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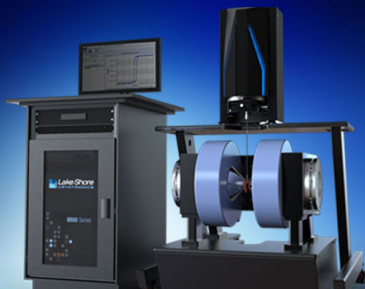
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Nanotube composite carbon fibers

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Single walled carbon nanotubes (SWNTs) were dispersed in isotropic petroleum pitch matrices to form nanotube composite carbon fibers with enhanced mechanical and electrical properties. We find that the tensile strength, modulus, and electrical conductivity of a pitch composite fiber with 5 wt % loading of purified SWNTs are enhanced by $\sim 90\%$, $\sim 150\%$, and 340% respectively, as compared to the corresponding values in unmodified isotropic pitch fibers. These results serve to highlight the potential that exists for developing a spectrum of material properties through the selection of the matrix, nanotube dispersion, alignment, and interfacial bonding. © 1999 American Institute of Physics. [S0003-6951(99)04635-5]

The discovery of carbon nanotubes has spawned a tremendous level of activity in carbon research, since the practical realization of their extraordinary properties would open endless possibilities for new materials that include super strong nanowires,^{1,2} nanosized electronic devices,³ charge storage devices in batteries,⁴ tiny electron guns for flat screen displays,⁵ and broadband optical limiters.⁶ Initially, most research efforts focused on understanding the fundamental properties of this quasi one-dimensional form of carbon. At the same time, there was always the appreciation that carbon nanotubes could form a foundation from which to develop a new generation of advanced materials with unique electrical, thermal, mechanical, and other properties. In this letter, we demonstrate the potential use of carbon nanotubes as a reinforcing filler in composite materials with enhanced mechanical and electrical properties.

The realization of the unique properties of nanotubes into engineering materials will in all probability require their incorporation into a suitable matrix. The aromatic character of commercial pitches derived from coal or petroleum suggests that there should be good compatibility with carbon nanotubes, and may even offer prospects for the utilization of unpurified or raw nanotubes. Moreover, pitches can be generated with a range of composition and properties, allowing latitude to match the matrix characteristics with that of the dispersed phase. In this regard, we have made a study to examine the synthesis and properties of composite carbon fibers produced via the addition and dispersion of purified single walled carbon nanotubes (SWNTs) in an isotropic pitch precursor. Other investigators have reported the dispersion of multiwalled carbon nanotubes in epoxide-based resin systems,^{7,8} poly(*m*-phenylenevinylene-co-2,5-dioctoxy-*p*-phenylenevinylene) (PmPV),⁹ and a urethane/diacrylate oligomer.¹⁰

Composite fibers are produced by extrusion in which it is possible that mechanical shear can be used to orient the nanotube bundles, much as a structure is developed by the shear-induced orientation of the liquid crystal phase during

the formation of fibers from mesophase pitch. The fiber form is particularly appealing as the steps to the commercial development of fibers for matrix reinforcement, in which the fibers themselves consist of a matrix-nanofiber composite, can be readily envisaged. In this preliminary study, we used Ashland A500 petroleum pitch as the matrix. This is an isotropic pitch that may be further treated to produce a mesophase pitch. While it is obviously of interest to see how the properties of high performance mesophase pitch fibers could be modified by nanotube addition, we have limited the present research to investigating the properties of the relatively much weaker carbon fibers that are obtained by spinning isotropic pitch. Due to the lack of molecular orientation in the isotropic pitch fibers, their tensile modulus is about 10–20 times less than the maximum attainable for mesophase pitch fibers, and their tensile strength is about five times less.¹¹

