Understanding the nanoscale local buckling behavior of vertically aligned MWCNT arrays with van der Waals interactions†

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The local buckling behavior of vertically aligned carbon nanotubes (VACNTs) has been investigated and interpreted in the view of a collective nanotube response by taking van der Waals interactions into account. To the best of our knowledge, this is the first report on the case of collective VACNT behavior regarding van der Waals force among nanotubes as a lateral support effect during the buckling process. The local buckling propagation and development of VACNTs were experimentally observed and theoretically analyzed by employing finite element modeling with lateral support from van der Waals interactions among nanotubes. Both experimental and theoretical analyses show that VACNTs buckled in the bottom region with many short waves and almost identical wavelengths, indicating a high mode buckling. Furthermore, the propagation and development mechanism of buckling waves follow the wave damping effect.

Introduction

Since their discovery in 1991,1 carbon nanotubes (CNTs) have attracted great interest in new materials research and the mechanical properties of CNTs have been reported extensively. Recently, with the outstanding fatigue, resilience and good damping effect, ultra long VACNTs and continuous CNT composites have shown promising potential as engineered nanotube architectures in future applications, such as artificial skin, energy absorbing materials and aircraft or wind turbine coatings. In these applications, the CNT arrays deform and recover together under compression, so the collective compressive behavior of CNTs has an influence on the compressive properties, and understanding of the collective compressive behavior becomes critically important.

There are numerous studies on the compressive properties of VACNTs, showing a large amount of evidence on the buckling of VACNTs. It was firstly reported2 that VACNT blocks exhibited viscoelastic behavior similar to soft-tissue, and a sharp stiffness increase in critical densification strain along with local buckling of VACNTs. The compression of VACNT films3 indicated that VACNTs exhibited foam-like viscoelastic behavior with local zigzag buckling waves and strong resilience. Similarly, local periodic buckling regions and stiffness of VACNTs under nano-indentation were reported4 in a low-cyclic compression. Also, local buckling behavior in the bottom region of VACNT turfs5 and VACNT arrays6–7 with many short buckling waves was observed in compression. The periodic buckling waves were observed during electrical conductivity characterization of a VACNT block.8 And the stress–strain curve analysis of dense VACNT brushes also indicates progressive propagating buckling behavior.9 Moreover, an in situ compression test10 revealed the progressive propagation of periodic buckling of VACNT bundles from bottom to top, and another in situ compression experiment11 also indicated the large scale structural buckling and collapse of long VACNTs. These local buckling behaviors of VACNT were observed in many experiments and there are some research studies3,5,6,9–11 which employed the classical Euler’s column buckling model14 with the formula: 

$$P = \frac{\pi^2EI}{L^2}$$

in order to predict the CNT buckling. Moreover, there are analytical modeling,13,15–18 numerical simulations,12,19 and experimental studies20–23 on buckling and post-buckling behavior of individual CNTs under an axial compression. However, the observed local buckling behavior is different from individual Euler column buckling due to the van der Waals interactions.
Waals interaction between nanotubes, so the compressive behavior of VACNT arrays is collective behavior and the nanotube interactions could change the buckling response significantly. The van der Waals interaction within bundles cannot be ignored due to the close distance between nanotubes, and CNTs are constrained by the van der Waals force from the adjacent nanotubes in the radial direction along the length, which can be considered as a lateral support. Consequently, VACNTs have lateral support effects from neighboring nanotubes and the buckling behavior may be different from individual Euler column buckling. Therefore, the van der Waals interactions between neighboring VACNTs cause CNT to buckle collectively as bundles and give rise to local buckling waves. There are many studies on the van der Waals interactions between parallel,23−25 and cross linked26 CNTs, and the interaction potential between CNTs,27 but no detailed studies have been reported on the effects of the van der Waals interactions on the collective buckling behavior of VACNTs.

