Functionalized Few-Walled Carbon Nanotubes for Mechanical Reinforcement of Polymeric Composites

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ABSTRACT Compared to single-walled carbon nanotubes (SWNTs) and more defective multiwalled carbon nanotubes (MWNTs), the thin few-walled carbon nanotubes (FWNTs) are believed to have extraordinary mechanical properties. However, the enhancement of mechanical properties in FWNTs-polymer composites has remained elusive. In this study, free-standing carbon nanotubes (CNTs)/polymer composite films were fabricated with three types (SWNTs, FWNTs, MWNTs) of functionalized CNTs. The mechanical properties of composite films have been investigated. It is observed that the Young's modulus of composite films with only 0.2 wt % functionalized FWNTs shows a remarkable reinforcement value of $dY/dV_f = 1658$ GPa, which is ~400 GPa higher than the highest value ($dY/dV_f = 1244$ GPa) that was previously reported. In addition, the Young's modulus increased steadily with the increased concentration of FWNTs. The results indicated that FWNTs are practically the optimum reinforcing filler for the next generation of carbon nanotube-based composite materials.

KEYWORDS: FWNTs · Young's modulus · PVA

To date, carbon nanotubes (CNTs) are the strongest single molecules measured and are known to have an extremely high Young's modulus of up to 1 TPa and tensile strength approaching 180 GPa.[1−3] They are lighter than existing fibers, and they are believed to increase the performance of structural composites, including those used in airplanes, space vehicles, and various leisure goods, *etc*. However, CNTs have provided only limited enhancements to the mechanical properties of polymer matrix and the composite processing is still limited to benchtop scale. Indeed, many well-known issues[4−6] still need to be resolved in order to take the maximum benefits from carbon nanotubes to polymer host. Among them, the main problems[7] are (1) the dispersion of nanotubes in matrix, (2) the load transfers between the nanotubes and polymer matrix, (3) the structure integrity (defect density) of the nanotubes, and (4) the purity and cost of the nanotubes. It is generally believed that high quality SWNTs are the best reinforcing filler because of their small size and high Young's modules. However, it is extremely hard to separate SWNT[8] from bundles into individual nanotubes in real applications. Additionally, the difficulty in purification and the high cost limit their large scale applications. For CVD-grown multiwalled carbon nanotubes (MWNTs), the cost is much lower, and it was recently discovered that MWNTs under certain conditions can provide better mechanical reinforcement of polymer composites.[9] However, CVD-grown MWNTs still have limited use in the application of composites because of their low structural perfection and uniformity.[10,11] Fortunately, few-walled carbon nanotubes (FWNTs)[12−14] provide a direction toward solving all these problems. FWNTs, defined as nanotubes with sidewalls of 2 to 5 layers, diameters ranging from 3 to 8 nm, and lengths around tens of micrometers, are unique small diameter MWNTs with near perfect graphitization structure (Figure 1b).[12] Here, we have investigated the application of such materials as reinforcing fillers in polyvinyl alcohol (PVA)-based composites. The results have demonstrated that such material is the best compromise as structural reinforcing fillers that combined the easiness in synthesis and purification, high structural perfection, and good tolerance to surface functionalization.

Recently, Coleman *et al*. reviewed the published data using dY/dV_f as a benchmark for composite reinforcement.[15,16] In this paper, we also used dY/dV_f value to compare the reinforcing property of different CNTs and the data collected from a review of current literatures.[9−11,17−28] To eliminate the effect of the quality of the nanotube samples made from different methods, different types of nanotubes (SWNTs, FWNTs, MWNTs) grown by similar CVD methods were produced (Figure 1), functionalized, and incorporated in a PVA

