Morphology-dependent load transfer limits the strength of carbon nanotube yarns

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ABSTRACT: The outstanding properties of individual carbon nanotubes (CNTs) have motivated interest in CNT fibers for composite materials, high-strength conductors and multifunctional textiles. However, despite advances in manufacturing, the strength of CNT fiber remains 10-100 fold less than individual CNTs. In light of the complex, multi-scale load transfer in CNT yarns, a hierarchical model taking into consideration the morphology-dependent mechanics is necessary to understand this limitation. We present a coupled analytical and finite element model of three-dimensional morphology and the full tensile behavior of CNT yarns. By incorporating load-induced changes in morphology, simulations of yarns in tension show different load paths such as fracture-type or stick-slip failure depending on the waviness and number density of CNTs.

The strength of untwisted pristine CNT yarns is shown to be limited to <10% of the intrinsic CNT strength, even at practical limits to CNT packing density and alignment. Load-induced changes in CNT morphology are verified by tensile testing of CNT yarns along with in-situ X-ray scattering. In addition, the nominal structure of the yarn is shown to strongly influence the improvement in strength achieved by densified and/or cross-linking, and a sublinear relationship between CNT contact enhancement and yarn strength is predicted. Thus, this work provides a means to investigate the complex load transfer mechanisms in CNT assemblies, and to further study the process-structure-property limits of CNT yarns

TEXT

Individual carbon nanotubes (CNTs) have outstanding tensile strength (~ 50 GPa)¹, high electrical conductivity ($3 \times 10^{-5} \Omega\text{-cm}$)² and thermal conductivity ($3000 \text{ W m}^{-1} \text{ K}^{-1}$), and low mass density ($< 2200 \text{ kg/m}^3$) relative to metals. In seeking to scale these and other properties to macroscopic composites, textiles, and wires, there has been considerable work towards manufacturing of continuous CNT yarns.^{1,3} Prominent CNT yarn manufacturing methods include spinning from CNT suspensions,⁴⁻⁶ dry drawing and twisting from multi-walled CNT forests,^{4,7,8} and drawing/spinning from a floating catalyst CVD process.^{4,9,10} As synthesized, the typical reported strength of CNT yarns is $\sim 0.1\text{-}4$ GPa/SG. While promising, these strength values remain only 1-10% of the verified strength of as produced defective CNTs, and are lower than commercially produced polymer fibers such as Kevlar (~ 3 GPa/SG) and Dyneema (~ 3.5 GPa/SG),⁹ and high-strength carbon fibers (~ 3 GPa/SG).

The mechanical behavior of CNT yarns is determined by the properties of the individual CNTs, the nanoscale interactions between contacting CNTs within the yarn, and the load transmission through the hierarchical, entangled and anisotropic morphology of the CNT network. Statistical approaches have shown that the distributions of intrinsic CNT strength and the strength of local CNT-CNT interactions influence yarn strength.¹¹ Tensile testing of yarns along with in-situ Raman spectroscopy¹² has suggested that ultimate strength is limited by relative slip between CNTs. Analysis of the CNT-CNT friction indicates that the adhesion generated by van der Waals forces provides only a small resistance to relative sliding of CNTs, making it the primary limitation for yarn strength.¹³ Multi-scale molecular dynamics (MD) simulation¹⁴ of twisted yarns comprised of idealized straight CNTs predicts that the structure of the yarn changes during loading, which in turn influences the mechanics.

As a result, multi-scale modeling efforts have sought to link the effect of both nominal and reinforced CNT-CNT interactions as well as statistical variations in geometry to yarn properties. Notably, Beese et al. utilize Monte-Carlo methods incorporating a statistical shear-lag model, in conjunction with experimental data on double-walled nanotube bundles and CVD-spun yarns, to study the effect of interfacial strength on the yarn strength and dominant failure mechanism.^{15,16} They find that yarns fall short of the intrinsic CNT bundle strength by a factor of 1.75 to 2.5, at the theoretical limits of density. However, this understanding of CNT yarn mechanics is limited by a simplified simulation framework and the assumptions of idealized morphology that does not incorporate waviness, which plays a significant role in determining internal load distributions in the yarn.^{17,18} As a result, the full stress-strain response of yarns has not been modeled and the relationship between morphology and load transfer within the yarn has not been explored. Furthermore, the morphology of the CNTs is a key factor in understanding and engineering load

transfer, because it governs spatial distribution of CNTs, packing density, and the distribution of CNT-CNT contacts. Another essential feature in a model is the ability to capture the effect of strain-induced alignment of CNTs on the contact distribution and strength.

