INVESTIGATION ON INTERFACIAL PROPERTIES OF CNT/ALUMINA NANOCOMPOSITES USING PULL-OUT SIMULATION BASED ON MOLECULAR MECHANICS

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1 Introduction
Carbon nanotube (CNT) has attracted widespread attention in the fields of polymer and ceramics based composites. As for mechanical properties of CNT/ceramics composites, the interfacial properties between CNT and ceramics matrix is a key issue. However, all of previous studies are limited to the interfacial properties between CNT and various polymer matrices, or between two neighboring walls in a multi-wall carbon nanotube (MWCNT) [1]. In this work, as an extension of our previous work [1], molecular mechanics (MM) simulations of the pull-out process of a CNT from an alumina matrix using the Materials Studio (Accelrys) were carried out, aiming at investigating the interfacial characteristics in CNT/ceramics composites.

2 Model Construction and Simulation Method
In a previous work [2], it was identified that CNTs were generally located in alumina (α-Al₂O₃) grain boundary (GB). Therefore, as shown in Fig. 1, a CNT was modeled to be located in GBs with only consideration of the effects of van der Waals (vdW) and electrostatic Coulombic interactions at interface. The average distance between the outermost wall of the CNT and the inner surface of alumina matrix was intentionally set to be 0.34nm. Four types of GBs [3], i.e., Σ19, Σ31, Σ3 and Σ7, were used. The pull-out process (Fig. 1) included the following two steps: (1) one end of alumina matrix (x=0) was fixed; and then (2) the opposite end of the CNT was pulled out gradually in the x-axis direction by a constant displacement increment ∆x (0.2nm). After each pull-out step, the structure was relaxed to obtain the minimum systematic potential energy.

3 Results of Single-Wall Carbon Nanotube
To explore the influence of GBs on the pull-out behaviors, a single-wall carbon nanotube (SWCNT), i.e., SWCNT(5,5) of the diameter D of 0.678nm and the length l of 5.165nm, was used. The energy increments (∆E) between two consecutive pull-out steps are shown in Fig. 2a), in which three distinct stages can be seen. Both stages I and III have the same pull-out displacement of 1.0nm (defined as a), which is close to the cut-off distance of the vdW interaction. Moreover, ∆E in the four curves have almost the same ∆Eₙ (the average energy increment in stage II). This suggests that the type of GB has a minor effect on the pull-out process. Therefore, only Σ31 was used in the subsequent simulations. We also found that the SWCNT length had no effect on ∆Eₙ. In stage II, as shown later, the resultant vdW interaction changes only within the region of 2a centered by the right end of the matrix. In the remaining embedded region, repetitive breaking and reforming of the vdW interaction happen and counterbalance mutually. This leads to the length-independent pull-out
behavior. Then, various SWCNTs with the same length of 5.165nm were used to explore the influence of CNT diameter $D$ (Fig. 2b)). A key feature in Fig. 2b) is that $\Delta E_{II}$ increases linearly with $D$, which was fitted as:

$$\Delta E_{II} = 52.04 \times D + 9.036$$

($\Delta E_{II}$ in kcal mol$^{-1}$, and $D$ in nm)  

(1)

Therefore, the SWCNT pull-out force in stage II can be simply calculated as:

$$F_{II} = \Delta E_{II} / \Delta x = 1.807 \times D + 0.314$$

($F_{II}$ in nN, and $D$ in nm)  

(2)

In view of that two new surface regions are generated at the two ends of CNT after each pull-out step (Fig. 1), the surface energy density $\gamma_{II}$ can be calculated as: $\gamma_{II} = \Delta E_{II} / (2\pi D \Delta x) = F_{II} / (2\pi D)$. The converged $\gamma_{II}$ was obtained as 0.303 N/m. This $\gamma_{II}$ is new for the interface of SWCNT and alumina matrix although there have been some previously reported $\gamma_{II}$, e.g., 0.09~0.12 N/m [4] and 0.1 N/m [5] between SWCNT and polyethylene matrix, and 0.14 N/m [1] between two neighboring CNT walls. The present $\gamma_{II}$ is much higher than those previous values [1,4,5], implying a stronger interface. Moreover, as shown in [1] for the pull-out among nested walls in a MWCNT, the maximum pull-out force occurs at the end of stage I if the capped effect is modeled. Similar to that in [1], we can predict this maximum pull-out force using the above $\gamma_{II}$.
Based on the above results, the interface shear stress (ISS) in stage II was analyzed. A SWCNT(5, 5) ($D=0.678 \text{ nm}$) with only a half repeated unit in the length direction, embedded in the middle position of matrix (Fig. 3a), was used. The obtained energy increment $\Delta E_{\omega}$ and the pull-out force $F_{\omega}$ for $\Delta x=0.1 \text{ nm}$ are shown in Fig. 3b). It can be found that the pull-out force only exists within the region of $2a=2.0 \text{ nm}$ centered by the right end of matrix. Therefore, the ISS can be solely distributed within the region of $2a$ in stage II (Fig. 3c)). The pull-out force was further averaged within the region of $2a$, i.e., $F^*_\omega$. By assuming that the ISS is uniform within this region ($2a$), the average of ISS $\tau_0$ in stage II can be defined from $F^*_\omega$ as: $\tau_0 = F^*_\omega / (2\pi Da)$ . The obtained converged $\tau_0$ from various unit cells of SWCNT with various diameters was 303 MPa.

