

MECHANICAL PROPERTIES OF CARBON NANOTUBE FIBERS

Jingna Zhao, Xiaohua Zhang, * Qingwen Li

Suzhou Institute of Nano-Tech and Nano-Bionics, Ruoshui Road 398, Suzhou 215123, China

** xhzhang2009@sinano.ac.cn*

Keywords: carbon nanotube, fiber, mechanical properties

Abstract

The factors contributing to the mechanical properties of carbon nanotube (CNT) fiber include the nano-scale tube structure, micro-scale inter-tube characteristics, and macro-scale spin parameters. In the spinning based on CNT arrays, liquid infiltration is an efficient way to strengthen CNT fibers. To improve the fiber strength, the tubes must be long and have a small diameter and thin walls, the spinning need to be performed at the optimal condition, the fiber should be highly densified with the aid of highly polar solvents, and long-chain or cross-linked polymers can be introduced into the fiber.

1 Introduction

Carbon nanotubes (CNTs) are the strongest nano-materials ever discovered by mankind, with tensile strength and modulus up to 100 GPa and 1 TPa, respectively [1]. For the purpose of engineering applications, especially the light-weight and high-strength ones, various methods have been developed to assemble CNTs into continuous fibers at the macro-scale, including the coagulation-based “wet spinning” [2,3], “direct spinning” from CNT aerogel [4,5] or similarly from preformed CNT film [6], and “dry spinning” from CNT arrays (also called “array spinning”) [7,8]. So far, the array spinning has become the most widely used method, as it allows the spun fibers to possess high purity, strong strength and low density.

As compared to their constituents, the tensile strength of CNT fiber is still 1—2 orders of magnitude smaller. The strongest but very short direct-spun fiber was measured in 2007 to be 8.8 GPa and 357 GPa in strength and modulus [9]. For the array-spun fiber, the current record was 3.3 GPa reported also in 2007 [10]. A recent study shows that the highest strength for the polymer-infiltrated CNT fiber was ~2.5 GPa [11]. Although these values are as comparable to many commercial high-performance fibers, there is still a big gap to fully utilize the superb performances of CNT. This is because many factors, from nano-, micro-, to macro-scale, contribute to the fiber’s mechanical properties. Here we study the way to strengthen CNT fibers. We find that, in order to obtain high-performance CNT fibers, the tubes must be long and thin-walled, and be highly compact. Long-chain or cross-linked polymers can be introduced into the fibers by liquid infiltration and a certain post-spin thermal treatment.

2 Materials and testing methods

The vertically aligned CNT arrays used for fiber spinning were synthesized by a sustained chemical vapor deposition (CVD) on SiO₂/Si wafers [12] and the chloride mediated CVD (CM-CVD) [13]. Based on carbon source (C₂H₂ or C₂H₄) and CVD method, the arrays are

divided into four groups, namely the C₂H₂-I and C₂H₂-II, C₂H₄, and C₂H₂-CM arrays [14]. As reported in Refs. [14,15], the fiber is made by drawing and twisting the continuous CNT sheet pull out of a CNT array, where the ratio between the draw and twist speeds $H = v_d/v_t$ is used to control the twist level while the fiber diameter is related to the width of CNT sheet w_{CNT} .

The fiber diameter was measured by the optical diffraction model where a 532 nm green laser was used. Tensile tests were conducted using a MTS Nano Bionix Universal Testing System, by Oak Ridge, Tennessee. The samples were mounted on paper tabs with a gauge length of 7 ± 1 mm. The extension speed was 0.001 mm/s.

3 Results and discussion

At the nano-scale, the structural parameters such as tube diameter, length waviness, and wall thickness can affect the mechanical properties of CNT fibers. As we have produced spinnable CNT arrays different tube structures, it is possible to systematically analyze the structural dependence. At the micro-scale, the influencing factors include tube arrangement and entanglement, and inter-tube load transfer. However, in the array spinning, they are strongly related to the quality of CNT array. Therefore, it is difficult to obtain a general dependence. In order to refine the inter-tube characteristics, CNT densification and polymer infiltration are two widely-used techniques. The contributing factors at the macro-scale are found to be the assembly parameters like fiber diameter and twist angle.