Therefore, we seek to develop a multi-scale model for a CNT yarn consisting of wavy CNTs (Fig. 1a), and use insights from tensile testing and X-ray scattering to explain structure-property relationships and changes during loading. We first describe the CNT morphology using space curves, which can be related to direct orientation measurement by X-ray scattering or image analysis. The shape of each individual CNT is described by its waviness amplitude and wavelength. From this, analytical formulations for the strength of each CNT-CNT contact are used to build a three-dimensional model of the yarn in tension, with sliding CNTs transferring load to fixed CNTs via contacts. The three dimensional arrangement of the CNTs in space varies along the axial coordinate due to the distribution of waviness among CNTs (Fig. 1c), with the center of each CNT deviating from the hexagonal arrangement at the fixed end. The changing contact distribution with each step is simulated using a step-wise finite element method (Fig. 1d). The contact locations, strength and stiffness are recalculated with each step, thus capturing how CNT yarn morphology evolves during loading. Recalculation of yarn geometry allows the model to capture the local variations in load sharing due to breaking and reformation of contacts. In addition, CNTs can locally separate once a contact is broken, preventing reattachment of the contact. As explained in later sections, this effect plays an important role in dictating mechanism, and yarn strength. Using this approach, we discuss how yarn strength is limited by CNT-CNT contact behavior, and predict that the organization of the CNTs in combination with the contact strength limits ultimate strength of CNT yarns.

CNT MORPHOLOGY AND CONTACT MODEL

To begin, we construct a mathematical representation of the anisotropic shape and arrangement of CNTs within a yarn. We describe the centerline of each CNT using a 3D parametric function, $r_j = [X, Y_j(X), Z_j(X)]$ (Equation 1), where j is the index of the CNT. We choose the 2D projections $Y_j(X)$, and $Z_j(X)$ to be sine functions^{17,19–21}.

$$r_j = \left[X, A_j \sin\left(\frac{\pi X}{\lambda_j} + \theta_1\right), A_j \sin\left(\frac{\pi X}{\lambda_j} + \theta_2\right) \right] \quad (1)$$

To capture the variation of CNT morphology within the yarn²², the amplitude A_j and phase parameters θ_1 and θ_2 , are selected from a normal distribution. Using this representation, the waviness of each CNT is conveniently parameterized by the ratio of amplitude (A_j) to wavelength (λ_j), and can be geometrically related to the Herman's orientation parameter by Equation 2 (see Supplementary Information).

$$\frac{A}{\lambda} = \frac{1}{\pi} \sqrt{\frac{1}{3}(1 - f)} \quad (2)$$

In the limiting case of perfectly aligned CNTs ($f = 1$), the ratio A/λ approaches zero, coincident with the amplitude becoming very small relative to the wavelength. As discussed later, the chosen representation lets us relate the yarn mechanics model to experiments, using small-angle X-ray scattering to measure the orientation parameter f during tensile testing.

It is well known that the attractive force between CNTs and other solid bodies causes deformation of the CNT cross-section; this has been observed and/or simulated for CNTs in contact with substrates,²³ among CNTs in pairs or bundles,^{24,25} and is known to cause self-collapse single-wall CNTs (SWNTs) with relatively large diameters.²⁶ We consider that CNT-

CNT contacts are the primary source of load transmission within yarns, both for pristine CNTs and for crosslinked bundles or junctions where atomic-scale separations are needed to form these bonds. Therefore, we analytically formulate how self-deformation, which is determined by the morphology of the CNTs at each contact location within the yarn, determines the strength of each respective contact.

To formulate the contact geometry, we use the defined 3D shapes of the CNTs and minimize the total potential energy between each pair of CNTs that are determined to be in contact within the yarn (Fig. 1b). A contact is formed between CNTs i and j when $|r_j - r_i| \leq \delta_{max}$, where δ_{max} is a critical separation beyond which the attractive van der Waals force is negligible. The potential energy (U_T) is the sum of the elastic strain energy of bending the CNTs (Ψ) and the potential energy per unit contact length (L_c) of the resulting contact (Π).

$$U_T = \Psi + L_c \Pi \quad (3)$$

We next describe the deflected shape of a CNT, identified by index k using a local 3D coordinate system representing a section of the CNT around the contact, $\langle x_k, y_k(x_k), z_k(x_k) \rangle$ where y_k and z_k are given by third order power series functions of the individual CNT's longitudinal coordinate x_k (Fig. 2a). Note that the orientation of this coordinate system can differ from the global coordinate system (Equation 1). The CNTs have the same diameter, and consequently the same flexural stiffness, and are assigned geometric boundary conditions analogous to fixed cantilever beams at the ends ($y_k = 0, z_k = 0$). Thus, their deflected shapes are similar in the vicinity of the contact,²⁷ and we define the local coordinate system such that the deflected CNTs are symmetric about the axial direction x_k . Further details of the derivation of the geometric shape function are given in Supplementary Information.

