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Enhanced Mechanical Properties of Prestressed Multi-Walled Carbon Nanotubes**

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It may sound a crazy idea to build up a space elevator for delivering payloads from the Earth into space. The ultimately extra-low delivery cost, possibly US\$10 per kilogram, makes the space elevator the only technology for exploiting solar power in a big way that could significantly brighten the world's dimming energy outlook.^[1] To meet the biggest challenges of building a space elevator, the key issue lies in creating a superstrong, lightweight cable that can stretch over 36 000 km between the Earth and a geostationary space station. This requires at the minimum a specific tensile strength (namely, the tensile strength–specific gravity ratio) of 48.5 GPa (for the graphite specific gravity 2.25), much higher than those of all natural or artificial materials, for example, 1.36 GPa for graphite whiskers or 0.08 GPa for high-carbon-steel wires, before the discovery of carbon nanotubes (CNTs).^[2] It is known that the sp^2 carbon bond is the strongest bond in nature. A single-walled carbon nanotube (SWNT) can be viewed as a cylindrical shell of sp^2 -bonded monolayered carbon atoms, and a multi-walled carbon nanotube (MWNT) an assembly of SWNT-like shells with interwall spacings of 0.34 nm on average.

Experiments^[3,4] have confirmed the predictions, based on both molecular dynamics simulations and first-principles calculations,^[5,6] that pristine SWNTs may have extremely high axial tensile Young's moduli (≈ 1 TPa) and specific strengths (70–100 GPa). This seems to promise many applications of CNTs in composite materials as mechanical reinforcements, much better than all other known fibers. However, actual reinforcement effects are far below expectations,^[7,8] and the measured axial strengths of individual MWNTs and bundles of CNTs are quite diverse and typically one or two orders of magnitude lower than in theory.^[4,9] The reason^[4] is that the

axial tensile load exerted on both ends of individual MWNTs, which are stuck and stretched by two atomic force microscopy (AFM) tips, would be borne mostly by the outermost shell of the tested MWNT since the load could be neither effectively transferred to nor carried by the inner shells due to the ultralow interwall shear strength, usually ranging from 0.08 to 0.3 GPa.^[4,10] A similarly poor load-transfer property is observed for CNT bundles.^[9] Thus, the ultralow interwall shear strength, a virtue that allows molecular bearings^[10] and gigahertz mechanical oscillators,^[11] becomes the primary obstacle on fabricating CNT-reinforced composites with excellent mechanical performance.

Various approaches have been proposed for improving the interwall or intershell load-transfer property of CNTs, which can be categorized as either the spun-yarn mechanism^[12,13] or the crosslink mechanism.^[14,15] With the spun-yarn method it is technically simple to produce continuous CNT yarns from short CNTs. The spun-yarn mechanism is essentially the pressure-induced friction. Twisting a CNT yarn harder will lead to higher inter-CNT friction on the one hand, but lower yarn axial components of both the tensile strength and Young's modulus of every constituent CNT in the yarn on the other hand. As a result, the CNT yarns may only have, for example, a specific strength of 0.31–0.58 GPa and a Young's modulus of 1–30 GPa,^[16] both two orders of magnitude lower than those of pristine SWNTs.

Several of the proposed methods can effectively introduce crosslinks in CNTs and remarkably enhance the interwall shear strengths. A theoretical study based on the ab initio total energy density functional shows that Wigner defects existing in SWNT bundles can form a link between the constituent tubes and increase the shear modulus by a sizeable amount.^[15] Molecular dynamics simulations^[17] show that a small number of defects may increase the interwall shear strength by several orders of magnitude. A breakthrough in the crosslink method was made by using moderate electron-beam irradiation inside a transmission electron microscope^[14] with carbon–carbon bond-type crosslinks generated at low doses of irradiation to increase the bending modulus up to 30-fold, which corresponds to an enhancement in the overall interwall shear strength of one order of magnitude. However, the discomfiture with the crosslink methods is that a small number of defects in a CNT can largely reduce its tensile strength,^[14,18] while removing the defects, for instance by annealing, usually leads to failure of the crosslinking mechanism—the interstitial-vacancy pairs (or Wigner defects) as crosslinks will disappear even at a temperature of around 500 K.^[19]

