parameters in order to match the results from a MD or multi-scale simulation [22]. Although many authors have been attracted by the simplicity of this approach, the EROM requires a more sophisticated simulation to tune the efficiency parameters and can only model singular filler configurations. The MT model, on the contrary, allows for the simulation of more complex configurations such as misoriented distribution of fillers, as well as curviness and agglomeration effects [23]. However, although the MT method apparently provides a favorable theoretical framework for the consideration of general arrangements of CNTs, a few research

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works in the literature report that the MT method may provide diagonally asymmetric stiffness tensors, as well as may violate the Hashin-Shtrikman-Walpole (HSW) bounds [24–27]. In the light of these deficiencies, some authors have sought alternative approaches. Amongst those, it is worth noting the contribution by Ferrari [28], and later extended by Dunn et al. [29] (DUN), who proposed to use the strain-concentration tensor given by that of the MT method for perfectly aligned fibers. Another relevant work was the one by Schjødt-Thomsen and Pyrz (STP) [30] who proposed a novel micromechanics approach based upon the direct integration of the MT stiffness tensor for perfectly aligned inclusions. More recently, Zhupanska [31] studied the applicability of the MT method to estimate the elastic moduli of buckypaper doped with Single-Walled CNTs (SWCNTs). In the case of randomly oriented SWCNTs, his results showed that the MT method only provides results comprised between the HSW bounds for moderate filler contents, yielding inadmissible results for high filler concentrations.

All studies agree on the detrimental impact of curviness on the mechanical properties of CNT/polymer nanocomposites. Finite element simulations were proposed by Fisher et al. [32] and Bradshaw et al. [33] to analyze the planar sinusoidal parametrization of CNTs proposed by Hsiao and Daniel [34]. Another noteworthy contribution was done by Shi et al. [23] who extended the MT method for three-dimensional helical CNTs. In that work, their results showed that composites doped with aligned wavy CNTs experience critical reductions in the longitudinal modulus, whilst the lateral moduli slightly increase. Yanase et al. [35] proposed an ad hoc Eshelby's tensor (YNS) to account for planar sinusoidal CNTs. In their model, the integration of localized changes in orientation was combined with the MT model to derive closed-form solutions of the effective stiffness. Matveeva et al. [36] studied both sinusoidal and helical models by finite element-based homogenization methods, analytical models and MD simulations. It was shown that both geometries significantly reduce the longitudinal elastic stiffness of the composite for fully aligned wavy fillers.

A second important feature of the microstructure is related to the tendency of CNTs to agglomerate in bundles. A noticeable contribution in this respect is the work by Shi et al. [23] who introduced a two-parameter agglomeration model. That approach consists of considering agglomerates as ellipsoidal inclusions so that one can conduct the homogenization process in two separate steps. Their results demonstrated substantial decreases in the elastic moduli of composites, what supports the widespread idea of agglomeration as microstructural defects. Although only a few works report about this issue, the two-parameter agglomeration method has been widely accepted. For instance, numerous efforts have been made to study the influence of agglomeration on the mechanical response of CNT-reinforced structural elements (see e.g. [37–40]).

In this study, a critical comparison of different mean-field homogenization approaches for the estimation of the elastic moduli of SWCNT-reinforced polymer composites is presented. For different filler axisymmetric orientation distributions, the suitability of the MT, SC, DUN and STP approaches is assessed in terms of diagonal symmetry and comparison against the HSW and VT/RS bounds. Microstructural features such as CNT volume fraction, aspect ratio, and chirality are also investigated. Afterward, approaches concerning waviness effects, namely the MT, STP and YNS models, are analyzed for both sinusoidal and helical geometries. The influence of CNT agglomeration is studied through the two-parameter agglomeration framework. Most studies limit themselves to the consideration of waviness and agglomeration effects acting independently. However, both phenomena are simultaneously found in practice. The results of this work show that the MT method fails to simulate the coupled effect of these two phenomena, given that its estimates for random filler arrangements are insensitive to waviness. In addition, it is evidenced that the MT predictions for composites doped with fully aligned wavy CNTs are highly asymmetric. By considering the combination of the YNS approach and the two-parameter agglomeration model, it is noted that the weakening effects of waviness and agglomeration add up when acting simultaneously. In addition, comparison analyses with experimental data are presented to illustrate the importance of the coupled effect of waviness and agglomeration for moderate filler contents. Finally, a case study is also presented to illustrate the coupled weakening effect of filler waviness and agglomeration on the macroscopic dynamic behavior of CNT-reinforced skew plates.