4 Results of Multi-Wall Carbon Nanotube

For MWCNTs, the number of walls ($n$) was limited to 2 and 3 for a double-wall carbon nanotube (DWCNT) and a triple-wall carbon nanotube (TWCNT) to reduce the computational cost. Two typical cases were studied, i.e., Case 1: simultaneous pull-out of all walls (Fig. 4a)); Case 2: only pull-out of the outermost wall with the fixed inner walls (see Fig. 4b)). The obtained $\Delta E_{II}$ was also found to be proportional to the diameter of the outermost wall of MWCNT ($D_o$) as follows:

- Case 1
  $\begin{align*}
  \Delta E_{II} &= 57.54 \times D_o + 4.36 \quad n = 2 \quad (3a) \\
  \Delta E_{II} &= 58.26 \times D_o + 6.50 \quad n = 3 \quad (3b)
  \end{align*}$

- Case 2
  $\begin{align*}
  \Delta E_{II} &= 93.61 \times D_o + 10.17 \quad n = 2 \quad (4a) \\
  \Delta E_{II} &= 96.60 \times D_o + 10.50 \quad n = 3 \quad (4b)
  \end{align*}$

For Case 1, the above results plus that for SWCNT are shown in Fig. 5. It can be found that the slope of linear Eq. (3a) ($n=2$) is 9.56% higher than that of Eq. (2) (SWCNT), which highlights the contribution of the first inner wall to $\Delta E_{II}$. However, the slope of Eq. (3b) ($n=3$) is only 1.24% higher than that of Eq. (3a) ($n=2$), which implies that the contribution of the innermost wall of TWCNT is remarkably weakened due to the increase of the distance of this wall to the sliding surface. Therefore, for MWCNTs with more walls over 3, $\Delta E_{II}$ is approximately equal to that of Eq. (3b). Based on the above $\Delta E_{II}$, the pull-out force $F_{II}$, the surface energy density $\gamma_{II}$ and the average ISS $\tau_0$ of DWCNTs and TWCNTs were obtained, which were 1.106 and 1.120 times higher than those of SWCNT, respectively. For Case 2, the results obtained from the sliding behavior between nested walls in a MWCNT were adopted [1]. It was found that $\Delta E_{II}$ of Eq. (4b) was approximately equal to the sum of $\Delta E_{cc}$ and $\Delta E_{s}$ of two independent sub-problems. As shown in Fig. 5c), $\Delta E_{cc}$ was the potential energy increment for a TWCNT when only the outermost wall was pulled out against the other two inner walls [1], i.e., $\Delta E_{cc} = 36.15 \times D_o - 15.75$ . Moreover, $\Delta E_s$ was the potential energy increment of the pull-out of a SWCNT from the alumina matrix, i.e., Eq. (2). Therefore, based on the combinations of various
Fig. 5 Effect of number of walls on \( \Delta E_{II} \) for cases of SWCNT, DWCNT and TWCNT

cases, e.g., Case 1 and Case 2 in the present work and those for sliding among nested walls in MWCNT [1], the pull-out force for an arbitrary pull-out of a CNT from the alumina matrix can be evaluated. In this case, the diameter of the critical wall (i.e., the wall immediately at the sliding surface) of the CNT should be used if the sliding interface does not exist between matrix and CNT.

5 Conclusions

In conclusion, we have investigated the pull-out process of a CNT from an alumina matrix, to clarify the interfacial properties of CNT/ceramics composites. The influences of CNT length, diameter, number of walls and type of alumina GB on the pull-out behaviors were explored. A set of universal formulae was proposed to predict the pull-out force from the outermost wall diameter of the CNT for the arbitrary pull-out.

References