As far as we are aware, how to enhance the interwall shear strength of a MWNT by several orders of magnitude without significantly reducing its tensile strength and/or tensile stiffness is still an unresolved problem. To obtain a solution, we consider a class of new MWNTs that have smaller interwall spacings than the average ($s_0 \approx 0.34$ nm) for normal MWNTs, and we call such nanotubes prestressed MWNTs (PMWNTs), which will be explained later. Recently, a novel irradiation annealing technique was found to be able to successfully shrink the interwall spacings of graphitic structures down to 0.22–0.28 nm for fullerene onions^[20] and 0.29 nm for MWNTs.^[21] The interwall pressures of such shrunken MWNTs were found

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to reach values higher than 40 GPa.^[21] Since in general higher pressure allows higher friction, we thus expect that PMWNTs would have higher interwall shear strengths and therefore better load-transfer capabilities than those of normal MWNTs, even though the constituent tubes of the considered PMWNTs would be perfect and thus there would be no interwall crosslinks. At the same time, we are also concerned with the axial tensile strengths and Young's moduli, the thermal stability of the reduced interwall spacing structure, and the axial strength sensitivity to defects for PMWNTs.

These studies are carried out using the second-generation reactive empirical bond order (REBO) potential^[22] approach, in which both the covalent bonding and van der Waals interactions are taken into account. We firstly constructed a number of PMWNTs that are stable and have reduced interwall spacings. Shown in the insert of Figure 1 is a typical PMWNT with six walls, which will be studied in more detail. This PMWNT is produced by first releasing the six zigzag SWNTs (5,0), (11,0), (17,0), (23,0), (29,0), and (34,0) from their concentric and usual structures, and then reaching the energy-optimization configuration, which is calculated using molecular dynamics. The resulting PMWNT has reduced interwall spacings ranging from 0.248 to 0.283 nm, and has an average 20% interwall spacing reduction compared with normal MWNTs.

To obtain the axial tensile strength and Young's modulus of the above PMWNT, we calculated the nominal stress σ while elongating the PMWNT using a periodic boundary condition with periodic length $L=4.26$ nm (ten times the zigzag lattice length), through fixing all atoms at one end of the PMWNT and moving all atoms at the other end. Stress σ is defined as the end force divided by the nominal cross-sectional area of the PMWNT with a diameter equal to the outermost tube diameter plus the average interwall spacing. In principle such calculated σ is independent of the chosen period length whenever it is an integral multiple of the zigzag lattice length. The curve of σ versus the relative elongation (or strain) ε is

plotted in Figure 1 (solid line). For comparison, the σ - ε curve for a normal MWNT is also shown (dashed line), and is in good agreement with those reported in the literature.^[18] The extremities of these σ - ε curves and the slopes of the curves at $\varepsilon=0$ correspond to the tensile strengths and Young's moduli, respectively. The results show that the axial tensile strength and Young's modulus of this specific PMWNT are about 20% higher than those of normal CNTs, and the failure strains of these prestressed and normal CNTs are almost the same (failure strain $\varepsilon_{cr}=18\%$). Similar results were obtained for other PMWNTs. Thus, PMWNTs have the potential to break the record for the highest tensile strength and Young's modulus of all known materials, which used to be held by pristine SWNTs. Meanwhile, since the mass density of the studied PMWNT is 20% higher than those of normal CNTs, its specific strength and Young's modulus are the same as those of normal CNTs.

To estimate how the interwall shear strength is enhanced, we considered the same supercell of the studied PMWNT with a length of 4.26 nm. We slowly axially slid an inner core, which consisted of the i -th shell and all its inside shells, relative to the outer tube consisting of the $(i+1)$ -th shell and all the outside shells. The interaction force against this sliding is a periodic function of the slide distance, and the force amplitude per unit area of the imaginary cylindrical interface between the inner core and the outer tube is defined as the interwall shear strength. The atomic simulation results of the interwall shear strength, $\tau(s)$, versus the interwall spacing s are plotted in Figure 2 (filled triangles). It is found that $\tau(s)$ of the studied six-walled zigzag PMWNT is greatly enhanced with reduced interwall spacing compared with the normal interwall spacing $s_0=0.353$ nm. An exponential law $\tau(s)=0.045e^{21.7(1-s/s_0)}$, where $\tau(s)$ is in GPa, is observed. Interestingly, for zigzag prestressed double-walled carbon nanotubes (PDWNTs), we obtained a similar exponential strength-spacing relation, as shown by the open circles in Figure 2. We also plotted the shear strengths (open squares) for three chiral PDWNTs, and

