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Highly Conducting Carbon Nanotube/Polyethyleneimine Composite Fibers**

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Carbon nanotubes have long been of interest as additives for increasing the mechanical and electronic properties of polymers, and considerable progress has been made.[1–6] However, melt-phase and solution viscosities ordinarily become too high for conventional processing when the nanotube component exceeds about 10 wt.-%, which limits the nanotube contribution to composite properties. In a groundbreaking development, Vigolo et al. have shown that composite fibers comprising largely nanotubes can be obtained by a process called polyvinyl alcohol (PVA) coagulation spinning.[7–9] In this process, a dilute surfactant-assisted single-walled carbon nanotube (SWNT) dispersion is coagulated into a gel state by spinning it into an aqueous PVA solution; this is followed by conversion into a solid fiber by a slow draw process, during which the water in the gel evaporates.[7–9] We recently reported improvements in this fiber-spinning technique that dramatically increased fiber strength and fiber-spinning rate.[10–12] These improved fibers (comprised of about 60 % SWNTs in a PVA matrix) have a capacity to absorb energy (a specific toughness of about 600 $\mathrm{J\,g^{-1}}$) that is much higher than any other natural or synthetic organic fiber. Additionally, these SWNT fibers have been successfully utilized in the fabrication of electrochemical devices, such as electromechanical actuators[1,12] and supercapacitors.[10,11] However, unless the polymer is removed by pyrolysis (which degrades the mechanical properties of the fiber), performance of these electrochemical devices is limited by the low electrical conductivity of the nanotube/polymer composite fibers and degradation of mechanical stability when the PVA in these fibers is converted into an ionic conductor.[11] We show here that fibers with useful mechanical properties can be spun if we replace the PVA coagulant with a polyethyleneimine (PEI) coagulant. Although the PEI used is ordinarily a liquid at room temperature, it interacts with the nanotubes to serve as an intertube binding agent. The resulting strain-to-failure and toughness of the PEI-containing fibers are far greater than those of the thermally annealed, binder-free SWNT fibers (which have the advantage of a somewhat higher tensile strength and electrical conductivity) that were spun using the pioneering superacid method developed by the Rice group.[13,14] While the fiber strength and toughness achieved here are far less than those of fibers obtained from the continuous spinning process of Dalton et al. for producing SWNT/PVA composite fibers,[10,11] the prospects of improving the mechanical properties of the SWNT/PEI fibers appear good. Moreover, the electrical conductivity of the SWNT/PEI composite fibers is over a hundred times that of the supertough SWNT/PVA composite fibers.

PEI and, in general, amines, are known to effectively interact with carbon nanotubes via physisorption on the nanotubes' sidewalls.[15–21] Thus, a method for separating metallic and semiconducting SWNTs has been developed that uses the higher affinity of an alkylamine for semiconducting SWNTs than for metallic nanotubes.[20] Semiconducting SWNTs used as drain–source channels in field effect transistors (FETs) can be coated with PEI to shift the device characteristics from p- to n-type, which is a result of electron donation from the amine groups to the SWNT sidewalls.[16,19] Additionally, respectable mechanical properties have been reported for PEI-containing SWNT/polyelectrolyte films with up to 50 wt.-% SWNTs.[21]

This high affinity for SWNTs led us to consider using PEI as a coagulant in fiber-spinning processes. We found that injection of aqueous SWNT dispersions into a rotating bath containing a PEI/methanol solution causes the SWNTs to collapse to form gel fibers. Like the SWNT/PVA gel fibers,[22] these new gel fibers commonly exhibit a flat, ribbon-like structure, as a result of skin formation on the nanotube disper-

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[**] Partially supported by the Defense Advanced Research Projects Agency Grant MDA972-02-C-0005, the Texas Higher Education Coordinating Board Grant 009741-0130-2003, and the Robert A. Welch Foundation. E. M. acknowledges funding from MEC (Ramón y Cajal Program). B. G. K. acknowledges support from University IT Research Center Project.

DOI: 10.1002/adma.200401648

sion during coagulation, and subsequent structure collapse as the methanol diffuses outwards. Strong, uniform, gel fibers several meters in length were easily obtained when dispersions of SWNTs that were produced by the high-pressure CO decomposition route ("HiPco" process[23]) were used. Extremely thin gel fibers were spun when more dilute SWNT dispersions were injected, in particular Triton X-100 dispersions of SWNTs produced by the pulsed-laser vaporization (PLV) method.[24] Finally, the gel fibers produced were extensively washed in methanol to remove excess PEI, and dried by pulling them from the solvent bath.

