ENHANCED CARBON NANOTUBE FIBER AND FILM BY A HIGH TOUGHNESS EPOXY

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Abstract:

The extraordinary mechanical and physical properties of individual carbon nanotube (CNT) have motivated considerable interest in fabricating macroscopic structures. Among which, CNT fibers and CNT films are two types of promising candidates as composite reinforcement for real applications. Here we report the effect of introducing a high toughness epoxy resin on the tensile properties of CNT fiber and CNT film, which were both fabricated from vertically aligned CNT arrays. Fig.1 schematically presents the preparation procedure. The CNT fibers were spun by drawing and twisting, and modified by soaking them in the epoxy/acetone solution, while the CNT films were modified during the winding process by in-situ spraying the epoxy solution onto the rotating mandrel. As a result, comparing to the as-prepared CNT fiber, the tensile strength and modulus of epoxy modified CNT fiber were improved to 1.41 GPa and 79.38 GPa, enhanced by 32.85% and 82.11%, respectively. The epoxy modified CNT film gave the strength and modulus up to 1.54 GPa and 58.58 GPa, 51.83% and 211.10% higher than the pure CNT film. This implicated that the direct spraying process in CNT film preparation is more efficient in modifying the CNT/epoxy interaction than the post treatment on the CNT fiber. The SEM, Raman, and infra-red spectrum analyses attribute the main mechanism of the improvement to the enhanced tube-tube interactions by the densification and higher degree of CNT orientation, as well as the interaction between the CNT and the epoxy molecules.

1 Introduction

The extraordinary mechanical and physical properties of individual carbon nanotube (CNT) have motivated considerable interest in fabricating CNT based macroscopic structures aiming at converting the unique property of microscopic CNTs to structure efficiency in engineering. Among which, CNT fibers and CNT films are two types of promising candidates as composite reinforcement for real applications. In the past two decades, extensive efforts have been devoted to the fabrication, reinforcement and performance of continuous CNT fiber. The first CNT fiber was fabricated through coagulation-based “wet spinning” method by Paul Pascal research center in 2000 [1]. “Direct spinning” CNT fiber was obtained from CNT aerogel in 2004 [2]. Since the super-aligned CNT arrays were synthesized on silicon wafers by Jiang et al. by chemical vapor deposition in 2002 [3], more interests have been attracted to the “dry-drawing” continuous CNT fibers from the CNT arrays. The studies focused not only on the process modification to get high performance of the CNT fibers, but also on the relationships between the structures and the fiber properties [4-12]. Researchers in University of Texas
at Dallas developed this dry-drawing method by introducing twist during spinning, and obtained high CNT fraction (96-98wt%) fibers with remarkable properties [13]. Above all, Zhang et al. [14] reported exceptionally high mechanical properties of this kind of CNT fiber with tensile strength and modulus up to 3.3GPa and 263GPa, respectively. Recently this dry-spun CNT fiber was proved can be significantly strengthened by solvent or polymer shrinking effect [15-20]. Jia et al. [21] showed that the nanotube structures, such as tube diameter, wall thickness, tube length and level of defects, had notable influences on the CNT fiber mechanical properties. Fang et al. [22] reported a considerable tensile strength improvement of the CNT fiber from 1.58 to 2.06 GPa by polyimide-infiltration and curing at high temperature, due to strong CNT-polymer interfacial shear stress. Additionally, the diameter of the CNT array-spun fiber can be kept constant by controlling the width of the CNT array by laser etching [23]. Especially in recent years, the characterization of mechanical and physical properties of CNT fiber, as well as the interfacial performance and functionalized application of CNT fiber based composites have been widely studied [24-27]. However, although significant advances have been made in the lab study of CNT fiber and its composites, an efficient synthesize process of high performance CNT composites for large-scale production is still lacking.

In order to realize high transfer efficiency of the unique property of CNT to industrial utilization, a novel approach for fabricating high performance CNT composite film has been developed recently, inspiring by the CNT array based dry-drawing method. Liu W. [28] reported a continuously preparation method of CNT/PVA composite film by coupling the spraying of a PVA solution with the winding process of CNT sheets from an array onto a rotating mandrel. During the winding process, ethanol was simultaneously sprayed to densify the winding sheets at the opposite side of the rotating mandrel using an alcohol spray gun. A new record has been reported by Wang X. [30], which developed the winding method to a stretch-winding process by adding a pair of rods before winding to stretch the CNT sheets. These researches showed that this CNT array based winding process is expected to realize continuous fabrication of high performance CNT composites and satisfy industrial demand.

