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Producing superior composites by winding carbon nanotubes onto a mandrel under a poly(vinyl alcohol) spray

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ABSTRACT

A simple method for processing high-performance carbon nanotube (CNT)/poly(vinyl alcohol) (PVA) composites by coupling the spraying of a PVA solution with the continuous winding of CNT sheets from an array onto a rotating mandrel is reported. This method allows the CNT composites to have a high CNT volume fraction, while having a high degree of alignment, long CNTs, and good integration with the matrix, which are extremely difficult to realize simultaneously by other processes. As a result, the composites have a toughness, strength and electrical conductivity up to 100 J/g, 1.8 GPa and 780 S/cm, respectively. Such a one-step synthesis process is promising for industrial productions and also works for different types of polymers.

1. Introduction

Carbon nanotubes (CNTs) are an order of magnitude stronger than current engineering fibers [1,2] 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 [3–6]. 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 a structure with the existing processing approaches, including the dispersion of CNTs in the polymer matrix and the infiltration of polymers into the interspace of the continuous CNT network [5].

The dispersion approach is widely used in the industrial productions of composite films and fibers/yarns, including the solution processing, melt processing, electrospinning, and coagulation spinning [5,7]. However the dispersion of long CNTs is hindered by their entanglement and aggregation, and the CNTs are often limited to a low fraction (<10 wt.%) and randomly orientated. Consequently, the reported strengths of the composites processed by this approach are usually under 400 MPa [8,9]. Further in situ polymerization or hot stretching has not been very effective in improving the mechanical properties [10,11]. It is intrinsically impossible for the dispersion approach to produce the CNT composites with desired structure of long CNTs, high volume fraction, and good alignment.

In the infiltration approach, the composites are synthesized by infiltrating polymers into CNT preforms, which are produced by using CNT fibers/yarns, sheets, arrays, or bucky papers [5,12]. It is easy to use long CNTs and to improve their alignment to some extent. However, the uniformity of

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infiltration becomes a problem because the preforms are already tightly packed. As a result, the un-infiltrated parts of the composites might become defects and limit the overall performance. For example, the poly(vinyl alcohol) (PVA)-enhanced CNT fibers (CNT fraction 70–80 wt.%) were just ∼300 MPa stronger than the un-infiltrated ones [13], as the thermoplastic PVA was difficult to infiltrate into the CNTs. Furthermore, it is not easy to control the degree of infiltration and over-infiltration does not benefit the improvement of properties. It has been reported that the over-infiltrated CNT/epoxy composites were only 231.5 MPa [14] in strength, and 402 MPa after shear pressing [15]. In these composites, the CNT fraction was 16.5 and 32 wt.%, respectively.

Due to the limitation and complexity of these methods, new and easy synthesis processes should be developed to produce CNT composites with improved properties. So far, the strongest un-functionalized-CNT composites have been reported to be stronger than 2 GPa [16]. In addition to the high-strength bismaleimide (BMI), it also contained long and aligned CNTs, and importantly the uniform mixing between BMI and CNTs at the CNT fraction of ∼60 wt.%. However, multi steps were used for those structural features, including the preparation of the bucky paper, stretching to align the CNTs, and the infiltration to get the mixed structure. Furthermore, it is a challenge to use stretching to align all CNTs that are initially randomly oriented in the bucky paper, which could become a limiting factor to the composite strength.

Here we demonstrate a one-step approach of “spray winding” to fabricate high-performance CNT composites, by using PVA as a testing matrix. In this method, CNT sheets, drawn out from CNT arrays [17], are continuously collected (wound) onto a rotating mandrel under the spray of a polymer solution. This allowed the homogenous integration between CNTs and polymer molecules, which are very critical in determining the properties of the composites. We found that in our spray-wound CNT/PVA composite films, the CNT fraction is tunable, and could be as high as 65 wt.% to reach the best mechanical properties. The best film produced here is very strong (1.8 GPa), stiff (45 GPa), and tough (100 J/g), much better than the fibers made by the same CNT and PVA [13,18] and many other CNT/polymer composites [5]. The high performance arises from *the long CNTs, highly-aligned tube morphology, and good interfacial bonding between CNT and PVA, which are obtained simultaneously*. The spray winding is easy to be scaled-up for industrial productions and works for both thermoplastic and thermosetting polymers.

2. Experimental

Fig. 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 sprayed area. By choosing an appropriate mandrel diameter, sheet width, and number of revolutions, unidirectional composites with 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.