From this, the bending strain energy of the deformed configuration can be calculated using the curvature in 3D, κ .

$$\Psi = 2 \int_0^{L_o-L_c} EI \kappa^2 dx_k \quad (4)$$

Next, we calculate the potential energy per unit contact length (Π), resulting from the deformation of the CNT cross-section at the contact. The deformed configuration (Fig. 2a) is modeled by a piecewise function for the radius, consisting of a flat contact region defined by sector angle α , a region of varying radius bounded by sector angle $\beta = \pi/2$, and a constant radius of the top, R_d between $\theta = \beta$ and $\theta = \pi$. Note that this shape is valid within the limits of self-collapse that is known to occur in large diameter SWNTs, causing potentially larger contact area due. The total potential energy of the contact region is the sum of the additional strain energy due to cross-section deformation V_s , and the van der Waals adhesion energy in the flat contact region V_c , and the non-contact cylindrical region V_{nc}

$$\Pi = V_s + V_{nc} + V_c \quad (5)$$

As a result of this formulation, the total potential energy, Ψ is a function of contact length, L_c and contact sector angle, α . Finally, the total potential energy is minimized with respect to L_c and α to calculate the dimensions of each geometrically derived contact within a complete three-dimensional CNT yarn model.

CNT-CNT CONTACT LENGTH AND STRENGTH

The equilibrium contact geometry therefore defines the static deformed configuration of each pair of CNTs in contact within the yarn, and the contact dimensions are used to determine the strength of each contact from the van der Waals force per unit area. We calculate the contact

length (Fig. 2b) for an exemplary case of a pair CNTs in close proximity, showing that CNT sizes (diameter, number of walls) with lower flexural rigidity (EI) form larger contact lengths (L_c) due to the lower bending strain energy required to form the contact. Beyond a critical separation, the attractive forces will not be sufficient to draw the CNTs into contact, as seen for CNTs with 10 nm diameter and 4 walls. This is due to the rapid increase in the strain energy for the bending deformation due to higher flexural rigidity (EI) corresponding with higher number of walls. Importantly, while larger diameter CNTs having the same number of walls have lower radial stiffness and thus form wider contacts, increasing CNT diameter disproportionately increases their flexural rigidity thus ultimately reducing the total contact area. As a result, single-walled CNTs with lowest flexural stiffness form the largest contact area for a given span length and initial separation.

To relate the contact area to the normal van der Waals adhesion force (F_n), and the static friction force (F_s) of CNT-CNT contact (Equations 6 and 7), we must know the contact strength. Previous studies employed molecular dynamics simulations and atomic force microscopy experiments to determine that CNT-CNT contact in shear can be represented by a single asperity microscale friction law^{28,29} Here, A is the Hamaker's constant, d is the separation between the outer walls of the CNTs, w and L_c are the contact width and length respectively.

$$F_n = \left(\frac{A}{6\pi d^3} \right) w L_c \quad (6)$$

$$F_s = \tau w L_c \quad (7)$$

Therefore, in nominal simulations we use $\tau = 0.24$ GPa as the interfacial shear strength for relative sliding between CVD grown CNTs.²⁹ In general, the interfacial shear strength depends

on factors such as CNT roughness, chirality, presence of other chemical groups and defect density.

Each CNT-CNT contact is loaded in a combination of shear and tension, as the CNTs tend to spring apart when they straighten as well as slide with respect to each other (Fig. 2c). Therefore, we define an effective strength based on the normal and shear components and the total area of the two contacting CNTs (Equation 8). To relate individual CNT-CNT contact strength to a common measure of yarn strength, we normalize by the specific gravity (SG), determined from the mass of the constituent nanotubes and total volume of the yarn (Equation 9).

$$\sigma_c = \frac{1}{2A_{cnt}} \sqrt{F_n^2 + F_s^2} \quad (8)$$

$$\sigma_{c,norm} = \left(\frac{1}{SG} \right) \frac{\left(\sqrt{F_n^2 + F_s^2} \right)}{2A_{cnt}L_c} \quad (9)$$

The CNT-CNT contact strength is strongly related to diameter and number of walls (Fig. 2d), on a per-contact length basis. With increasing diameter, the reduced flexural stiffness of the CNT walls results in a greater contact width and therefore a greater specific contact strength per unit length. However, the improvement in specific contact strength becomes small for larger D/n as further increases in contact width impose a high strain energy penalty. The secondary y-axis shows the contact strength for a contact length of 100 nm. Thus, even for the higher limit of contact lengths and strengths possible in a highly wavy, entangled structure, the contacts remain weaker than their constituent CNTs (~ 25 GPa/SG).

