MULTISCALE MODELLING OF CARBON NANOTUBE–REINFORCED POLYMER COMPOSITES

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Abstract In this article, a multiscale modelling that combines molecular dynamics (MD) with micromechanics and homogenisation techniques was developed to determine the effect of carbon nanotube's (CNT) waviness and agglomeration on the bulk properties of CNT-reinforced thermoset composites. MD simulations were first conducted to determine the effective elastic modulus at the nanoscopic level using a constant-strain energy minimization technique. To account for the marked discrepancy in the literature between existing modelling predictions and experimental findings, CNTs of different curvatures and bundle sizes were appropriately considered in our simulations. To scale up the elastic properties to the microscopic level, micromechanics approach of the Mori-Tanaka type was then used. The predictions of the current multiscale model are in good agreement with existing experimental findings indicating that waviness and agglomeration of CNTs limit their reinforcement effect and thus explain the reasons for the marked discrepancy between existing grossly idealised models and the experimental findings.

INTRODUCTION

Owing to their remarkable mechanical and physical properties, a few weight percentages of CNTs can significantly improve the mechanical, electrical, and thermal properties of CNT-reinforced polymer composites [1-4]. The presence of CNT agglomerates limits the reinforcement effect of the CNTs due to their slippage within the bundle [2]. This slippage limits the stress transfer between the CNTs within the bundle as well as between the CNTs and the surrounding polymer matrix [2]. Due to their extremely high aspect ratio and very low bending stiffness, CNTs tend to curve when dispersed in polymer matrices, resulting in a nanocomposite with properties that vary significantly in different directions [1]. Earlier models that considered polymer nanocomposites reinforced with isolated well-dispersed straight CNTs predicted mechanical properties that are much higher than the experimental measurements [2, 3]. To overcome these simplified models, we developed a multiscale model, based on molecular dynamics simulations and micromechanical modeling techniques, to evaluate the effect of CNT waviness and agglomeration on the elastic properties of CNT-polymer nanocomposites. First, MD simulations of a wavy CNT embedded in an epoxy matrix was conducted to determine the effective elastic moduli at the nanoscale level. Then, Mori-Tanaka micromechanical technique was used to scale up the nanoscale properties to the microscale level. The obtained numerical results were validated with recently obtained experimental findings. Our results reveal the detrimental effects of CNTs waviness and agglomeration on bulk properties.

MULTISCALE MODELING

All MD simulations were conducted with large-scale atomic/molecular massively parallel simulator (LAMMPS). Interactions between the CNT and the polymer molecules were nonbonded interactions that originate from the van der Waals (vdW) and electrostatic forces. Epoxy matrix based on DGEBA resin and TETA curing agent was used in the current study. The properties of the neat epoxy were taken from our earlier study [2]. MD simulations were conducted for RVEs reinforced with either well dispersed or agglomerated wavy CNTs of different waviness (curvatures). To study the effect of CNT waviness, CNTs were considered to have a sinusoidal shape; as defined by:

$$y = a\cos\left(\frac{\pi z}{2\lambda}\right) with\ z \in [0, \lambda] \tag{1}$$

where a and λ are the amplitude and the quarter wavelength of the wavy CNT, respectively. The parameter $\alpha = a/\lambda$ is used as a shape parameter that defines the degree of curvature of the CNT. Seven curved single wall CNTs were generated and equilibrated before using them as reinforcements in the RVE of the nanocomposites. Armchair (5, 5) CNTs of length 256 Å were considered for all the simulations. The combined influence of CNT waviness and agglomeration was examined by considering RVEs reinforced with individual and agglomerated bundles of wavy CNTs, as shown in Fig. 1. Curved CNTs have reinforcement effects on both the chord and the transverse directions. Therefore, in order to determine the properties of a nanocomposite reinforced with wavy CNTs, the RVEs were assumed to be orthotropic. Accordingly, nine independent material constants are required to fully define the elastic stiffness matrix of the RVE. A series of MD simulations were carried out to determine the elastic moduli of the RVEs using the constant-strain energy minimization method. Predefined displacements were applied on the MD unit cell and the obtained viral stress tensor was then used to determine its effective stiffness constants. The averaged stress tensor of the MD unit cell was defined in the form of a virial stress [2]; as follows:

$$\sigma = \frac{1}{V}\sum_{i=1}^{N}\left(\frac{m_i}{2}{v_i}^2 + F_i\, r_i\right) \tag{2}$$

