

Improving the tensile strength of carbon nanotube yarn via one-step double [2+1] cycloadditions

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Abstract—The tensile strength of a CNT yarn was improved through simple one-step double [2+1] cycloaddition reactions that crosslinked the constituent CNTs using a polyethylene glycol (PEG)-diazide crosslinker. The FT-IR spectrum confirmed that the azide groups in the PEG-diazide were converted into aziridine rings, indicating that the cycloaddition reaction was successful. The generation of crosslinked CNTs was also supported by the observation of N1s peak in the XPS spectrum and the increased thermal stability of the material, as observed by TGA. The tensile strength of the CNT yarn was increased from 0.2 GPa to 1.4 GPa after the crosslinking reaction when twisted at 4000 twists/meter. The appropriate selection of the crosslinker may further optimize the CNT yarn crosslinking reaction. The simplicity of this one-step crosslinking reaction provides an economical approach to the mass production of high-strength CNT yarns.

Keywords: Carbon Nanotube Yarn, Crosslinking, (PEG)-diazide

INTRODUCTION

Carbon nanotubes (CNTs) have several excellent material properties, including good mechanical strength, a high electrical conductivity, and chemical stability [1]. Among these, the remarkable tensile strength of CNTs offers a unique opportunity for use as a one-dimensional material in the transportation, aerospace, and defense industries [2,3]. Before CNTs may be effectively utilized in these applications, the individual nanotubes need to be assembled into a one-dimensional macroscopic structure called a CNT yarn. Several techniques were recently developed for spinning CNT yarns [3]. Some representative yarn-spinning methods include (i) spinning from a CNT solution [4]; (ii) spinning from a superaligned array of CNTs [5]; and (iii) spinning directly from chemical vapor deposition synthesis [6]. The strengths of the CNT yarns prepared by these methods are much lower than the strength of an individual CNT and are not competitive with other commercial high-performance fibers, such as carbon fibers [7].

The main reason for the weak strength of CNT yarns is that CNTs interact with each other via weak van der Waals forces [8]. To increase the tensile strength of a CNT yarn, there have been efforts to develop post-treatment processes. Efforts toward maximizing

the interactions among CNTs in a CNT yarn have tested both physical and chemical approaches. Physical approaches include shrinking and twisting [9], and tensioning [10], which can share the existing knowledge of textile engineering. In contrast, chemical approaches are required to develop new methods, because CNTs are highly resistant to chemical reactions. In this sense, compared to physical approach, chemical approach still has much room to contribute to the improvement of the strength of CNT yarns. Thus, the development of new chemical route is imperative.

Most common chemical approaches have involved the infiltration of polymers into the CNT yarns to create CNT/polymer composite yarns [4,11-15]. Polymers such as polyvinyl alcohol [11,14, 16] and poly(ethylenimine) catechol [12], a type of adhesive polymer, have been inserted into the CNT yarns. The infiltrated polymers fill the voids inside the CNT yarns to increase the load transfer efficiency and tensile strength. Recently, it was reported that covalent crosslinks between CNTs improved the tensile strength of the CNT yarns [17]. Covalent bonding is much stronger than van der Waals forces, and the CNTs can be held together more tightly in a crosslinked network.

Here, we report a simple method for crosslinking CNTs via one-step cycloadditions to improve the tensile strength of the CNT yarns. As linker molecule, PEG-diazide (2,000 g/mol) was selected in which the PEG polymer bear an azide group at either end. The method described here draws on the merits of both polymer infiltration and crosslinks among CNTs. In this work, the crosslinking reaction is characterized using commercial multi-walled carbon nano-

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tubes (MWCNTs), and the chemistry is applied to CNT yarns spun from a CNT forest. The crosslinked CNT yarn exhibits a seven-fold increase in tensile strength. The simple one-step cycloaddition reaction is expected to be readily applied to the mass production of high-strength CNT yarns.

