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Mechanical and electrical property improvement in CNT/Nylon composites through drawing and stretching

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ABSTRACT

The excellent mechanical properties of carbon nanotubes (CNTs) make them the ideal reinforcements for high performance composites. The misalignment and waviness of CNTs within composites are two major issues that limit the reinforcing efficiency. We report an effective method to increase the strength and stiffness of high volume fraction, aligned CNT composites by reducing CNT waviness using a drawing and stretching approach. Stretching the composites after fabrication improved the ultimate strength by 50%, 150%, and 190% corresponding to stretch ratios of 2%, 4% and 7%, respectively. Improvement of the electrical conductivities exhibited a similar trend. These results demonstrate the importance of straightening and aligning CNTs in improving the composite strength and electrical conductivity.

1. Introduction

Carbon nanotubes (CNTs) have highly desirable mechanical, thermal and electrical properties. They are promising candidates as reinforcement for the next generation of high performance composites. Significant effort has been focused on developing CNT composites over the last two decades. Methods for fabricating CNT composites include: dispersing short CNTs in polymer matrix [1–3], infiltrating CNT buckypaper with polymer solutions [4,5], and reinforcing with CNT fiber assemblies [6–8].

Studies of CNT composites [9–11] so far have largely focused on improving the nanotube dispersion quality and the interface with the matrix. To achieve good quality CNT/polymer dispersion, short CNTs in low volume fractions are typically utilized. Although short CNT composites have some advantages in certain low volume fraction applications, such as thermally and electrically conducting materials, their mechanical properties fall far short of traditional high performance structural composites. It results largely from the short CNT length (usually <10 μm), which cannot efficiently transfer a mechanical load across the weakly bonded interface. Chemical modification may improve interfacial shear strength, at the expense of introducing defects in the CNT structures and thus degrading the properties [12]. Achieving high volume fractions of dispersed CNTs in polymer is difficult because the resulting high viscosity complicates further processing.

Another approach is to infiltrate CNT films (also known as buckypapers) with thermoplastic polymers or epoxy resin [4,13]. The CNTs in the buckypaper sheets have no preferential orientation and each nanotube is curved and wavy. CNT fibers (yarns) can also be used to fabricate composites. They include plied or braided CNT fiber assemblies [6,7] and long spun fibers infiltrated by polymer [8]. The most significant component in these composites is the CNT fiber. Techniques for making CNT fibers are classified into "liquid" methods [14], where CNTs are dispersed into a liquid and solution-spun into fibers, and "solid" methods [15,16], where CNTs are directly spun into ropes or yarns. The last 10 years have seen rapid progress in the "solid" fiber spinning approach [17–24]. While the mechanical properties of these fibers are promising, they both have limitations. The "liquid" method requires short CNTs for solution spinning, which limits the mechanical properties, while the "solid" method involves fiber twisting, which is a slow and expensive process. Scaling-up of these technologies presents a major obstacle for engineering applications.

In a recent work by Cheng et al. [25], a high volume fraction of highly aligned CNTs was homogeneously dispersed in an epoxy matrix. The CNT/epoxy composites were produced by drawing and stacking CNT sheets from aligned CNT arrays, and then infiltrating the stacked CNT sheets with epoxy. This method alleviates

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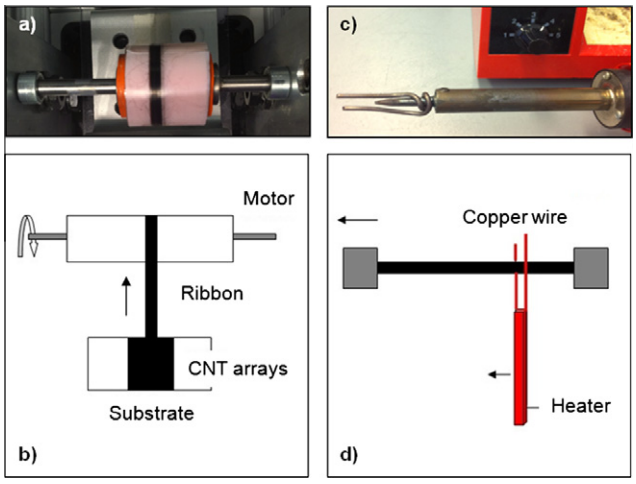

Fig. 1. (a) Rotary winding device. (b) A schematic of the drawing and winding process. The nylon solution was added on the as-wound ribbons using a dropper. (c) A piece of copper wire attached to a heating device provided local heating of the CNT composite. (d) A schematic of the local heating and stretching process.