As-prepared SWNT (Carboxex, Inc.) were purified using the hydrothermal method which briefly, involves a refluxing of as-prepared nanotube material in distilled water at 373 K for 12 h, followed by drying in air at 333 K for 12 h and a final wash in 6 M hydrochloric acid to remove the catalyst particles.¹² The purified SWNTs were then dispersed in the pitch, which is solid at room temperature, as follows: the pitch was first dissolved in quinoline (Aldrich Chemicals) by stirring the mixture for ~ 2 h at 60 °C. The SWNTs were then added to the low viscosity hot solution, and a high power ultrasonic wand (Fischer Scientific) was used to disperse the nanotubes (500 W for 2 min). Afterwards, the mixture was transferred to a vacuum distillation apparatus, where the quinoline was completely removed. By this procedure, nanotube-pitch mixtures were prepared with nominal nanotube loadings of 1, 5, 8, and 10 wt %. The cooled nanotube-pitch mixtures, now solid were ground and each in turn was transferred to a single hole fiber spinning apparatus (Fig. 1). This consists of a heated reservoir that is pressurized with nitrogen (80 psi), a single hole die (300 μm in diameter) and a speed controlled wind-up drum onto which the fiber is pulled. With the reservoir heated to ~ 310 °C and the wind-up drum speed of 400 rpm, composite fibers with an

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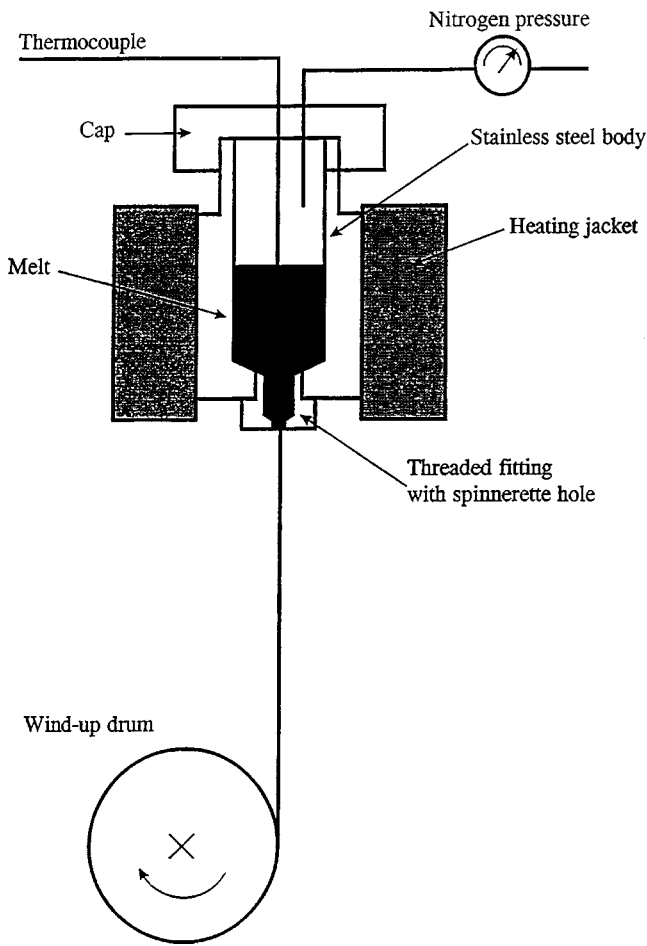


FIG. 1. Schematic of a single-hole spinnerette for composite carbon fiber production.

average diameter of $\sim 18 \mu\text{m}$ were produced.¹³ Pitch is generally spun at $\sim 50^\circ\text{C}$ above its softening point to ensure low pitch viscosity for fiber drawing. At the same time, it is necessary to keep viscosity sufficiently high to allow the drawn fibers to retain their continuity and shape prior to solidification in air. We found in our study that the temperature at which the nanotube-pitch mixture could be spun increased with the addition of nanotubes by $\sim 10^\circ\text{C}$ per 2 wt % increase in nanotube loading. This behavior, appears to be due to an increase in the viscosity of the molten pitch, i.e., possibly a change in the viscosity-temperature relationship

