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14. ABSTRACT The objectives of this project were (1) establish proof of principle by demonstrating enhanced polymer properties by the addition of single-walled nanotubes (SWNTs), (2) provide guidelines for materials selection that give improved mechanical, electrical and/or thermal properties, and (3) define processing methods most appropriate for the materials identified. Our study of SWNT-polymer composites focuses on thermoplastics, because these materials can be readily drawn into fibers. As we have shown previously, the extensional flow exerted on the composite during fiber spinning aligns the SWNT to an unprecedented level. The anisotropic orientation of SWNT in these composite fibers provides an advantage when looking for changes in macroscopic properties, particularly tensile strength. Composite processing and composite characterization received comparable effort in this project. Processing efforts include our coagulation method as well as in situ polymerization of nylon in the presence of well-dispersed SWNT. In addition to mechanical testing of the SWNT-thermoplastic fibers, we established methods for testing the electrical and thermal conductivity of these highly anisotropic materials. We used scattering methods for quantifying the extent of dispersion within the composites, a widely appreciated and longstanding question in nanocomposites.						
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Contract Information

Contract Number	N000140010720
Title of Research	Nanotube / Polymer Composites: Materials Selection and Process Design
Co-Principal Investigators	Karen I. Winey and John E. Fischer
Organization	University of Pennsylvania

Technical Section

Technical Objectives

- (1) Establish proof of principle by demonstrating enhanced polymer properties by the addition of single-walled nanotubes (SWNTs).
- (2) Provide guidelines for materials selection that give improved mechanical, electrical and/or thermal properties.
- (3) Define processing methods most appropriate for the materials identified.

Technical Approach

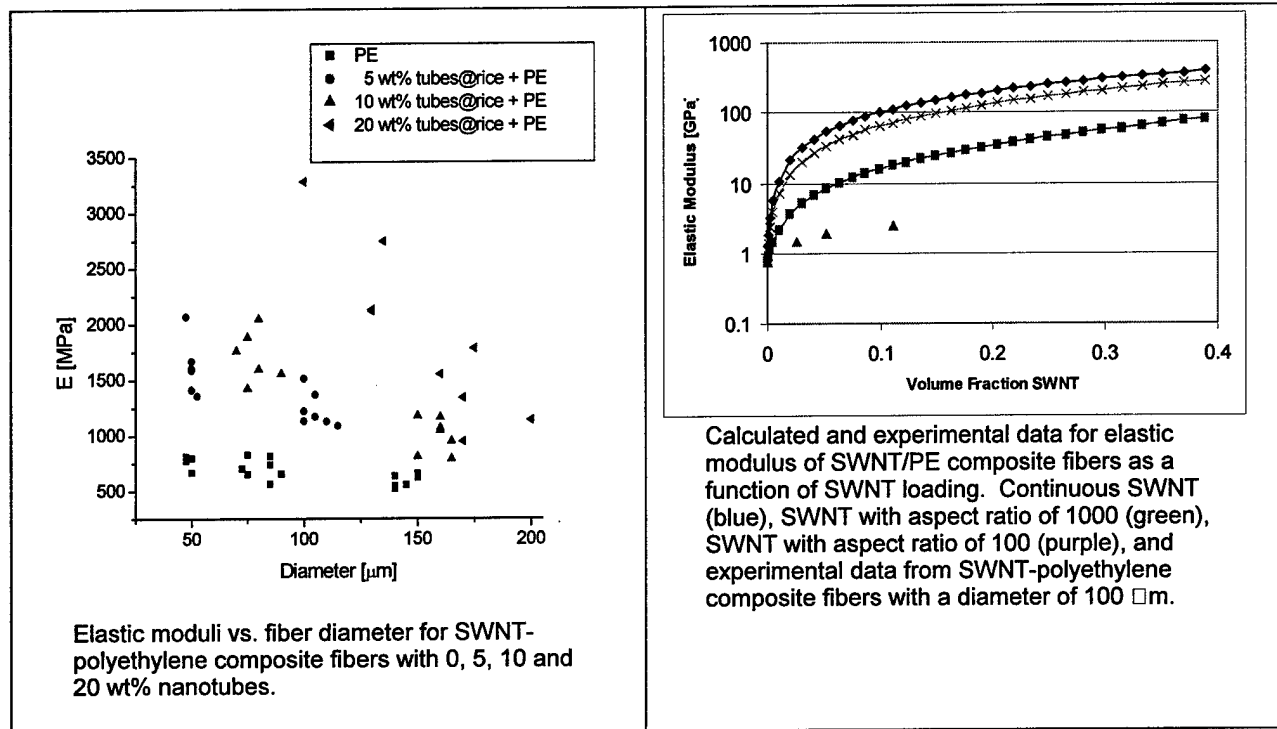
Our study of SWNT-polymer composites focuses on thermoplastics, because these materials can be readily drawn into fibers. As we have shown previously, the extensional flow exerted on the composite during fiber spinning aligns the SWNT to an unprecedented level. The anisotropic orientation of SWNT in these composite fibers provides an advantage when looking for changes in macroscopic properties, particularly tensile strength.