Scanning electron microscopy (SEM) images indicate that the ribbon-like gel fibers dried to form much thinner ribbons (1–5 μm in thickness) that rolled up and otherwise, partially collapsed to form tubular (Fig. 1a) and less regularly collapsed fiber structures, which were about 15–50 μm in width (Fig. 1b). A closer view of the cross sections (Fig. 1c) reveals that the SWNT bundles were coated less extensively by polymer than the PVA-spun fibers,[10–12] and that the coagulation process occurred via the formation of an extremely thin PEI skin (Fig. 1d).[22] Thermogravimetric analysis (TGA) indicated a PEI content of no more than about 25 wt.-% in the fibers. Additionally, the presence of "beads" (probably excess PEI), typically 20 to 60 nm in diameter (Fig. 1c), is a feature that was not observed for SWNT/PVA composite fibers.

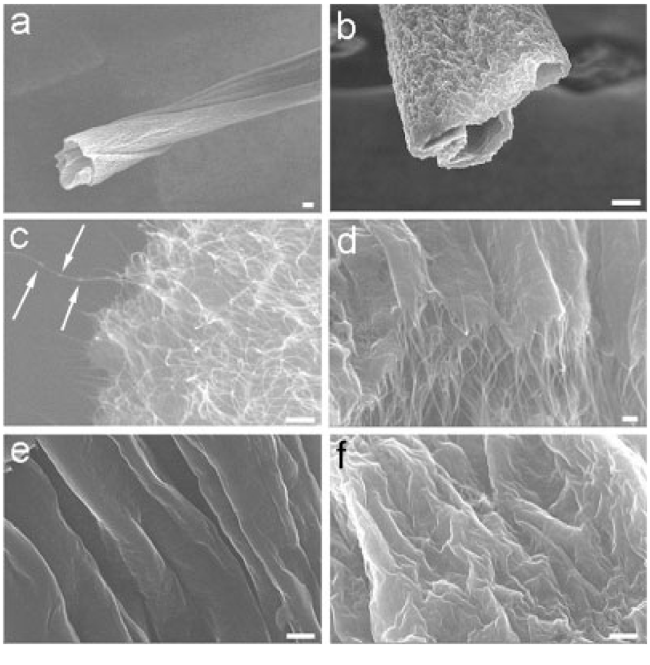

Figure 1. SEM images of SWNT/PEI composite fibers. a,b) SEM images of fibers spun using HiPco SWNTs and cetyltrimethylammonium bromide (CTAB) as surfactant showing that coagulation occurred to form thin ribbons that, when dried, folded to form the pictured "hollow fibers" (scale bars: 10 μm). c) SEM image of the cross section of an SWNT/PEI fiber spun using HiPco SWNTs and lithium dodecyl sulfate (LDS), showing that the degree of polymer incorporation was less extensive than for PVA-spun fibers [10–12]. The arrows indicate the location of beads (probably PEI) along the SWNT bundles (scale bar: 200 nm). d) Image showing part of the sidewall and the cross-section of a SWNT/PEI fiber spun using PLV SWNTs and Triton X-100 as surfactant, showing the thin PEI skin that coated these SWNT/PEI composite fibers (scale bar: 200 nm). e,f) Different morphologies of the surface of SWNT/PEI fibers spun using HiPco SWNTs and LDS surfactant (e) and PLV SWNT and Triton X-100 surfactant (f) (scale bars: 1 μm).

SEM images (Figs. 1e,f) indicate that the outer fiber surface is corrugated, with the axis of corrugation lying approximately parallel to the fiber axis. Similar corrugations parallel to the fiber axis (called "elementary filaments") have also been observed for spun PVA fibers[22] and binder-free SWNT fibers.[14] These corrugations, about 0.5–1 μm in apparent diameter, are typically observed along the outer surface of fibers spun using HiPco SWNT dispersions and anionic surfactants (Fig. 1e). This type of structural organization on the fiber surface is, however, not observed in fibers spun using other surfactants (Fig. 1f). Electron dispersive spectroscopy (EDS) data indicates the absence of sulfur in the fibers spun using PEI/methanol coagulation solutions and sulfur-containing anionic surfactants in the spinning solutions, suggesting that the nanotube-associated surfactant was removed during the coagulation process.

The Raman spectra of the nanotubes in the PEI/SWNT composite (Figs. 2a,b) are similar to those of SWNT/polypeptide dispersions,[25] suggesting that PEI possibly behaves similarly to polypeptides, and at least partially intercalates into SWNT bundles. Additionally, the transitions observed in differential scanning calorimetry (DSC) studies (Fig. 2c) of pure PEI (a liquid polymer at room temperature) and SWNT/PEI composite fibers—in particular, the transitions between 22 °C and 47 °C for the PEI spun fibers–also indicate the molecular-level nature of the nanotube/polymer interaction. These results might be related to introduction of order in the PEI due to efficient interfacial interaction between the polymer and the nanotubes,[26] which facilitates the fabrication of stable gel fibers and solid fibers using a liquid polymer for coagulation.