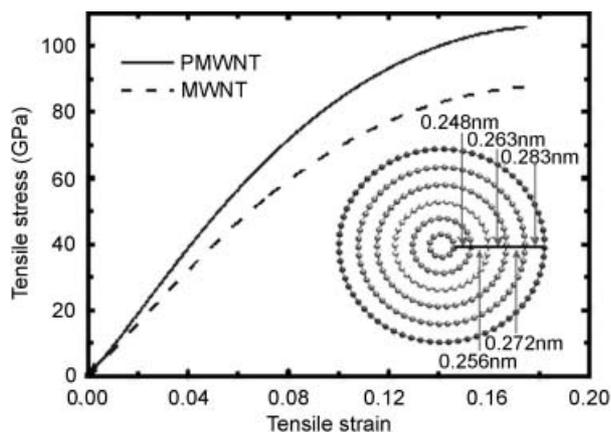


Figure 1. Axial tensile stress–strain curves of the studied PMWNT and a comparative six-walled normal MWNT (5,0)@(14,0)@(23,0)@(32,0)@(41,0)@(50,0). Insert: Energy-optimization configurations of the studied PMWNT and the reduced interwall spaces varying from 0.248 to 0.283 nm from the inner to the outer shells.

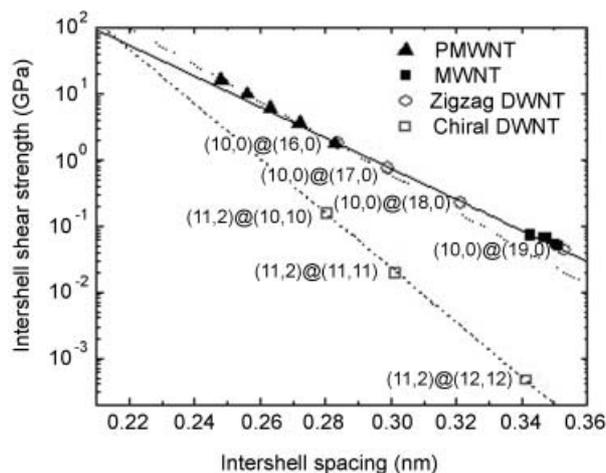


Figure 2. Enhancement effects of reduced intershell spacings on interwall shear strengths for the studied six-walled zigzag PMWNT (\blacktriangle), normal six-walled zigzag MWNT (\blacksquare), zigzag PDWNTs (\circ), and chiral PDWNTs (\square).

observed that the enhancement effect was even higher for chiral PDWNTs, with the value $\tau(s) = 1.8$ GPa at 20% spacing reduction for DWNT (10,0)@(16,0) being four orders higher than the value for interwall shear strength of the normal DWNT (11,2)@(12,12). Furthermore, the interwall shear strengths for normal DWNTs may differ by two or three orders of magnitude due to chirality^[23,24] (also see Figure 2). Significantly, the results shown in Figure 2 indicate that such chirality-dependent diversity will disappear at the reduced interwall spacing $s = 0.22$ nm. This property allows us to produce more uniform and reliable PMWNTs without taking into account various chirality combinations.

