Mechanical and Electrical Properties of Carbon Nanotube / Polydimethylsiloxane Composites Yarn

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ABSTRACT

Carbon nano tube (CNT) yarn is an axially aligned CNT assembly. It has great potential many applications. In this study, the mechanical and electrical properties of the aerogel-spun CNT yarns and CNT/Polydimethylsiloxane (PDMS) composite yarns were investigated. The CNT/PDMS yarn was fabricated by droplet infiltration of PDMS solution into the aerogel-spun CNT yarn. The mechanical properties of the CNT/PDMS yarns were significantly improved with an average strength of 837.29 MPa and modulus of 3.66 GPa, over 100% improvement compared to the original CNT yarns. The electrical conductivity of the CNT/PDMS yarn increased from 1636 S/cm to 3555 S/cm. The electromechanical properties of CNT/PDMS yarns demonstrated that such CNT yarn could be suitable for strain sensors.

Keywords*:* carbon nanotube, PDMS, composites yarn, mechanical properties, electrical conductivity.

INTRODUCTION

Carbon nanotubes (CNTs) have a unique atomic structure and excellent properties such as high tensile strength and Young's modulus [1, 2], excellent piezoresistivity [3, 4] and good electrical and thermal conductivities [5, 6]. They have shown great potential in many applications including high performance composites [7], sensors [8] and smart textiles [9]. With the development of different technique to synthesize CNTs, various forms of raw CNT assemblies can be obtained, including CNT powder, fiber [10], buckypaper [11], and arrays [12]. The macroscopic and wire-like morphology of CNT fibers (yarns) has generated a large body scientific research and led to the development of a variety of engineering applications. They could be used as light weight electrical wires or for weaving multifunctional fabrics with for high mechanical performance, electrical conductivity or strain sensing. However, before CNT fibers are utilized in a specific practical application, their properties which are important to that application should be investigated in depth.

CNT yarn, assembled by axially aligned CNTs, can be obtained by indirect dry spinning from aligned CNT arrays [13] or CNT film [14], and direct dry spinning from CNT aerogel using a chemical vapor deposition (CVD) reaction [15]. CNT yarn exhibits good mechanical properties and good electrical conductivity. Direct aerogel spinning has proven to be an efficient way for mass producing high quality CNT yarns [16]. However, aerogel-spun CNT yarns exhibit a wide range of variation in diameters, strengths and conductivities. Further, due to the interfacial slippage among bundles or CNTs, CNT yarn shows electrical and mechanical property deficiencies [17, 18].

To improve the performance of the CNT yarn, much work has been done using polymer infiltration to fabricate CNT composites yarn in order to enhance the physical interaction of CNTs [19-24]. For example, Liu improved the tensile strength of the CNT yarn from 0.55 Gpa to 2.0 Gpa by incorporating polyvinyl alcohol (PVA)/dimethyl sulphoxide (DMSO) solution into the CNT yarn during the yarn spinning process [19]. Recently, Jung and his coworkers applied this method to aerogel spun CNT yarn by using a dilute (0.05 wt. %) solution of polystyrene (PS), polyacrylonitrile (PAN) and PVA. It is found that the CNT/PVA composites yarn yielded the greatest improvement, 100% improvement of specific strength and nearly 50% improvement in electrical conductivity [22]. A post polyester coating

procedure was also applied to CNT multi-yarn by Misak et al. through a direct glue coating method. However, the mechanical properties of the CNT multi-yarn did not show improvement [23].

In this study, the aerogel-spun CNT coating yarns were fabricated by a continuous sizing method using a dilute PDMS and toluene solution with different solution concentrations. The microstructure, tensile performance, electrical properties and the electromechanical response of the CNT yarn before and after coating were investigated.

EXPERIMENTAL

Aerogel-Spun Carbon Nanotube Yarn

The CNT yarns were received from the Suzhou Institute of Nano-Tech and Nano-Bionics (Suzhou, China). They were spun directly from the CNT aerogel by a floating catalyst CVD reaction with a liquid source of carbon and floating nano-iron catalyst, similar with the method reported by Li et al. [25]. Ethanol, ferrocene, and thiophene were injected into the heated reactor (1300℃) at a rate of 0.15 ml/min. Ar-H_2 mixture with a volume ratio of 1:1 was injected into the reactor at a rate of 4000 sccm. The aerogel-like CNTs grew spontaneously and were blown out using air. They were twisted into yarn and collected onto a take-up roller. During the collection process, the CNT bundles were preferentially aligned and assembled into a free standing yarn with uniform diameter.