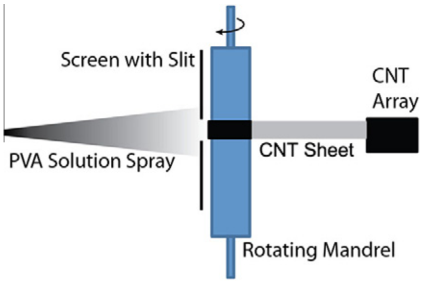

Fig. 1 – Schematic view of spray winding. A CNT sheet is drawn out of a drawable array and continuously wound onto a rotating mandrel on which micrometer-sized droplets of PVA solution are deposited. A screen with a slit is used to control the spray area.

The CNTs used here were grown in the form of arrays by a sustained chemical vapor deposition on SiO_2/Si wafers coated with a thin Fe film as the catalyst [19]. The CNT array was vertically aligned and highly drawable, i.e., continuous CNT sheet could be pulled out. The tubes were about 300 μm long, mainly 6-walled, and 8–10 nm in diameter [18]. The PVA solution was prepared by dissolving PVA (molecular weight 85,000–124,000, 99+% hydrolyzed) in a solvent containing equal volumes of deionized water and ethanol. The solution was sprayed under 10 psi onto the winding sheet with a width of 3–5 mm, drawn at a speed of 18 mm/s, which was the linear velocity on the surface of the mandrel with a diameter of 3 cm and a rotational speed of 11.5 rpm. The solution droplets were micrometer-sized using a commercially available Badger 200NH airbrush. The composite films were prepared by rotating the mandrel for 1 h, with a solution-dependent thickness of 10–20 μm, measured by a micrometer and confirmed by scanning electron microscopy (SEM) image. 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 at a strain rate of 8.3% per min. The conductivity of the composites was measured by a 4-probe Agilent 34410A 6.5 digit multimeter along the CNT direction. The contact areas for the probes were coated with silver sputtering. 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.

3. Results and discussion

Our method of spray winding has an advantage of fabricating composites with a high and tunable CNT fraction. As the mandrel diameter, rotating speed, spray pressure, and the distance between the airbrush and the mandrel were fixed in this study, CNT/PVA films with different CNT fraction were obtained by using PVA solutions with different concentration, namely 0.5, 1, 1.5, 2, 5, and 10 g/L. With increasing concentration, the CNT fraction decreases. Fig. 2a shows the tensile strength as a function of the CNT weight fraction, estimated

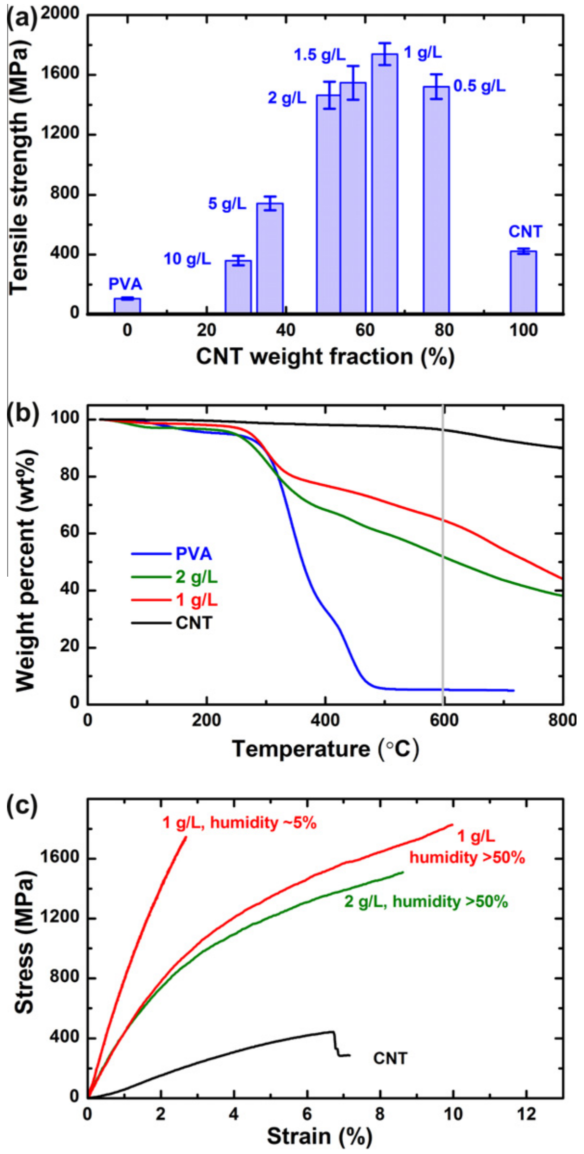

Fig. 2 – (a) Tensile strength of the CNT/PVA composites as a function of the CNT weight fraction. The corresponding concentrations of PVA solutions are labeled. (b) TGA curves for a pure CNT film, two CNT/PVA films, and a pure PVA film. The fraction in a film was estimated by using the TGA results at 600 °C, similar to Liu et al. [20]. (c) Stress–strain curves of a pure CNT film and three CNT/PVA films, under different ambient humidity.