To confirm that PMWNTs can effectively transfer loadings from the outermost shell to inner shells, we first considered a simple load-transfer problem (Figure 3a) for either a prestressed or a normal DWNT of length L , outer shell diameter D_o , and inner shell diameter D_i . All the left-end atoms are fixed and a uniform shear force q per unit area is

applied on a right section of length L_o of the outer shell. We can immediately obtain the axial stress, σ_i^{end} , of the inner shell at the left end and its upper bound, σ_i^{cr} , as follows:

$$\sigma_i^{\text{end}} = \frac{D_o + D_i}{2D_i s} \int_0^L \tau(x) dx, \quad \sigma_i^{\text{cr}} = \frac{D_o + D_i}{2D_i s} L \tau_s \quad (1)$$

where s is the average interwall spacing, $\tau(x)$ the intershell shear stress, and τ_s the intershell shear strength. It can be seen from Equation 1 that ideally the σ_i^{end} as a character of the load-transfer capability may reach the critical value $\sigma_i^{\text{end}} = \sigma_s$ of SWNTs if L is sufficiently long. Substituting the data $D_o = 1.5$ nm, $D_i = 0.8$ nm, $\tau_s = 0.043$ GPa, and $\sigma_s = 80$ GPa into the criterion $\sigma_i^{\text{max}} = \sigma_s$ yields the maximum possible value of σ_i^{max} , which is about 68% of the strength σ_s if, for instance, $L = 30$ nm. However, this maximum possible load-transfer capability would only be achievable when all outer- or inner-shell atoms were consistently confined by the intershell van der Waals interaction potential corrugation, which is not realistic because DWNTs are deformable. The molecular dynamics simulation results of σ_i^{end} and σ_o^{end} versus the increasing applied loads q (Figure 3b) for the normal DWNT (10,0)@(19,0) with lengths $L = 30$ nm and $L_o = 20$ nm reveal that the actual load-transfer capability is much depressed. In comparison, for the prestressed DWNT (10,0)@(16,0) with the enhanced intershell shear strength $\tau_s = 1.8$ GPa, we see the full load-transfer capability from the simulation results shown in Figure 3c.

Annealing is an important technique to reduce defects and impurities in normal CNTs to produce pristine CNTs with theoretical strengths. Therefore, the thermal stability of the reduced interwall spacing structure of PMWNTs at high temperatures is a matter of concern. Molecular dynamics simulations under canonical ensemble for various temperatures show that the PMWNT under study is thermally stable up to 2000 K for 2 ns (after the thermal equilibrium state was reached, which ensures thermal stability during further heat treatment). Interestingly, the simulations show that above this critical temperature the sp^2 -bonded innermost shell (5,0) transformed quite uniformly into sp^3 -bonded or diamond nanowires, and above 3000 K the two-walled core (5,0)@(11,0) transformed into diamond nanowires; in comparison, random sp^3 -bonds appear at 2800 K for normal MWNTs.^[25] Further calculations show that the diamond nanowires produced by annealing are also stable, which implies a systematic method to produce diamond nanowires without the application of extra-high external pressures that has already been proved experimentally.^[26]

We may also understand the mechanism of the interwall shear strength enhancement in the light of continuum mechanics. The six constituent shells of the studied PMWNT can be modeled as isotropic elastic thin shells fitted together with interferences.^[6,27] Comparison of the diameter of each constituent shell in the energy-optimized configuration with that in its SWNT state reveals circumferential prestrains ε_p of all the constituent shells, which are -8.13 , -4.65 , 2.69 , 5.13 , 7.33 , and 9.64% , respectively, from the innermost to the

