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Influence of carbon nanotube waviness on the stiffness reduction of CNT/polymer composites

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ABSTRACT

The degree to which the non-straight shape of carbon nanotube (CNT) affects the mechanical properties of CNT-based composites is studied. The effective scale of CNT curvature is determined using top-down scanning and then appropriate representative volume element encompassing of several straight and/or non-straight CNTs is defined. A multi-scale modeling relying on bottom-up approach is employed and CNT curvature is taken into account as a random parameter to capture any arbitrary non-straight shapes of CNTs. Comparing obtained results from developed modeling with available experimental data, the developed modeling procedure is validated. The results demonstrate that non-straight shape of CNT considerably reduces its efficiency to reinforce polymer matrix. It is observed that low contents of CNT enhance Young's modulus of polymer more efficiently due to the lower level of CNT waviness and agglomeration. The results exhibit non-linear variations in the Young's modulus of CNT-based composites versus CNT contents which was approved by experimental observations.

1. Introduction

Possessing exceptional mechanical, thermal and electrical properties, carbon nanotubes (CNTs) are received extreme interests among researchers as a potential reinforcing agent of polymeric composites [1–3]. Predicting mechanical properties of CNT/polymer composites plays an important role in their development process and industrial applications. The experimentally observed significance growth in mechanical properties of polymer by adding small portion of CNTs [4,5] has stimulated several researchers to develop proper technique to predict mechanical properties of CNTRP (Carbon Nanotube Reinforced Polymer).

Direct application of developed micromechanics rules to CNTRPs are not recommended, since basic assumptions of these rules are not valid for them. Reinforcing agents are considered as a continuum media in micromechanics, while CNT is a lattice structure. Moreover, due to the non-bonded van der Waals (vdW) interactions between CNT and surrounding polymer, the assumption of perfect bonding between reinforcing agent and surrounding resin which is treated in micromechanics rules are not applicable to CNTRP.

It is revealed that embedded CNTs significantly appear in the form of non-straight shapes in matrix [6–8]. This stems not only from their very high aspect ratios (L/D) which will be resulted in low bending modulus (EI/L); but also from induced uncertainties during the processing of CNTRP. The non-straight shapes of CNTs play a key role in weakening capability of CNT as reinforcement in comparison with straight CNTs. Consequently, neglecting non-straight shapes of CNTs is the key factor in different studies mechanical properties determined by theoretical models and corresponding ones measured experimentally.

Performing a review on literature, it can be understood that considerable efforts have been dedicated to the theoretical studies to predict mechanical properties of CNTRP [9,10]; while limited embedded CNT in polymer [11–21]. All aforementioned studies are suffering from common shortcomings which can be outlined as below.

In almost all conducted studies, CNT was simply replaced with 1-TPa solid fiber to determine the influence of CNT curvature on mechanical properties of CNTRP [11–21]. Therefore, actually the influence of fibrous-inclusion curvature on the mechanical properties is studied. In addition to the ignorance of CNT lattice structure, perfect bonding is also assumed between CNT and surrounding polymer by neglecting interphase region. In the majority of aforesaid investigations, sinusoidal pattern accounts for non-straight shapes of fibrous inclusion failing to address generalized form of non-straight shapes. More importantly, the selected unit-cell in mentioned researchers contains one single embedded wavy CNT which is not representative of total analyzed material region. Li and Chou [22] have studied the failure of CNT/polymer concentrating on a material region enriched with several CNTs; whereas the other abovementioned drawbacks are still pertinent to their study.

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Some researchers have modified available micromechanics rules to fit experimental data by introducing correction factor in the formula to capture agglomeration and/or waviness issue [23–25]. Determination of introduced correction factor is performed using sets of experimental observations.

The main objective of this article is to study the influence of non-straight shape of embedded CNT on reduction of stiffness CNT/polymer composite using multi-scale modeling technique. A proper modeling is developed to overcome aforementioned shortcomings of current methods for studying the influence of non-straight CNT on stiffness reduction in CNTRP. The developed modeling procedure is explained and it is executed to obtain mechanical properties of CNTRP in presence of any arbitrary non-straight shapes of CNT. The effective scale wherein waviness affects the properties is identified and then suitable RVE (Representative Volume Element) containing numerous curved CNTs are defined and analyzed.

2. Modeling procedure

CNT is a reinforcing agent at nano-scale; however, mechanical properties of CNTRP (Carbon Nanotube Reinforced Polymer) are subjected to be characterized at macro-scale. The wide ranges of involved scales, starting from nano and lasting in macro scale necessitate employment of multi-scale modeling approach. A top-down scanning is performed to distinguish effective parameters of different involved scales. The material region at macro-scale is partitioned into smaller constitutive blocks as shown in Fig. 1. Random volume fraction is assigned to each and every single constructive block in order to capture the material inhomogeneity originated from non-uniform dispersion of CNTs. The average of volume fractions in each block is consistent with the overall volume fraction of investigated material region.

The mechanical properties (Young's modulus and Poisson's ratio) of each block are evaluated at the lower scale of meso. At this scale, CNTs are oriented in different directions and they can appear in both straight and/or non-straight shapes. They can also locally concentrate inside the block to form local agglomerations at this scale. Therefore, both agglomeration and waviness issues have to be considered at the scale of meso. Mechanical properties of these blocks can be calculated using improved Mori–Tanaka model which was successfully developed by Shi et al. [17]. Moreover, it is able to address the random orientations of inclusions and interaction between them. The improved Mori–Tanaka model considers reinforcement in the form of cylindrical inclusion.