Composite processing and composite characterization are now receiving comparable effort in this project. Processing efforts were expanded this year to include in situ polymerization of a thermoplastic in the presence of well-dispersed SWNT. In addition to mechanical testing of the SWNT-thermoplastic fibers, we have established methods for testing the electrical and thermal conductivity of these highly anisotropic materials. We have also begun to explore the scattering methods for quantifying the extent of dispersion within the composites, a widely appreciated and longstanding question in nanocomposites.

Progress

(1) Improved mechanical properties in SWNT-polyethylene (PE) fibers. As an extension of our work with poly(methyl methacrylate), we established that similar improvements in the elastic modulus are found in SWNT-polyethylene fibers. This study included developing a protocol for preparing the composite using a widely-applicable melt mixing method and for melt spinning the composite into fibers (50 - 200 nm diameter). The extent of SWNT alignment was tested using Raman spectroscopy and was found to increase as the fiber diameter decreases due to higher extensional flows. Melt fiber spinning, which we pioneered in SWNT-polymer composites, remains the best way to align SWNT. We also determined that the improved mechanical properties were not the result of substantial changes in the crystallinity of the PE matrix. The improvement in tensile modulus is as high as five times for the case of 100 nm diameter fibers with 20wt% SWNT in PE relative to a PE fiber. A comparison was made between the measured elastic moduli and the predicted moduli assuming perfect interfacial adhesion and complete dispersion. This work was published in the *Journal of Nanoscience and*

Nanotechnology. A somewhat less extensive study of SWNT-polystyrene composites was also completed.



(2) **In situ polymerization method for SWNT-nylon.** The general melt mixing method developed for thermoplastics alluded to above involves suspending SWNT in a volatile solvent and dripping this suspension into a molten polymer while it's under shear. This is applicable to thermoplastics with glass transitions temperatures below $\sim 150^\circ\text{C}$. Unfortunately, SWNT-nylon composites could not be made following this scheme, because it softens at $\sim 300^\circ\text{C}$.