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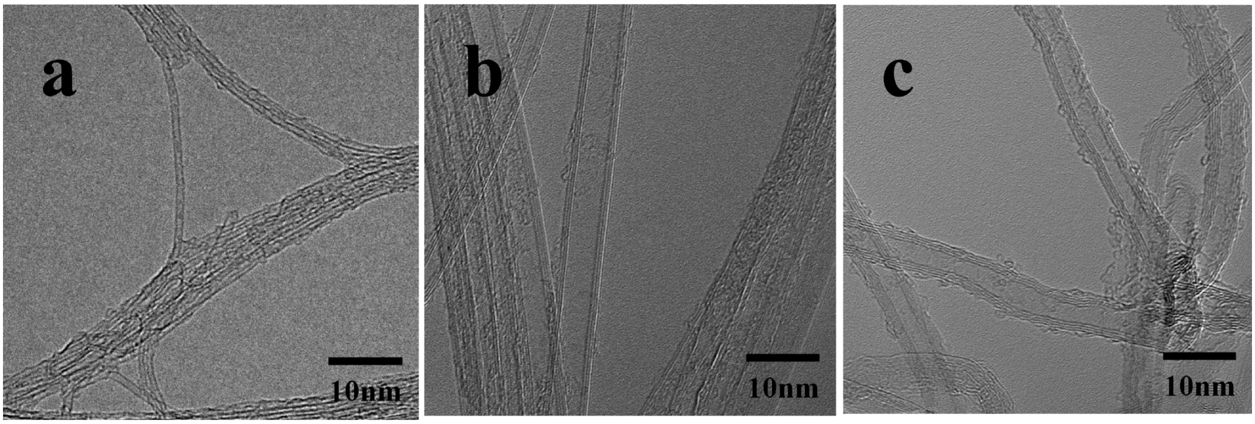

Figure 1. HRTEM images of (a) SWNTs. (b) FWNTs. (c) MWNTs.

matrix. All of the samples were prepared using the same thermal CVD in a horizontal tube furnace. Details of nanotube synthesis can be found in Supporting Information. Free standing CNT/PVA films with similar thickness were fabricated. The mechanical properties of the composite films were investigated with a DMA 2980 tensile tester from TA Instruments. It shows that FWNTs are easier to produce, easier to purify than SWNTs, and have better structural integrity than MWNTs. These properties, plus the significantly improved reinforcing property measured in this study, allow us to predict that FWNTs are highly suitable, if not the best reinforcing filler, for the next generation of composite materials. The consistently better performances from FWNTs in our study also confirm the previous analysis.[11]

RESULTS AND DISCUSSION

It is known that poor dispersion of nanotubes in solvents and polymer matrices is a key problem in making high performance CNT composite materials. Covalent functionalization of the nanotubes is a promising strategy to not only improve nanotube dispersion but also provide a means for creating microscopic interlinks between nanotubes and polymer. However, too much defect under extreme chemical treatment can compromise the mechanical properties of the nanotubes. Therefore, in this study, a moderate functionalization method was employed (Supporting Information II) to obtain good dispersion of CNTs in polymer matrix without creating too high defect density on nanotubes. The method was chosen to be the mildest treatment that will prepare a stable water suspension to prepare composite films without noticeable aggregations of nanotubes. Raman spectroscopy (Figure 2) clearly indicates the covalent functionalization of the CNTs. The defect concentration of CNTs before and after functionalization can be estimated by the intensity of the D-band (I_D) at ~1300 cm^{-1} relative to the intensity of the G-band (I_G) at ~1590 cm^{-1}. As can be seen from Figure 2, after functionalization, the relative intensity of D bands of all type of CNTs are higher as the functional groups are attached to the sidewalls. We also noticed that the suspension of functionalized CNT and PVA mixture is very uniform without any visible aggregations, while large agglomerates still exit with unfunctionalized CNTs (Supporting Information III).