EXPERIMENTAL

1. Reagents and Materials

MWCNTs (95+%, outer diameter 10–20 nm, inner diameter 2–5 nm, length 10–30 nm) were purchased from Nanostructured & Amorphous Materials, USA. Polyoxyethylene bis(azide) (2,000 g/mol, PDI<1.2) was purchased from Aldrich (polyoxyethylene bis(azide) will be denoted as “PEG-diazide” throughout, for simplicity). Teflon membrane filters, 0.2 μm pore size (0.47 cm diameter) were purchased from Avanteq. All other reagents were purchased from Aldrich and used without further purification.

2. Crosslinking of the MWCNTs

A 100 mg sample of MWCNTs was added to 50 mL 1, 1, 2, 2-tetrachloroethane (TCE), and the solution was sonicated for 10 min. The solution was then heated at 180 °C with stirring, after which 2 mL of a TCE solution containing 25 mg PEG-diazide, which had been sonicated for 2 min, was injected at a rate of 10 mL/h using a syringe pump. The solution was then stirred for 10 min. After the reaction had reached completion, the brown-colored supernatant was decanted and the remaining solid was washed with TCE to remove by-products. The product was then washed with tetrahydrofuran (THF) to remove TCE. The remaining solid was dried at room temperature under vacuum overnight.

3. CNT Yarn Preparation

The yarns were directly spun from CNT forests grown on a Si wafer bearing a 300 nm oxidized layer. The growth of the spinnable CNT forests is described in detail elsewhere [18]. The wafer was first coated with a 10 nm film of Al₂O₃ using atomic layer deposition (ALD), after which the wafer was coated with a 1 nm Fe layer using electron beam evaporation. The CNT forest was grown by chemical vapor deposition (CVD) using a Lindberg Blue M (HTF55322) tube furnace with a quartz tube 4 cm in diameter and 70 cm in length. The prepared substrate was positioned in the middle of the tube furnace, and the temperature was ramped to 670 °C over 17 min under a 400 sccm Ar flow. Once the target temperature was reached, a gas mixture of C₂H₂ (19 sccm), H₂ (95 sccm), and Ar (286 sccm) was introduced into the furnace over 3 min to grow the CNT forest.

The diameter and length of the CNTs in the forest were 10–20 nm and 300 μm, respectively. The as-synthesized CNT forests were spinnable, and yarns were spun directly from the CNT forest. Initially, a CNT sheet with a two-dimensional geometry was pulled such that the width was controlled at approximately 1 cm, to ensure consistent sample preparation. The pulled CNT sheet was subsequently twisted using an electric motor with various numbers of twists per meter (t/m), followed by immersion in ethanol. During the twisting and immersion steps, the CNT sheet shrank and formed a one-dimensional yarn that was then dried in a vacuum oven overnight.

4. Crosslinking the CNT Yarns

A CNT yarn sample was dipped in PEG-diazide and heated to

180 °C under a N₂ atmosphere before injecting 2 mL TCE. The temperature was maintained for a further 10 min and the reactor was cooled to room temperature. The resulting CNT yarn sample was washed with TCE and a THF solution to remove the un-reacted PEG-diazide and dried under vacuum overnight.

5. Characterization

Fourier transform infrared (FT-IR) spectra of the samples were obtained from powdered samples (Spectrum GX & Auto Image model, Perkin Elmer).

X-ray photoelectron spectroscopy (XPS) was used to analyze the crosslinked CNTs (EXCALAB 250 XPS surface analysis system, VG Scientific). The chamber was evacuated to a base pressure of ~1×10⁻¹⁰ Torr. A hemispherical energy analyzer was used for electron detection. XPS spectra were collected using an Al-Kα X-ray resource. High-resolution spectra were collected at a pass energy of 50 eV in 0.05 eV steps for the major elements to study the relevant chemical structures. High-resolution data were subsequently peak-fitted, plotted, and tabulated to illustrate the chemical species present for each major element detected.

SEM images were obtained with a field emission scanning electron microscope (Philips Electron Optics B.V.XL30S FEG) with a resolution of 1.5 nm at 10 kV or higher and 1.5 nm at 1 kV. The beam current range was 1 pA–25 nA.

