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Interphase effect on the macroscopic elastic properties of non-bonded single-walled carbon nanotube composites

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ABSTRACT

Compared to the small diameter of a carbon nanotube (CNT), the thickness of the CNT–matrix interphase in a CNT–composite is considerable. Hence, the interphase property can significantly influence the macroscopic properties of the composite. This paper applies an effective multi-scale method to explore such an interphase effect on the properties of nano-composites reinforced by single-walled CNTs. The method integrates the van der Waals (vdW) gap interphase, the dense interphase, and the randomly distributed wavy CNTs in a matrix to realize an accurate prediction of macroscopic properties with a nanoscopic resolution, by using a conventional finite element code commercially available. The study concluded that with the same volume fraction, increasing CNT waviness and diameter reduces the composite Young's modulus, and that ignoring either the vdW gap interphase or the dense interphase can lead to an erroneous characterization, and that both interphases can be ignored in some circumstances.

1. Introduction

Many experimental and theoretical studies on carbon nanotubes (CNTs) have shown that they have exceptional mechanical properties [1]. Hence, CNTs, both single-walled (SWCNT) and multi-walled (MWCNT), have been considered to be promising reinforcing materials to make engineering nano-composites of tailored mechanical properties. CNT–matrix interphase is a transient region between the external surfaces of CNTs and the bulk matrix of a CNT–composite. Compared to the small diameter of a CNT, the thickness of the interphase is considerable, which bonds the CNTs to the matrix and plays an important role in determining macroscopic properties of the composite [2,3]. In the case of a non-bonded CNT–composite, there are two distinct interphase regions. One is the vdW interphase, which is the gap distance between the CNT atoms and those in the internal surface of the matrix surrounding the CNT [4]. The other is the adsorption layer interphase, which often has a greater density than the bulk matrix [5,6], hence is called a dense interphase. In some studies the vdW gap interphase was assumed to be the only interphase region [7–9] with certain thickness and mechanical properties. The effect of the vdW interphase on the nano-composite properties have been investigated to a certain extent. For example, Tan et al. [10] studied analytically and reported that the vdW interphase debonds and weakens the composite when the material is subjected to a large strain. The spring element in a finite element has been used to treat CNT–composites [11–14]. For example, Shokrieh and Rafiee [12] used spring elements in a finite element analysis to treat the vdW interactions between the CNT atoms and the surrounding matrix. They claimed that the CNT–composite would have a non-linear behaviour under a large strain. Using the atomistic simulation, Tsai et al. [7] characterized the vdW interphase considering the non-bonded energy between an SWCNT and matrix. They found that the interphase has a major effect on the transverse Young's modulus of aligned SWCNT–composites. The role of the dense interphase has also been studied. Odegard et al. [3] developed a continuum-based elastic micromechanical model and concluded that the interphase influence would diminish if the diameter of a nano-filler is greater than 200 nm. Wang et al. [15] developed an FE code to include the interphase effect on the overall properties of nano-composites with different inclusion shapes. They concluded that the interphase is effective when the nano-filler diameter is less than 20 nm. Although the shape and

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material of SWCNTs is different from those studied by Odegard and Wang, the diameter of an SWCNT (~1 nm) is much less than the maximum effective diameter claimed by Odegard and Wang. Thus one can imagine that the interphase of SWCNTs is very effective. In their micro-mechanical model, Yang et al. [5] treated the combined vdW gap interphase and SWCNT as an inclusion, but the combined dense interphase and matrix as a new matrix. They reported that a weaker interphase would make the elastic modulus smaller, except that in the longitudinal direction of the SWCNTs.

Recently, the authors [6] proposed a comprehensive nano-scale representative volume element (NRVE) for characterizing SWCNT–PVC composites. This NRVE is capable of accommodating the coupled contribution of all phases associated with a CNT–composite unit: the matrix, the dense interphase, the vdW gap interphase and the SWCNT. The vdW gap interphase and the SWCNT were regarded as an equivalent solid fibre (ESF). They then characterized the elastic properties of each phase by atomistic simulation and implemented within a three-phase continuum-based FE model. Their investigation showed that the NRVEs have transversely isotropic properties and that the vdW gap interphase is softer but the dense interphase is stiffer than the bulk matrix. They concluded that ignoring an interphase region would bring about erroneous predictions of the elastic parameters of the NRVE, particularly its transverse Young's modulus and the out-of-plane shear modulus. However, their results were limited to a special case with straight SWCNTs. In reality, nevertheless, CNTs in a composite are highly wavy because of their flexibility and extremely high aspect ratio of length to diameter [16,17]. To the best of our knowledge, the effect of interphase on the overall elastic properties of composites with wavy SWCNTs has not been studied yet.