Thus, in this paper, we have investigated and unraveled the buckling response of VACNTs with the van der Waals interactions as lateral supports by coupling experiments and modeling. This is the first time to interpret the unique local buckling behavior of VACNTs by considering the van der Waals interaction and to understand the propagation of local buckling with a wave damping effect.

### Experimental and modelling

#### Characterization of buckling in quasi-static compressions

To study the buckling response of VACNTs under compression, uniform compression testing was performed using an Instron ElectroPuls E3000 machine at room temperature. Since the VACNTs (3 mm × 5 mm × 0.63 mm) were grown on a silicon substrate, the VACNT array with the silicon substrate was placed in the bottom compressive fixture, having the substrate contact with the bottom surface of the fixture with a pre-load of 0.02 N. Compressive strains were applied along the longitudinal direction of the VACNTs downwards under displacement control. All the tests were performed at the applied quasi-static loading rate of 100 μm min−1. The specimens were compressed from 4.7% to 80% strain by flat platens. The actuator kept the strain for 1 min and then released the strain, allowing the specimen to recover. The compressed VACNT arrays after recovery were monitored through SEM characterization and the buckling region was imaged for each strain-increase step.

#### van der Waals interaction modelling for lateral support

In order to explain the high mode buckling behavior of VACNTs observed in experiments, we developed analytical CNT models to take into account the van der Waals interaction between neighboring nanotubes, and then developed a finite element model accordingly. For the CNT model, the interaction between inter-tubes within a MWCNT is neglected, which simplifies the MWCNT to the equivalent CNT column. Therefore, the CNT is assumed to be a prismatic hollow continuous column with a ring cross-section. Since the distribution of VACNTs, the CNTs within bundles are assumed to be parallel to each other. The van der Waals interaction between CNTs was modeled with the Lennard-Jones pair potential28 and the interaction force between two parallel nanotubes is:23

\[
F(d) \approx F(d_0) + \frac{\partial F(d_0)}{\partial d} (d - d_0)
\]

\[
= \pi^2 \sigma^2 \sqrt{R} \left( \frac{35A}{64d_0^{15}} - \frac{46189B}{131072d_0^{10.5}} \right) + \pi^2 \beta^2 \sqrt{R} \left( \frac{315A}{128d_0^{5.5}} - \frac{96996B}{262144d_0^{11.5}} \right) (d - d_0)
\]

Therefore, the CNT is assumed to be a prismatic hollow column with a ring cross-section. Since the distribution of VACNTs, the CNTs within bundles are assumed to be parallel to each other. The van der Waals interaction between CNTs was modeled with the Lennard-Jones pair potential28 and the interaction force between two parallel nanotubes is:23

\[
K = \pi^2 \sigma^2 \sqrt{R} \left( \frac{35A}{64d_0^{15}} - \frac{46189B}{131072d_0^{10.5}} \right) + \pi^2 \beta^2 \sqrt{R} \left( \frac{315A}{128d_0^{5.5}} - \frac{96996B}{262144d_0^{11.5}} \right) (d - d_0)
\]

Thus, the equivalent spring constant per unit length is:

\[
\sigma_{cr} = E_{CNT} \left( \frac{m \pi r}{L} \right)^2 / 4 + \frac{K}{\pi} \left( \frac{L}{m \pi r} \right)^2
\]

where \(d\) and \(d_0\) are the distances between the interacting atoms, \(R\) is the radius of nanotubes, and \(A\) and \(B\) are attractive and repulsive constants, respectively.

With the supporting effect of van der Waals interaction, the corresponding lateral support is represented by converting the van der Waals interaction to the elastic modulus of the supporting medium accordingly:29

\[
\sigma_{cr} = E_{CNT} \left( \frac{m \pi r}{L} \right)^2 / 4 + \frac{K}{\pi} \left( \frac{L}{m \pi r} \right)^2
\]

\(m\) is the number of half waves, \(L\) and \(r\) indicate the length and the radius of CNTs, and \(K\) is the equivalent spring constant, representing the van der Waals interaction between CNTs.