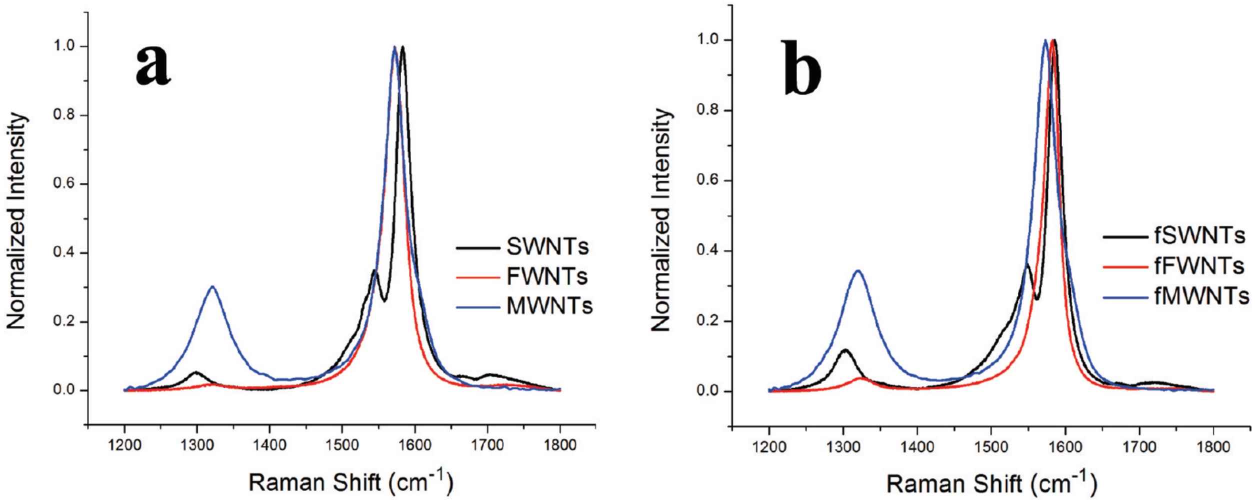

Figure 2. Normalized Raman spectra of different type of CNTs (a) before and (b) after functionalization.

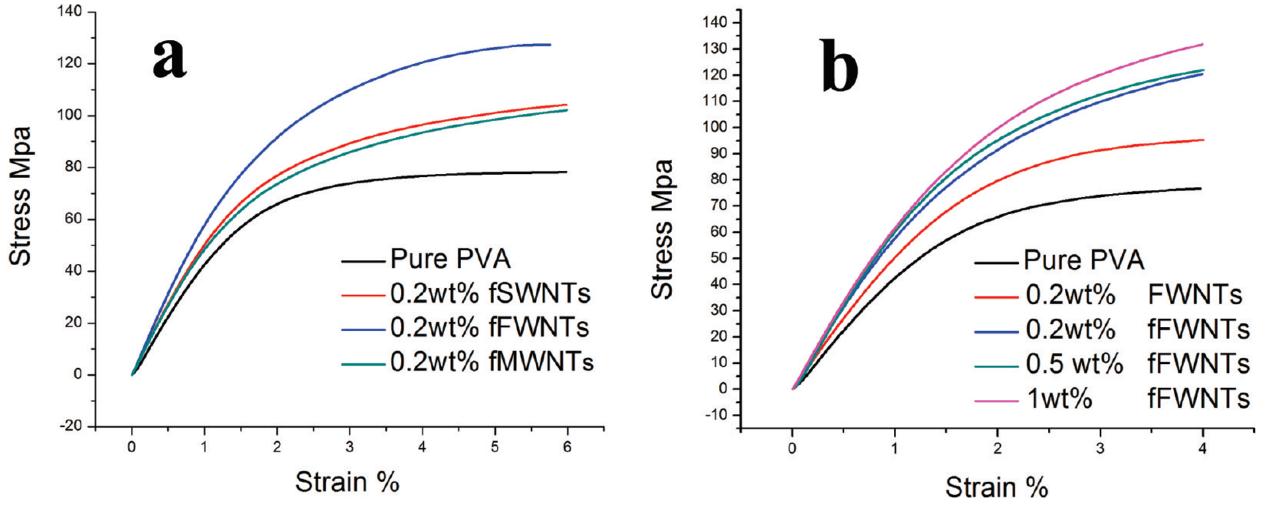

Figure 3. Stress−strain curves of composite films containing (a) 0.2 wt % of different types of CNTs; (b) different concentration of fFWNT.

The mechanical properties of different types of CNTs (SWNTs, FWNTs, MWNTs) in PVA composite have been investigated. The typical stress−strain curves for the PVA-based composite are given in Figure 3 and their mechanical properties are summarized in Table 1. Results indicate that all of composite films with as little as 0.2 wt % nanotube show higher Young's modulus and higher tensile strength than those of pure PVA materials. In particular, the improvement is more pronounced with functionalized FWNT (fFWNT) films. Composite films with 0.2 wt % fFWNT exhibit the highest Young's modulus of 6.33 GPa, which is 1.99 GPa higher than that of pure PVA film, coupled with a 42 MPa increase in tensile strength (Figure 3a, Table 1). This represents a reinforcement of dY/dV_f = 1658 GPa which is $\sim$400 GPa higher than the highest value of dY/dV_f = 1244 GPa previously reported[11] in PVA-CNTs composites. In the case of SWNTs and MWNTs, the reinforcement (dY/dV_f = 741 and 767 GPa, respectively) is much lower than that of FWNTs.