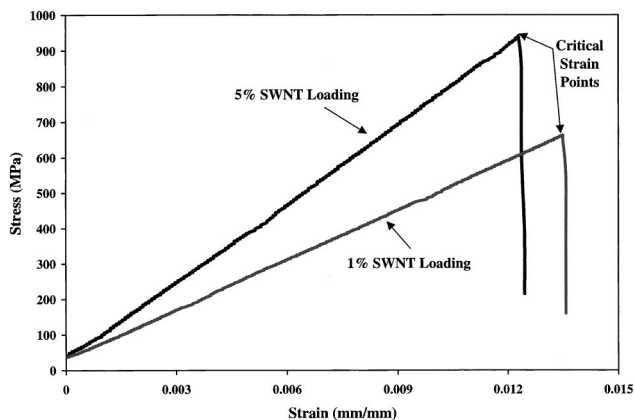


FIG. 2. Typical stress-strain plots for composite carbon fibers with 1 and 5 wt % nanotube loadings.

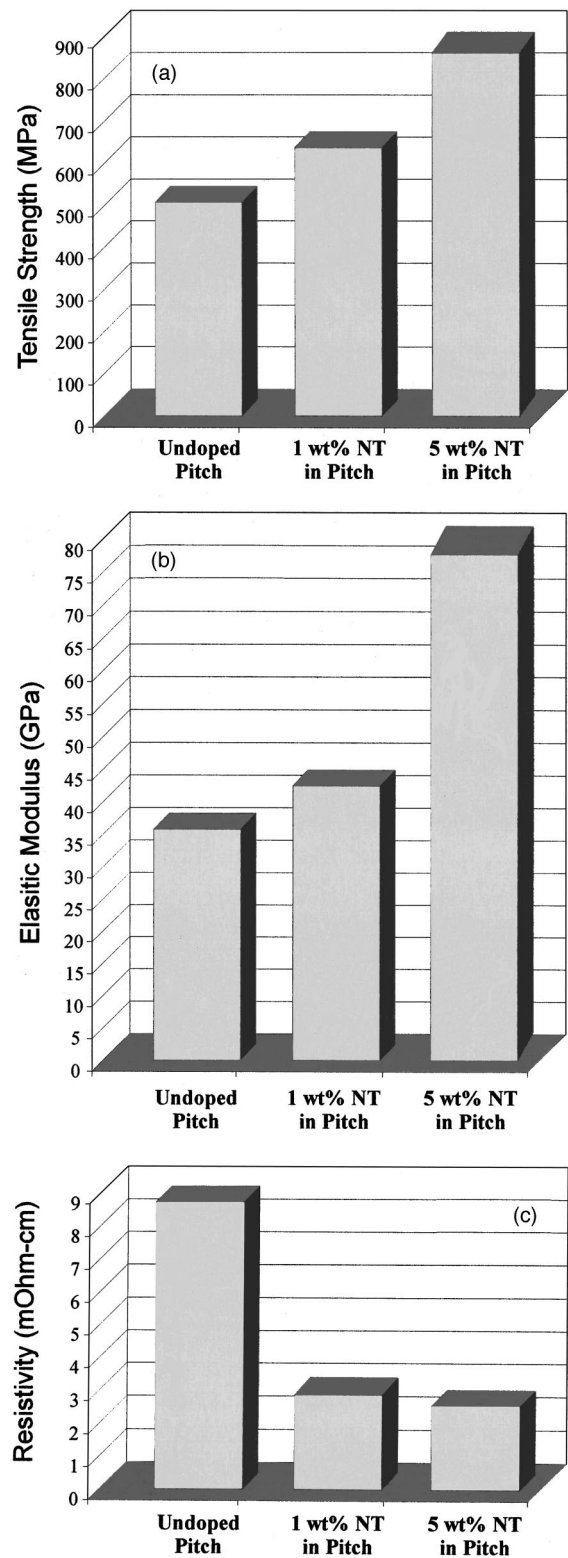


FIG. 3. A comparison of the tensile strength (a), modulus (b), and electrical resistivity (c) of composite carbon fibers with 1 and 5 wt % nanotube loadings to the corresponding values in unmodified isotropic pitch fibers. Each data point in this figure represents an average value for strength, modulus or resistivity obtained from 12 composite fibers. Standard deviations of experimental values are: strength $< 15\%$, modulus $< 15\%$, and resistivity $< 20\%$.

due to the presence of the nanotubes. At loadings of 8% and 10%, while the melt temperature could be used to lower the pitch viscosity to the point where it could be extruded, the melt was then too weak to maintain its shape and form a fiber. The raw fibers that were produced at lower loadings

were oxidatively stabilized by heating at 1 °C/min to 310 °C under 1 L/min air flow. The stabilized fibers were then carbonized under 2 L/min nitrogen flow in a tubular reactor at 20 °C/min to 1100 °C.