Thermo gravimetric analysis (TGA) was performed using a thermal analysis system (Q600, TA instruments, U.S.A) over the temperature range 30–1,000 °C with a heating at a rate of 10 °C/min under a N₂ atmosphere.

6. Strength Measurements of the CNT Yarns

The tensile strengths of the CNT yarns were measured with a nano universal testing system (NANO Bionix, Agilent Technologies), shown in Fig. S1 in Supporting Information. The maximum load and load resolution were 500 mN and 50 nN, respectively. After calibration, the sample experienced strain at a set strain rate of 0.0027/s until failure was detected. The length of each sample was 10 mm. Unlike normal universal tensile machines (UTM), Nano UTM measures the force/displacement curves using a nanomechanical actuating transducer (NMAT) assembly. As the mechanical motor applies an upward tensile force to the sample, the sensor measures the load used to balance its position.

RESULTS AND DISCUSSION

The mechanism through which CNTs were crosslinked using PEG-diazide as a crosslinker is shown in Fig. 1. PEG-diazide underwent addition reactions with the sidewalls of MWCNTs to form covalent bonds. PEG-diazide includes an azide group at either end of the molecule. Thermal treatment of the azide group generates singlet and triplet nitrenes accompanied by N₂ extrusion [19]. The singlet nitrenes can then attack the sidewalls of the MWCNTs through an electrophilic [2+1] cycloaddition, and the triplet nitrenes with two p-orbitals bearing un-paired electrons can react with the π systems of the sidewalls. Both nitrene groups tend to react with the sidewalls of distinct MWCNTs to form aziridine rings.

This reaction has two advantages as a method for crosslinking CNTs in a CNT yarn. First, the reaction is a single step. Previously reported crosslinking method consists of two steps: sidewall modi-

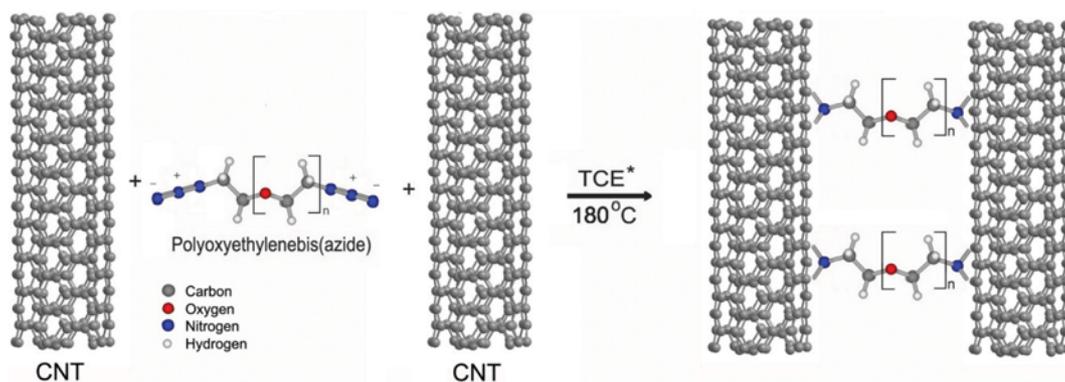


Fig. 1. Schematic representation of the covalent crosslinking of CNTs through the [2+1] cycloaddition mechanism using a polyoxyethylene bis(azide) crosslinker (gray=carbon, red=oxygen, blue=nitrogen, and white=hydrogen). TCE is 1, 1, 2, 2-tetrachloroethane.

fication and crosslinking [17]. In our reaction, the linker molecule directly forms chemical bonds to the sidewall of CNT. Thus, it can be readily applied to a mass production process. Second, the reaction can occur at the sidewalls of CNTs as well as at the end tips. The end tips of a CNT are generally more susceptible to chemical reactions than the sidewall [20]. The reaction can occur at any position on the surface of a CNT and, thus, can maximize the effects of crosslinking. In this work, a two-step approach was employed. The crosslinking reaction was first confirmed using MWCNTs, and then the reaction was applied to CNT yarns in an effort to improve the tensile strength.

