Super-strong and highly conductive carbon nanotube ribbons from post-treatment methods

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ABSTRACT

In this study, we present a simple and effective mechanical densification method that uses carbon nanotube (CNT) fibers synthesized via a floating-catalyst technique to produce highly dense CNT ribbons. After being infiltrated with epoxy, the resulting cross-linked CNT ribbons exhibited impressive improvements of an increase in strength by 13.5 times and an increase in stiffness by more than 63 times, the best improvement factors reported in the literature. The strength and stiffness of the post-treated fibers reached as high as 5.2 GPa and 444 GPa respectively, while their electrical conductivity reached up to 12,000 S/cm. The knot-strength efficiency of the cross-linked CNT ribbons approached 78%, which is much higher than that of many commercial high-strength fibers. The performance of the post-treated ribbons was comparable to that of commercial PAN carbon fibers, suggesting that our combined post-treatment of CNT fibers is a promising method for achieving cost-effective mass production of high-performance CNT fibers.

1. Introduction

Due to their strong carbon–carbon covalent bonds and unique atomistic structures, carbon nanotubes (CNTs) possess extraordinary mechanical, electrical, and thermal properties [1]. Therefore, they have great potential in numerous applications, such as multifunctional composites [2], engineering fibers [3], and electronic [4] and electrochemical devices [5]. Many methods have recently been developed to assemble CNTs into structures with controlled morphologies such as continuous CNT fibers [6–8], CNT films [9], and CNT aerogels [10], in order to take advantage of the superior axial properties of the CNTs. Among them, CNT fibers and sheets with aligned CNTs along their direction have drawn extensive attention. Their excellent anisotropic properties, which stem from these aligned morphologies, make them attractive candidates for a broad range of applications, such as reinforcements for high-performance composites, transmission lines, biosensors, and microelectrodes [5]. Their unique properties combine the high electrical and thermal conductivities of metals with the flexibility and strength of textile fibers [11].

To date, there are three main methods for the production of continuous CNT fibers: spinning from CNT solutions [6], dry-state spinning out of a CNT array [8], and direct spinning from CNT aerogels or via the floating-catalyst method [7]. Owing to the weak van der Waals interaction between individual CNTs and CNT bundles, the mechanical properties of CNT fibers are significantly lower than those of the individual CNTs, resulting in their low performance [12]. Over the last decade, several efforts have been made to improve CNT fiber performance by controlling the CNT length, number of CNT walls, CNT diameters [13,14], CNT alignments [15], inter-tube load transfer [16–19], and nanotube entanglement [13]. The inter-tube load transfer between the CNTs could be enhanced by increasing their van der Waals interactions through densification [18] and their covalent cross-links through irradiations [17], or creating cross-link bonds between the tubes through polymerization [16,19]. Of these post-treatments, densification and polymer infiltration are the most widely used methods since they are simple but highly effective [16,19].

The as-spun CNT fibers usually have porous structures [7,8,16,18], allowing them to be further densified to obtain more close-packed structures with better alignments. The van der Waals interaction strongly depends on the contact areas between the CNTs. If there is much space and many pores between the CNT bundles, the degree of van der Waals interaction is lower. Through the densification process, the densified CNT yarn can have much less interspace between the CNTs and improve their contact area,
resulting in the increased van der Waals interaction. Therefore, these highly dense structures have more van der Waals interactions between the CNTs and CNT bundles, and hence improve the fiber performance [16,18,20,21]. CNT fibers can be densified with the application of a mechanical force in their lateral direction. The densification methods could be classified into two categories: indirect approaches (such as liquid densification, twisting [16,18], and drawing through dies [22]) and direct approaches (such as rubbing and pressurized rolling [23]). The drawback of the indirect approaches is their low densifying forces. The liquid densification method, for example, employs the surface tension of volatile solvents such as acetone or ethanol to densify the CNT fibers. Its densifying forces are therefore limited by the low surface tension of the solvents used [18].

With the twisting method, the densifying forces are produced by the twisting torque, which is limited by the fiber structures. It has been reported that highly twisted CNT fibers tend to snarl or coil rather than being densified further, and their strength is also reduced [24]. Similarly, the compressive forces produced by drawing CNT fibers through a die to densify them into more compact structures result from the drawing forces and the difference between the cross-sectional areas of the fiber and the dies used. However, these drawing forces are limited by the tensile strength of the fibers, while a significantly small die could damage the fiber structures, resulting in their poor strength [22]. Due to these limitations, the CNT fibers could not be densified completely with these methods, and their performance remained unsatisfactory.

