CARBON NANOTUBE / POLY(VINYL ALCOHOL) COMPOSITES FORMED BY SPRAY WINDING

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Introduction

Carbon nanotubes (CNTs) are an order of magnitude stronger than current engineering fibers [1] making them ideal reinforcement for advanced composites. After decades of extensive research it still remains a great challenge to synthesize high-performance CNT composites in a manner conducive to large-scale production [2]. In order to fully utilize the unique properties of CNTs, it is desired to uniformly distribute among the matrix the unidirectionally-aligned long tubes at a high fraction. However, it is difficult to realize such structure with the existing processing approaches.
In this study, we demonstrate a one-step approach of spray winding to fabricate high-performance CNT composites, by using poly(vinyl alcohol) (PVA) as a testing matrix. The composites film has a tensile strength of 1.8 GPa and Young's modulus of 45 GPa at the CNT mass fraction of 65 wt%. It is much better than the many other CNT/polymer composites [3]. The high performance arises from the long tube length, highly-aligned tube morphology, and good interfacial bonding between CNT and PVA, which are obtained simultaneously through spray winding.

Experimental

Figure 1 shows schematically the spray winding approach for fabricating CNT/PVA composites, where a CNT sheet is drawn out of a drawable CNT array and wound on a rotating mandrel. During the processing, a dilute PVA solution was sprayed into tiny droplets and deposited on the sheet. A screen with a rectangular slit can be put between the nozzle and mandrel to control the area of spray. By choosing an appropriate mandrel diameter, sheet width, and number of revolutions, unidirectional composites with the desired size and thickness can be produced. Finally, the composites are compressed between two hot platens at 160 °C, slightly below the melting temperature of PVA, to remove air bubbles and to improve the CNT-polymer integration.

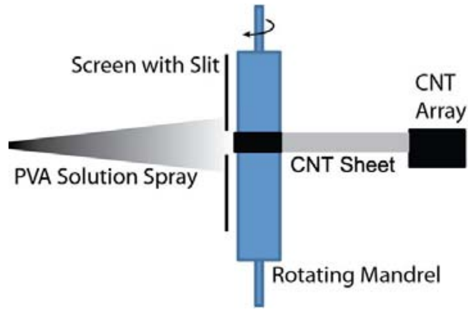


Figure 1: Schematic view of spray winding.

The CNTs used here were grown in the form of arrays by a sustained chemical vapor deposition on SiO_2/Si wafers [4]. The tubes were about 300 μm long, mainly 6-walled, and 8–10 nm in diameter. 1-g/L PVA solution was prepared by dissolving PVA (molecular weight 85,000–124,000, 99+% hydrolyzed) in a solvent containing equal volume of deionized water and ethanol. The composite films were prepared by rotating the mandrel for one hour. For the tensile tests, the films were cut into 1.5 cm×0.5 mm pieces (gauge length 6 mm) and tested on a Shimadzu EZ-S testing machine with a load cell of 100 N. In order to estimate the CNT weight fraction, thermogravimetric analysis (TGA) were conducted in nitrogen (99.999%) in a Perkin Elmer Pyris 1 at a heating rate of 10 °C/min.

Results and Discussion

Figure 2a provides the stress-strain curves for a pure CNT film (by layering hundreds of sheets with spraying the mixture of water and ethanol) and for three films made by using the 1-g/L PVA solutions. The pure CNT film was only 420 MPa in strength, due to the weak van der Waals interaction between tubes. In such a film, CNTs might slide against each other under external loads. When PVA was sprayed into CNTs, the long and flexible polymer molecules not only wraps and stick on CNTs, but also interact and bridge CNTs that are not in close contact. Therefore, the interfacial shear stress was improved greatly, resulting in high tensile strength of 1.82 GPa, Young's modulus of 47 GPa and toughness of 100 J/g.

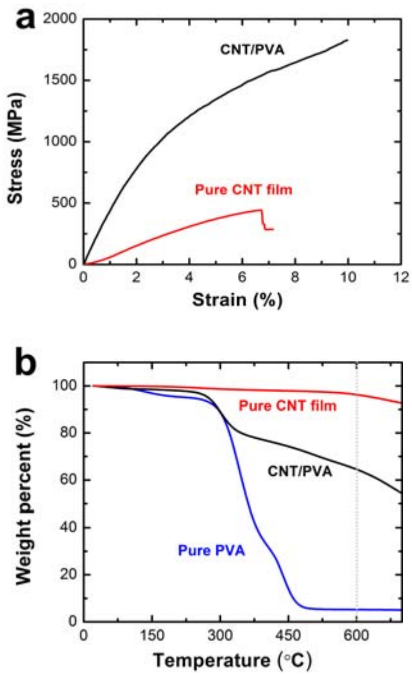
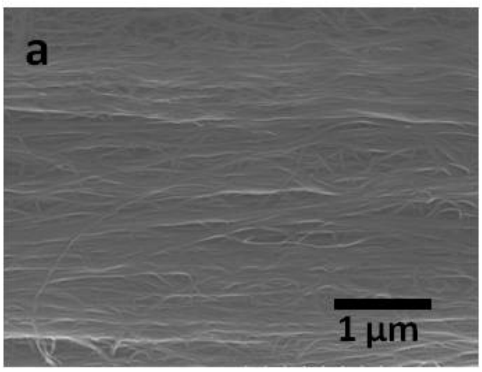


Fig.1 (a) Stress-strain curve of the pure CNT film and CNT/PVA composites; (b) TGA curve of the pure CNT film, CNT/PVA composites and pure PVA.

The high performance of our composites arises from the uniform integration of the high mass fraction of aligned long CNT and the polymer matrix. The mass fraction of CNT is calculated [5] to be 65 wt% based on the TGA curve of the composites (Fig.2b). Scanning electron microscope (SEM) image, as shown in Fig.3a, also indicates a highly alignment of CNT in the composites. This is because the alignment of nanotube in the CNT sheet was well maintained during the process and even can be improved after the hot pressing. Fig. 3b showed the fracture surface of the composites where the tubes have only short pull-out lengths from the uniformly wrapped polymer matrix. The good and uniform integration of CNT and PVA are contributed by the capillary force during the solvent evaporation.



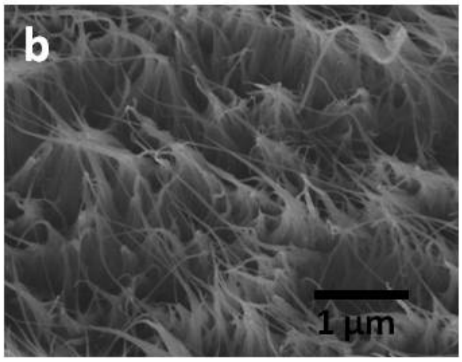


Fig. 3 (a) SEM image of the CNT/PVA composites side view; (b) SEM image of the fracture surface of the CNT/PVA composites.

Conclusion

In summary, a novel spray winding method was developed to fabricate CNT-PVA composites with mechanical properties outperforming other CNT-thermoplastic composites. The spray winding technique produced CNT composites with the desired structural features of high CNT mass (volume) fraction, long CNTs, good CNT alignment, and excellent mixing of the CNTs and matrix. The method can be applied to both thermoplastic and thermosetting matrix CNT composites, which overcomes some limits of previously reported techniques. Besides the thermoplastic PVA used here, this method can be also used to make thermosetting polymer-based composites with ultrahigh mechanical properties.

Reference

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