Preparation of CNT Composites Yarns

A PDMS toluene solution with 1% concentration was prepared by adding PDMS (Sylgard 184 from Dow Corning) base polymer and curing agent (1:10 weight ratio to base polymer) into toluene. The mixture was mechanically stirred for 2 hours at ambient temperature. To avoid untwisting or disintegration of the yarn, a simple droplet infiltration method was adopted to fabricate the composite yarn. As shown in *Figure 1*, the yarn was drawn out from the spool and passed through a liquid droplet of PDMS solution, guide pins and dried by a device heated to 80°C. The first guide pin supports the droplet and allows the yarn to pass through it without breaking; the other two guide pins remove excess solution from the yarn. The pre-cured composite yarns were placed in a drying cabinet to cure for 12 hours. For comparison, CNT yarns treated with toluene droplets were obtained by the same method.

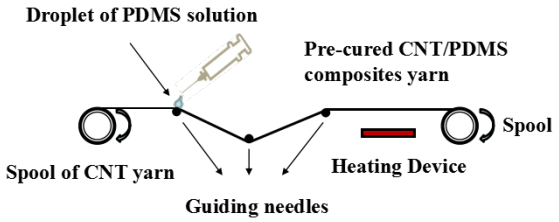


FIGURE 1. Schematic view of droplet infiltration method.

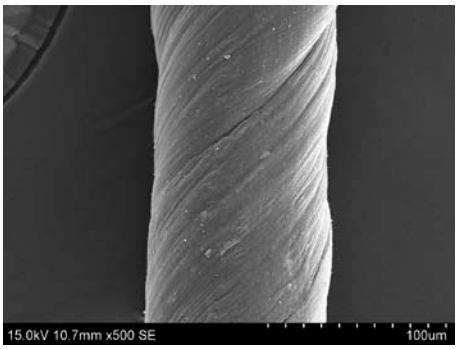
Characterization

The structural observations of CNT yarns were conducted by scanning electron microscopy (SEM) (Hitachi TM3000, 5 kV) and field emission SEM (FESEM, Hitachi S4800, and 5 kV). In order to estimate the polymer weight fraction of the composite yarn, Thermogravimetric analysis (TGA) was conducted in nitrogen using a Perkin-Elmer TGA 4000 at a heating rate of 20 ℃/min. The tensile properties of the original CNT yarn, toluene treated CNT yarn and CNT/PDMS composite yarn were characterized under both monotonic and cyclic loading on a displacement-controlled XQ-2 tensile tester at a gauge length of 10 mm and a stretch rate of 0.5 mm/min. An Agilent 34410A digital multi-meter was used to measure the electrical resistance.