Since CNT based composite is widely regarded as the next generation of composites to meet the stringent performance requirements of future aero-space structures, the combination of CNT with aviation used resin matrix become one critical issue. Epoxy resin, with good resistance to heat, impact, moisture, fatigue and radiation, as well as other comprehensive performance, is one of the critical matrixes for the manufacture of aircraft, missiles, rockets, satellites and space shuttles. However, existing reports has not adopt epoxy resin to modify the CNT array based films, especially the in-depth knowledge of the modification mechanism is required. The fundamental study of the CNT/epoxy composites is important for the realization of next generation composites for future aerospace application.

In this study, we adopted an epoxy resin to modify the tensile properties of CNT fiber and film, which were both fabricated from vertically aligned CNT arrays. Results showed that the tensile properties of the CNT film was improved by adding the epoxy resin, and the enhancing mechanism was systematically discussed.

2 Experimental

The CNT films used in this study were fabricated by horizontally drawing continuous CNT sheet from vertically aligned CNT array and directly winding onto a rotating polytetrafluoroethylene (PTFE) mandrel. During the winding process, ethanol was simultaneously sprayed to densify the winding sheets at the opposite side of the rotating mandrel using an alcohol spray gun.
air brusher. As comparison, CNT fibers were also prepared by drawing and twisting the CNT sheets from the same CNT array of CNT films, and densified by adding a drop of ethanol at the tip of the triangular CNT strip. For the CNT/polymer composite films and fibers, the ethanol was replaced by epoxy solutions (HJ-815, Dasen Materials and Technology Ltd., dissolved in acetone with a weight fraction of 0.1%). For convenient, the ethanol and epoxy solution infiltrated films (fibers) were denoted as pure CNT film (CNT fiber) and CNT/epoxy composite film (CNT/epoxy composite fiber), respectively. For the epoxy-CNT film, a curing process at 70°C for 6h was conducted to reduce porosity within the film. The preparation procedure of the CNT fiber and film were shown in Fig.1.

After preparation, the CNT fiber diameter was measured by the optical diffraction method using 532 nm green laser. The thickness of the CNT films was tested by a micrometer caliper. The surface and fracture morphology of CNT fibers and films were observed by a Scanning Electron Microscope (SEM, Apollo 300, Cam Scan, England). The CNT weight fraction of the CNT/polymer composite films was measured by thermo gravimetric analysis (TGA), with a heating rate of 10°C/min in Argon gas from 25°C to 800°C. The alignment degree in the CNT films was characterized by the decrease of normalized G’-band intensity from polarized Raman spectroscopy when the polarization axis of the incident laser beam was change from parallel to perpendicular with the film [31, 32].

As to the mechanical performance of the array based CNT assembles, single fiber tensile tests were conducted on a MTS Nano Bionix Universal Testing System (Oak Ridge, Tennessee, shown as Fig.2), with the extension speed of 0.001 mm/s.

For the tensile test of the CNT films, the as-prepared films were cut into small rectangular pieces with 15mm in length and 0.5 mm in width, which were glued onto a window-frame with a rectangular opening in the center, and tested on a Shimadzu EZ-S testing machine with a load cell of 100N at a strain rate of 8.3% per min. The gage length was 6±1 mm for all the CNT fibers and films, as shown in Fig.3.
3 Results and Discussion

Both pure CNT film and CNT/epoxy composite film were prepared from the same CNT array to investigate the effect of introducing epoxy on the tensile properties of CNT films, with the mandrel diameter and rotating speed fixed the same during the winding process. Fig.4 provides the tensile test results of pure and epoxy modified CNT fibers and films. The pure CNT film was only 1.01 GPa in strength and 18.83 GPa in modulus, approximately the same strength as that of the pure CNT fiber, but much lower in stiffness. The relative low strength of the pure CNT film derives from the weak van der Waals interactions between nanotubes as within the CNT fiber, leading to easily slide between neighbouring nanotubes under external tensile loads. After the epoxy spraying, the tensile strength and modulus of CNT/epoxy composite film increased up to 1.54 GPa and 58.58GPa, while the data CNT/epoxy composite fiber also rise up to 1.41GPa and 79.38 GPa, respectively. The spraying of epoxy solution into the carbon nanotube during the fabrication process enables well penetration of the macromolecular into the nanoscale CNT bundles due to the yarn-like structure of the CNT assembles. The penetration of the epoxy molecular makes the relatively separated CNT bundles wrapped by a three-dimensional network, and the effect of acetone densification makes the loose CNT bundles well compact, both of which can render more tube-tube or tube-polymer contact sites to improve the load transfer efficiency within the CNT assembles, resulting in higher tensile strength.