Direct approaches are the best solutions to overcome these issues. As the densifying forces are applied directly to the CNT fibers with these approaches, the forces can densify the fibers into much more dense structures [23]. Indeed, it has been reported that CNT fibers densified by the pressurized rolling system showed highly packed structures and an impressive average strength of 4.34 GPa, the highest extrinsic CNT fiber strength reported so far [23].

In polymer infiltration treatment, the inter-tube load-transfer efficiency of CNT fibers can be effectively enhanced by the cross-links formed between the CNT bundles through the infiltration process, leading to better performance of the CNT fibers [16,19,21]. For example, it has been reported that by using dimethyl sulfoxide (DMSO) as a densifying liquid and polyvinyl alcohol as an infiltrated polymer, the CNT fiber strength could reach as high as 1.95 GPa [16]. This impressive strength is 255% higher than that of the as-spun fiber. Similarly, it was found that solvent methanol and polymer poly(ethyleneimine) catechol used in a combined post-treatment of CNT fibers could increase the fiber strength by 2.4 times (from 0.91 GPa to 2.2 GPa) and the stiffness by 1.8 times (from 65 GPa to 120 GPa) [19].

Knotted fibers or ropes are widely used in many applications involving heavy loads, such as lifting heavy cargo, securing heavy loads, and rescuing people from hazardous environments. The knots may weaken the fibers or ropes due to the sharp bends formed at the knots. To ensure safety, both the tensile strength and knot-strength efficiency of the knotted fibers or ropes should be determined. CNT fibers consisting of aligned CNT bundles have yarn-like properties [25]. They are flexible and able to tolerate bending in such a way that traditional fibers such as carbon fibers, wool, and silks cannot. These excellent properties were demonstrated by the good performance of the CNT fibers in a knot test.

Indeed, the knot test provides information on transverse properties, as it tests the response of fibers not only to tension, but also to bending, compression, shear, and possible high-stress concentration. Although many researchers have reported the positive effects of post-treatments on CNT fiber performance and shown that treated CNT fibers are still flexible and knottable [16], there have been no comprehensive studies of the effects of these post-treatments on the yarn-like properties of the CNT fibers, such as the knot strength. Since the post-treatments modify the structures of the CNT bundles, it would be expected that the yarn-like characteristics of the CNT fibers would be altered after these post-treatments are applied.

In this paper, we report a simple but effective method based on direct approaches to mechanically densify CNT fibers synthesized with a floating-catalyst technique. After the mechanical densification, epoxy was infiltrated within the fibers to form cross-links between the CNTs and CNT bundles, enhancing their mechanical performance significantly. For the first time, we also attempted to characterize the performance of the knotted CNT fibers after their post-treatments were applied. The experimental results strongly support the potential use of CNT fibers as high-strength commercial fibers.

2. Experimental section

2.1. Synthesis of CNT fibers

Continuous CNT fibers were synthesized with a horizontal CVD reactor at 1100–1200 °C using the floating-catalyst method, as shown in Fig. 1 below. A pre-heated feedstock consisting of methane (carbon source), ferrocene (catalyst precursor), thiophene (promoter), and hydrogen (carrier gas) was injected into a furnace, with flow rates of 160–250, 100–400, 10–20, and 1000–2000 ml/min, respectively. The CNT aerogels continuously formed in the furnace were mechanically pulled out with a cold rod and spun continuously with a motorized winding system at a winding rate of 25 m/min. During the pulling-out process, the CNTs were oriented into fibers with good alignment along the fiber axis.

Before the fibers were collected by the winder, a sprayer was used to spray ethanol on the as-prepared fibers to enhance their CNT packing. Ethanol and nitrogen were mixed, and sprayed to form a fine mist for fiber densification. The spraying conditions were optimized with the winding rate to produce a stable and consistent fabrication process for the CNT fibers. The content of iron particles in the as-spun fibers varied between 18 and 21 wt%. Their tubes were mainly multi-walled, with a diameter of ~15 nm and approximately 15–20 walls. More details of the CNT-fiber morphologies can be found in our previous work [3].