It should be noted that nanotube diameters, lengths along with the amount of impurities and structural defects may vary among samples from different batches and different laboratories. Thus, experimental results using the same type of nanotubes from different researchers may show a discrepancy. In this study, our aim is to investigate the optimum type of nanotubes as reinforcing filler in practical applications. The fact that a higher value of dY/dV_f (741 GPa) was observed with the SWNTs used here compared with the highest reported value (305 GPa) in PVA/SWNTs composite[20] verified that the SWNTs used here are of high quality (Supporting Information IV) and our experimental comparison is appropriate. The same is true for MWNTs used in this study.

We found that FWNTs shows a remarkable reinforcement value of dY/dV_f = 1658 GPa (Figure 3, Table 1), much better than the results from SWNTs and MWNTs. It is known that dispersion of CNTs in polymer is the most fundamental issue in composite systems. Ideally, individual nanotubes must be uniformly dispersed in polymer matrix in order to achieve uniform stress distribution and efficient load transfer. Theoretically, to maximize reinforcement, we will need nanotubes with small diameters to obtain greater surface area and maximized interaction with the matrix. Therefore, if we could routinely produce individually dispersed high-quality SWNT in polymer matrix, they should show best performance in the composite material compared with other types of CNTs with same defect density, length, *etc.* However, in real applications, a true solvent for any unfunctionalized individual carbon nanotubes is yet to be achieved. The fabrication of uniform polymer composite with SWNTs is more challenging because of severe bundling of the nanotubes. Although any type of carbon nanotubes tend to form bundles, the strong in-

TABLE 1. Mechanical Properties of 0.2 wt % CNTs/PVA Composite Films

	pure PVA	0.2 wt % of fSWNTs	0.2 wt % of fFWNTs	0.2 wt % of fMWNTs
tube diameter (nm)		0.7−1.4	3−8	>8
tube length (μm)		up to 1	up to 20	up to 2
tube aspect ratio		up to 1429	up to 6667	up to 250
Young's modulus (GPa)	4.34 ± 0.017	5.60 ± 0.014	6.33 ± 0.059	5.26 ± 0.062
V_f (%)		0.17	0.12	0.12
dY/dV_f (GPa)		741.18	1658.33	766.67
tensile strength (MPa)	80.49 ± 2.29	114.21 ± 2.12	122.45 ± 2.87	108.47 ± 3.53

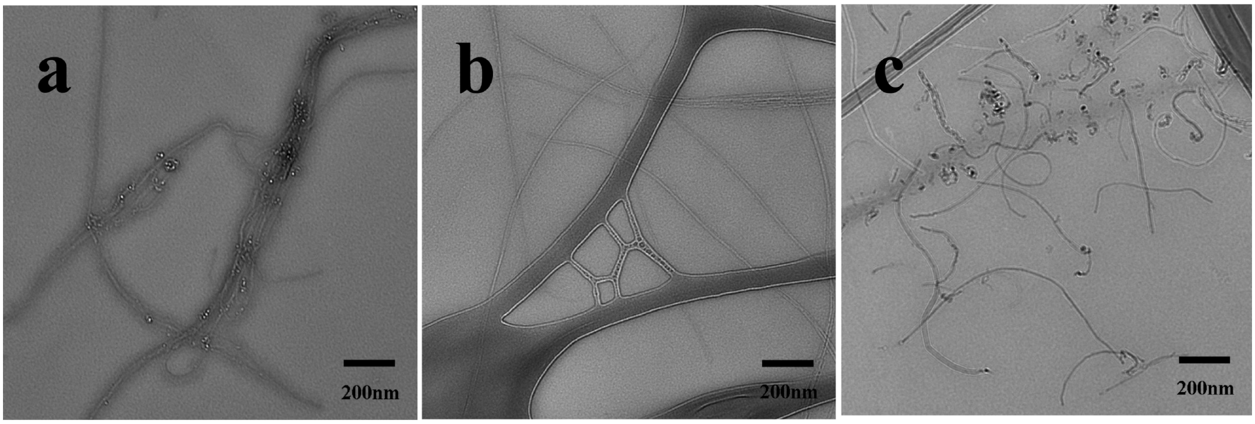

Figure 4. TEM-micrographs of PVA filled with 0.2 wt % functionalized (a) SWNTs, (b) FWNTs, (c) MWNTs.

trinsic van der Waals attractions in SWNTs (~0.5ev/nm for SWNT−SWNT contact)[29] produce larger bundles, making them more difficult to be dispersed in any solvents or polymer matrices. Although chemical modification can improve the dispersion of SWNTs in matrix materials, covalent functionalization can severely disrupt their single layer structure. Additionally, the modulus can also be considerably reduced by even small nanotube curvature[30,31] and SWNTs tend to be "wavier" than others.