1. Characterization of the Crosslinked CNTs

The covalent crosslinking was confirmed using a variety of analysis techniques, including FT-IR, XPS, and TGA. Fig. 2 shows the FT-IR spectra of the PEG-diazide, crosslinked MWCNTs, and pristine MWCNTs. Organic azides display a strong FT-IR absorption band in the region 2,080-2,170 cm^{-1} due to an asymmetric vibration [21]. The FT-IR spectrum of PEG-diazide revealed an asymmetric vibration peak at 2,113 cm^{-1} . A peak due to the symmetric

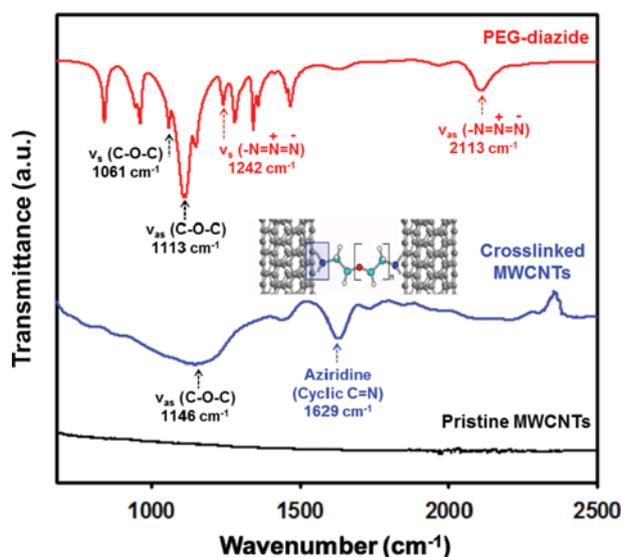


Fig. 2. FT-IR spectra of the PEG-diazide (red), crosslinked MWCNTs (blue), and pristine MWCNTs (black).

vibration of the azide groups was observed at 1,242 cm^{-1} [21]. These peaks were absent from the FT-IR spectrum of the crosslinked MWCNTs. Instead, a peak at 1,629 cm^{-1} was observed, indicating a possible cyclic imine structure [22]. The disappearance of the azide peaks and the appearance of a cyclic imine peak indicate that the azide groups were converted into aziridine rings as they formed chemical bonds with the MWCNTs. In the pristine MWCNTs, no significant peaks were observed.

Fig. 3 shows XPS survey spectra collected from the crosslinked MWCNTs and pristine MWCNTs. In the crosslinked MWCNTs, an N1s peak was observed at 399 eV, whereas no N1s peak was observed in the pristine MWCNTs. The atomic content of N in the crosslinked MWCNTs was 0.89% (Table 1). The presence of N indirectly supports the conclusion that the PEG-diazide formed chemical bonds to the MWCNTs and was not washed away. The O1s peak was more intense in the crosslinked MWCNTs than in the pristine MWCNTs as the PEG-diazide contained O atoms bonded to the MWCNTs. The atomic content of O increased from 2.78% to 3.79% (Table 1).

The successful crosslinking of MWCNTs by PEG-diazide was also supported by the TGA results. TGA curves obtained from the

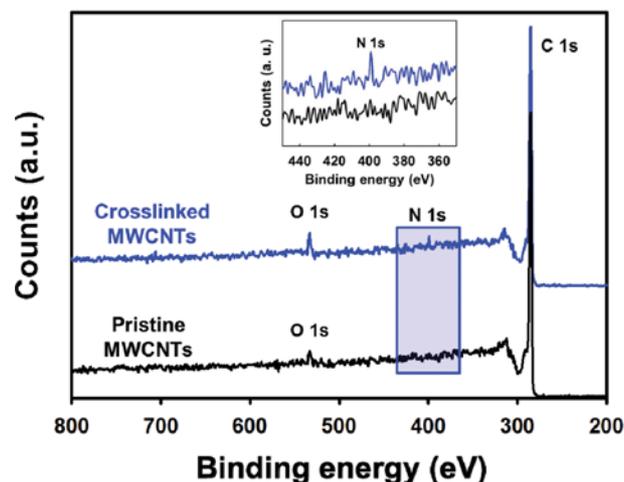


Fig. 3. XPS survey spectra of crosslinked MWCNTs and pristine MWCNTs.