from the TGA curves (Fig. 2b) in a similar way reported by Liu et al. [20]. The highest strength of 1.82 GPa was found for the film containing 65 wt.% of CNTs, by using the 1 g/L PVA solution. The average strength among more than five samples here was 1.74 GPa (Fig. 2a). These films were much stronger than other CNT/PVA composites (100–600 MPa) [8,12,21,22]. The strength was also much higher than that of the composite fibers (1.2 GPa) comprising the same CNTs and PVA [13], and was comparable to that of the strongest CNT/PVA fiber (~2.05 GPa) reported very recently [20]. We believe that a better integration between CNTs and PVA can be obtained by this spray winding than by the infiltration. However, the strength varies significantly with the change of the CNT fraction. Increasing the fraction to 78 wt.%, by using the diluter PVA solution (0.5 g/L), the strength became lower (1.52 GPa). When there was only 28 wt.% of CNTs, the strength decreased significantly to 359 MPa, just 253 MPa higher than that of the pure PVA film. These results suggest that the optimal PVA concentration is 1 g/L, when other synthesis parameters remain constant. However, as one can find in Fig. 2a, when the solution concentration was from 0.5 to 2 g/L, all the composites were stronger than 1.5 GPa, indicating that the spray method is efficient for dilute solutions.

Fig. 2c 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- and 2-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. For example, in the tensile test there was a sudden drop of stress, corresponding to the sliding. When PVA was sprayed into CNTs during winding, it can easily penetrate the thin CNT ribbon during the spray winding, which enables uniform and complete dispersion of the CNTs in the PVA matrix. This makes it easier for the long and flexible polymer molecules to wrap around individual CNTs and bridge neighboring CNTs. Therefore, the interfacial shear stress was improved greatly, resulting in high tensile strength. Note that both the CNT film and the composite film were densified due to the capillary force caused by the evaporation of the solvents.

The tensile behavior is also found to depend on the relative humidity (RH), see the two red curves in Fig. 2c, because PVA is hydrophilic. When the RH is high, there is a large amount of water absorbed to increase the plasticity of the PVA matrix. As a result, the film deforms easier under stretching than the one containing less water. The strongest CNT/PVA film had a strain to failure of 10% when being tested under >50% RH, and only of 2.8% if the RH was 5%. Thus the modulus and toughness were also humidity dependent (it had negligible influence on the strength as the CNT–PVA interfaces were not changed). When measured under >50% RH, the modulus was 40–56 GPa and the toughness ranged from 65 to 112 J/g, for the films stronger than 1.5 GPa. The toughness was much higher than those of the strongest CNT/PVA fiber [20] and CNT/BMI composites [23]. A recent study showed a similar toughness (~121 J/g) for a CNT/PVA composite film via a layer-by-layer assembly [12]. However, such super-tough composites had a larger strain at failure of 20–40% and a smaller strength of 504 MPa. Under the dry environment of 5% RH, the modulus was doubled (96 GPa), and the toughness was still large, up to 38 J/g. These results demonstrate the influence of matrix plasticity on the mechanical properties of CNT composites.

The high performance of our composites arises from long CNT length and high degree of alignment. As the CNTs were pulled out from drawable arrays, their tube length of ~300 μm (aspect ratio of ~30,000) [18] was not changed and was one order of magnitude longer than the tubes that are normally used for dispersion in a polymer matrix [21,24]. It is obviously important for high-performance composites.