The bulk modulus (K) and shear modulus (G) of mentioned block is obtained by improved Mori–Tanaka model using below equations [17]:

$$K = K_{out}\left[1 + \frac{\mu\left(\frac{K_{in}}{K_{out}} - 1\right)}{1 + \alpha(1-\mu)\left(\frac{K_{in}}{K_{out}} - 1\right)}\right] \tag{1}$$

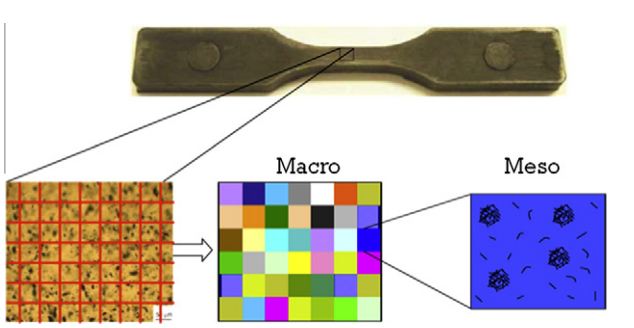

Fig. 1. Partitioning CNTRP at macro scale into constitutive blocks at meso scale.

$$G = G_{out}\left[1 + \frac{\mu\left(\frac{G_{in}}{G_{out}} - 1\right)}{1 + \beta(1-\mu)\left(\frac{G_{in}}{G_{out}} - 1\right)}\right] \tag{2}$$

where μ accounts for volume fraction of aggregates with respect to the total volume of the block and κ denotes volume fraction of CNTs inside the aggregates. Therefore, the improved Mori–Tanaka model is a two-parameter model taking into account agglomeration [17]. Other parameters in Eqs. (1) and (2) are calculated using below formulations [17]:

$$\alpha = \frac{1 + \nu_{out}}{3(1 - \nu_{out})} \tag{3}$$

$$\beta = \frac{2(4 - 5\nu_{out})}{15(1 - \nu_{out})} \tag{4}$$

$$K_{out} = K_m + \frac{f_r(1-\kappa)(\delta_r - 3K_m\alpha_r)}{3[1 - \mu - f_r(1-\kappa) + f_r(1-\kappa)\alpha_r]} \tag{5}$$

$$G_{in} = G_m + \frac{f_r\kappa(\eta_r - 2G_m\beta_r)}{2(\mu - f_r\kappa + f_r\kappa\beta_r)} \tag{6}$$

$$G_{out} = G_m + \frac{f_r(1-\kappa)(\eta_r - 2G_m\beta_r)}{2[1 - \mu - f_r(1-\kappa) + f_r(1-\kappa)\beta_r]} \tag{7}$$

$$\nu_{out} = \frac{3K_{out} - 2G_{out}}{6K_{out} + 2G_{out}} \tag{8}$$

where K_m, G_m and f_r are the bulk modulus of matrix, shear modulus of matrix, CNT volume fraction, respectively. α_r and β_r are Hill constants for cylindrical inclusion [17].

Prior to the application of improved Mori–Tanaka model at the scale of meso, two modifications are employed to adjust the model for investigated constitutive block.

Firstly, in contrast with other investigations wherein micromechanics rule is directly applied to obtain the properties, indirect application of improved Mori–Tanaka is employed using equivalent fiber phenomenon. Equivalent fiber consists of CNT and its surrounding interphase which is perfectly bonded to polymer. In other word, the constitutive block at the scale of meso comprises of equivalent fiber instead of CNT accounting for CNT and polymer interaction. A full range of equivalent fiber properties is obtained by Shokrieh and Rafiee [26] for different ranges of CNT length using FEM at micro-/nano-scale. They have considered non-bonded vdW interactions between CNT and polymer. It was reported that developed equivalent fiber is a transversely isotropic material. The longitudinal Young's modulus of equivalent fiber versus CNT length is shown in Fig. 2. It can be understood from Fig. 2 that Young's modulus is significantly lower than 1-TPa value as a Young's modulus of isolated CNT. It should be pointed out that when the length of CNT is more than 10,800 nm, the Young's modulus of equivalent fiber approaches to a bonding value as 649 GPa. Transverse modulus of equivalent fibers is 11.2 GPa regardless of CNT length. The probability density function of CNT length distribution in matrix is experimentally characterized by Wang et al. [27]. They have reported that dispersed SWCNT length varies from 150 to 1700 nm in resin. Consequently, each length of CNT is considered as a new inclusion phase in the Mori–Tanaka model.

Second modification is applied in order to capture the non-straight shape of embedded CNTs. Transverse and longitudinal stiffness of the unit-cell containing straight equivalent fiber is calculated for each and every length of CNT. The stiffness of a unit-cell containing non-straight equivalent fiber along longitudinal/transverse direction is placed between two aforementioned bounding limits depending on the non-straight shape. Thus, a random value is selected between dictated bounding values reflecting any arbitrary non-straight shape. Reflecting any desired non-straight shape, the explained strategy will reduce effective longitudinal/