### Results and discussion

#### Structural and morphological characterization

Fig. 1 shows structural and morphological characterization results of commercially available VACNTs. The CVD grown MWCNTs are vertically aligned and have a uniform length around 0.63 mm. Fig. 1A confirms the vertically aligned distribution of the MWCNTs. The MWCNTs are aggregated together as bundles (Fig. 1B) and have an average distance of several nanometers between adjacent CNTs (Fig. 1C), indicating the CNTs are very close to each other within the bundles and the effect of van der Waals interactions between them could be critical during compression. The outer diameter of these MWCNTs ranges from 7 nm to 10 nm, while the inner diameter ranges from 5 nm to 8 nm, and the number of graphitic layers of each nanotube is found to be around 3 (Fig. 1D). The aspect ratio of VACNTs is estimated to be nearly \(6 \times 10^4\), which is extremely high. The characterization results provide clearly the structural and morphological features of VACNTs for experiments and modeling.

To have further information on the defect degree of the VACNTs, which could also affect the stability and buckling behavior of CNTs, Raman spectroscopy with 633 nm excitation was employed (Fig. 2). We conducted the Raman spectroscopy
measurements with 5 different VACNT samples and different characterization positions along the longitudinal direction of each sample. The Raman spectrum shows D-, G-, and 2D bands at 1323.5 cm\(^{-1}\), 1594.1 cm\(^{-1}\), and 2638.1 cm\(^{-1}\), respectively. In the Raman spectra of VACNTs, the average ratio of \(I_D/I_G\) peaks is around 0.78 before compression and 0.77 after compression; the standard deviation is less than 5%, indicating that the intrinsic properties of VACNTs do not change much during the compression process. This Raman spectrum result indicates the existence of disorder and defects in the graphitic structure of the VACNTs,\(^{30}\) which could lead to relatively weak resistance to an applied force and contribute to the instability of CNTs and propagation of buckling behavior during the compression process.

**Buckling behavior characterization in quasi-static compressions**

With all necessary structural and morphological properties of VACNTs, we utilized a strain increase compression test to investigate the buckling behavior of VACNTs. The SEM images in Fig. 3 indicate that the VACNTs exhibit local buckling behavior which develops progressively as the strain increases. Note that the buckling behavior develops from the bottom of the VACNT arrays. It could be attributed to the unbalanced friction between the bottom of the VACNTs and the silicon substrate, leading to a higher instability of VACNTs and also the smaller diameter of CNTs in the bottom as the effective catalyst size shrinks in the diffusing process to the substrate.\(^{31}\) As seen in Fig. 3A and D, the buckling waves develop progressively upward with new buckling waves propagating above the buckled region as the strain increases. Interestingly, the wavelength of the new buckling waves appears to be constant with the old ones. This buckling propagation and developing mechanism has not been studied in detail yet. And it could be explained in accordance with a wave damping effect,\(^{14}\) which was observed in previous experiments and modeling results, especially in shell buckling.\(^{32-36}\) Generally, a cylindrical shell under a uniform axial compression will have many axis-symmetrical buckling waves in the longitudinal direction due to the surrounding constraint force from its continuous shell structure, and the amplitudes of buckling waves will gradually decrease upwards, and eventually go to zero. Due to the van der Waals interactions from neighboring nanotubes, CNTs are constrained in the radial direction along the length and consequently have lateral support effects. Analogous to the shell buckling, the VACNT buckling with van der Waals lateral support also have many short buckling waves, which represents a high mode buckling, and the amplitudes of waves will decrease gradually under the wave damping effect. The detailed buckling propagation and the developing process are shown in the representative stress–strain curve in Fig. 3F with the corresponding buckling conditions (Fig. 3A–E). The stress–strain curve can be divided into the widely reported three-regions according to the buckling developing process: elastic region (0–5%), plateau region (5–60%), and densification region (70–85%). When strain is in the elastic region (<5%),
interaction, have determined the length of all waves under
ture and Young
needs a little more stress to force new buckling waves. Among
the SEM images. The amplitudes of buckling waves are large in the
the CNTs have only elastic deformation and there are no
buckled waves. When the strain increases and exceeds the criti-
cal buckling strain, the buckling waves start to propagate from
the bottom and the elastic modulus decreases correspond-
ingly, indicating the critical buckling condition in Fig. 3A.
With the strain increase, the bottom parts of CNTs deflect
rapidly and then CNTs buckle at the first crests of the half
buckling wave nearest to the bottom substrate. After the first
half-wave is deformed, the second buckling half-wave sequen-
tially begins to grow rapidly and so on. In this way, the buck-
ning waves will gradually decrease down to zero upwards
in the buckling region and the rest parts of CNTs will still
remain straight, following the wave damping effect.