After the tensile test, the surface and fracture morphology of CNT films and fibers were characterized. The SEM images in Fig.6 (a) and Fig.6 (c) showed well integration of epoxy molecular with individual CNT bundles. It is more porosity in the pure CNT film in Fig.5 (a) and Fig 5 (c), thus the CNT bundles are easily slide against each other under external stress, resulting in irregular fracture morphology after tensile test as shown in Fig.5 (b) and Fig5. (d). In contrast, it can be seen from Fig.6 (a) and
Fig. 6 (c) that the epoxy solution was uniformly and completely penetrate into the pores between nanotuber bundles, which is vital for increasing the load transfer efficiency within the CNT film. In addition, the well integrated CNT/polymer network bridge the pristine separated CNT bundles together when response to external tensile loads, that is why the relatively more neat fracture morphology in Fig. 6 (b) and Fig. 6 (d) emerge after the tensile test.

![Fig.5. The SEM images of surface and fracture morphology after tensile test for (a, b) pure CNT fiber and (c, d) pure CNT film.](image)

In addition to the good infiltration of epoxy with CNT, the high degree of CNT alignment in the epoxy spraying composites is the second key factor benefiting its mechanical properties. Polarized Raman spectroscopy is widely regarded as an effective approach to estimate the CNT alignment degree in CNT nanocomposites. Fig. 7 and Table 1 presents the Raman results of pure and epoxy modified CNT films.

![Fig.7 Raman spectra for (a) pure CNT film and (b) CNT/epoxy film at different polarized angle. The G'-band intensity decrease with increasing polarized angle, and decreased more when epoxy is sprayed to the composite film.](image)

**Table 1 Normalized intensity of G’-band peak at different angle between the tested film and the polarization axis of the incident laser beam.**

<table>
<thead>
<tr>
<th></th>
<th>0°</th>
<th>20°</th>
<th>40°</th>
<th>60°</th>
<th>80°</th>
<th>90°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure CNT film</td>
<td>1</td>
<td>0.93</td>
<td>0.80</td>
<td>0.68</td>
<td>0.56</td>
<td>0.52</td>
</tr>
<tr>
<td>Epoxy-CNT film</td>
<td>1</td>
<td>0.84</td>
<td>0.63</td>
<td>0.55</td>
<td>0.42</td>
<td>0.32</td>
</tr>
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</table>

For the pure CNT film, the normalized G’-band
intensity decreased to 0.52 when the polarized angle is 90°, higher than the 0.32 of CNT/epoxy composite film, indicating that the degree of CNT alignment in the film is improved by epoxy spraying. Obviously, lower CNT alignment is not as efficient as the higher CNT alignment degree system in load transfer under external stress because of the weak tube-tube interaction due to limited contact area in the curly fluffy CNT structure.

The enhanced tensile mechanical performance of the CNT/epoxy composite film also arises from its high CNT load. The TGA curves in Fig.8 gave evidence that the CNT/epoxy composite film has a high CNT weight fraction of 49.84%. The CNT weight fraction in the CNT/epoxy film was calculated from the results at 600°C, as shown by the cross point of the dash line with the TGA curves.

![Fig.8 TGA curves of pure CNT film and pure epoxy resin and epoxy solution sprayed CNT/epoxy film.](image)

In conclusion, the high mechanical property of CNT/epoxy composite film arises from good wetting ability of resin with nanotube, higher degree of CNT alignment, and high CNT load by dilute solution spraying.

4 Conclusions

The effect of introducing a high toughness epoxy resin on the tensile properties of CNT fiber and CNT film, which were both fabricated from vertically aligned CNT arrays were reported. As a result, comparing to the as-prepared CNT fiber, the tensile strength and modulus of epoxy modified CNT fiber were improved to 1.41GPa and 79.38 GPa, enhanced by 32.85% and 82.11%, respectively. The epoxy modified CNT film gave the strength and modulus up to 1.54 GPa and 58.58 GPa, 51.83% and 211.10% higher than the pure CNT film. This implicated that the direct spraying process in CNT film preparation is more efficient in modifying the CNT/epoxy interaction than the post treatment on the CNT fiber. The SEM, contact angle, Polarized Raman and TGA analysis attributed the main mechanism of the epoxy modification on the tensile performance of CNT film to three aspects, i.e. good wetting ability of CNT film with epoxy, high degree of CNT alignment, and high CNT load in the epoxy sprayed CNT film.

5 References

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