SIMULATION OF CNT YARNS IN TENSION

Hierarchical model framework

To enable simulation of the load-displacement behavior of the CNT yarns in tension, we build a finite element model (FEM) of a yarn segment, wherein the shape of each CNT is governed by Equation 1, and the population of CNTs is represented by normal distributions as described above. Non-dimensional parameters for yarn waviness, X_w and area-normalized number density, X_d are introduced.

$$X_w = \frac{A_m}{D} \quad (10)$$

$$X_d = \left(\frac{\pi}{2\sqrt{3}} \right) \frac{D^2}{S^2} \quad (11)$$

Here, A_m represents the mean of the waviness amplitude distribution, S is the nominal center-to-center spacing of the CNTs, and D is the CNT diameter.

A representative three-dimensional unit of the yarn is created by arranging the first point of the centerlines of the CNTs in a hexagonal grid, with nominal center-to-center spacing (S_m). The CNTs have a distribution of amplitudes and wavelengths, which satisfies the geometric relationship with the Herman's orientation parameter (Equation 2). Half of the CNTs are fixed at their ends (i.e., the left end of the unit), and a displacement boundary condition is applied on the other CNTs (right end). This results in two groups of interdigitated CNTs, as described earlier. The applied displacement causes the CNTs to stretch, as well as slide relative to each other against the adhesion force at the contacts. The size of the model (i.e., the number of CNTs) was chosen to consist of 25 CNTs, each 2 μm long, such that the breaking of contacts does not render the computation unstable, while allowing convergence of results. Further details about the mesh and ANSYS elements are listed in Supplementary Information.

Within the finite element framework, the CNT yarn unit contains two element types. The CNTs are modeled by beam elements having linear elastic constitutive behavior^{30–33} and the contacts are represented as springs connected between the CNTs. The contacts are modeled using spring elements connecting each pair of CNTs determined to be within a critical separation. A typical profile of the contact breaking force versus separation between contacting CNTs is shown in Supplementary Information.

Notably, this representation for the CNT-CNT interface differs from the classical shear-lag theory as it does not directly provide a function for the stress distribution in the CNT elements along the contact length. However, it represents an averaged value for the contact. The main reason for choosing this representation is that the spring element allows dynamic simulation of load transfer and sharing between adjacent CNTs both prior to and post contact failure because its stiffness drops to zero when the contact strength is exceeded. Finally, the model allows for reformation of the contact with a lowered contact length and strength after sliding, when the CNTs still remain within the range of van der Waals adhesion, thus providing elastic-plastic behavior analogous to the shear-lag model.³⁴

Simulated tensile behavior of model CNT yarns

The results of a simulation of a typical MWNT yarn consisting of CNTs with 10 nm diameter and 4 walls ($X_w = 1$, $X_d = 0.84$), and strength 1.59 GPa/SG, are shown in Fig. 3. The stress-strain behavior is initially linear, followed stick-slip behavior with decreasing stress beyond the peak load. To understand the mechanism of load transfer, we plot the normalized number of contacts remaining at each load step relative to the initial number, N_c/N_0 (Fig. 3a). Next, we analyze the contact forces in the yarn, by plotting the cumulative histogram of the forces on

individual contact elements (Fig. 3b). As the stress in the yarn increases, the contacts are progressively loaded; this is seen in the upward shift of the cumulative contact force distributions at 0%, 0.2% and 1.3% strain, respectively. Simultaneously, the weaker contacts break, and in the vicinity of broken contacts, the CNTs detach and relax. As a result, these CNT segments do not carry any load, although they remain intact. Visualization of the force distribution on CNT elements (Fig. 3c) shows that distinct load paths emerge due to the contact distribution in the yarn. Even as the stress increases, bundled CNT segments may relax and separate as the contacts break, and carry no load. Because the individual CNTs are very stiff, there is a high strain energy penalty for reformation of contacts once the initial morphology is disrupted. Thus, with each load step, fewer of the initial contacts reform, and the number of contacts remaining within the yarn drops.