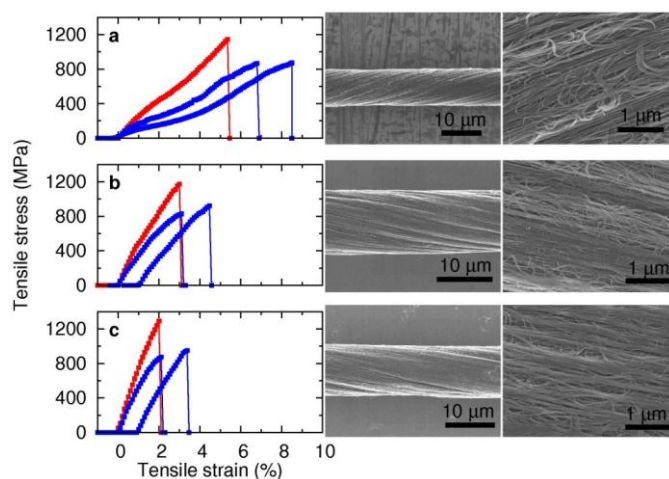


Figure 1. Tensile test and fiber morphology of C₂H₂-II fibers with large (a), medium (b), and small (c) tube wavinesses. In each panel, results of two as-spun fibers (blue) and one PVA-infiltrated fiber (red) are shown.

3.1 Effect of nanotube waviness

The waviness is studied at first. This is because even for the same type of CNT array, that is, all the tubes possess the similar nano-structures, the waviness can be quite different. However, our results show that, the waviness has only effects on the tensile behavior and therefore the modulus, rather than on the magnitude of tensile strength, see Figure 1. (We compared the fibers with the similar fiber diameter of 10–15 μm and twist angle of 15–20 °.) For the fiber with large tube waviness, tensile stress does not increase linearly upon stretching. As the alignment is increased, the modulus goes up and the strain at break decreases. However, these C₂H₂-II fibers with different morphologies are almost of the same tensile strength, ~830–880 MPa. This is because that in the fibers, the filaments of CNT bundles are tightly compact and therefore contribute in carrying external loads. Upon the external load, the stretching effect makes wavy tubes straight, resulting in the large strain at break. If the waviness is sufficiently large, the fiber morphology will probably be refined, as indicated by the initial state in tensile

behavior shown in Figure 1a, where the stress does not go up quickly until a certain strain threshold is reached. Therefore, the modulus increases with decreasing the waviness. Interestingly, even after poly(vinyl alcohol) (PVA) infiltration, the similar tensile behavior can be observed for different tube wavinesses, see the red curves in Figure 1.

3.2 Effect of nanotube structure

The structural parameters for C₂H₂-I, C₂H₂-II, C₂H₄, and C₂H₂-CM tubes are given in Table 1. According to the wall number, we also use another way to name the CNTs [16,17]. The C₂H₄ tubes were the typical few-walled CNTs (FWCNTs). The C₂H₂-II array and fibers were often studied with comparison to the FWCNT, and therefore referred as the multi- or many-walled CNT (MWCNT).

	C ₂ H ₂ -I	C ₂ H ₂ -II	C ₂ H ₄	C ₂ H ₂ -CM
Diameter (nm)	8—10	8—10	≤6	≥17
Walls	8—10	~6	2—3	≥15
I_G/I_D	0.88	0.99	1.27	1.65
Height (μm)	320	320	260	1000
Strength (MPa)	689	866	1170	383
Modulus (GPa)	10.1	16.0	53.5	6.5

Table 1. Tube diameter, number of walls, I_G/I_D ratio, array height, strength and modulus of CNT fibers.