Table 1. Atomic contents of PEG-diazide, the pristine MWCNTs, and the crosslinked MWCNTs analyzed by XPS

	PEG-diazide	Pristine MWCNTs	Crosslinked MWCNTs
C1s	67.14	97.22	95.32
N1s	1.81	-	0.89
O1s	31.04	2.78	3.79

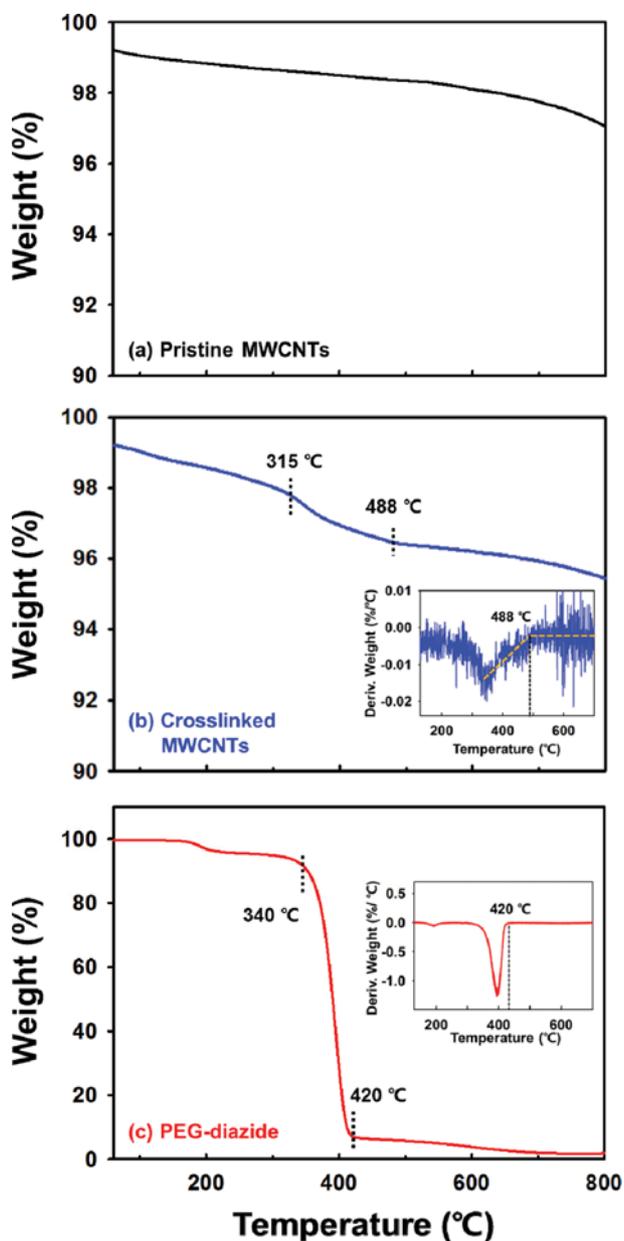


Fig. 4. TGA curves of (a) the pristine MWCNTs, (b) the crosslinked MWCNTs, and (c) the PEG-diazide. The insets in (b) and (c) show the first derivatives of (b) and (c) with respect to temperature, respectively.

pristine MWCNTs, the crosslinked MWCNTs, and PEG-diazide are plotted in Fig. 4. The thermal decomposition range was identified by calculating the first derivatives of the TGA curves with respect to temperature, as shown in the insets of Fig. 4(b) and Fig. 4(c).