While the number of contacts decreases, the strength distribution of the remaining contacts shifts upward due to greater alignment of CNTs within the yarn upon loading. As a result, the average area of each remaining contact increases. We quantify this increase in alignment by estimating the Herman's orientation parameter from the deformed yarn geometry, f_m relative to the initial orientation, f_0 (Fig. 3d). The maximum alignment and the onset of stick-slip occur at comparable strain. During stick-slip and after the peak load, both the load and contact number fluctuate slightly while the load decays monotonically. Thus, stick-slip is characterized by the failure and reattachment of subpopulations of contacts within the yarn due to incremental strain.

In the stick-slip regime, there is no significant shift in the contact force distribution (i.e., Fig. 4a, between 1.3% and 2% strain). Above 4% strain, the stress drops significantly, corresponding to widespread failure of contacts, within a small incremental strain. Ultimately, the stress drops to zero as the total strength of remaining contacts becomes negligible, resulting in separation of the

yarn segment. Therefore, reformation of contacts with increasing load is vital to maintain the homogeneity and capacity of load transfer within a CNT yarn.

In situ X-ray testing

To validate our simulation finding that the internal morphology of the CNT yarn changes during loading, we performed in-situ tensile testing of twisted MWNT yarns (made by dry spinning),⁷ while collecting small-angle X-ray scattering (SAXS) data from the center of the suspended section (Fig. 5a, inset). To observe orientation changes during loading, we calculate the Herman's orientation parameter by azimuthal integration of X-ray scattering intensity. The strain was cycled four times with increasing strain per cycle (Fig. 4a, 4b), with the yarn eventually failing at 12.6% engineering strain. The permanent deformation of the yarn increased after each cycle, resulting in an initial strain offset before the yarn began to carry load in the subsequent cycle, because the stress remained zero until the slack was taken up. The Herman's orientation parameter increased with strain within each loading cycle (Fig. 4c) and the maximum value normalized by the initial value (f_m/f_0), increases with successive cycles (Fig. 4d). There was also significant hysteresis in each cycle, suggesting changes in the microstructure of the yarn. Thus, tensile loading causes permanent changes in the CNT morphology, and energy is dissipated upon release of the load, both of which occur by breakage and reformation of contacts within the yarn.

Morphology-driven limits of CNT yarn strength

We now use our model to explore how the CNT characteristics (diameter, number of walls, nominal strength) and collective morphology (waviness, density) influence the strength, stiffness, and failure mechanism of CNT yarns. Yarns with different diameters and number of

walls are simulated with constant waviness parameter ($X_w = 1$). The nominal spacing between CNTs is dependent on diameter, and thus the density parameter varies and is reported on Figure 6a. First, as expected from the contact model, we find that yarn strength is directly related to the nominal strength of contacts (Fig. 5a), when yarn strength is normalized by the mass density of the yarn (units = GPa/SG). For instance, SWNTs with diameter 2 nm have contact strength of 0.08 GPa/SG-nm, while 4-walled CNTs with diameter 10 nm have contact strength of 0.01 GPa/SG-nm. Consequently, single-walled CNT yarns generally have higher strength compared to multi-walled ($n = 4$) yarns.

However, we find strikingly that both SWNT and MWNT yarns have ultimate strength significantly below (6% and 2.5% respectively) the intrinsic CNT strength. Fig. 5a shows the strength of simulated MWNT yarns (10 nm, 4 walls) in both absolute and relative terms compared to the strength of the constituent CNTs. Although CNT-CNT contacts can be strong on a per-length basis, the intrinsic waviness of CNTs in the yarn, which is unfortunately an outcome of all presently known CNT yarn and fiber manufacturing processes, limits contact area and ultimately contact strength. Next, we vary waviness and density parameters (Equations 10 and 11) for MWNT yarns (10 nm diameter, 4 walls) yarns, and show (Fig. 5b) that a reduction in CNT waviness increases yarn strength due to higher contact strength. For example, reducing the waviness parameter X_w from 5 to 1 results in a factor of 3.4 increase in strength from 0.35 GPa/SG to 1.2 GPa/SG for density parameter, $X_d = 0.68$. A simultaneous increase in the CNT density to $X_d = 0.85$ (with $X_w = 1$) increases the yarn strength to 1.7 GPa/SG.

Further insight is gained by simulating yarns with one or more parameter values approaching practical limits, and analyzing the role of contact breakage and reformation. When the contact area is maximized, i.e. when the yarn has high density and low waviness ($X_w = 1$, $X_d = 0.82$; Fig.