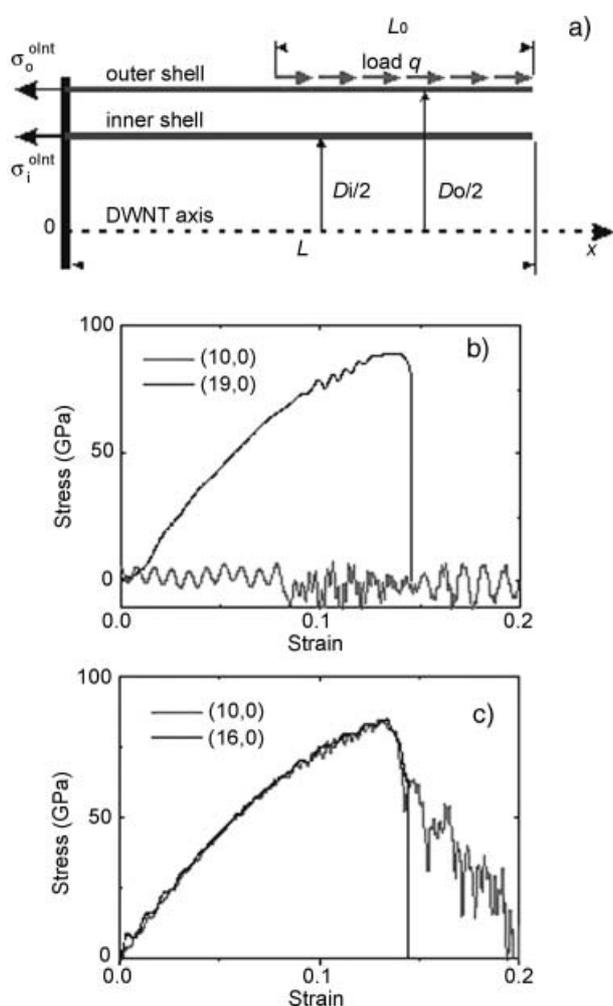


Figure 3. Load transfer in normal or prestressed DWNTs characterized by the end stress σ_i^{end} (thin line) and σ_o^{end} (thick line) for inner and outer shells, respectively. a) Illustration of the loading applied on the DWNTs in simulation. b) Load transfer in a normal DWNT (10,0)@(19,0) with $L = 30$ nm and $L_o = 20$ nm. c) Load transfer in the prestressed DWNT (10,0)@(16,0) with $L = 30$ nm and $L_o = 20$ nm.

outermost shell, all below the failure strain limit (about 18%). The two innermost shells are circumferentially compressed and the others extended. The circumferential membranous force per unit axial length sustained by the i -th shell is roughly $N_i = Yt\varepsilon_i$, which is actually caused by the interwall pressure difference inside and outside the shell. Force balance leads to the equation $2N_i = 2Yt\varepsilon_i = p_{i-1,i} D_{i-1,i} - p_{i,i+1} D_{i,i+1}$, where $Yt = 0.34$ TPa nm is the tensile rigidity, and $p_{j,j+1}$ and $D_{j,j+1}$ denote the interwall pressure and interface diameter between the j -th and $(j+1)$ -th shells, respectively, as schematically illustrated in Figure 4a. By jointly resolving the equations for all the shells, we estimate all the interwall pressures as 173, 122, 73.1, 40.2, and 17.7 GPa, which are basically consistent with the results 114, 78.2, 52.5, 33.5, and 17.7 GPa by directly calculating the van der Waals forces between the interwall carbon atoms. The existence of such high interwall pressures is very likely the primary mechanism of the interwall shear

strength enhancement. Since the interwall pressures are self-equilibrated, we thus call interwall-spacing-reduced MWNTs prestressed ones.

Two more insights are gained from the above-mentioned analysis. Firstly, the pressure over 100 GPa acting on the innermost core shell implies that a PMWNT may not be stable without a very small core. To ascertain this point, we studied the two- to five-walled tubes generated by drawing out the inner shells from the PMWNT concerned. As shown in Figure 4b, the energy-optimized configurations of the two- to four-walled tubes are indeed collapsed with only insignificant enhancement of the interwall shear strength. Secondly, since a pressure as high as several to dozens of GPa may lead to an sp^2 - sp^3 transition^[28] at high temperature, the very high interwall pressures explain our previous result of sp^2 - sp^3 transformation at 2100 K or higher temperature without any external pressure.

The very high interwall pressure, however, gives rise to concern as to whether the tensile strength of prestressed MWNTs would be more sensitive to defects than that of normal ones. We thus investigated prestressed (10,0)@(16,0) in comparison to the normal (10,0)@(19,0) for three defect cases: one-atom vacancy in the inner layer, one-atom vacancy in the outer layer, and one-atom vacancies in both layers. From the calculated stress-strain curves, we observed that the vacancy effects of reducing the tensile strengths for both types of DWNTs are almost the same – less than 5% reduction for a one-atom defect in either the inner or outer tube, or 23.0% reduction for one-atom vacancies in both tubes. A similar phenomenon is well known in the mechanics of materials. For example,^[29] the maximum stress in an infinitely large isotropic plate containing a small circular hole sustaining remote biaxial stretching tractions q_x and q_y with $0 < |q_y| < q_x$ is equal to $3q_x - q_y$. This, in turn, may be smaller (as $q_y > 0$) or larger (as $q_y < 0$) than that for the unidirectional stretching problem ($q_y = 0$). Since the outer and inner tubes of a prestressed DWNT are affected by both prestretched and precompressed stresses, respectively, the overall influence may become insignificant.