2.2. Mechanical densification

We have successfully developed a modified densification method, as shown in Fig. 2 below. 20-cm-long CNT fibers were slightly straightened, and their tops and ends fixed on a sheet of A4 paper with plastic tape. After another sheet of A4 paper was placed on top of the fibers, both sheets were fixed to a very flat surface with plastic tapes, to stabilize the sandwich structure during the densification process. A stainless-steel spatula with a flat edge was then used to press on the A4 paper at one end of the fibers with an applied force of approximately 100 N, at 45° to the fiber axis. After that, the spatula was slid across the A4 paper, along the fiber axis, to compress and mechanically densify the fibers into a ribbon shape while the compressive force was still maintained.

To optimize the microstructure and properties of the densified CNT fibers, CNT ribbons, the pressing and sliding were repeated at least five times. The estimated contact area between the spatula edge and the flat surface the fibers were applied to was 3 mm². When more than 100 N was applied, no further reduction in the fiber thickness was observed under the microscope, indicating that the fibers were densified into the densest structures that this method could produce.
2.3. Epoxy infiltration of CNT ribbons

The epoxy-infiltration process was prepared by the solution-mixing method. The epoxy Epikote 1004 (Polymer Technologies Pte Ltd, Singapore) was used; it contained bisphenol A and epichlorohydrin as its resins and aliphatic amines as its hardener. First, the resin and hardener were mixed at a mass ratio of 5:2. The mixture was then completely dissolved in acetone at a weight fraction of 30%, the best fraction for producing strong in mixture was then completely dissolved in acetone at a weight fraction of 30%, the best fraction for producing strong in mixture was then completely dissolved in acetone at a weight fraction of 30%, the best fraction for producing strong in mixture was then completely dissolved in acetone at a weight fraction of 30%, the best fraction for producing strong CNT ribbons after the optimization of several different weight fractions [26,27]. At this optimum weight concentration, the viscosity of the epoxy solution was low enough for the solution to infiltration the porous CNT ribbon structures while enabling a sufficient amount of the epoxy to be maintained to strongly cross-link the individual CNTs and CNT bundles of the CNT ribbons. Finally, the CNT ribbons were immersed in the solution for five minutes. After that, the composite ribbons, called cross-linked CNT ribbons, were dried and cured completely after 24 h at room temperature, following the curing process suggested by the vendor.

2.4. Knot formation of the CNT fibers, CNT ribbons, and cross-linked CNT ribbons

With the aid of metal tweezers and a magnifier lamp for illumination, overhand knots were loosely tied in the CNT fibers and their post-treatment counterparts. The knots were then pre-tightened via the hanging of a weight of 1 mg on one end of the fiber. All the knots were formed at a specific position (2–3 mm from the middle of the gage length of the test samples), so that the breaking positions after the knot test could be compared.

2.5. Characterization and analysis

The surface morphologies and dimensions of the CNT fibers, CNT ribbons, cross-linked CNT ribbons, and their knotted counterparts were investigated and measured with a field emission scanning electron microscope (FE-SEM, Model S-4300, Hitachi). Due to the micro size of the CNT ribbons, it was challenging to position the ribbon such that the tilt angle between the CNT ribbon width and the laser beam was 0°. Therefore, we could minimize errors only by measuring the thickness of the ribbons at the tilt angle 0 < 15°. To determine the cross-sectional area of the ribbons or fibers, we measured at 10 different positions along their lengths. The diameter, length, width, and cross-sectional area at each position were determined by the SEM. The cross-sectional areas of 10 different positions were then averaged. The maximum relative error of the cross-sectional area of the CNT fibers, CNT ribbons, and cross-linked CNT ribbons was less than 5%.

Tensile tests of all the samples were performed on a fiber tensile tester (XS(08)XT-3, Shanghai Xusai Co., China), which was equipped with a load cell of 15 N and precision of 0.01 cN. The samples were sandwiched between two pieces of cardboard and clamped with micro-pneumatic grips. A total of 120 samples were tested at a gage length of 10 mm, with an extension rate of 1.2 mm/min [28]. Stress was calculated by dividing the applied force by the sample cross-sectional area determined by FE-SEM.

The electrical resistance of the CNT fibers, CNT ribbons, and cross-linked CNT ribbons was measured with a two-probe method using a Fluke 73III multimeter [3]. For better electrical contact, the two ends of the samples were fixed to two separate glass slides with silver paste. The electrical conductivity of the fibers was then calculated by inverting their resistivity.