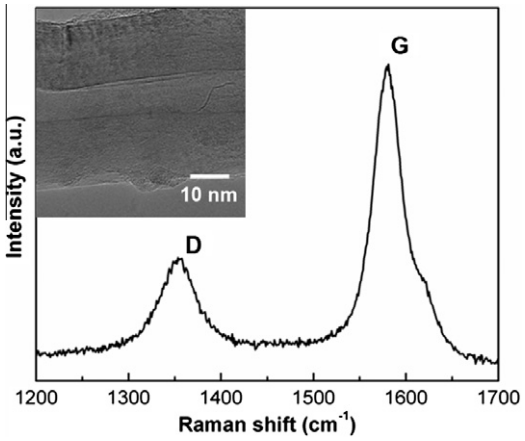

Fig. 2. Raman spectrum of the CNTs prepared by one-step CVD method [26] and used to make CNT composite in this study. The inset is a TEM image of a thick-walled CNT that was used in this study.

many limitations of other CNT processing methods. However, wavy nanotubes are still present, which reduces the mechanical properties of the composites.

Here we report a strategy, mechanical stretching of aligned CNT composites, to address the issue of CNT waviness. This approach involves drawing and winding thin CNT ribbons from free-standing CNT arrays, infusing a nylon 6,6 solution between layers of the CNT ribbon without disturbing the pre-existing alignment and stretching the composite while locally heating it to reduce the CNT waviness. The mechanical and electrical property results of this work identify a new mechanism of maximizing mechanical properties of CNT composites.

2. Experimental

2.1. Rotational winding CNT ribbons into composites

Vertically aligned CNT arrays with a height of ~700 μm were synthesized on a quartz substrate with iron chloride ($FeCl_2$) powder using a thermal chemical vapor deposition (CVD) method described in literature [26]. The CNTs were drawn from the arrays onto a rotating cylindrical polytetrafluoroethylene (PTFE) spool (as depicted in Fig. 1a and b). Continuous CNT tows were placed on the rotating spool while tension was applied in order to well pre-align the ribbons. Meanwhile, nylon 6,6 (1.14 g/cm^3 at 25 °C, molecular weight = 262.35, Sigma Alderich) solution (1 wt.% in phenol) was infused between the layers of the as-wound CNT ribbons using a dropper. After approximately one hundred winding revolutions at a speed of 1.1 m/min, unidirectional CNT/nylon 6,6 composites (10 cm long, 0.5 cm wide and 20 μm thick) were produced.

2.2. Locally heating and stretching the CNT composites

The as-wound CNT/nylon 6,6 composite was removed from the PTFE spool. Precise stretching was performed on a tensile testing machine (Shimazu EZ-S). The composite was locally heated by a fabricated heating element with dual prongs. The temperature between the two extended wire ends (see Fig. 1c and d) reached approximately 160 °C, which was measured by a thermocouple. The heating element moved along the composite at a speed of 3 mm/s so that the composite was heated and stretched uniformly along the length direction at a speed of 0.1 mm/min. The low applied load and the moving local heating source ensured that the whole composite was uniformly stretched without premature failure. The stretched CNT composites were hot pressed in a vacuum oven at 160 °C for 1 h.

2.3. Materials characterization and testing

Tensile test specimens were cut from the CNT/nylon 6,6 composite films into strips with dimensions of 10 mm long and 0.3 mm wide. CNT alignment was parallel to the longitudinal direction of the tensile loading. Edge defects were minimized by cutting the sample with a sharp razor and then hot-pressing it at 160 °C, which allowed the polymer molecules to partially reconfigure to smooth sample edges. Sample width was measured using a calibrated scale bar in an optical microscope (30×) and the sample thickness was measured using a micrometer. The composite specimens with gauge length of 6 mm were tested at room temperature using the tensile testing machine at a crosshead speed of 0.5 mm/min. Five specimens were tested for each CNT/nylon 6,6 composite. Resistance was measured using the four-probe method. Transmission electron microscopy (TEM) analysis of the nanotubes was performed using a JEOL 2010F microscope at an acceleration voltage of 200 kV. Scanning electron microcopy (SEM) analysis of the ribbons and composite fracture surface was carried out on a JEOL 6400F microscope with an acceleration voltage of 5 kV.