Mechanical tests provided information about the stress transfer resulting from this strong interfacial bonding (Fig. 3): density-normalized tensile strengths and failure strains, typically ranging from 70 to 100 MPa cm^3 g^{-1} and from 7 to 13 %, respectively, result in energy-to-break values of about 5–6 J g^{-1} for HiPco SWNT/PEI fibers. This toughness is about three times higher than that of similarly spun, undrawn, PVA composite fibers, which have a reported maximum tensile strength and failure strain of 115 MPa cm^3 g^{-1} and 3 %, respectively.[7] The measured tensile strengths of these SWNT/PEI fibers are close to those of superacid-spun fibers (100–130 MPa cm^3 g^{-1}),[13,14] but far below those of predrawn, supertough SWNT/PVA composite fibers (1.2 GPa cm^3 g^{-1}).[10–12] Lower mechanical properties (specific tensile strength ~50 MPa cm^3 g^{-1}, toughness ~2 J g^{-1}) were measured for PLV SWNT/PEI fibers. A maximum density-normalized Young's modulus of ~6 GPa cm^3 g^{-1} was measured at the start of drawing for HiPco SWNT/PEI composite fibers. This modulus is close to that measured of similarly spun, undrawn, PVA composite fibers (7–11 GPa cm^3 g^{-1}),[7] but significantly lower than that of superacid-spun fibers (110–140 GPa g^{-1} cm^3)[13,14] and of continuously spun, predrawn, PVA composite fibers (55 GPa g^{-1} cm^3).[10–12] Specific

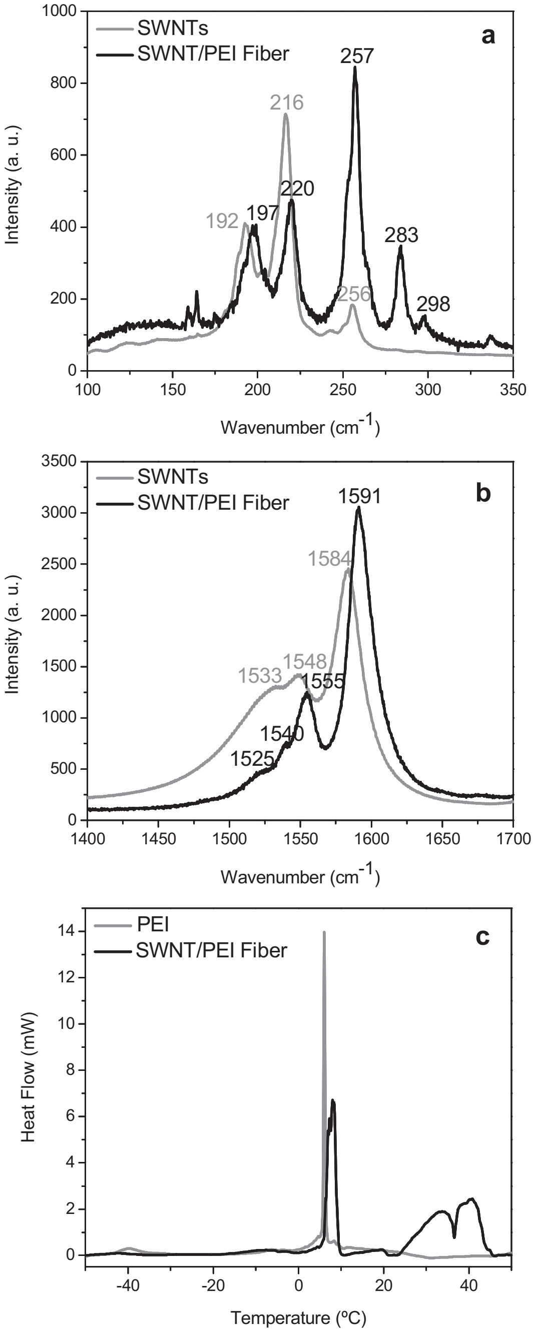

Figure 2. Raman a) radial breathing modes and b) tangential modes of SWNTs in a SWNT/PEI composite fiber, compared with those for the starting HiPco nanotubes. c) DSC plots of pure PEI, and PEI in a HiPco SWNT/PEI composite fiber.

strengths and moduli are reported (using measured force/strain curves and fiber weight per length), since these results are much more reliable than absolute tensile strengths for fibers that typically have hollow and irregular cross sections.