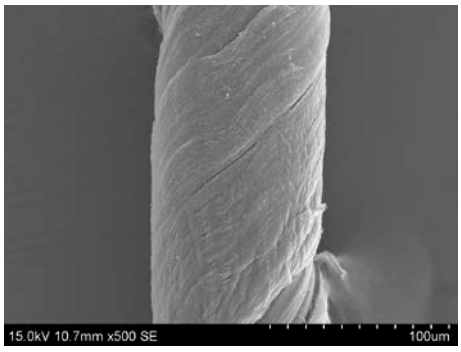
RESULTS AND DISCUSSION

Structure of CNT Yarn and Composite Yarn

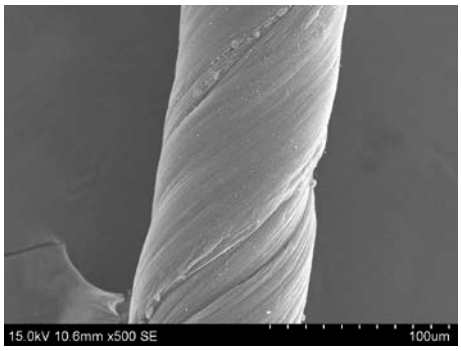
The SEM images of the original CNT yarn, toluene treated CNT yarn and the CNT/PDMS composites yarns are shown in *Figure 2*. The original CNT yarn (*Figure 2a*) showed a smooth surface with an apparent twist angle of 45 degrees. The toluene treated CNT yarn (*Figure 2b*) displayed a more uniform surface with a twist angle of 45° as well. The CNT/PDMS composite yarn surface (*Figure 2c*) is the smoothest of the three. This indicates that the toluene penetrated the CNT bundles and capillary forces drew neighboring CNTs together during toluene evaporation [7], causing the yarn to shrink from 99 μm to 94 μm. When the CNT yarn was treated with a 1% PDMS solution, the molecules of the PDMS base polymer infiltrated into the CNT yarn and bonded the CNTs upon evaporation of the toluene. After the PDMS was cured, a stable, dense network of CNT and polymer was formed, decreasing the diameter of the composite yarn to 88 μm. The fact that the twist angle of the yarns is unchanged indicates there is no stretching force during the droplet infiltration process.



(a) Original CNT yarn



(b) Toluene treated CNT yarn



(c) CNT/PDMS composite yarn

FIGURE 2. SEM image of the surface of original CNT yarn, toluene treated CNT yarn and CNT/PDMS composite yarn.

Figure 3 shows the TGA results on the original CNT yarn, CNT/PDMS composite yarn and PDMS film. The weight ratio of PDMS in the composite yarn was calculated to be 5.3% based on the weight losses of the CNT yarn, PDMS film and the composites yarn at a temperature of 780°C, the highest temperature the machine is capable of achieving.

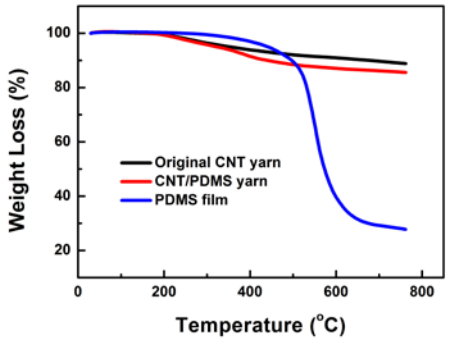


FIGURE 3. TGA results of original CNT yarn, CNT/PDMS composite yarn and PDMS film.

Tensile Properties

Figure 4 provides a comparison of the mechanical properties of the original CNT yarn, toluene treated CNT yarn and CNT/PDMS composite yarn. For the original CNT yarn, the average strength and Young's modulus were 408.53 MPa and 1.44 Gpa, respectively. After toluene treatment average strength and modulus of the CNT yarn increase to 680.37 MPa and 1.78 Gpa, respectively. The CNT/PDMS composite yarn showed further improvement with average strength increasing to 837.29 MPa and modulus to 3.66 GPa, over twice the original CNT yarn in each case. The measured breaking stress of the composite yarn was 925.7 MPa. The droplet infiltration process with dilute polymer solution showed great advantages over the previously mentioned polyester glue coating method, in which the tensile strength of the as-received CNT multi-yarn was improved from 209±4.9 MPa to 220±6.1 MPa [23].

Typical stress-strain curves of original CNT yarn, toluene treated CNT yarn and CNT/PDMS yarns are provided in *Figure 5*. The original CNT yarn shows a failure strain of 30 percent. The high strain of CNT yarn resulted from the rearrangement of CNT alignment during tensile loading. The toluene treated CNT yarn has a more stable structure which could be extended to 40% before breaking. However, the CNT/PDMS composites yarn showed a lower failure strain of slightly over 20 percent. As the PDMS combined with CNT in the composites yarn, a dense and firm structure was obtained, which inhibited CNT rearrangement during stretching. However, the composite yarn required much higher loading to achieve similar deformation to either the original CNT yarn or the toluene treated CNT yarn.