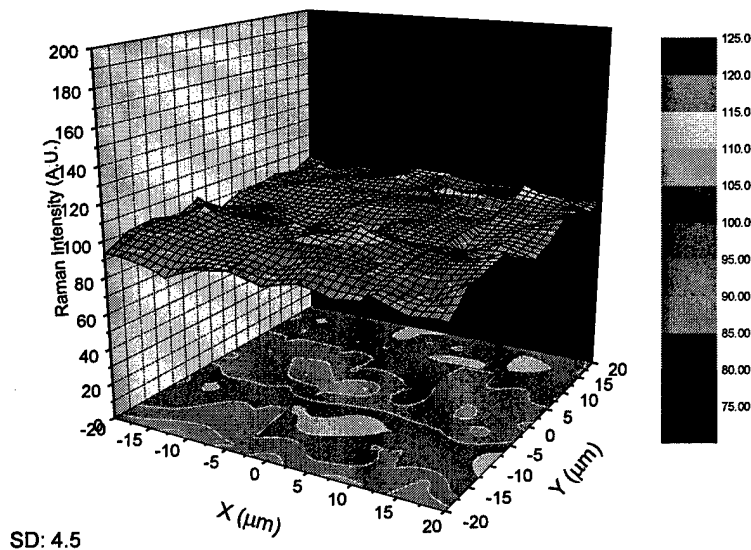
We have developed an alternative approach for nylon that involves polymerizing nylon in the presence of suspended SWNT. In particular, we use a two-phase polymerization route in which the SWNT can be dissolved in the aqueous or the organic phase prior to the reaction. Using an acid chloride monomer allows this interfacial reaction to occur at room temperature to high yield when the system is vigorously mixed.

During the previous year our attempts to improve the preparation of SWNT/nylon composites have met only limited success. We have successfully functionalized the nanotubes, but the dispersion within the composites is only fair. At present we are attempting to improve the dispersion using an amine terminated functional group that can participate in the step growth polymerization of nylon.

(3) **New method for measuring nanotube dispersion in SWNT composites.** As our ability to disperse nanotubes improves, optical microscopy is no longer sufficient to access the special distribution of nanotubes in a polymer matrix. Thus, we have recently demonstrated an imaging method with 1-micron resolution that is based on Raman spectroscopy. Raman spectroscopy has a specific absorption for SWNTs and that intensity can be mapped across a 40×40 micron area. To quantify this we have normalized the intensities, such that the mean intensity corresponds to 100 counts. The standard deviation of the mean provides a measure of the homogeneity of the SWNT distribution over this length scale. Our most recent method (described below) of preparing SWNT/PMMA composites has proven to be quite homogeneous

in SWNT distribution, unlike our SWNT/nylon composites. The method of Raman imaging provide a quantitative measure of SWNT dispersion. Currently we are developing SEM methods to evaluate the SWNT dispersion at an even finer length scale.

Figure shows the Raman intensity corresponding to SWNT as a function of x-y on the surface of a purified SWNT/PMMA composite prepared by the coagulation method containing 1 wt% nanotubes. The mean intensity has been normalized to 100. The standard deviation from the mean of 100 is given in the table below for 10 separate scans. These standard deviation is considerable lower than in pSWNT/nylon composites.

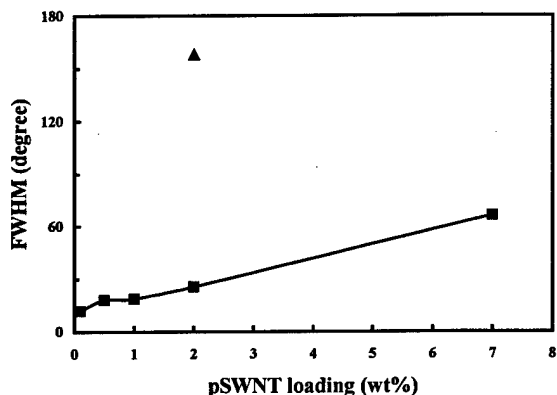


	1	2	3	4	5	6	7	8	9	10
SD	4.52	4.82	4.69	4.38	4.54	4.43	4.49	4.80	4.59	4.50

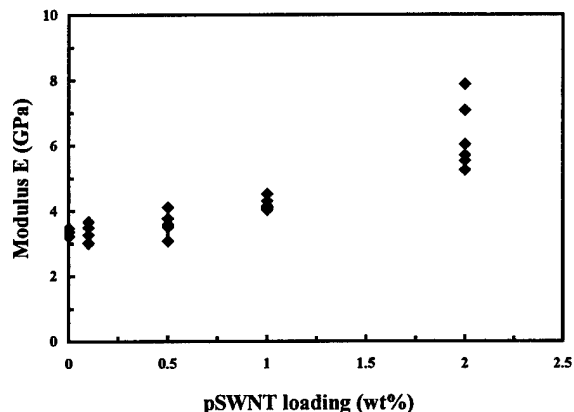
(4) **Coagulation Method for Preparing SWNT composites.** Coagulation is the method of recovering a polymer from a solution by pouring a polymer solution into a non-solvent. We have adapted this method to the preparation of SWNT composites to considerable success. In a recently accepted paper (Du, et al. *Journal of Polymer Science: Polymer Physics Edition*), we have detailed this method and demonstrated the improved SWNT dispersion. Composites were prepared in three forms: fibers, aligned composites, unaligned composites.