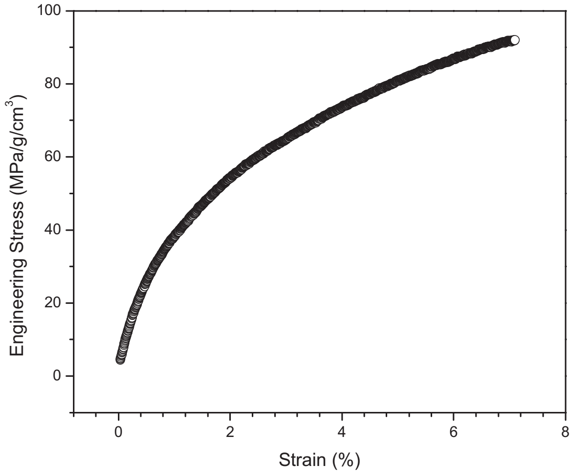

Figure 3. Engineering stress versus strain for a SWNT/PEI composite fiber spun using HiPco SWNTs and CTAB surfactant.

The described structural differences between SWNT/PEI and SWNT/PVA composite fibers, and the nature of the cited polymers, also account for their different electronic conductivity properties: conductivity values typically ranging between 100 and 200 S cm^{-1}, and between 10 and 30 S cm^{-1} were measured in PEI-spun fibers containing PLV SWNTs and HiPco SWNTs, respectively. These values are significantly higher than those that we obtained for PVA composite fibers (0.01–2.5 S cm^{-1}).

This work has shown that SWNT/PEI composite fibers can be successfully spun using a PEI solution as a coagulant, and different SWNT materials and surfactants in the spinning solution. The strong interfacial bonding between PEI and the nanotubes provides interfiber stress transfer. These fibers have moderate tensile strengths and toughness, and over a hundred times the electronic conductivity of previously reported SWNT/polymer composite fibers. The fiber strength and modulus can likely be significantly increased by crosslinking the PEI.[21,27,28] The presence of reactive amine groups on the polymer-coated nanotubes, as well as the possibility of chemically modifying these groups, might be usefully employed for incorporating these fibers in different matrices for fabrication of composites, as well as for sensor applications. Additionally, the proton conduction of PEI in the presence of suitable acids,[29] and its ability to form ionically conductive complexes with alkali metal salts,[30,31] might provide electrochemical-device capabilities for these SWNT/PEI composite fibers.

Experimental

As-produced HiPco SWNTs (Carbon Nanotechnologies, Inc., CNI) [23] and PLV SWNTs (Tubes@Rice) [24] were used in this study. 0.4 wt.-% HiPco SWNT dispersions in 1.2 wt.-% aqueous solutions of anionic (lithium dodecyl sulfate (LDS) and sodium dodecylbenzene sulfonate) and cationic (cetyltrimethylammonium bromide (CTAB)) surfactants were prepared by probe sonication. The PLV SWNT materials were provided in the form of a highly purified 0.16 wt.-% SWNT dispersion in 0.6 wt.-% of the non-ionic surfactant Triton X-100 [32]. These SWNT dispersions were injected at 1 mL min^{-1}

through 20-gauge (nominal inner diameter: 0.6 mm) needles into rotating 40 wt.-% PEI (branched; average molecular weight, $M_w \sim 25\,000$; water-free; Aldrich) solutions in methanol.

The SWNT/PEI composite fibers were characterized by SEM (LEO 1590 VP microscope) and micro-Raman spectroscopy (Jobin–Yvon Horiba high-resolution LabRam micro-Raman spectrometer; helium–neon Spectra Physics laser, model 127, with excitation wavelength, $\lambda_{exc} = 632.8$ nm; resolution =~ 1 cm^{-1}). The mechanical properties of these fibers were measured at room temperature with an Instron MicroTester (using a 1 cm gauge length and a constant strain rate of 0.9–1.2 % min^{-1}. Four-probe electrical conductivities were obtained from resistance values measured using a Keithley 2000 Multimeter and using the fiber-shell area (not including the area corresponding to the void space in the cross section). Thermal analysis was performed using a thermogravimetric analyzer (PerkinElmer Pyris 1 TGA) and a differential scanning calorimeter (PerkinElmer Pyris Diamond DSC).

Received: October 6, 2004
Final version: December 2, 2004

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An Axisymmetric Flow-Focusing Microfluidic Device[**]

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This paper describes a microfluidic axisymmetric flow-focusing device (AFFD) fabricated in poly(dimethylsiloxane) (PDMS) that produces polymer-coated droplets with size distributions significantly more narrow than those generated using conventional microencapsulation methods.[1–3] The AFFD confines droplets in the central axis of a microfluidic channel; this confinement protects droplets from shear, or from damage re-

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[**] This research was supported by DARPA. S.T. received an overseas research scholarship from the Ministry of Education, Culture, Sports, Science and Technology of Japan. P.G. thanks the Foundation for Polish Science for a postdoctoral fellowship. D.B.W was a recipient of a postdoctoral fellowship from the National Institutes of Health (GM067445).

DOI: 10.1002/adma.200401738