Fig. 3. A photograph of the flexible CNT/nylon 6,6 composite film (before stretching) made by the drawing and winding method.

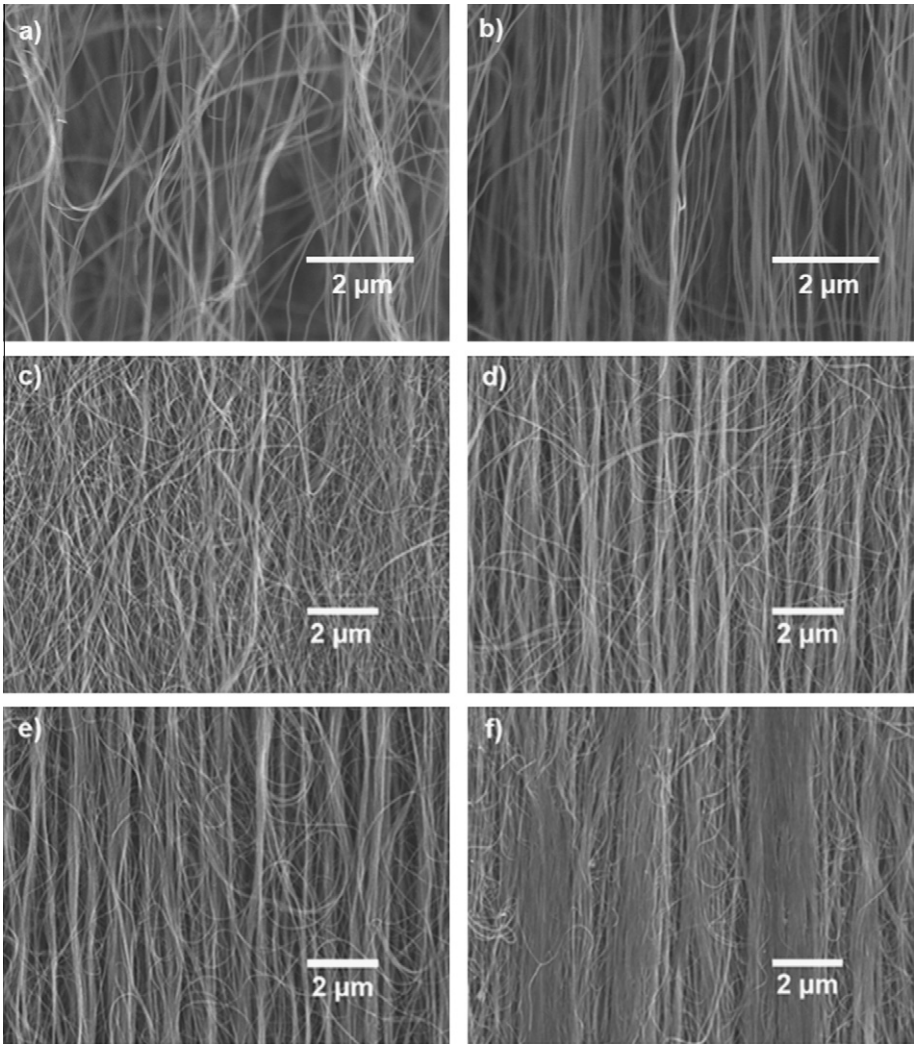

Fig. 4. SEM images of (a) as-drawn CNT dry ribbon showing wavy nanotubes, (b) stretched CNT dry ribbon representing reduced CNT waviness, (c) non-stretched CNT/nylon 6,6 composites showing wavy nanotubes, and CNT/nylon 6,6 composite after stretching with different ratios: (d) stretched for 2%, (e) stretched for 4% and (f) stretched for 7%. The polymer was removed during TGA.