Some models have been developed to study the effect of wavy CNTs. Some of them treated the CNTs as uniform fibres of a sinusoidal wavy shape [18,19], and simplified them as a bow wavy shape [20,21]. These assumptions are inconsistent with the actual geometries of wavy CNTs in a CNT–composite [16,17]. Recently, the authors proposed a technique for characterizing the waviness of CNTs, together with the new defined concept of waviness angle an algorithm was developed to generate wavy CNTs consistent with experimental observations [22]. Their method was verified by experimental and can be considered reliable for studying the effect of SWCNT waviness.

This paper will develop a multi-scale method to explore the impact and contribution of each of the interphases outlined above on the overall elastic properties of non-bonded, randomly wavy SWCNT–composites. 1D (aligned) and 3D distributed SWCNTs with different waviness angles will be constructed and implemented in an FE platform for stress analysis.

2. Multi-scale modelling

The primary strategy of our multi-scale modelling is illustrated in Fig. 1. The basic element includes a theoretically infinitely long straight SWCNT embedded in an amorphous PVC matrix [6] and thus the shear lag effect is not studied. Since the dimension of the element is much less than 100 nm, it is called an NRVE. In a CNT–composite, the volume fraction of CNTs is always low, rarely reaching 20% (*e.g.* Ref. [23]). It is therefore rational to assume, when the CNTs are dispersed well in the composite in manufacturing, that each CNT is surrounded fully by the matrix, and that the distance between individual CNTs is much larger than the thickness of an individual CNT–matrix interphase. Hence, the contact between CNTs and that between CNT–matrix interphases does not need to be considered in the modelling. As a result, the atomistic model of NRVE (A-NRVE) under a periodic boundary condition can be big enough to avoid any artificial effect of interphase or CNT contacts. Although, A-NRVE has been characterized with the aid of molecular dynamics (MD) and molecular mechanics (MM) [6], the authors have proposed an efficient and flexible continuum based three-phase model [6] enables to characterize a minimum NRVE dimension confined by the external diameter of the dense interphase layer, called 3P-NRVE model, as shown graphically in Fig. 1. With 3P-NRVE model, we can evaluate the transversely isotropic elastic properties of the 3P-NRVE, which takes into account all the atomistic interactions. When the 3P-NRVE is applied to a greater scale analysis, it can be treated as a homogeneous solid NRVE (S-NRVE). In this way, the calculation will be efficient but the lower scale (atomistic and interphase) effects are already included. A series of S-NRVEs can then be assembled to build up a randomly wavy SWCNT-fibre, as illustrated in Fig. 1. Compared to a square cross section, a circular cross section fibre can be a better representative of CNTs. In an FE modelling, however, it needs a fine mesh generation on the cross section. In contrast, square cross section fibres can be assembled with a series of single cubic homogenized elements which need much less computational cost while including all nanoscopic effects. A micro-scale representative volume element (MRVE) can therefore be obtained by assembling such SWCNT-fibres with the surrounding PVC matrix. Such an MRVE is ready to be used for an efficient finite element analysis but with the atomistic and interphase effects counted. More details about the S-NRVE of the above strategy will be explained in the following sections.

2.1. Elastic properties of S-NRVE

The elastic properties of S-NRVE can be obtained by transferring those of 3P-NRVE using the method developed by the authors previously [6]. A 3P-NRVE includes three phases: the ESF, the dense interphase and the bulk matrix, as illustrated in Fig. 1. To explore the diameter effect on the properties of the 3P-NRVE, a variety of SWCNTs, with typical diameters ranging from 6.76 Å of SWCNT (5, 5) to 26.18 Å of SWCNT (20, 20), were used to construct the corresponding 3P-NRVEs. The elastic properties of ESF were from our previous work [6]. It has been shown that the dense interphase of PVC has a thickness of 3 Å, Young's modulus of 17 GPa, and Poisson's ratio of 0.40 [6]. The Young's modulus and Poisson's ratio of the bulk PVC are 3.6 GPa and 0.38, respectively [24]. The overall elastic properties of 3P-NRVE can therefore be obtained by a 3D finite element analysis as explained in detail in Ref. [6]. This gives rise to the five elastic moduli of the corresponding S-NRVE, as listed in Table 1. Rows A–D represent the schemes of: (A) all phases included, (B) vdW gap interphase excluded, (C) dense interphase excluded, and (D) both dense interphase and vdW gap excluded. The elastic properties of the bulk PVC from our previous atomistic simulation [6] and the experimental results available [24] are $E_m = 3.6$ GPa and $\nu_m = 0.38$ [25].

2.2. Elastic properties of MRVE

The wavy SWCNT-fibres could be generated based on the algorithm developed by Ref. [22] in which a wavy SWCNT-fibre is assembled as a cord of a sequential random walking segments. Each cord starts from a boundary plane of an MRVE and continues in a random direction (it in most cases goes across another boundary plane). Each new point on the cord is generated on the base of a right circular cone, see Fig. 2. The apex of the cone is located at the end point of the last segment and the axis of the cone is coincident with the orientation of that segment. With a pre-determined walking distance of d_s, the only variable is the waviness angle, θ_{max}, which is the maximum angle of the cones that can be