The increase in array height results in the increase in tensile strength, similar to the spun CNT fibers [18]. Furthermore, the CNTs were aligned in the form of array or sheet. The aligned structure can be investigated by polarized Raman spectroscopy [25,26], as shown in Fig. 3a. For a pure CNT film, the normalized G'-band Raman intensity decreased to 0.669 when the angle between the film and the polarization axis of the incident laser beam was changed from 0° to 90°. The tubes were not fully aligned due to their own waviness in the array [18] and the weak tube–tube interaction. It appears that spraying the PVA solution further improved the alignment of CNTs in the composites. As shown in Fig. 3a, when there was PVA, the normalized G' peak at 90° became smaller, to 0.566 and 0.493, before and after the thermal pressing to densify the composites, respectively. In Fig. 3b, the Raman spectra of the strongest CNT/PVA films are provided. Both the G' band and the G band peaks decreased significantly for the hot-pressed film at the angle of 90°, indicating that the alignment had indeed been improved. It is not clear what caused the improved CNT alignment in the composites. It is our belief that the capillary force, which draws individual CNTs into closely packed CNT bundles, played an important role in improving CNT alignment.

As mentioned above, the tensile properties strongly depend on the CNT fraction. The optimal concentration of the PVA solution was 1 g/L, corresponding to the CNT fraction of 65 wt.%. Shown in Fig. 4 are the SEM images of the cross-sections and top views of the CNT composite films produced by the 0.5-, 1-, and 2-g/L PVA solutions. Below 1 g/L, there were micrometer-sized voids within the film due to the lack of PVA matrix (Fig. 4a and d). These voids will act as defects to fail the composites prematurely. When more polymers were sprayed, there was excessive matrix around the tubes (Fig. 4c and f), which leads to low CNT volume fraction and consequently low strength. In contrast, the 1-g/L solution produced an optimized structure with relatively high CNT fraction and no voids. This structure produced the highest composite strength shown in Fig. 2a.

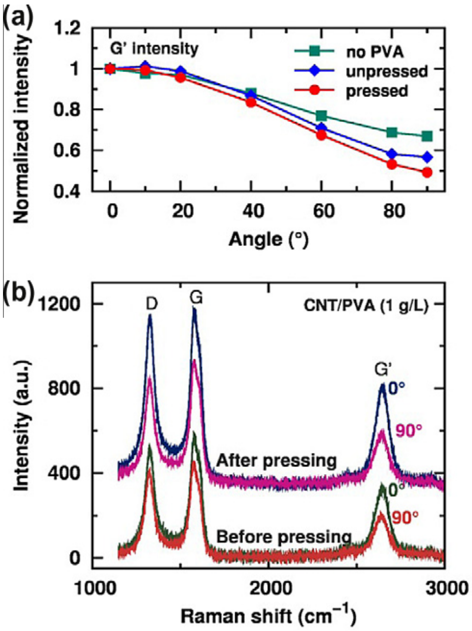

Fig. 3 – (a) Normalized intensity of G'-band peak versus the angle between the sample's longitudinal direction and the polarization axis of the incident laser beam. The normalized intensity at 90° becomes smaller when PVA is introduced into the composites, and further decreases after the hot pressing. (b) Raman spectra at 0° and 90°, before and after the hot pressing. All the composite films were produced by using the 1-g/L PVA solution.

The CNT/PVA composite films are also good electrical conductors (see Fig. 5). For the films made by the 0.5- and 1-g/L PVA solutions, their conductivity of 780 and 690 S/cm were larger than the pure CNT film (570 S/cm). It is counter intuitive that the incorporation of PVA matrix, which is insulating, into the CNT ribbon led to increase in the electrical conductivity, as compared to the pure CNT film. In the aligned CNT composites processed here, the electrical conductivity is largely controlled by the contact area between CNTs. When a PVA/(water + ethanol) solution is sprayed onto CNTs, the capillary force produced by the solution draws neighboring tubes together, which increases the inter-tube contact area. On the other hand, the wrapping of PVA molecules around individual CNTs or multiple CNTs presents an insulating barrier that decreases the inter-tube contact area. However, when the PVA solution is dilute, the PVA molecular wrapping is not complete. For dilute PVA solutions, the PVA molecules help maintain the close contact after the evaporation of the solvents, which led to enhanced conductivity. A similar increase of electrical conductivity was also reported in CNT/PVA fibers by Liu et al. [20]. However, when a high concentration PVA solution was used, the PVA wrapping around CNTs became dominant, which led to decreased contact area and consequently lower conductivity. The combination of these two contradicting factors led to an optimum concentration of PVA solution for the highest conductivity, as shown in Fig. 5.

Interestingly, the highest conductivity was obtained in samples processed with 0.5 g/L PVA solution (Fig. 5), while the highest strength was obtained in samples processed with 1 g/L PVA solution. This is because the conductivity is determined by the inter-tube contact area while the strength is affected mostly by the interfacial strength. This led to different optimum volume fraction for the PVA matrix.