3. Result and discussion

3.1. Morphologies of the CNT fibers, CNT ribbons, and cross-linked CNT ribbons

As can be seen in Fig. 3a below, the as-spun CNT fibers had good uniform diameters, with an averaged diameter of 13.5 ± 0.21 μm. The CNTs and CNT bundles observed in Fig. 3b showed fair alignment with the fiber axis, with several pores, although the fibers were densified in situ by ethanol during the synthesis. The CNT alignment could be enhanced by modifying the synthesis recipe such as using different carbon sources, promoters or temperature. The higher-density elastic smoke allows collecting more CNT filaments with the better CNT alignment.

The SEM images in Fig. 4a and b below show that the CNT fibers were turned into fiber-like ribbons after the densification. The ribbon width was 22 ± 1.1 μm and the ribbon thickness was 0.65 ± 0.12 μm. Comparing these images with the structure of the CNT fibers in Fig. 3b, it is obvious that the CNTs and CNT bundles in the CNT ribbons were highly packed with fewer pores, and have better alignments along the fiber axis, as can be observed in Fig. 4c.

After the epoxy-infiltration process, the cross-linked CNT ribbons (Fig. 4d-f) had smoother surfaces as the epoxy filled up all the pores and spaces, although a few wavy areas could still be observed. Moreover, the epoxy was coated on the CNTs and CNT bundles, resulting in slight increases in the width and thickness of the ribbons, to 23.5 ± 1.2 μm and 1 ± 0.2 μm respectively.
3.2. Mechanical properties of the CNT fibers, CNT ribbons, and cross-linked CNT ribbons

The stress-strain curves of the tested CNT fibers, CNT ribbons, and cross-linked CNT ribbons are plotted in Fig. 5a below. On the three curves, a transition from elastic response to plastic deformation before failure may be observed. The curves are linear and typically exhibit a sharp increase in slope at low strains (1–2%), and a gradual decrease in slope at high strains, suggesting that the tested samples had ductile behavior. Overall, the mechanical performance of the CNT samples was significantly enhanced after each applied treatment.

Fig. 5b reveals the mechanical performance of the CNT fibers, CNT ribbons, and cross-linked CNT ribbons. The CNT fibers had an average tensile strength and an average stiffness of 0.27 GPa and 4.28 GPa respectively. Their elongation of 12% indicated that the
fibers were very flexible [23]. These values also indicate that the as-
spun CNT fibers gave a fair performance, although the values are
also in the range of as-spun MWNT fibers reported in the literature
[5]. This fair performance may stem from the loose structures of the
CNT fibers, although the CNT fibers were densified by the ethanol
spraying during their synthesis process. As several pores and spaces
existed in the fiber structures, the bonding between the CNTs and
CNT bundles was weak, leading to their low mechanical strength.
These findings are supported by the large strain to break together
with the large plastic regions of the fibers, which were evidently a
result of the easy sliding of the CNTs and CNT bundles over each
other, owing to their weak van der Waals interactions [12]. The
results, therefore, suggest that liquid densification, especially the
ethanol spraying, may not be an effective method to densify and
improve the CNT fiber performance.

The mechanical properties of the CNT ribbons, however, showed
remarkable improvement. After the mechanical densification, the
ribbons had a stiffness of 78.72 GPa and a strength of 2.81 GPa, on
average—an increase in stiffness and strength by 18 and 10 times,
respectively, compared with their as-spun counterparts. This sig-
nificant enhancement was evidently due mainly to the reduction in
the cross-sectional area of the CNT fibers after the densification
from 143.1 μm² to 14.3 μm², as shown in Fig. 5c. In addition, the
high level of packing of the CNT ribbon structures also contributed
to this improvement by modifying the CNT interactions. The SEM
image in Fig. 4c suggests that the mechanical densification treat-
ment may have increased the CNT bundle size and inter-CNT con-
acts, and induced better alignment, resulting in a slight increase in
the bearing load from 3.81 to 4.01 cN (Fig. 5c).
The reduction in elongation before the failure of the CNT ribbons
after the densification also evidently supported the stronger van
der Waals interaction between the CNTs. In addition, the reduction
of CNT waviness, as shown in Fig. 4c, may also have contributed to
the improvement in the mechanical properties of the fibers, since
the load bearing of the CNTs and CNT bundles in the fibers was
more uniform [13]. These findings are consistent with other reports
that the CNT ribbons could be densified by pressurized rolling
methods [23], and suggest that mechanical densification could be
an effective method to densify CNT fibers into highly dense struc-
tures with better performance.