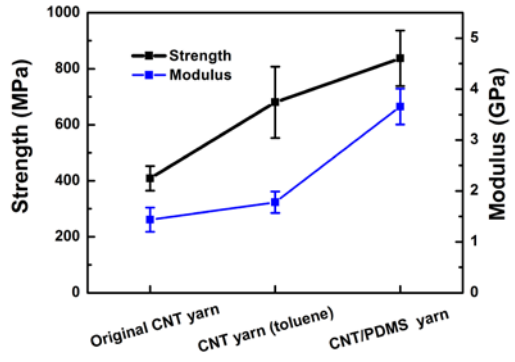


FIGURE 4. Tensile strength and Young's modulus original CNT yarn, toluene treated CNT yarn and CNT/PDMS yarn.

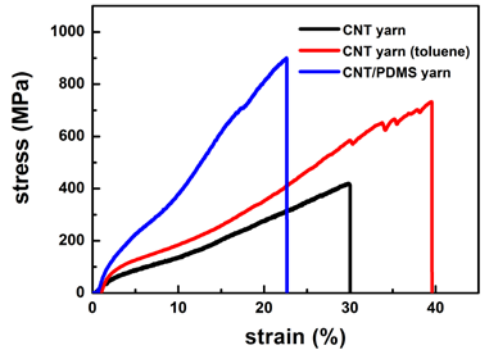


FIGURE 5. Typical stress strain curves of original CNT yarn, toluene treated CNT yarn and CNT/PDMS yarn.

The stress-strain curves, shown in *Figure 5* also indicated different stages of deformation behavior of the yarns. When the pristine CNT yarn was initially stretched, the entangled and misaligned CNT bundles rotated to similar orientations, resulting in very low modulus at a very low strain (< 0.5%). When the tensile strain increased from 0.5% to 2%, the aligned CNT bundles required higher load for deformation and thus showed a higher modulus. However, as the tensile strain increased continuously from 2% to 15%, the CNT bundles slipped and reoriented resulting in a decrease in tensile modulus in this strain range. After the CNT bundles reoriented into a more aligned and compact structure, modulus increased again until failure. The toluene treated CNT yarn and CNT/PDMS yarn showed similar trends in modulus change as a function of strain that of the pristine CNT yarn. Due stronger interactions between CNT bundles, the toluene treated CHT yarn and the CNT/PDMS yarn both showed higher modulus and ultimate strength compared to the CNT yarn.

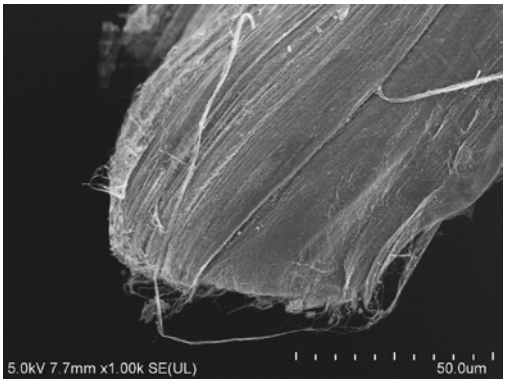


FIGURE 6. SEM image of the breaking area of CNT/PDMS yarn after tensile testing.

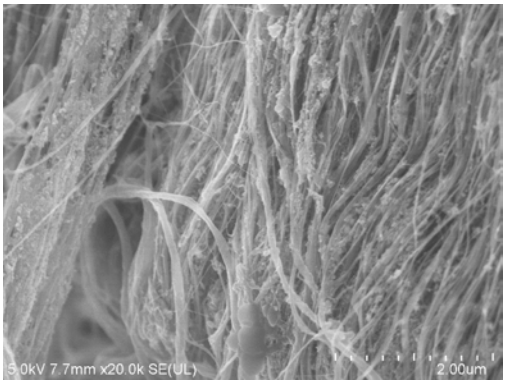


FIGURE 7. Higher magnification of *Figure 6.*

As shown in *Figure 6*, the broken ends of the CNT/PDMS yarn show clear fracture surfaces with very short pullout lengths of CNTs. This indicates that the PDMS and CNTs formed a good interface in the yarn. The SEM image of the composite yarn under higher magnification in *Figure 7* revealed\\s that the PDMS infiltrated into the CNT bundles in the yarn.