Figure 2 shows the stress-strain curves for different CNT fibers. The general trend is that the fibers spun from thinner-walled CNTs, with smaller diameters as well, show higher tensile strength. It can be clearly seen by comparing the two groups of C₂H₂ fibers, where the only difference is the wall number while the tube diameter and length were similar. As decreasing the wall number from 8—10 to ~6, the fiber became stronger, from 689 to 866 MPa. In fact, as only the outmost layer of CNT carries the load before the fracture [18], there should be no difference as changing the wall thickness. However, the defects might become more and more as increasing the number of walls, indicated by the ratio I_G/I_D of the G- and D-band intensities of the Raman scattering spectrum which was 0.88 and 0.99 for the C₂H₂-I and C₂H₂-II fibers. It suggests that the thinner C₂H₂-II might be stronger. Furthermore, the tube-tube contact area can be different for these different tubes, because the CNTs with fewer walls can be flattened or collapsed more easily, giving rise to more efficient inter-tube load transfer.

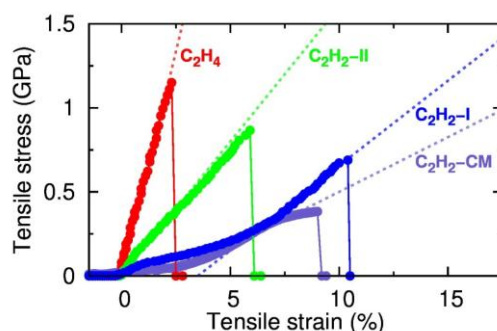


Figure 2. Results of tensile tests on different CNT fibers.

3.3 Effect of array height (tube length)

It is generally known in the traditional textiles that the longer filament length, the higher strength of yarn (fiber). Similarly, for CNT fibers, the longer tube length increases the tube-tube contact area and also the migration chances from fiber surface to the interior of the fiber, resulting in higher effective load transfer between the tubes. Furthermore, there are reduced

end-to-end contacts which act as the assembly defects. Figure 3 shows the fiber strengths of the C₂H₂-I, C₂H₂-II, C₂H₄, and C₂H₂-CM fibers, averaging more than 20 samples, as functions of array height. All the fibers became stronger as increasing the array height until a maximum was reached, which for different arrays was 500, 350, 260, and 1000 μm , respectively. When further increasing the height, by adding the growth time, the strength decreased significantly. This phenomenon can be explained by the growth mechanism of CNT arrays [14]. There are two typical stages during the growth. At the first several minutes, the array height increases linearly with time. Within this linear growth, the tube diameter does not change from the array top to the bottom, and neither does the number of walls. However, afterwards, the growth rate slows down, and the number of walls grows up greatly at the bottom of the array. Due to the increase of tube thickness, further growth of the array height is suspended, together with a loss of the tube alignment at the array bottom. Therefore, the best array height is the one just before the end of the linear growth, rather than the maximum one out of the full growth.

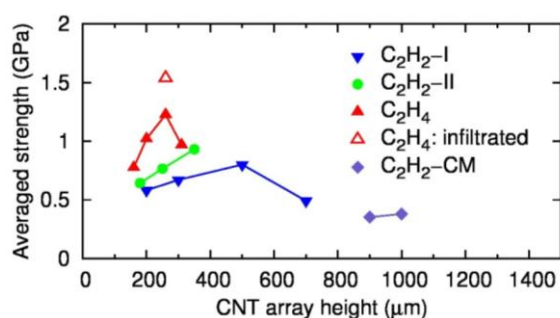


Figure 3. Fiber strength as a function of array height. The PVA-infiltrated C₂H₄ fiber is also plotted.

3.4 Effect of fiber diameter

In order to spin a CNT fiber with constant fiber diameter d_f , the width of CNT sheet w_{CNT} is fixed during the spinning. Therefore, it is possible to study the diameter effect. Contrary to popular belief that a thinner fiber might be stronger, Figures 4a and b show that as increasing d_f from sub-5 μm to $\sim 15 \mu\text{m}$, both the fiber strength σ_f and modulus E_f increase slightly. The reason is that a thinner fiber is less compacted due to the smaller radial pressure inside the fiber, as can be checked using the ratio between w_{CNT} and d_f^2 (Figures 4c and d), a quantity proportional to the fiber density. It means that the fiber density increases with increasing diameter [15]. However, when further increasing d_f , there might be decreases in σ_f and E_f [19,20]. This result arises out of the fact that the outermost layers of the fiber are usually more compressed than the interior as the interior is always shielded. Therefore, we suspect that for larger fiber diameter, less fraction of CNTs (only the fiber surface) can carry the external load, resulting in the weaker mechanical performances.