5c, curve 1), the yarn strength still remains below 2.5% of the intrinsic CNT strength. Thus, even at high levels of order, CNT-CNT contact strength limits yarn strength. The CNT morphology also affects the yarn failure mode. As shown in Figure 5d, for high density yarns ($X_d = 0.82$), there is first a brief increase in the number of contacts due to strain-induced alignment. After this, the contact number decreases, and has dropped by approximately 80% at 1% strain. Beyond this point, the highly ordered yarn fails by progressive stick-slip, and its ultimate strength is governed by the CNT-CNT contact strength and density of contacts.

The above case represents an ideally high density of CNTs. In order to represent a yarn with SG of around 1.5, which is comparable to the high SG of 1.3 to 1.8 measured for densified CNT yarns made by direct spinning from CVD,³⁵ the waviness parameter is increased and the yarn density is lowered ($X_w = 2$, $X_d = 0.68$). Here (Fig 5c, curve 2), abrupt brittle-type failure of the yarn is predicted because the contacts are weaker than those in higher-density yarns. As seen in Figure 6d, the low density yarn shows sudden widespread failure of the contacts, and stick-slip is negligible. As a result, large segments of CNTs detach during loading. As the CNTs separate, the van der Waals force drops and is no longer able to balance the strain energy associated with the contact, and contacts are not reformed because of the large average separation between CNTs due to the low density of yarn. Thereby, post-slip re-attachment of CNT-CNT contacts is limited. Based on this, we conclude that high CNT density is also critical for high strength yarns by enabling reformation of broken van der Waals contacts upon loading. This allows load-induced alignment and strengthening of contacts in the initial stages of loading, finally resulting in higher contact survival and higher total stress transmitted.

We also explore the influence of CNT quality. Although individual CNT strength as high as 63 GPa has been measured,³² all populations of CNTs have statistically distributed strength over

micron-scale lengths due to the development of defects during growth and post-processing. Moreover, defective CNTs have $< 20\%$ the theoretical strength of CNTs.³² We simulate defective CNTs by reducing the CNT strength to 10% of its nominal value (40 GPa reduced to 4 GPa) on 50% of the CNT elements. In this case, yarn failure is sudden after an initially linear stress-strain behavior (Fig. 5c, curve 1d). When CNTs are highly defective and have low strength, the CNT segments can fail before the contacts, and thus both the broken defective CNT and neighboring segments of other CNTs do not carry any load. This mixed-mode failure also lowers overall yarn strength, in this case from 1.2 to 0.7 GPa.

DISCUSSION

We can now reflect on the reported mechanical properties of CNT yarns made by various methods, and assess the potential for significant improvement in these properties. In Fig. 6 we compare the strengths of CNT yarns manufactured by a variety of methods. The CNT yarns have strengths between 0.1 and 3.7 GPa/SG, and in the chart are grouped by their basic synthesis process and distinguished by post-processing methods. The CNT yarn values are compared to individual CNTs and prominent industrially produced fibers.^{7,9,32,35–43}

A widely used post-processing method is densification, in which a low-density CNT yarn is compacted by capillary forces upon exposure to solvent vapor or by passing the CNTs through a liquid bath. Densification of CNT yarns drawn and/or spun from floating catalyst CVD, and spun from CNT forests, has resulted in approximately 2-fold and 10-fold strength increases, respectively. For simulated exemplary MWNT yarns ($X_w = 5$, Figure 5b), our model predicts a 3-fold strength increase, from 0.1 GPa/SG to 0.3 GPa/SG, when the density is increased from $X_d = 0.4$ to 0.68. The simulated strength improves 12-fold to 1.2 GPa/SG when the increase in

density is also accompanied by a reduction of waviness (to $X_w = 1$). Thus, more significant gains in strength are possible when densification is accompanied by an overall reduction in CNT waviness, resulting in higher contact area. Further, a recent study by Wang et al. reported notably strong (3 GPa/SG) yarns of few-walled CNTs that were made by floating catalyst CVD followed by ethanol vapor densification and mechanical pressing.³⁵ Guided by our simulation results that exemplary SWNT yarns have twice the strength of MWNT yarns, , we can attribute the high strength reported by Wang to be achieved by both mechanical densification as well as and high contact deformation of CNTs with low wall stiffness. Both of these attributes favor increased CNT contact area and therefore higher absolute contact strength.