Regarding the infiltration treatment, the cross-sectional areas of
the cross-linked CNT ribbons surprisingly increased by more than
1.6 times after the treatment (Fig. 5c). This result is totally different
from the findings of most other work that used the combined
treatment of liquid densification and infiltration, namely that there
was a reduction in the cross-sectional areas [16,19]. These findings
again support the effectiveness of our mechanical densification
method, which ensures that the epoxy solution has no further
densifying effects on the CNT structures. In fact, the coating of the
epoxy on the CNTs and CNT bundles was the main reason for the
increase in the cross-sectional area of the cross-linked CNT ribbons.
Since the bearing load of the samples after the infiltration treat-
ment increased by about 2 times, the strength of the infiltrated
ribbons only showed a slight increase of more than 1.2 times,
reaching 2.9–5.2 GPa, with an average of 3.6 GPa.

Although this improvement in the strength of the cross-linked
CNT ribbons was much lower than the improvement in the strength
of the CNT fibers treated by combining liquid densification and
infiltration, as reported in other research [16,19], the enhance-
ment in their stiffness was remarkable. After the treat-
ment, their stiffness increased to 187–444 GPa, with an average of
266 GPa, over three times higher than that of the CNT ribbons.
These results may be because the polymer infiltration significantly
enhanced the interfacial load transfer between the CNTs and CNT
bundles. After the infiltration treatment, the epoxy had infiltrated
the CNT structures well, cross-linking the CNTs and CNT bundles

Fig. 5. (a) Stress–strain curves of tested samples, (b) tensile strength and stiffness of the CNT samples, (c) cross-sectional area, tensile load, and elongation to failure of the CNT samples, (d) electrical conductivity of the CNT samples. (A colour version of this figure can be viewed online.)
with strong bonds and minimizing the inter-tube slippage [29]. Therefore, the inter-tube interactions substantially improved, leading to the noteworthy increase in the stiffness of the cross-linked CNT ribbons. The remarkable decrease in both elongation before failure and the plastic region was evidently a result of the hindering effects of the infiltrated epoxy on interbundle slippage [29]. These results are also supported by the considerably short fracture length of the cross-linked CNT ribbons, compared with the CNT fibers and CNT ribbons (Fig. 51).

Furthermore, the improvement in the mechanical performance of the cross-linked CNT ribbons might have been due to the decrease in the CNT waviness after the densification. The results were consistent with the increase in the elastic modulus of the CNT/epoxy array when the CNT waviness was reduced [21]. Due to the fact that up to 21 wt % of iron particles were distributed randomly along the CNT samples, the wide range of the mechanical strength and stiffness of our CNT fibers, CNT ribbons, and cross-linked CNT ribbons was to be expected. These defects would have acted as stress raisers and initiated fractures during the tensile test. The impurities, however, can be reduced by optimizing the synthesis reaction or applying proper post-treatments [15,23].

3.3. Electrical properties of the CNT fibers, CNT ribbons, and cross-linked CNT ribbons

Fig. 5d presents the electrical performance of the CNT fibers, CNT ribbons, and cross-linked CNT ribbons. As can be observed, the CNT fibers had the lowest electrical conductivity, with an average value of 1657 S/cm. This could be explained by the loose structures of the CNT fibers. The many pores in the fiber structures are believed to be the main reasons for the poor contact between the CNTs and CNT bundles, resulting in their low electrical performance.

The electrical properties of the CNT ribbons, however, showed a significant improvement. After the mechanical densification, their electrical conductivity approached an impressive value of approximately 12,000 S/cm, seven times higher than that of their as-spun counterparts. As with the improvement of their mechanical properties, this impressive enhancement stemmed from the reduction of the cross-sectional area and the high packing of the CNT ribbon structures. The increased contact between the CNTs and CNT bundles within the ribbon structures also contributed to the better electrical performance of the CNT ribbons.

Regarding the infiltration treatment, the reduction in the electrical conductivity of the cross-linked CNT ribbon to 4887 S/cm was to be expected, since the epoxy was electrically non-conductive, and its infiltration increased the insulated fraction of the samples.