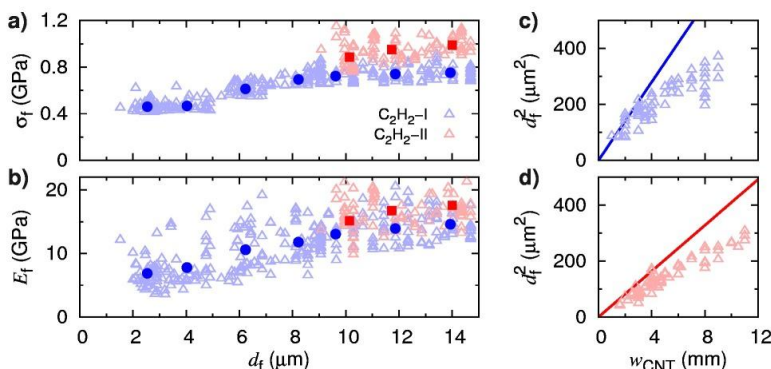


Figure 4. (a,b) Fiber strength and modulus generally increase with fiber diameter. (c,d) Square of fiber diameter as a function of the width of CNT sheet.

3.5 Effect of fiber's twist angle

In the array spinning, the surface twist angle θ_s of CNT fiber is related to the ratio between the draw and twist speeds $H = v_d/v_t$ by $\theta_s = \arccos\{H/[(\pi d_f)^2 + H^2]\}^{1/2}$. Generally speaking, the twist improves the filament (CNT bundle)-filament interfaces and frictional forces, making the load transfer more efficient. This improvement is dominant when increasing the angle to the optimal one about 15—20° (Figure 5). However, at over twists, although the load transfer is improved and the fiber is densified as well, the load (upon stretching) compresses the fiber rather than acting along the fiber axis due to the large angle between the filament and the axis. Therefore, the strength drops beyond the optimal twist angle. This normal peak obviously corresponds to the optimal spin condition for high-performance CNT fibers.

However, a new strength peak was surprisingly observed when increasing θ_s up to >30° and ~27° for the C₂H₂-I and C₂H₂-II fibers, respectively. This totally new strength peak cannot be observed in the traditional yarns, and should be attributed to the collapse transformation of the special hollow structure of CNTs. The collapse makes the CNT bundles much stronger and reduces their cross-sectional areas, as predicted by our molecular-dynamics simulations [21]. The new peak indicates possible post-spin treatments to strengthen CNT fibers, such as over-twisting and stretching [15].

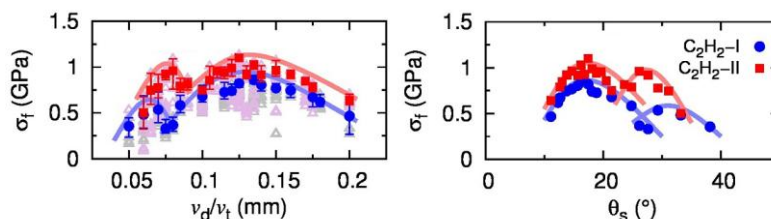


Figure 5. Double-peak strength behavior of CNT fibers with increasing twist angles (or decreasing the speed ratio v_d/v_t). Here only fibers with diameter larger than 10.5 μm are plotted.