The extent of SWNT alignment in the composites was evaluated by measuring the azimuthal spread in the form factor x-ray scattering; more SWNT loading in the composites reduced the extent of alignment (increased the FWHM). The mechanical properties of the fibers show a modest increase with SWNT loading. The electrical conductivity shows a percolation threshold as a function of SWNT concentration in the isotropic composite. Note that the conductivity is much lower (at 2wt% loading) in the aligned composites; this result highlights the influence of alignment on transport properties. Our paper concludes that the percolation threshold in nanotube composites will depend on the dispersion (isolated nanotube or bundles), aspect ratio of nanotubes (or bundles), orientation of nanotubes (or bundles), nanotube purity, as well as the concentration of nanotubes. We have already demonstrated the importance of the alignment and are currently pursuing experiments to investigate the nanotube aspect ratio and the dispersion on electrical and thermal properties.

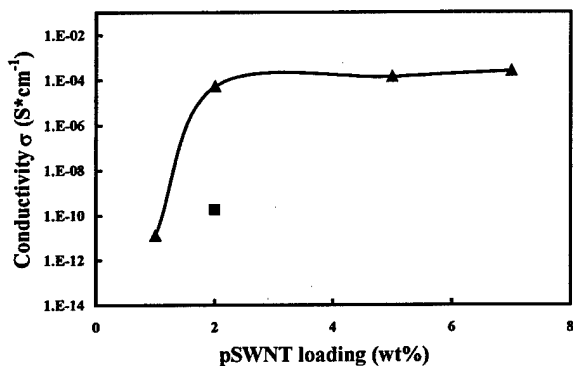
Finally, we observed improved thermal stability for the pSWNT/PMMA composites as illustrated by a reduction in the maximum rate of weight loss and an increase in the temperature of the maximum rate. We are collaboration with Dr. Takashi Kashiwagi of NIST in pursuing the fire retardation properties of SWNT in these composites. A joint publication has been submitted to *Macromolecular Rapid Communication*.



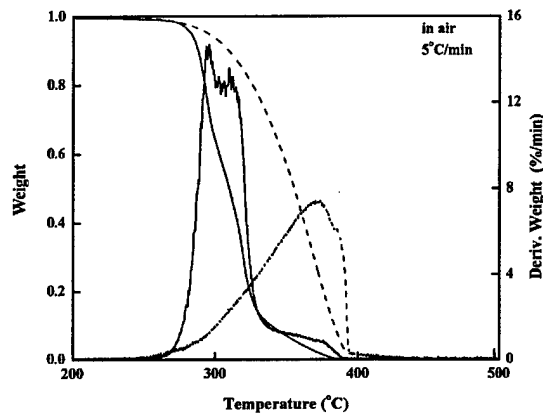
FWHM of the Lorentzian function fitted to the azimuthal distribution of the SAXS intensity from the pSWNT/PMMA composites, both unaligned composite (▲) and aligned composite (■), as a function of pSWNT loading.



Elastic tensile modulus of the pSWNT/PMMA composite fibers as a function of the pSWNT loading.



Electrical conductivity of the pSWNT/PMMA composites, both unaligned composite (▲) and aligned composite (■), as a function of the pSWNT loading.



TGA analyses of normalized weight loss and its rate by the initial sample weight at a heating rate of 5°C/min in air: (solid) pure PMMA; (dash) 0.5% pSWNT/PMMA composite.