3.4. Knot-strength properties of the CNT fibers, CNT ribbons, and cross-linked CNT ribbons

Fig. 6 below presents the SEM images of the knots formed with tweezers in the gage lengths of the CNT fibers, CNT ribbons, and cross-linked CNT ribbons. The stress–strain curves of the CNT samples and tensile strength of the cross-linked CNT ribbons, together with those of their knotted counterparts, are plotted in Fig. 7 below. It is clear that the stress–strain curves of the knotted samples have an extra region at the low strain (2–8%), unlike the curves of the unknotted samples. These extra regions correspond to the tightening process of the knots, and vary with the initial degree of tightening.

The stresses in the knot-tightening curves of the CNT fibers and CNT ribbons are extremely low (Fig. 7a and b), indicating that very low loads were required to tighten their knots. Importantly, there was no degradation of the strength of the CNT fibers and CNT ribbons observed in their stress–strain behavior and strength results (Fig. 52), due to the knots. Moreover, the testing samples broke at random positions along the gage length, most of which were remote from the knots themselves. These findings suggest that CNT fibers and CNT ribbons have a knot efficiency of 100%, and that mechanical densification therefore has no negative effects on the yarn-like properties of CNT fibers. We believe that although the CNT bundles in the CNT ribbons are modified after the mechanical densification, their van der Waals interactions are still preserved, allowing the CNT ribbons to maintain their yarn structures with high flexibility and have excellent performances in knot tests.

In contrast, the knot region in the stress–strain curve of the cross-linked CNT ribbons showed complicated behavior, with many local peaks and their knots requiring at least 0.1 GPa to be tightened (Fig. 7c). Furthermore, the cross-linked CNT ribbons had a slight reduction in their strength, as indicated by their stress–strain behavior and strength results, shown in Fig. 7c and d. In addition, all the tested samples broke at the knot, suggesting that there were stress concentrations at the knot positions. The strength of the knotted cross-linked CNT ribbons was 2.8 GPa on average, resulting in a knot efficiency of 78%.

The behavior of the CNT fibers, CNT ribbons, and cross-linked CNT ribbons in the knot test can be explained by investigating the surface morphologies of the CNT samples at the knot area. The SEM image in Fig. 8a below suggests that the CNT fibers and CNT ribbons had a few kinks that formed at the bending surfaces of their knots. According to the previously mentioned results, as the yarn structures of the CNT fibers and CNT ribbons were still maintained, the kinks at their knots had no negative influence on their mechanical performance. Therefore, they had excellent knot-strength performance, with efficiency of 100%.

On the other hand, severe kink bands and micro-cracks were observed at the knot of the cross-linked CNT ribbon (Fig. 8b). It is well known that kink bands formed at the bending portions of many fibers, such as nylon or polyester fibers, can weaken their mechanical performance [30]. These observations suggest that the strong bonds formed between the CNTs and CNT bundles after the infiltration treatment alter the nanostructures of the cross-linked CNT ribbons, causing them to have less flexibility. Therefore, micro-cracks and kink bands are formed at the knot of the cross-linked CNT ribbon and act as stress raisers, leading to low failure strength of the samples under tensile stress. In addition, these findings also provide an explanation for the formation of the complicated knot-tightening regions in the stress–strain curves, with many local peaks of up to 0.5 GPa, as shown in Fig. 7c. In these regions, many micro-cracks may be produced and propagated to a specific extent before the whole sample structures became load-bearing. Hence, these pre-cracks weaken the sample structures, resulting in the lower strength of the knotted cross-linked CNT ribbons.

3.5. Advantages of the developed post-treatments for property enhancement of the as-spun CNT fibers

The mechanical densification method has been used to densify CNT products such as CNT arrays with biaxial densification [17] and rolling [31], and to convert CNT hollow tubes into ribbons [23]. We modified the previous densification technique by applying both compressive stress along the fiber axis and protective layers to densify the CNT fibers into highly packed structures. The sliding effect may slightly apply shear stress along the fiber axis, which can significantly enhance the CNT alignment. Furthermore, using two A4 papers as the protective layers can also (i) prevent damage caused by the combination of shear and compressive effects during the densification, and (ii) help obtain the maximum number of packed structures.
Fig. 6. SEM images of knot formed in the (a) CNT fiber, (b) CNT ribbon, and (c) cross-linked CNT ribbon.