3.6 Effect of liquid densification

Liquid infiltration is often used during the array spinning [14,19]. When the liquid is solvent without any polymer molecules, there is purely the densification effect, which is generally explained as results of the surface tension or capillary force during the evaporation of solvent. Therefore, volatile solvents like ethanol and acetone are widely used. However, this might not be correct [22]. For example, dimethyl sulfoxide (DMSO) has a surface tension of 43.7 mN/m (at 20 °C), larger than acetone (23.7 mN/m) but smaller than water (72.8 mN/m). But DMSO strengthens CNT fibers more than the other two solvents. In the following, CNT fibers were produced out of the FWCNT (C₂H₄) arrays.

Figure 6 shows the strengthening abilities of different solvents, where according to the dipole moments the solvents are sorted and grouped into non-polar, polar aprotic, and polar protic solvents. For non-polar solvents, toluene and styrene have the best strengthening results, because their aromaticity introduces π - π stacking with CNTs and as leaving out of the fiber makes the tubes more compact than the others. To get a clear polarity dependence, non-aromatic polar solvents were used. For polar protic solvents which contain dissociable H⁺, there is no clear dependence on polarity. Water is the worst solvent and only improved the fiber strength up to 742—971 MPa. Methanol has an infiltration result as comparable as ethanol (~1.05 and ~1.08 GPa, respectively). This seems that the infiltration is limited by the large surface tension. It is correct for water, because the strong H-bonding increases the melting and boiling points, solubility, viscosity, and surface tension. Ethylene glycol shows a surprisingly high infiltration result, making CNT fibers as strong as 1.33—1.58 GPa. The

reason is that the viscosity of ethylene glycol (16 cP) is still low enough for a rapid wetting, and that its two polar –OH groups result in more dipole- π interactions. Therefore, during the evaporation a large capillary force is generated to draw CNTs together. However, for the 1,3-propanediol which has only an additional –CH₂– group, its large viscosity (52 cP) strongly limits the infiltration into CNTs. For polar aprotic solvents, the polarity dependence can be more clearly seen. After the infiltration, the local dipole moment of solvent can induce dipole moment on CNT, resulting in an attractive binding energy. The highly polar solvents like *N,N*-dimethylformamide (DMF), DMSO, and *N*-methyl-2-pyrrolidone (NMP) improved the fiber strength up to 1.14–1.35 GPa, higher than ethanol (~1.08 GPa). However, for acetone whose molecular structure is similar to DMSO, its dipole moment is ~1 D smaller and the infiltration result was only ~1.03 GPa. The results of ethyl acetate and acetonitrile also agree very well with the polarity dependence.

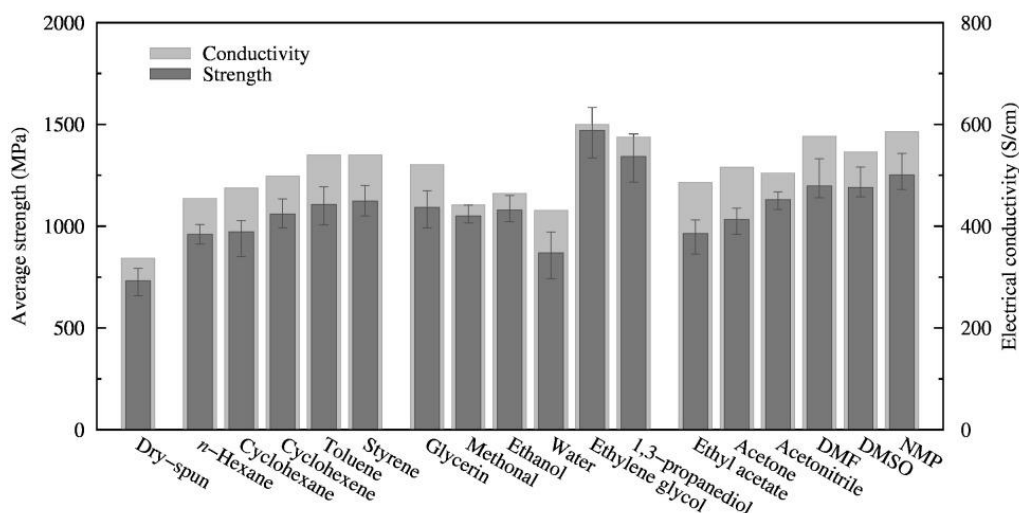


Figure 6. Tensile strength and electrical conductivity of CNT fibers after different solvent infiltration. All the fibers were spun from the same array.