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where V is the volume of the RVE; v_i, m_i, r_i and F_i are the velocity, mass, position and force acting on the ith atom, respectively. The obtained stiffness tensors of the RVEs from the MD simulations were then used as an input to the micromechanical model to aid in the determination of the bulk properties.

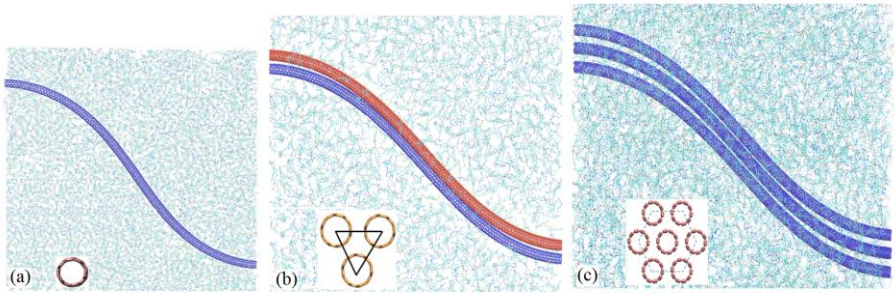
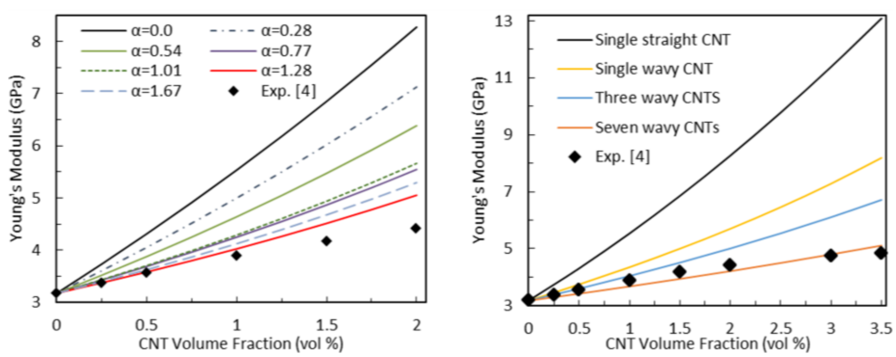


Fig. 1. MD unit cells representing RVEs reinforced with (a) single CNT (α=0.54), (b) bundle of three CNTs (α=0.54), and (c) bundle of seven CNTs (α=0.54).

RESULTS AND DISCUSSION

Figure 2(a) shows the predicted variation of Young's modulus of nanocomposites reinforced with randomly oriented wavy CNTs. The model predicts that the bulk elastic properties of the nanocomposite are reduced significantly with increasing the CNT curvature. However, the effect of waviness stabilizes after α=0.75, due to a reduction in the longitudinal and the simultaneous increase in the transverse elastic constants of the effective fiber upon reaching this curvature. Figure 2(b) shows the variation of the effective Young's modulus of the nanocomposite with the CNT loading for the three agglomeration cases, the well-dispersed straight case, and the experimental results for a similar nanocomposite system obtained from the literature [4]. The results indicate that the CNT agglomeration has a significant effect on the bulk elastic properties of the nanocomposite and this effect increases with the increase in the number of CNTs in the bundle.



(a) (b)

Fig. 2. Effect of CNT (a) waviness and (b) agglomeration on the bulk Young's modulus of CNT-epoxy composites.

CONCLUSIONS

We developed a multiscale model to determine the effect of CNT waviness and agglomeration on the bulk elastic properties of CNT-reinforced epoxy composites. The results show good agreement between the developed model and the reported experimental results; thus validating the modeling procedures developed in this study and emphasizing the importance of the inclusion of CNT waviness and agglomeration in future models.

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