As we have discussed, the uniform integration between the PVA and CNTs (Fig. 4b) leads to the improved mechanical and electrical properties of their composites. In fact, similar integration has already been realized by other techniques, especially for high-performance CNT/PVA fibers which were 1.8–2.06 GPa in strength [7,20,27]. The coagulation-based wet spinning allowed the intimate bonding of PVA to the CNTs [7,27]. The traditional infiltration can be significantly improved by using dimethyl sulphoxide (DMSO) that can wet hydrophobic CNTs [20]. The evaporation of water or DMSO can also shrink the CNT ribbon and fiber. However, the wet-spun multi-walled CNT composite fibers do not show comparable mechanical properties [28]. Although the single-walled CNT/PVA fibers have high strength, they have to be assembled into composite pre-pegs, which usually have a strength that is less than 50% of the fiber strength.

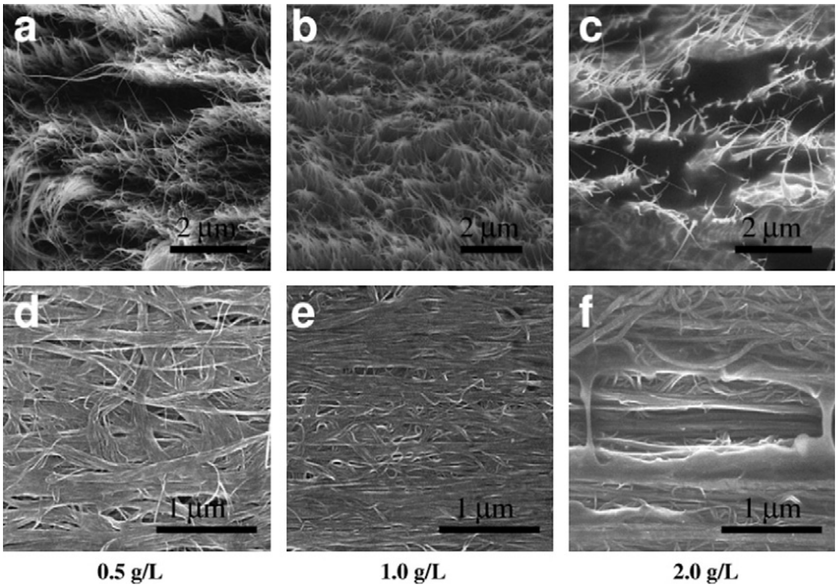

Fig. 4 – SEM images of the cross-sections (a–c) and the top views (d and f) of CNT/PVA films produced by using the 0.5-, 1-, and 2-g/L PVA solutions. For a small PVA fraction, large empty spaces can be observed either between different CNT layers (a) or between CNTs in the same layer (d). In contrast, over-spraying of PVA led to excessive matrix around the CNTs (c and f).

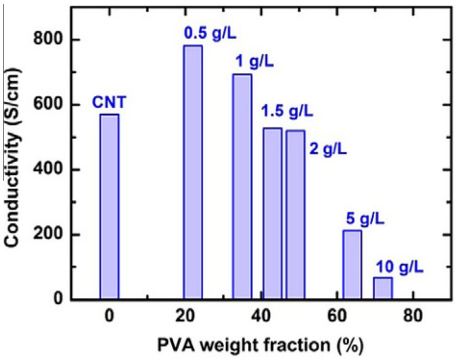

Fig. 5 – Electrical conductivities of CNT/PVA composites as a function of the PVA weight fraction.

4. Summary

We have synthesized high-performance CNT/PVA films by a new and simple method of spray winding. In this method, several advantages can be easily achieved simultaneously in one step, including the high CNT fraction, use of long CNTs, the improved CNT alignment, and a uniform distribution of PVA molecules among the CNT network. By using the CNTs with a large aspect ratio of ~30,000, the strongest composite films were measured to have a strength of ~1.8 GPa, a modulus of 40–96 GPa, and a toughness of 38–100 J/g. The production speed of the CNT composites depends only on the rotation speed of the mandrel, and is much higher than the existing techniques such as the resin transfer molding [14] and the layer-by-layer assembly [12,29,30], making it conducive to large-scale production at low cost. Besides the thermoplastic PVA used here, this method can be also used to make thermosetting polymer-based composites with ultrahigh mechanical properties.

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