The polarity dependence observed here is important for making high-performance CNT fibers, and can be well extended for the production of CNT composites.

3.7 Effect of polymer infiltration

To avoid the large difference in CNT densification, ethanol, DMF, DMSO, and NMP were used to dissolve different polymers. Polymers such as dodecylamine, PVA, and polyurethane (PU) can be directly introduced into CNT fibers through infiltration because their molecular weights are not huge. However, for the polymers with cross-linked networks, such as polyimide (PI) and bismaleimide (BMI), the usual way is to cure the fibers containing their prepolymers or resins. A molecular weight dependence can be obtained. Dodecylamine and BMI resin are the smallest polymers, molecular weight of just hundreds of g/mol. Different from the solvent evaporation that draws CNTs together, these molecules stay between and separate neighboring CNTs. As a result, the fiber strength was even ~100–200 MPa smaller than the pure solvent densification. When long-chain polymers like PVA was used, due to the bridging between and wrapping around the CNTs, the fiber strength was improved up to 1.34–1.54 GPa. The CNT fiber enhanced by PI prepolymer had a moderate strength of ~1.09 GPa as the molecular weight is in between dodecylamine and PVA.

PU, PI, and BMI are three different cross-linked polymers. In our study, PU was introduced into the fiber directly by infiltration, while PI and BMI were formed inside the fiber by curing

their prepolymers or resins. The direct infiltration of PU was limited by the large molecular weight, resulting in the average fiber strength of only 1.09 GPa. However, both PI and BMI led to efficient load transfers between CNTs, as their network structure was formed inside the fiber which can well connect CNTs with each other. PI- and BMI-reinforced CNT fibers had the strength of 1.97 and 2.38 GPa, respectively. Figure 7 provides the comparison between stress-strain curves for five different CNT fibers [22]. Generally, as strengthening the CNT fibers, the modulus goes up and the strain at break decreases.

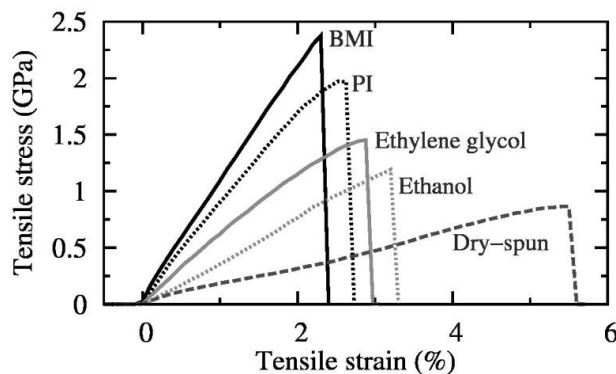


Figure 7. Stress-strain curves for dry-spun, ethanol-densified, ethylene glycol-densified, PI-reinforced, and BMI-reinforced CNT fibers.

4 Summary

The mechanical properties of CNT fibers are studied. For high-performance fibers, attention should be paid to the tube structure, twist angle, packing density, and filament-filament interfacial properties. Highly polar solvents can be used to improve the densification level and help the polymer infiltration for modifying the interfacial bondings.