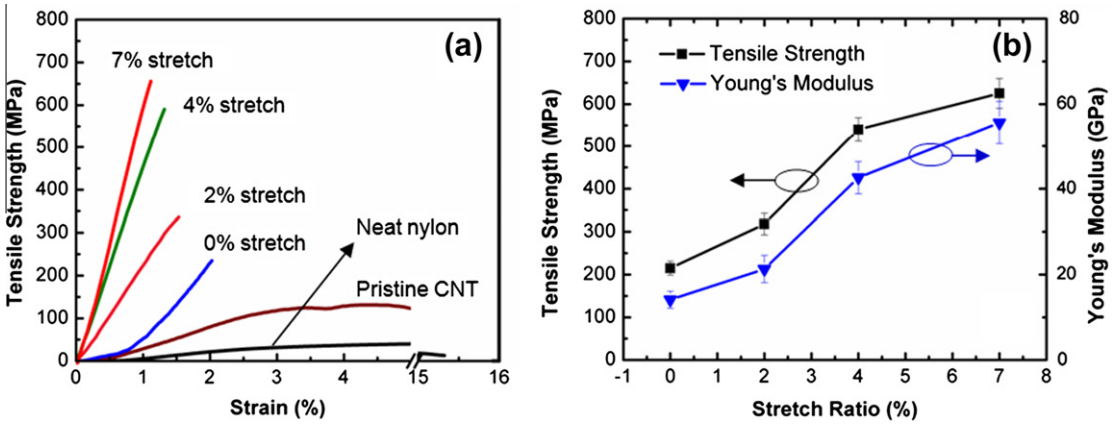

Fig. 5. Enhanced mechanical properties of CNT/nylon 6,6 composites. (a) Typical stress–strain curves of the stretched CNT/nylon 6,6 composites, pristine CNT ribbon and neat polymer, illustrating significant improvement of strength and modulus through stretching. (b) Comparison of tensile strength and Young's modulus of the CNT/nylon 6,6 composites with different stretch ratios.

Table 1
Comparison of the mechanical and electrical properties of pristine CNT ribbons, neat nylon 6,6 and aligned CNT/nylon 6,6 composites with different stretch ratios. S stands for stretch.

Samples	Tensile strength (MPa)	Young's modulus (GPa)	Conductivity (S/cm)
Pristine CNT ribbons	92	3	520
Neat nylon 6,6	44	1.6	2.0×10^{-15}
0% S-CNT/nylon 6,6	215	14	136
2% S-CNT/nylon 6,6	318	21	185
4% S-CNT/nylon 6,6	540	43	335
7% S-CNT/nylon 6,6	625	56	417

Thermogravimetric analysis (TGA) was completed on a Perkin Elmer Pyris 1 in nitrogen (99.999%) with a heating rate of 10 °C per minute.

3. Results and discussion

3.1. CNT/nylon 6,6 composites

The CNTs used to fabricate composites in this study were characterized by Raman and TEM (Fig. 2). A sharp G band peak (due to graphitic carbon) at 1583 cm^{-1} and a weak D band peak (due to disordered carbon) at 1357 cm^{-1} were observed in the Raman spectrum, indicating that the as-synthesized nanotubes were well-crystallized. The TEM image shows a nanotube having 50 walls and a diameter of 45 nm (inset in Fig. 2). These nanotubes were highly drawable from the array and had a high aspect ratio of approximately 15,000 indicating a large interaction interfacial area with the nylon matrix. Fig. 3 is a photograph of a typical aligned CNT/nylon 6,6 composite as prepared by the drawing and winding method.

3.2. Alignment strategies

Alignment of CNTs is a major issue for fabricating high performance composites [27,28]. The drawing process aligned the CNTs by applying tension during uptake on the PTFE spool. Another advantage of this method is the ease with which wide CNT sheets are formed, which facilitates more rapid fabrication of large engineering structures. Although the CNTs were aligned, a significant amount of waviness was present and diminished the mechanical strength and stiffness.

In order to maximize the load-carrying efficiency, the waviness of CNTs within the composites was minimized. To accomplish this goal, we used a simple local heating and stretching method to uniformly stretch the nanotubes together with the polymer matrix. Stretching has proven to be effective by Cheng et al., whose nanotube preforms started out with low preferential alignment [29]. In this work we applied the stretching technique to well aligned CNT composites.