How to effectively produce PMWNTs is the key issue. Banhart et al.^[20] found that by using electron irradiation within certain temperature circumstances (about 600 °C), normal carbon onions, as assemblies of concentric spherical shells of sp^2 -bonded carbon atoms with interwall spacings of about 0.34 nm, could be transformed into smaller carbon onions with reduced interwall spacings ranging from 0.22 to 0.28 nm. Sun et al.^[21] found MWNTs with reduced interwall spacing (≈ 0.29 nm) from irradiation-reconstruction processes after electron irradiation for tens of minutes (12–50 min) with a beam density of about 200 A cm^{-2} at 600 °C in FEI Tecnai F-30, and their estimate of the intershell pressure was consistent with our results. Such a shrunken mechanism can be explained as follows. Electron-beam irradiation can knock off atoms from carbon onions or MWNTs in equilibrium states, thus inducing defects and vacancies. Since the entirely sp^2 -bonded state is the most energy-favored, annealing reconstruction could circumferentially shrink the constituent shells with a reduction of spacings that generates very high intershell pressures for the nanoscale shell dimensions. To

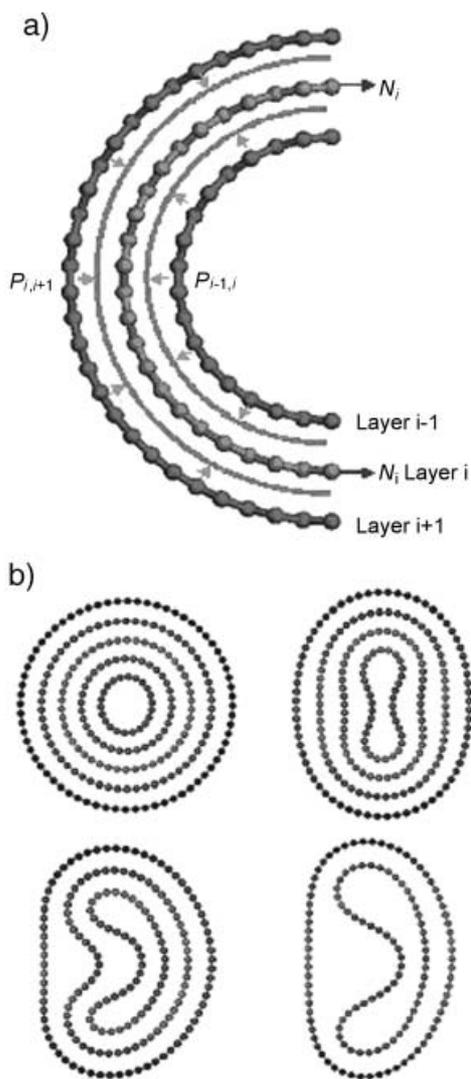


Figure 4. Interwall shear strength enhancement mechanism and instability. a) Balance of circumferential force N_i and interwall pressures $p_{i-1,i}$ and $p_{i,i+1}$. b) Energy-optimized configurations of the five- to two-walled tubes generated by drawing out the inner shells from the investigated PMWNT.

confirm this concept, we removed lines of atoms from the outer shell in the double-walled carbon nanotube (10,0)@(19,0) and then equilibrated the system at 500 K. After 200 ps, the vacancies in the graphite lattice are healed and the interwall spacing is reduced with perfect sp² bonding structure. These results indicate that PMWNTs could be produced at a reasonable cost. Such PMWNTs, with their ultimate specific strength of about 80 GPa, may serve as the sole candidate for fabricating the cables of space elevators to deliver payloads from the Earth into space.

Keywords:

carbon nanotubes · mechanical properties · molecular dynamics simulations · stress

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