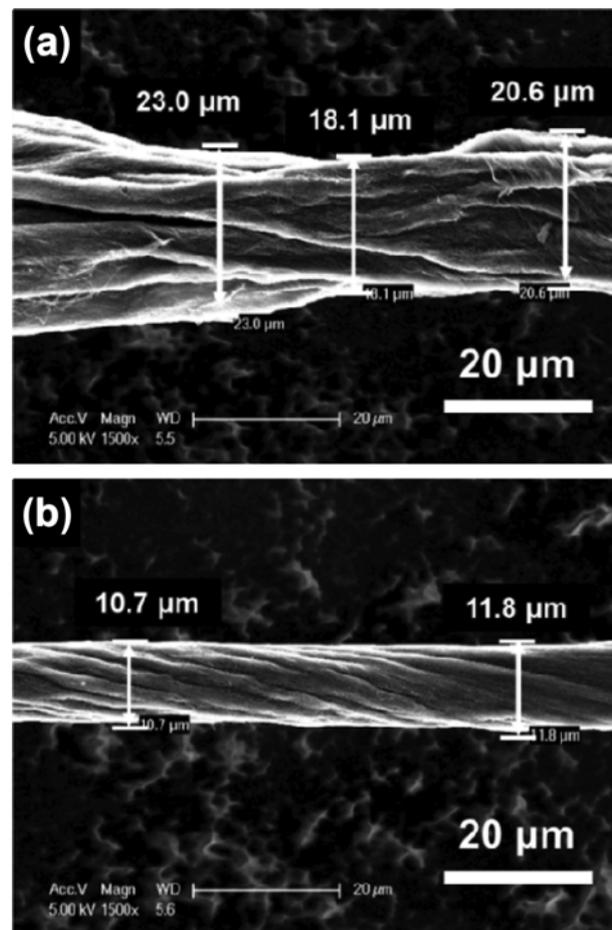


Fig. 5. SEM images of the CNT yarns (a) before and (b) after shrinking.

The TGA curve obtained from the pristine MWCNTs revealed a smooth decrease as the temperature was increased. In contrast, the crosslinked MWCNTs displayed a rapid decrease in the TGA curve over a temperature range extending from 315°C to 488°C. This decrease is attributed to the decomposition of the linker molecules. Note that the temperature at which the decomposition reached completion in the crosslinked MWCNTs exceeded that measured for the pure PEG-diazide sample. This result indicates that the thermal stability of the MWCNTs increased upon formation of the PEG-diazide-crosslinked MWCNT networks.

2. Strength Improvement in the CNT Yarns

The [2+1] cycloaddition chemistry was applied to CNT yarns in an effort to improve the tensile strength of the material. Prior to the chemical treatment step, the as-spun CNT yarns were twisted and shrunk using ethanol. Ethanol shrinking effectively formed a compact yarn structure. SEM images of the CNT yarns before and after ethanol shrinking are shown in Fig. 5. Fig. 5(a) shows that the CNT yarn has a larger diameter and is non-uniform along its axis direction. This result indicates that a significant number of voids are irregularly distributed throughout the CNT yarn. After shrinking, the diameter of the CNT yarn is found to decrease and become more uniform, as shown in Fig. 5(b).