In Fig. 3F, when the strain is in the densification region
(>~70%), the elastic modulus will increase dramatically. The
behavior of CNTs was changed from buckling to packing and
folding in this region. Under these conditions, the collapse of
the nanotube forest happens throughout the material and
buckled nanotubes touch and press against one other as
shown before in Fig. 3E. When this happens, the stress–strain
curve rises sharply and the corresponding stiffness would
simply be proportional to the relative density of bulk samples.
Fig. 3E gives the corresponding buckling response in the den-
sification region, showing almost uniform buckling half-waves
along the longitudinal direction, which covers more than half
the length of VACNTs. The gradually decreasing amplitudes in
the top waves and the periodic developed half waves in the
middle and bottom regions follow the wave damping effect
when the strain keeps increasing up to a higher level. The
observed half-wavelengths from the SEM images are around
9 µm at the top and middle region, and 6–8 µm at the bottom
region. This slight increase in the wavelength indicates that
the waves are heavily folded at the bottom and have weak
recovery when the applied force is released. The difference in
the wavelength between the top and bottom region is also
reported in Cao et al.’s work. Overall, at a large strain, the
decrease of the buckling wave amplitudes and the periodic
propagating waves still follow the wave damping effect.

van der Waals interaction modeling characterization
With the above equations, a finite element CNT buckling
model with lateral support was developed by converting the
van der Waals interaction into a supporting medium and the
simulation results are shown in Fig. 4. In Fig. 4A, the critical
buckling mode keeps the 1st mode (whole column Euler buck-
ling) when the aspect ratio is under ~60. The critical buckling
mode will become a high mode after that and the mode
number will gradually increase with the aspect ratio. When the
aspect ratio exceeds ~6000, the critical buckling mode starts to
remain constant around the 30th mode and the buckling
region decreases from almost whole nanotube to nanotube
ends. According to FEA analysis, with lateral support, the
buckling mode of VACNTs will quickly increase to a high mode
after the aspect ratio of 60 and have a nearly proportional cor-
relation with the aspect ratio, but when the aspect ratio is over
~6000, the local buckling behavior occurs and the buckling
mode will start oscillate around number 30. Fig. 4B shows the
simulation result of critical buckling conditions of VACNTs
under experimental conditions (aspect ratio of 6 × 10^4), where
the CNT buckles in the bottom region with ~30th buckling
mode, indicating the observed buckling response in the SEM
images. The amplitudes of buckling waves are large in the
bottom and gradually decrease to zero upwards, suggesting a
wave damping effect. The half wave number of the FE result is
around 15 at one end, which is higher than the experimental
The unique buckling behavior of VACNT arrays under compression was characterized experimentally and interpreted properly by employing the van der Waals interaction between VACNTs as the lateral support. Since van der Waals force from the adjacent nanotubes can constrain a VACNT in the radial direction, the buckling of VACNTs becomes a high mode buckling with many half buckling waves. The propagation and developing mechanism of VACNT buckling starts from the bottom of the nanotube and follows the wave damping effect. Furthermore, the study on such buckling behavior of VACNTs will significantly improve the understanding of collective mechanical properties of VACNT arrays and VACNT composites in compression, which could contribute to the use of engineered nanotube architectures in the building of synthetic biomaterials.

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