Fig. 7. Stress–strain curves of the (a) CNT fibers, (b) CNT ribbons, and (c) cross-linked CNT ribbons, compared with those of their knotted counterparts. (d) Strength of the cross-linked CNT ribbons compared with that of their knotted counterparts. (A colour version of this figure can be viewed online.)

Fig. 8. SEM images of knotted area of the (a) CNT fiber and (b) cross-linked CNT ribbon.
In fact, the thickness of the resulting ribbons was determined by the gap between the A4 papers produced by the compressive forces during the densification. While the CNT fibers could be damaged if there was excessive rolling performed via the pressurized rolling method [23], our developed technique enables as many CNT fibers as possible to be densified without causing any damage to the CNT fiber structures. In addition, although 20-cm-long fibers were used in this study, our technique could also be automated to fabricate ribbons of unlimited length with the simple addition of a discrete control system with two winding rollers. This set-up is similar to the concept of the pressurized rolling system [23]. Therefore, our developed densification method has great potential to be scaled up to produce CNT ribbons that meet industrial-standard requirements.

The most noteworthy feature of our developed hybrid post-treatments is their outstanding enhancement of the electrical and mechanical performances of the MWNT fibers. Fig. 9a below compares the enhancement factors of the mechanical performances of CNT fibers produced by different post-treatments, such as liquid densification, a combination of liquid densification and polymer infiltration [16], acid treatment [32], laser treatment [33], and mechanical densification [23]. As can be observed, the combined post-treatments employed in our study showed the best effects, with enhancement factors of more than 13.5 for tensile strength and 63 for stiffness. The results indicate that the hybrid post-treatment method combining mechanical densification and polymer infiltration is a promising approach to improve the performance of CNT fibers.

Importantly, the high strength and stiffness of our CNT ribbons and cross-linked CNT ribbons were better than those of the CNT fibers and their post-treated counterparts fabricated by the other methods. After the first mechanical treatment, our condensed CNT ribbons achieved a tensile strength much higher than that of the best CNT fibers spun with the wet-spinning and array-spinning methods, as shown in Fig. 9b below. Once further combined with the epoxy infiltration, the cross-linked CNT ribbons reached significantly high strength (up to 5.2 GPa) and stiffness (up to 444 GPa), which are very comparable to those of commercial PAN carbon fibers. Furthermore, while the strength of our cross-linked

![Fig. 9. (a) Comparisons of enhancement factors of different post-treatments in this work, including liquid densification [16], acid treatment [32], laser treatment [33], a combination of liquid densification and polymer infiltration [16], mechanical densification [23], and a combination of mechanical densification and polymer infiltration. (b) Comparisons of mechanical properties of the best CNT fibers from array spinning [12] and wet spinning [11], ribbons from aerogel spinning, and PAN carbon fibers [23].](image)

![Fig. 10. Plot of knot-strength efficiency against fiber strength for a variety of fibers. The values of Kevlar 49, Dyneema, Carbon T300, and Twaron were obtained from Ref. [25]. The value of the graphene oxide fiber was obtained from Ref. [34], while the others were derived from Ref. [30].](image)
CNT ribbons was comparable to that of the best DWNT ribbons produced by the floating-catalyst method [23], their stiffness was much higher. The results indicate that with the application of proper post-treatments, the performance of MWNT fibers with low electrical and mechanical properties could reach the performance of many other high-strength fibers.

A further highlight of our study is the high performance of our CNT fibers, CNT ribbons, and cross-linked CNT ribbons in the knot test. As shown in Fig. 10 below, the CNT ribbons was slightly lower (78%) due to the alteration of the epoxy-infiltration and curing of mussel-inspired catecholamine polymer, Adv. Mater. 22 (24) (2010) 4959–4963.

4. Conclusions

In summary, a modified mechanical densification method based on direct approaches was successfully developed to fabricate CNT ribbons with high performance. With the cross-links formed between the CNTs and CNT bundles with the epoxy-infiltration treatment, the cross-linked CNT ribbons gained excellent enhancements in both their electrical and mechanical properties, making those properties comparable to those of PAN carbon fibers. While the mechanical densification had no effect on the yarn-like properties of the CNT fibers, the cross-linking treatment altered those properties and reduced their knot-strength performance from 100% to 78%. However, the performance of our post-treated CNT fibers was still much better than those of many other commercial high-strength fibers. This work demonstrates that our combined post-treatment has great potential to produce high-performance and conductive CNT fibers at industrial scale, and at low cost.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2015.12.048.

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