Table 1
Abbreviations used throughout the present paper for proper handling.

DE	Dilute Eshelby
MT	Mori-Tanaka
SC	Self-consistent
STP	Schjødt-Thomsen and Pyrz
DUN	Dunn
YNS	Yanase
L-HSW	Hashin-Shtrikman-Walpole lower bound
U-HSW	Hashin-Shtrikman-Walpole upper bound
RS	Reuss bound
VT	Voigt bound

The remainder of this paper is organized as follows: Section 2 concisely presents the micromechanics approaches used in this research work. Section 3 presents the used approaches for analyzing the waviness effects, both for planar sinusoidal and helical geometries. Section 4 describes the basis of the two-parameter agglomeration model. Finally, Section 5 includes the numerical results and discussion, and Section 6 concludes the paper.

Throughout the paper, a boldface letter stands for a fourth-order tensor, $\mathbf{A} \equiv A_{ijkl}$, and a colon between two tensors denotes inner product, $\mathbf{A}:\mathbf{B} \equiv A_{ijkl}B_{klmn}$.

Abbreviations. To distinguish the regarded methods, several abbreviations have been introduced as a reference for readership in Table 1.

2. Mean-field micromechanics modeling

2.1. Fundamentals of effective medium theory

Let V denote the Representative Volume Element (RVE) of a polymer matrix doped with a sufficient number of CNTs in such a way that the overall properties of the composite are statistically represented [41]. It is assumed that CNTs are transversely isotropic inclusions dispersed according to an arbitrary Orientation Distribution Function (ODF). The matrix is defined as isotropic and perfect bonding between phases is assumed. In accordance with the notation of Hill [42] and Walpole [43], the tensor of elastic moduli of CNTs, $\mathbf{C}_f$, can be noted as $\mathbf{C}_f = (2k_r, l_r, n_r, 2m_r, 2p_r)$, where k_r, l_r, m_r, n_r and p_r are fiber Hill's elastic moduli; k_r is the plane-strain bulk modulus normal to the fiber direction, n_r is the uniaxial tension modulus in the fiber direction, l_r is the associated cross modulus, m_r and p_r are the shear moduli in planes normal and parallel to the fiber direction, respectively. Similarly, the matrix phase can be noted as $\mathbf{C}_m = (3\kappa_m, 2\mu_m)$, with κ_m and μ_m being the matrix's bulk and shear moduli, respectively. In conjunction with the used notations, the constitutive matrix for inclusions with transversely isotropic properties (with $x_1''-x_3''$ as the isotropy plane) takes the form:

$$\mathbf{C}_f = \begin{bmatrix} k_r + m_r & l_r & k_r - m_r & 0 & 0 & 0 \\ l_r & n_r & l_r & 0 & 0 & 0 \\ k_r - m_r & l_r & k_r + m_r & 0 & 0 & 0 \\ 0 & 0 & 0 & p_r & 0 & 0 \\ 0 & 0 & 0 & 0 & m_r & 0 \\ 0 & 0 & 0 & 0 & 0 & p_r \end{bmatrix} \tag{1}$$

In order to describe the filler orientations, a reference local coordinate system $\mathrm{K}'' \equiv \{0; x_1'' x_2'' x_3''\}$ is fixed in each fiber. In this paper, it is assumed that all the inclusions are equal and defined as ellipsoids with aspect ratios $a_1 = a_3 < a_2$, being the semi-major axis aligned in the local