With a low glass transition temperature (~50 °C) and large strain-to-failure, nylon is a suitable matrix for stretching. As compared to cold stretching, which can result in inhomogeneous elongation during necking, local heating allows for a more uniform elongation of the composite. At temperatures close to the melting point of nylon, the polymer chains are much more mobile and can reconfigure more easily under applied strain, allowing the CNTs to straighten.

SEM images indicated that the post-strained CNTs (Fig. 4b) were much straighter and better aligned than the CNTs in the as-drawn ribbon (Fig. 4a). The morphologies of CNT networks in the non-stretched and the stretched composites are shown in Fig. 4c–f. The nylon matrix was removed by heating the composite samples to high temperatures in a TGA furnace under an inert atmosphere. The non-stretched composite (Fig. 4c) showed that CNTs were very wavy along the axial loading direction. Consequently, only a small fraction of the CNTs in the composite would carry load effectively during tensile testing. The SEM images in Fig. 4d–f showed improved CNT alignment in the stretched samples. The straightened nanotubes have a larger fraction of their length aligned with the loading direction, which resulted in higher mechanical strength and stiffness. However, there was only a slightly discernable difference in the SEM images of composites stretched for 2%, 4% and 7% due to the limited stretch ratio. Attempts to stretch the composite with local heating to over 7% without breakage were not successful.

The CNT–polymer interface interaction is another potential factor that may affect the properties of CNT composites. In this work, CNTs with a high aspect ratio were used to produce composites. The CNT's aspect ratio was much larger than the minimum that was required to effectively transfer load across the CNT–polymer interface. In addition, the dilute nylon solution was delivered into each layer of the CNT ribbon, which allowed the CNTs or their bundles to be integrated with the nylon molecules at the molecular level and thus increased the effectiveness of load transfer. The stretching process only increased the overall alignment of the CNTs but did not affect the CNT–polymer interface.

High volume fraction and good CNT dispersion in the polymer matrix were achieved by using a dilute polymer solution for composite fabrication. However, as the volume fraction of CNTs was increased by decreasing the nylon concentration, the heated stretching became more challenging. Methods of simultaneously enhancing nanotube mass fraction while increasing the stretch ratio are currently under investigation. Following the stretching step, hot-pressing reduced the thickness of the CNT composites by approximately 20% with a final thickness of 16 ± 1 μm. The mass fraction of the CNT/nylon 6,6 composites was determined using TGA. The differences in the mass losses (TGA curves) of nylon 6,6 and the composite sample were measured and a mass fraction of 20% was estimated. Given the densities of nylon 6,6 and CNTs as 1.14 and 2.1 g/cm^3, respectively, the volume fraction of CNTs in the composites was estimated to be 15%.

3.3. Mechanical properties

Typical tensile strength curves for the pristine CNT ribbon, pure nylon 6,6, CNT/nylon 6,6 composites with increasing stretch ratios are shown in Fig. 5 and summarized in Table 1. The dry CNT ribbon, which was densified with ethanol, was formed using the same winding method as the other composite samples. The dry CNT ribbon exhibited a tensile strength of 90 MPa and elastic modulus of 3.2 GPa. The tensile strength of as-wound CNT/nylon 6,6 composites was 220 MPa. The strength of the composites with stretch ratios of 2%, 4% and 7% were improved to 320, 540 and 630 MPa, respectively, corresponding to 50%, 150% and 190% improvement over those of the non-stretched composite. The Young's modulus of CNT/nylon 6,6 composites without stretching was 14 GPa. This was increased to 21, 43, 56 GPa with three different stretch ratios of 2%, 4% and 7%, respectively, which corresponded to 50%, 200% and 290% increase over those of the non-stretched composite. These observations are consistent with other reports in the literature. Bradford et al. [30] used a tensile testing machine and stretched resin infused CNT preforms to a strain of 5% before curing and observed a 33% increase in tensile strength and 50% increase in Young's modulus. Fig. 4 showed that stretching 2–7% resulted in improved alignment of the CNTs in the composites. With increasing stretch ratio, more nanotubes were straightened and the average space between the nanotubes became smaller. Through enhanced alignment and densification of CNT network, the tensile mechanical properties of the composites were significantly improved. In this study, aligned CNTs were achieved macroscopically