References

- [1] Ruoff R.S., Qian D., Liu W.K. Mechanical properties of carbon nanotubes: theoretical predictions and experimental measurements. *C. R. Phys.*, **4**, pp. 993-1008 (2003).
- [2] Vigolo B., Pénicaud A., Coulon C., et al. Macroscopic Fibers and Ribbons of Oriented Carbon Nanotubes. *Science*, **290**, pp. 1331-1334 (2000).
- [3] Ericson L.M., Fan H., Peng H., et al. Macroscopic, Neat, Single-Walled Carbon Nanotube Fibers. *Science*, **305**, pp. 1447-1450 (2004).
- [4] Zhu H.W., Xu C.L., Wu D.W., et al. Direct Synthesis of Long Single-Walled Carbon Nanotube Strands. *Science*, **296**, pp. 884-886 (2002).
- [5] Li Y.L., Kinloch, I.A. Windle, A.H. Direct Spinning of Carbon Nanotube Fibers from Chemical Vapor Deposition Synthesis. *Science*, **304**, pp. 276-278 (2004).
- [6] Ma W., Liu L., Yang R., et al. Monitoring a Micromechanical Process in Macroscale Carbon Nanotube Films and Fibers. *Adv. Mater.*, **21**, pp. 603-608 (2009).
- [7] Jiang K., Li Q., Fan S. Spinning continuous carbon nanotube yarns. *Nature*, **419**, p. 801 (2002).
- [8] Zhang M., Atkinson K.R., Baughman R.H. Multifunctional Carbon Nanotube Yarns by Downsizing an Ancient Technology. *Science*, **306**, pp. 1358-1361 (2004).
- [9] Koziol K., Vilatela J., Moisala A., et al. High-Performance Carbon Nanotube Fiber. *Science*, **318**, pp. 1892-1895 (2007).
- [10] Zhang X., Li Q., Holesinger T.G., et al. Ultrastrong, Stiff, and Lightweight Carbon-Nanotube Fibers. *Adv. Mater.*, **19**, pp. 4198-4201 (2007).
- [11] Ryu S., Lee Y., Hwang J.-W., et al. High-Strength Carbon Nanotube Fibers Fabricated by Infiltration and Curing of Mussel-Inspired Catecholamine Polymer. *Adv. Mater.*, **23**, pp. 1971-1975 (2011).

- [12] Li Q., Zhang X., DePaula R.F., et al. Sustained Growth of Ultralong Carbon Nanotube Arrays for Fiber Spinning. *Adv. Mater.*, **18**, pp. 3160-3163 (2006).
- [13] Inoue Y., Kakihata K., Hirono Y., et al. One-step grown aligned bulk carbon nanotubes by chloride mediated chemical vapor deposition. *Appl. Phys. Lett.*, **92**, art. no. 213113 (2008).
- [14] Jia J., Zhao J., Xu G., et al. A comparison of the mechanical properties of fibers spun from different carbon nanotubes. *Carbon*, **49**, pp. 1333-1339 (2011).
- [15] Zhao J., Zhang X., Di J., et al. Double-Peak Mechanical Properties of Carbon Nanotube Fibers. *Small*, **6**, pp. 2612-2617 (2010).
- [16] Fang C., Zhao J., Jia J., et al. Enhanced carbon nanotube fibers by polyimide. *Appl. Phys. Lett.*, **97**, art. no. 181906 (2010).
- [17] Meng F., Zhang X., Xu G., et al. Carbon Nanotube Composite Films with Switchable Transparency. *ACS Appl. Mater. Interfaces*, **3**, pp. 658-661 (2011).
- [18] Yu M.F., Lourie O., Dyer M.J., et al. Strength and Breaking Mechanism of Multiwalled Carbon Nanotubes under Tensile Load. *Science*, **287**, pp. 637-640 (2000).
- [19] Liu K., Sun Y., Lin X., et al. Scratch-Resistant, Highly Conductive, and High-Strength Carbon Nanotube-Based Composite Yarns. *ACS Nano*, **4**, pp. 5827-5834 (2010).
- [20] Fang S., Zhang M., Zakhidov A.A., et al. Structure and process-dependent properties of solid-state spun carbon nanotube yarns. *J. Phys.: Condens. Matter*, **22**, art. no. 334221 (2010).
- [21] Zhang X., Li Q. Enhancement of Friction between Carbon Nanotubes: An Efficient Strategy to Strengthen Fibers. *ACS Nano*, **4**, pp. 312-316 (2010).
- [22] Li S., Zhang X., Zhao J. et al. Enhancement of carbon nanotube fibres using different solvents and polymers. *Compos. Sci. Technol.*, doi: 10.1016/j.compscitech.2012.05.013.