Solution spinning of high-quality SWNTs dispersed in superacids has produced fibers having a very high degree of orientation (Herman's parameter 0.986).^{37,39} To our knowledge, these CNT fibers have the highest alignment achieved to date, yet their strength is only approximately 1 GPa/SG. Therefore, we expect that the presence of residues from dispersion and spinning that do not actually cross-link CNTs can hinder CNT-CNT load transfer by reducing the interfacial shear strength, further emphasizing the role of contacts in determining CNT yarn strength.

In light of our finding that even highly ordered yarns do not possess contact strength equal to CNT strength, we believe that current CNT yarns with strengths exceeding ~2 GPa/SG have essentially reached the limit of strength possible by van der Waals adhesion alone. Notably, the highest reported CNT yarn strengths of 6-9 GPa/SG, by Koziol et al.,⁹ were obtained over short (~1 mm) gage lengths, compared to less than 1 GPa/SG measured over longer gage lengths. In both cases, the strength was statistically distributed but possessed a low strength peak and a high strength peak. It can be assumed that the shorter gage length captured at least a small number of continuous CNTs that spanned across the entire length of the sample.

A promising direction to improve CNT yarn strength may therefore be to increase the CNT interfacial adhesion by chemical modification or crosslinking.⁴⁴ For example, molecular dynamics (MD) simulations validated through in situ Transmission Electron Microscopy (TEM) mechanical measurements determined that the interfacial strength can be increased to 400 MPa between overlapping CNT bundles by cross-linking the CNTs with PMMA oligomers. The crosslinked value is 67% greater than the 0.24 GPa interfacial strength derived for pristine CNTs due to van der Waals forces, and used in the simulations described in this work.²⁹

To examine the potential advantages of increased contact strength by crosslinking or addition of an interfacial material, we simulate the stress-strain response of CNT yarns having increased contact strength, and report the relative improvement of yarn strength (Figure 7). The simulations show that the structure of the yarn determines the factor of improvement in yarn strength, and there is always a sublinear increase in relative yarn strength with increased contact strength. Yarns with high density and low waviness, ($X_d = 0.85$, $X_w = 1$) fail by gradual stick-slip weakening of contacts as shown previously. In this type of yarn, the failure mode is preserved even as contact strength is increased. Thus, the yarn strength increases only by a factor of 2 for a 6-fold increase in contact strength. However, a yarn with low density and higher waviness ($X_d = 0.68$, $X_w = 2$) shows brittle-type fracture due to widespread failure of a large number of contacts. In this case, improvement in contact strength leads to a larger relative increase in yarn strength. Thus highly dense yarns made by mechanical pressing of as-synthesized yarns would not proportionally benefit from cross-linking at CNT-CNT contacts, compared with as-synthesized yarns. However, as illustrated previously, dense yarns ($X_d = 0.85$) are nominally twice as strong as yarns with lower density ($X_d = 0.68$). As a result, dense yarns are predicted to have a strength of around 3.3 GPa/SG for a factor of 6 increase in contact strength, which represents a 50%

increase over the high strength yarns densified by mechanical pressing.³⁵ However, it must be noted that chemically cross-linked contacts would not reversibly reattach after they fail, and instead transition to adhesion by weaker van der Waals forces. This would further limit the ability of the yarn to sustain load in the stick-slip regime.

Also, as presented in this paper, the CNT yarn model assumes that all CNTs have the same diameter, equivalent length, and equivalent intrinsic fracture strength (except when defects are introduced, e.g., Fig. 5c). While this may affect the strength of individual contacts, it does not alter the overall failure mode. Further, the influence of impurities such as surface-bound amorphous carbon, surfactant residues, and unreacted catalyst material, is not considered. Therefore, future work may be focused on adapting the 3D finite element geometry to include lateral constraint provided by macroscopic twist; capturing the diameter, length, and strength distributions of CNT populations; and extending the size of the model while maintaining computational stability.

CONCLUSIONS

We have presented a hierarchical framework for modeling the tensile behavior of CNT yarns, which reveals how macroscopic mechanical properties are governed by CNT diameter, number of walls, density and alignment. In-situ tensile testing is used to simultaneously collect X-ray scattering data to capture load-induced changes in morphology. A multiscale three-dimensional finite element model is formulated to capture the waviness of CNTs, and examine changing contact distributions during tensile loading, enabling direct simulation of the full tensile stress-strain behavior of CNT yarns. The simulations reveal that progressive stick-slip and failure of CNT-CNT contacts causes isolated load paths to emerge, leading to yarn failure at <10% of the

intrinsic CNT strength. Finally, the failure mode and ultimate strength are governed by the structural parameters of the yarn and load transfer mechanism. The benefits of post-processing methods such as densification and cross-linking vary based on the nominal structure of the yarn, and are not necessarily linear with respect to the strength of an individual contact. This knowledge is critical to envision the extent to which significant improvements in the strength and toughness of CNT fibers can be made, and whether CNT fibers will realize multifunctional uses such as load-bearing lightweight conductors, or textiles for improved ballistic protection. Also, with appropriate modifications, the methods presented here could be applied to study the thermal and electrical behavior of CNT assemblies, and to elucidate how CNT-CNT load transmission influences growth and processing.