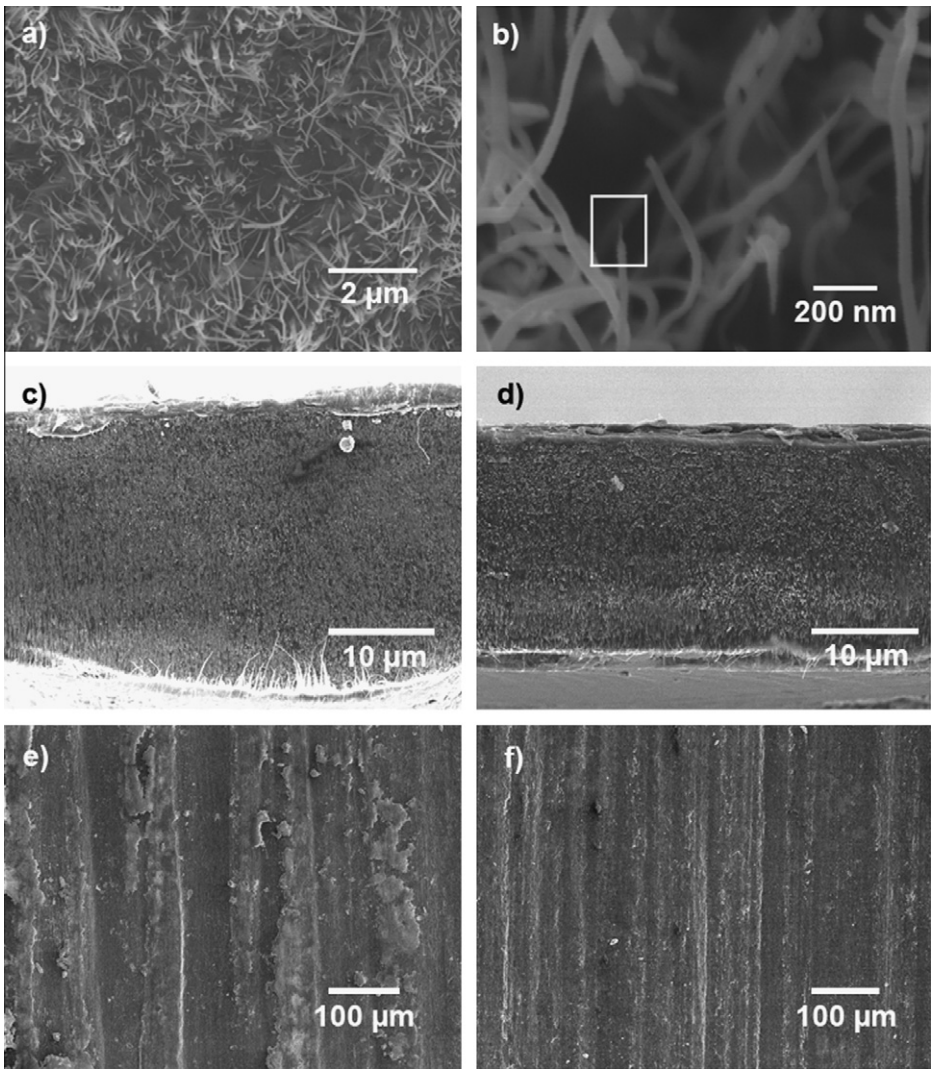

Fig. 6. SEM images of (a) the fracture surface of the CNT/nylon 6,6 composite stretched for 7%, (b) fractured sheath–core tips of the MWNTs, side views of a stretched composite, (c) before hot-pressing, (d) after hot-pressing and top views of a stretched composite, (e) before hot-pressing and (f) after hot-pressing.

through the drawing and winding process. Further reduction in the microscopic waviness by stretching made the strength enhancement even more notable. This is in good agreement with the models and simulations on the effect of nanotube waviness in composites [31–33].