Electrical Properties

The electrical conductivities of the original CNT, toluene treated CNT and CNT/PDMS yarns are summarized in *Figure 8*. The average electrical conductivity of the original CNT yarns is 1636 S/cm. The toluene treated CNT yarn had an increased electrical conductivity of 2152 S/cm and the CNT/PDMS yarn showed the highest electrical

conductivity of 3555 S/cm. It is interesting CNT yarn with an insulator such as PDMS incorporated shows has improved electrical conductivity over the original CNT yarn. This is because that the conductivity of CNT yarn is mainly dependent on the contact resistance of the CNTs. For the composite yarn, although the polymer had infiltrated into the yarn, the decreased diameter and resulting densification of the yarn as a result of the imbibing process and the binding effect of the PDMS combined to increase the contact between CNT's and overcame any insulating effect provided by the PDMS.

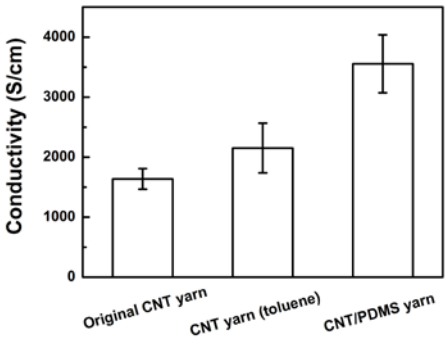


FIGURE 8. Electrical conductivity of original CNT yarn, CNT yarn (toluene) and CNT/PDMS yarn.

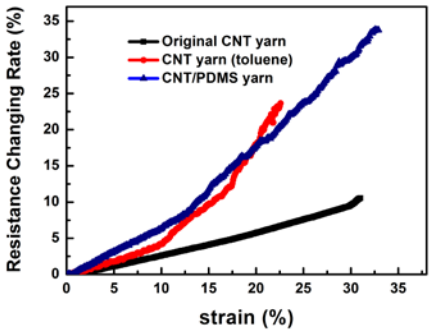


FIGURE 9. Resistance change rate as a function of strain for original CNT yarn, CNT yarn (toluene) and CNT/PDMS yarn.

The electromechanical properties of the original CNT yarn, toluene treated CNT yarn and CNT/PDMS yarn were investigated by active resistance measurement. This was done by measuring in situ resistance of CNT yarns during tensile stretching. Their resistance change rate was calculated by the ratio of changed resistance during tensile loading to the unstrained resistance of CNT yarns. *Figure 9* shows the resistance change rate as a function of the tensile strain. For the original CNT yarn, the resistance change rate increased linearly with increasing tensile strain. In the cases of both the toluene treated CNT yarn and CNT/PDMS yarn, the resistance change increased at similar, and much higher linear rates than the CNT fibers with increasing strain. To evaluate the correlation between resistance and strain of CNT yarns, the gauge factor (GF), a measure of the sensitivity of the strain gauge, was calculated using Eq. (1).

$$\mathrm{GF} = \frac{\Delta \mathrm{R} / R}{\Delta L / L} = \frac{\Delta R / R}{\varepsilon} \tag{1}$$

where ΔR is the change in strain gauge resistance, R is the unstrained resistance of strain gauge and ε is the strain. The gauge factor of original CNT yarn is 0.35. For the toluene treated CNT yarn and CNT/PDMS composites yarn, the gauge factors improve to 1.24 and 1.73 accordingly, which indicated the toluene treated CNT yarn or the composite yarn can be used as strain sensing materials.

CONCLUSION

In this study, CNT/PDMS composites yarn was fabricated by droplet infiltration of PDMS solution into the aerogel-spun CNT yarn. The composite yarn showed a smoother surface with decreased diameter. The mechanical properties of the CNT/PDMS composites yarn were improved by more than 100% over the original CNT yarn, with average strength of 837.29 MPa and modulus of 3.66 GPa. The electrical conductivity of the CNT/PDMS yarn improved to 3555 S/cm from 1636 S/cm in the case of the CNT yarn. The electromechanical properties of CNT/PDMS yarn demonstrated a gauge factor of 1.73, indicating this yarn is suitable for use as a strain sensor.

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