FIGURES

Figure 1. Hierarchical morphology of a CNT yarn and analytical-numerical model implementation. (a) SEM images of dry spun MWNT yarn, with high magnification view showing entangled and wavy microstructure in the yarn. (b) A section of the discretized 3D morphological model of the CNT yarn with a hexagonal arrangement of CNTs, and each CNT having specified waviness, and displacement-controlled tension boundary condition in the finite element model. The shape of each CNT is described by a waviness amplitude and wavelength. (c) Cross-sectional view showing the location of CNT centers at the fixed end ($x/L = 0$) and mid-axial location ($x/L = 0.5$), showing anisotropy due to the tortuous shape of CNTs (d) Model framework, where morphology and contact geometry are re-calculated prior to incrementing the strain and solving the finite element model with each load step.

Figure 2: Scaling of contact strength and length for a single CNT-CNT joint as a building block of a CNT yarn. (a) Schematic showing bending and cross-section deformation of CNTs due to van der Waals forces, and nomenclature defined by contact length L_c , equilibrium wall position $r(\theta)$, sector angles α and β , and contact width $2w$. (b) Normalized contact length versus horizontal spacing (S) divided by CNT radius (R) for different combinations of CNT diameter and number of walls. (c) Free-body diagram showing typical loads on a contact, which is represented as a spring with a sliding stiffness and breaking force. (d) Specific contact strength for the CNT-CNT joint, loaded in tension, versus wall-normalized thickness. Right y-axis shows absolute contact strength for a contact length of 100 nm. Each curve in (d) represents a different number of walls (n); the CNTs in the pair have identical diameter and number of walls.

Figure 3: Simulated tensile behavior of a CNT yarn consisting of CNTs with diameter 10 nm and 4 walls. (a) Exemplary stress-strain curve, along with the fraction of contacts remaining versus applied strain. (b) Cumulative distributions of the force on CNT-CNT contacts with increasing strain applied to the yarn. (c) Colormaps of force on individual CNTs and contacts within the simulated yarn segment, showing relaxation of CNT segments in the vicinity of broken contacts and consequent emergence of dominant load paths where force is highest. (d) Herman's orientation parameter versus strain, normalized to initial value before loading, showing increasing orientation of CNTs with increasing load, and saturation following the onset of stick-slip around 1% strain.

Figure 4: Validation of the CNT yarn model by cyclic tensile loading of dry-spun MWNT yarns during X-ray scattering, with increasing applied strain. (a) Stress-strain for load-unload cycles 1 and 2. Inset shows suspended yarn and X-ray beam direction orthogonal to loading. (b) Cycles 3 and 4, which proceeds to failure. (c) Herman's orientation parameter (f) of CNTs during the loading stage of each of the 4 cycles, showing that orientation increases significantly upon each loading cycle, and is reversed upon unloading. (d) Normalized maximum Herman's parameter for each cycle, and maximum strain reached at each cycle.

Figure 5: Influence of CNT geometry, waviness, density, and quality on yarn mechanics, as predicted by the integrated model. (a) Exemplary stress-strain curves of yarns consisting of single-walled ($n = 1$) and multi-walled ($n = 4$) CNTs. All yarns have the same waviness ($X_w = 1$), but the area-normalized density is diameter-dependent and varies slightly even though the nominal CNT center-to-center spacing is the same. (b) Relationships between specific strength and waviness and number density. (c) Influence of CNT quality and yarn morphology on yarn strength, showing that low-quality and/or wavy yarns fail by brittle fracture, yet higher quality and less wavy yarns fail by stick-slip pull-out. (d) Contact fraction versus strain for high and low density yarns from (c) showing higher density CNT yarns exhibit improved load transmission due to improved contact survival.

Figure 6: Comparison of the reported strength of CNT yarns manufactured by a variety of synthesis and post-processing methods.

Figure 7: Relationship between relative yarn strength (X_f) and contact strength (X_c), for selected combinations of waviness and density. The sublinear relationship between relative contact strength and yarn strength shows that yarns that fail due to bulk contact failure show a higher relative increase in strength.

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