The morphology changes of CNT yarns after crosslinking reac-

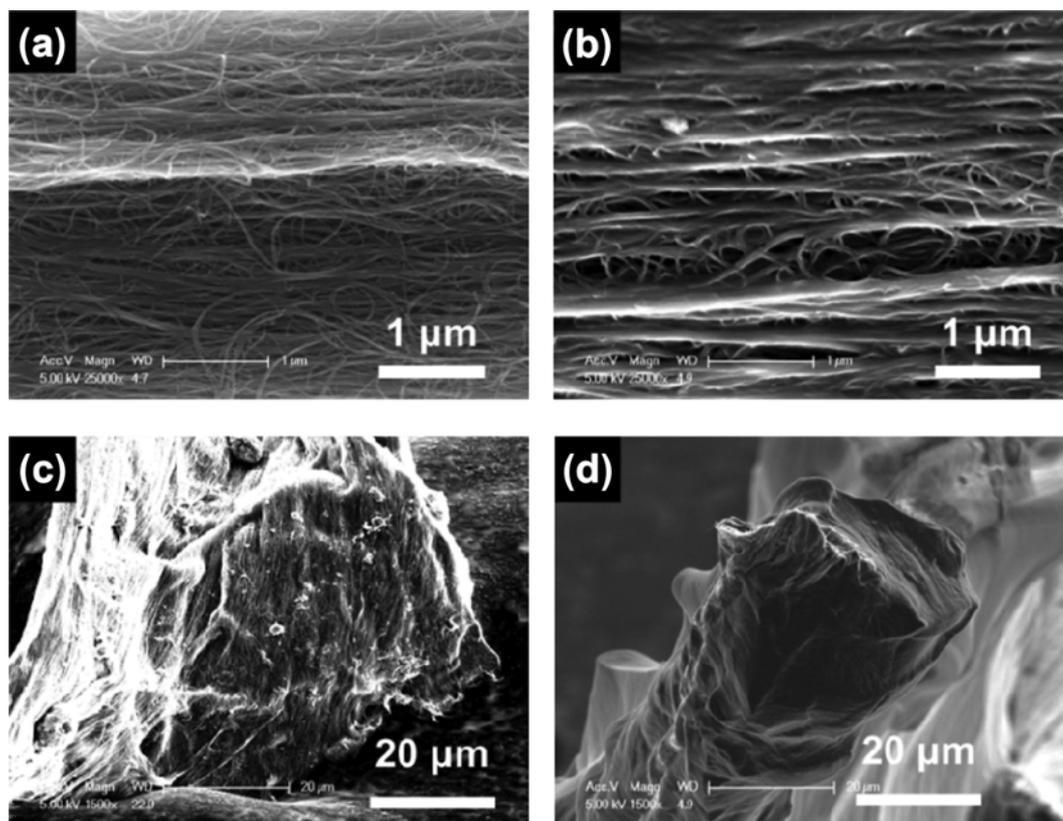


Fig. 6. SEM images of the CNT yarn surfaces (a) before and (b) after chemical treatment, and the tensile fracture surface of CNT yarns (c) without and (d) with chemical treatment.

tion were also observed. Fig. 6 shows the morphology of CNT yarns without crosslinking in the left column (a), (c), and after PEG-diazide crosslinking in the right column (b), (d). Fig. 6(a) shows that thin CNT bundles and individual CNTs could be identified in the absence of crosslinking. After crosslinking, the CNTs became glued together to form thicker bundles, as shown in Fig. 6(b). Figs. 6(c) and 6(d) compare the tensile fracture surfaces of the CNT yarns before and after chemical treatment. The chemically treated CNT yarn is densely infiltrated with the PEG-diazide, whereas the untreated CNT yarn displays a sparser structure. The alignment among the CNTs appeared to improve slightly after applying chemical treatments.

The linker molecule was selected in view of the molecular weight of the molecule. The molecular weight of the PEG-diazide linker used in this work was 2,000 g/mol, which is relatively low for polymers. If the chain length is too long, the polymer will have difficulty in infiltrating into the spaces between CNTs. On the contrary, if the chain length is too short, the crosslinking between CNTs may be difficult due to the intertube distance. The chain length of the linker polymer may potentially be further optimized to ensure that polymer crosslinking is maximized.

The tensile strengths of the CNT yarns were measured before and after chemical treatment. Since the strength of a yarn is dependent on the degree of twist, CNT yarns were prepared with various degrees of twist, from 1,300 twists/meter to 6,600 twists/meter. The tensile strengths are plotted in Fig. 6. Regardless of the degree of twist, the tensile strengths increased after chemical treatment.