The drawing and stretching method has produced CNT/nylon composites superior to other CNT/nylon composites reported in the literature. Comparing to CNT/nylon composites fabricated by solution processing [34], melt processing [35] and in situ polymerization [36], the CNT composites in this work showed promising mechanical properties due to long CNTs, well controlled alignment and reduced waviness. Conventional methods rely on short fiber dispersion, in which inefficient load transfer, random orientation and low volume fraction make it challenging to significantly enhance mechanical properties. In the multi-walled carbon nanotube (MWCNT)/nylon composites functionalized with amine groups [37], 1 wt.% of CNTs were incorporated into the matrix by melt compounding, which resulted in limited strength and modulus improvement (up to 59.3 MPa and 3.56 GPa, respectively). Although the CNTs were chemically functionalized with the aim to accomplish good nanotube dispersion and a strong interfacial adhesion with the matrix, the properties of the composites were not improved significantly. Another work [38] on the surface modification of CNTs suggested that only a small degree of functionalization could be applied, otherwise either the damaged surface of CNTs or excessive bonding with the matrix would lead to brittle failure of the materials. Even with moderate surface modification, it is challenging to obtain exceptional mechanical properties due to low CNT volume fraction [39]. While CNT length and alignment have been previously shown to be important for high performance CNT composites, this work demonstrates that reducing waviness is also a critical factor for making high performance CNT composites.

3.4. Fracture morphologies

Fig. 6a and b show the fracture surface morphology of a composite sample stretched for 7%. Rather than peeling off of the CNT sheets as reported in CNT buckypaper/BMI composites after stretching [29], Fig. 6a showed individual CNTs at the fracture surface. CNTs were also homogeneously distributed throughout the cross-section area and the polymer penetrated well between the nanotubes and their bundles. A sheath–core tip was observed on a few CNT ends after failure (Fig. 6b) indicating slippage between the CNT walls. It is believed that stress transfer between walls within MWNTs is low in composites [40]. The nanotubes prepared in this work had an average diameter of 45 nm with approximately 50 walls. With such a large number of walls, it

was assumed that the maximum stiffness of the composite was negatively affected. The pull-out length of CNTs was approximately one micrometer. Fig. 6c and d are the side views of the composites stretched for 7% before and after hot-pressing. During the hot-pressing process residual solvent was evaporated, the polymer was softened and the sample thickness was reduced. Pressed composites had higher tensile strength and Young's Modulus than un-pressed ones. It was assumed that the pressing minimized voids and defects in individual layers so that more intimate contact between polymer and CNTs was developed. Comparison of the surface of the pressed sample (Fig. 6f) with that of the un-pressed sample (Fig. 6e) revealed that hot-pressing decreased the surface roughness of the samples.

3.5. Electrical properties

Electrical conductivity of the CNT/nylon 6,6 composites are summarized in Table 1. Nylon is an insulator and the electrical conductivity of the neat nylon 6,6 is $\sim 10^{-14}$–10^{-16} S/cm [41]. The electrical conductivity of pristine CNT sheets and non-stretched composites were 520 S/cm and 140 S/cm, respectively. When the composite was stretched by 7%, the electrical conductivity was increased to 420 S/cm, which was two times higher than their non-stretched counterparts. This value is much higher than the electrical conductivity of composites prepared by conventional dispersion methods [42]. This is a result of higher volume fraction and enhanced CNT alignment. These results are also consistent with reports on the effect of CNT alignment on the electrical conductivity of their composites [43,44].

Future work will include investigations on a more efficient stretching solution and larger CNT volume fraction. In addition, CNT arrays with few-walled CNTs will be utilized to assess the importance of CNT wall number on mechanical properties of aligned CNT composites. Moderate surface modification will also be used to enhance the interfacial shear strength between nanotubes and the polymer.

4. Conclusion

A novel drawing and stretching approach was developed for fabricating CNT/nylon 6,6 composites with good CNT alignment, high CNT volume fraction and straight nanotubes. The winding method created aligned CNT composites, while the local heating and stretching strategy led to further reduction of CNT waviness. Both mechanical and electrical properties showed substantial increases (191%, 294% and 207% for tensile strength, Young's Modulus and electrical conductivity, respectively) as the stretch ratio was increased to 7%. Macroscopically aligned CNTs and microscopically reduced waviness are critical to improving mechanical properties of CNT composites. These new insights may lead to further development of other types of CNT-based high performance materials.

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