Individual carbonized composite fibers were mounted on to fiberboard testing plaques using colloidal graphite (Ted Pella, Inc.) as the adhesive, and tensile strength and modulus of elasticity were measured on a materials testing system following an American Society for Testing and Materials method (D638M modified for fiber geometry). Typical stress-strain curves are shown in Fig. 2. They exhibit a linear relation between stress and strain until the fiber breaks at a critical stress value. The maximum stress at the break is the tensile strength (σ) and the slope of the stress-strain curve is the modulus of elasticity (E). Since the nanotube loading is much less compared to anisotropic pitch in the composite carbon fibers used in the experiment, it is not surprising that similar strain to failure values were obtained from Fig. 2. The electrical resistivity (ρ) was measured using the standard four probe technique by passing a known current (1 mA) through the composite carbon fiber and measuring the voltage drop. Figure 3 summarizes the results obtained for σ , E , and ρ as a function of the nanotube addition. As noted earlier, uniform fibers could not be spun from the nanotube-pitch composites prepared at 8 and 10 wt % nanotube additions. We find that the tensile strength, modulus and electrical conductivity of a pitch composite fiber with 5 wt % loading of purified nanotubes are enhanced by $\sim 90\%$, $\sim 150\%$, and $\sim 340\%$ respectively, as compared to the corresponding values for unmodified isotropic pitch.¹¹ These results serve to highlight the potential that exists for developing a spectrum of material properties through the selection of the matrix, nanotube dispersion, alignment, and interfacial bonding. Wagner *et al.*¹⁰ obtained the Young's modulus, tensile strength, and failure strength of multiwalled carbon nanotubes (MWNTs)-containing thin polymer films as 2 GPa, 60 MPa, and 0.075. It should be noted that the weight percent loading of the MWNTs in the composite film was not reported.¹⁰ Furthermore, from their recent experiments they estimated ~ 150 GPa for the compressive strength of MWNTs. In an analogous molecular reinforced matrix, an improvement in compressive strength (20%–30%) has been reported for a molecular composite fiber consisting of a 14 wt % of a rigid rod polymer, (poly{(benzo-[1,2-*d*:5,4-*d'*]bisoxazole-2,6-diyl)-1,4-phenylene}) in a thermoset resin matrix.¹⁴ A 5 wt % loading of MWNTs in a PmPV polymer composite exhibited $\sim 90\%$ increase in the electrical conductivity compared to the value in pristine PmPV.⁹

In summary, we have shown that isotropic pitch composite fibers prepared with a few weight percent loading of purified SWNTs yield composite materials with enhanced

tensile strength, modulus, and electrical conductivity compared to the original pitch fibers. We believe that these enhanced properties result from the dispersion and incorporation of SWNT bundles in the petroleum-derived pitch matrix and that the SWNT bundles behave as unidirectional reinforcing nanofibers within the composite fiber. Direct observation of the dispersion and alignment of the carbon nanotube bundles in the petroleum pitch matrix was difficult to detect using electron microscopy. We also believe that more careful control and quantification of nanotube dispersion and alignment combined with appropriate matrix characteristics can lead to nanotube composites with more extraordinary physical and electrical properties. The recent finding by Chen *et al.*¹⁵ that SWNT bundles can be dissolved in organic solvents to obtain soluble nanotubes offers opportunities for enhancing nanotube dispersion. We are presently investigating the synthesis of composite carbon fibers derived from different precursors and soluble nanotubes.

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