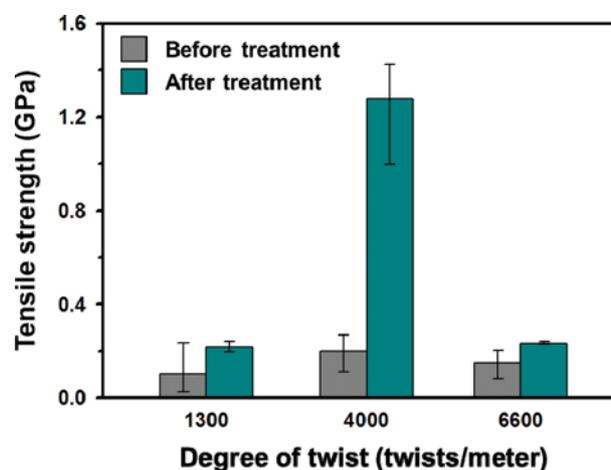


Fig. 7. Tensile strengths of the CNT yarns before and after chemical treatment.

The optimum degree of twist was 4,000 twists/meter. The maximum tensile strength was found to be 1.4 GPa. Remarkably, the tensile strength increased by a factor of 7 after chemical treatment at 4,000 twists/meter. This result suggests that the method could potentially increase the CNT yarn strength.

CONCLUSIONS

We report a one-step double [2+1] cycloaddition reaction to im-

prove the tensile strength of a CNT yarn by crosslinking the constituent CNTs using a PEG-diazide crosslinker. The FT-IR spectra confirmed that the azide groups in the PEG-diazide polymer were converted into aziridine rings, indicating that the cycloaddition reaction occurred successfully. The presence of an N1s XPS peak and the increased thermal stability observed in the TGA curves also support the successful crosslinking of the MWCNTs. The tensile strength of the CNT yarn increased from 0.2 GPa to 1.4 GPa after crosslinking measured from 10-mm long samples.

A variety of candidate crosslinker molecules bearing more than two azide groups at their ends may potentially be tested in an effort to further improve crosslinking and optimize the tensile strength of CNT yarns. The simplicity of this one-step crosslinking reaction provides an economical approach to the mass production of high-strength CNT yarns.

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SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at <http://www.springer.com/chemistry/journal/11814>.

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Supporting Information

Improving the tensile strength of carbon nanotube yarn via one-step double [2+1] cycloadditions

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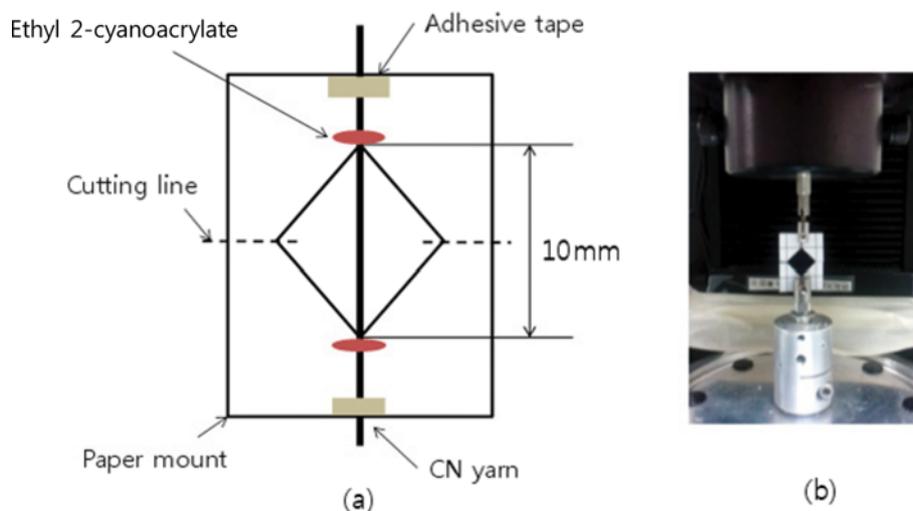


Fig. S1. (a) Structure of the set up for tensile strength measurements. (b) Photograph of paper mount fixed in the nano universal tensile machine (UTM). After calibration, the samples experienced strain at a set strain rate of 0.0027/s until failure was detected. The length of each sample was 10 nm. Unlike normal UTM, the nano UTM has a force/displacement measurement part; called a nano-mechanical actuating transducer (NMAT) assembly. As the mechanical motor applies an upward tensile force to the sample, the sensor measures the load used to balance its position.