In the case of MWNTs, they have diameters of more than 8 nm and can be well dispersed in polymer matrix (Figure 4c) after functionalization. However, the interfacial area is compromised with the increase of diameter compared with that of SWNTs. Moreover, the biggest I_D/I_G ratio in RAMAN spectrum (Figure 2) of pristine MWNTs suggested their high defect density and low structural uniformity, which may also contribute to limit their mechanical improvement in composites.

FWNTs are unique small diameter (3−8 nm) MWNTs in terms of their morphology. The length of FWNTs is as long as 20 μm and their aspect ratio can be reached to as high as ~6600 (Table 1). Their bigger diameter and thicker wall made FWNTs much easier to be individually dispersed in solvent or polymer than SWNTs. The quality of the CNTs dispersion in composite films has been evaluated by TEM micrograph (Figure 4). Figure 4b shows the uniform FWNTs distribution in PVA matrix. It is believed that the good dispersion of functionalized FWNTs in PVA provides huge surface area and more uniform stress distribution, minimizing the presence of stress concentration centers. Meanwhile, SWNTs are extremely difficult to be debundled even after functionalization compared to FWNTs and MWNTs (Figure 4a). Therefore, the effective modulus values for SWNT bundles are far below those theoretically expected for their individuals, and the large agglomerates may also originate cracks in composites rather than reinforce their mechanical strength. Additionally, SWNTs are more chemically unstable. As can be seen from Figure 5a, some of SWNTs are shortened and their conjugated single-layer structures are destroyed under the same reaction condition, which may compromise their mechanical properties to certain degree. In the case of FWNTs, the very low I_D/I_G ratio indicates that FWNTs have the perfect structure compare with all other CVD-grown carbon nanotubes. They should be the most robust in load transfer from matrix to nanotubes. Moreover, as can be seen from Figure 5, FWNTs are chemically stable than SWNTs and MWNTs, they can retain straight morphology and structural integrity even after covalently functionalizing. We believe that all of these factors—the easiness in synthesis and purification, the tolerance against chemical functionaliza-

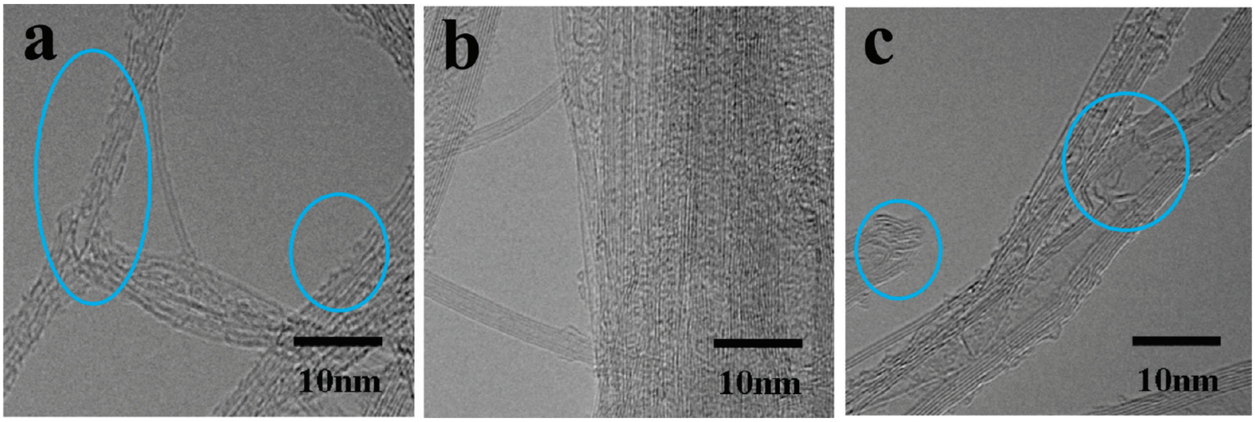

Figure 5. HRTEM images of functionalized (a) SWNTs, (b) FWNTs, (c) MWNTs.

TABLE 2. Mechanical Properties of Different Concentration fFWNTs/PVA Composite Films

	pure PVA	0.2 wt % of FWNTs	0.2 wt % of fFWNTs	0.5 wt % of fFWNTs	1 wt % of fFWNTs
Young's modulus (GPa)	4.34 ± 0.017	5.31 ± 0.025	6.33 ± 0.059	6.80 ± 0.037	7.10 ± 0.028
V_f (%)		0.12	0.12	0.30	0.61
dY/dV_f (GPa)		808.33	1658.33	820.00	452.46
tensile strength (MPa)	80.49 ± 2.29	104.55 ± 3.35	122.45 ± 2.87	127.27 ± 2.63	132.57 ± 3.82

tion, the formation of stable and uniform dispersion in polymer, and good structural perfection of the materials, have contributed to the observed higher reinforcing capability of the FWNTs, making them an optimum, if not the best, choice as structural filler in composite materials.

The mechanical properties of composites as they correlate to the concentration of fFWNTs have also been investigated (Figure 3b, Table 2). In general, the Young's modulus and tensile strength increased steadily with the concentration of functionalized FWNTs (ranging from 0.2 wt % to 1 wt %), indicating that the PVA films become more resistant to deformation. Additionally, as can be seen from Figure 3b, 0.2 wt % functionalized FWNTs have reinforcement of $dY/dV_f = 1658$ GPa which is notably higher than that of pure FWNTs/PVA composite. This suggests that the unfunctionalized FWNTs have large nanotube agglomerates, while the modified FWNTs have improved dispersion (Supporting Information III, Figure S1) and higher interface area and therefore possess higher mechanical enhancement of the composite materials. Results also demonstrate that the rate of increase of Young's modulus slows with the increase of fFWNT concentration, indicating more functional groups are needed to further improve the dispersion and avoid the aggregation at higher fFWNTs loading. This could be resolved by carefully modifying the condition of the chemical reaction.

CONCLUSION

In summary, this research explored the question of optimum reinforcing filler for polymeric composites materials, based on different CNTs/PVA composite and the multitude of factors that affect their mechanical properties. We conclude that the mechanical properties of CNTs/PVA composite vary with CNTs materials. Variations in defect density, diameter, length, aspect ratio, surface-functionalization, dispersion state, nanotube loading, and the interfacial adhesion between the nanotubes and the polymer matrix are all factors that could change the mechanical properties of the composite. From our research, it is shown that the optimum candidates, if not the best, for polymer reinforcement are functionalized FWNTs. Compared with other type of CNTs, they can be produced and purified more easily;[12] they can keep the structure uniformity after functionalization; their smaller diameters give them better dispersion in the matrix materials and therefore larger interfacial area, stronger interfacial adhesion, and more efficient load transfer between the nanotubes and the polymer host. It is foreseeable that our investigation of the extraordinary mechanical properties of FWNTs will encourage more exploration of their diverse applications, especially in composite materials.

METHODS

PVA was used as a prototype matrix to investigate the effect of different types of nanotubes on the enhancement of mechanical properties. It (from Aldrich, molecular weight 86000 g/mol, 99+% hydrolyzed) was dissolved in distilled water at 90 °C and subsequently cooled to room temperature. The nanotubes used were purified SWNTs, FWNTs, MWNTs (Figure 1), prepared by our thermal CVD method (Supporting Information I IV, Figure S2, S3). Water-soluble CNTs were obtained *via* mild sonication-mediated oxidation in 3 M HNO_3 (Supporting Information II). The composites were prepared with PVA and a functionalized carbon nanotube solution. To fabricate free-standing composite films, an appropriate amount of functionalized CNTs was mixed with a PVA aqueous solution at room temperature *via* tip sonicator. Highly uniform free-standing films were fabricated by casting this mixture solution in molds and the evaporation of excess water. The thickness of the resulting film was about 40 μm. The films were peeled off the substrates and cut into strips to facilitate mechanical properties testing. Prior to testing, all specimens underwent an additional drying procedure for 1 h at 60 °C, to ensure the evaporation of any remaining water. The volume fraction of CNT in each film was calculated from the mass fraction using the densities: (1) 1300 kg/m^3 for PVA, (2) 1500 kg/m^3 for SWNTs, and (3) 2150 kg/m^3 for MWNTs and FWNTs. Tensile testing was carried out using a DMA 2980 tensile tester. A speed of 1 N/min was used to obtain the tensile modulus, *Y*. In all cases, at least four strips were measured and the mean and standard deviation of *Y* were calculated.

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Supporting Information Available: Synthesis and purification of SWNTs, FWNTs, and MWNTs. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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