

PREPARATION OF MULTIWALLED CARBON NANOTUBE POLYMER COMPOSITES

R. Andrews¹, B. Dickey², D. Qian², B. Knutson², B. Safadi¹, B. Moore¹ and F. Derbyshire¹

¹University of Kentucky Center for Applied Energy Research,
2540 Research Park Dr., Lexington, KY, USA 40511.

²Chemical and Materials Engineering,
177 Anderson Hall, University of Kentucky, Lexington, KY, USA 40506.

Introduction

Our broad objectives are to explore the development of advanced composite materials in which carbon nanotubes serve as the reinforcing element in polymer matrices and in carbon matrices that are derived from pitches or polymers. In this presentation, we describe the results of preliminary investigations to prepare composites consisting of multiwalled nanotubes (MWNT) in selected polymers, to investigate the influence of different techniques on MWNT dispersion, and to determine the properties of the resulting artifacts.

Experimental, Results and Discussion

MWNTs were produced by the catalytic decomposition of a ferrocene - xylene mixture at ~700 °C and at atmospheric pressure, as described elsewhere [1]. By selecting the reaction conditions, the MWNTs can be produced in selectivities approaching 100%. Typically, their diameter is in the range 20 to 30 nm, and the length ranges from about 20 microns upwards.

Three polymer systems were examined: polystyrene; polyfurfural resin; and nylon 6.

Polystyrene

Dispersions of MWNTs in polystyrene (PS) were produced, and the effect of mixing time on nanotube dispersion was studied. MWNTs were added to a solution of 10% PS (45,000 M_w) in toluene to yield a 0.5wt% MWNT/PS product. The solution was sonicated, using an ultrasonic wand dismembrator at 300 watts, for various times between 0.5 and 120 minutes. Thin polymer films were cast from this solution and toluene removed by evaporation. The MWNT dispersion within the films was examined by SEM and TEM analysis. Dispersion increased with sonication time and times in

excess of 30 minutes apparently resulted in the dispersion of MWNTs as individual tubes.

Under TEM, a crack was propagated within the film by concentrating the electron beam, and the resultant failure mechanism of the MWNT/PS interface observed. MWNT-matrix pullout was seen, as was extension and bridging of MWNTs across the crack. In many cases, a single MWNT could be traced from one side of the polymer matrix, bridging the crack, and anchored into the other side of the matrix.

Using the previously described technique, MWNTs were dispersed in a 10% PS (280,000 M_w) / 90% toluene solution (1 wt% MWNT in PS) by sonication for 30 minutes. As before, thin films were cast and the toluene removed by evaporation. Blank films (10% PS in toluene) were also cast by the same technique. The electrical conductivity of these films was measured using a 4-point contact method. While the polystyrene blanks are insulating materials, the films doped with MWNTs are conductive (conductivity ~ 7.1·10⁻² Ω⁻¹ cm⁻¹).

Film samples were also tested for tensile strength, modulus and strain at yield (ASTM D882). The strength and modulus of the doped films were about 25% higher than the PS blanks and the strain at yield increased by 10%, Table 1. Hence, the presence of MWNTs enhanced the mechanical properties of this polymer.

Polyfurfural Resin

Bars of material (approximately 50 x 15 x 3 mm) were formed by the polymerization of furfural resin in a mold, using hexamethylene tetramine as a catalyst. The resin was cured in two stages: to 140°C for ~10 mins to effect partial polymerization; it was then introduced to the mold and held at ~170°C for 60 mins on a hot platen press (~10 MPa). For MWNT-doped polymers, 0.5wt% MWNTs was added to the resin and the mixture was sonicated for ~30 minutes using the ultrasonic wand dismembrator at 300 watts to disperse the nanotubes. Subsequently, the

catalyst was added and the mixture was molded and cured as before.

The resulting bars were analyzed to determine their electrical conductivity and their flexural strength (ASTM D790), Table 2. The addition of MWNTs, even at this low loading, considerably increased the electrical conductivity of the polymer, as was found for the PS films. In terms of mechanical strength, MWNT addition effects a dramatic improvement to the polymer flexibility. In contrast to the PS films, the flexural strength is lowered (by a factor of over 4), and the flexural modulus is reduced (by a factor of more than 7), while the mean strain at yield is increased by about 50%.

Nylon

The aims of this work were to explore the use of supercritical CO₂ formation of polymer-MWNT composite membranes. Supercritical anti-solvents have been used to create unique polymeric morphologies including microparticles, films, and fibers. These morphologies are obtained by first dissolving the polymer in an organic solvent and contacting this solution with a supercritical fluid. Novel microstructures obtained by this process are attributed to the rapidness of the precipitation process, which is the result of simultaneous evaporation of the solvent into the carbon dioxide phase and the expansion of the organic phase. Membrane formation achieved using a supercritical anti-solvent is analogous to traditional phase inversion membrane formation processes. Membrane morphology, and therefore separation selectivity and membrane permeability, are dictated by phase inversion process variables such as solvent choice, nonsolvent choice, temperature, and initial polymer concentration. Precipitation with a supercritical fluid anti-solvent offers the additional process variable of pressure for the tuning of membrane morphology to a specific application.

Polymer-nanotube composite membranes were formed by the rapid precipitation of a nylon-6/2,2,2 trifluoroethanol solution containing suspended MWNTs at a concentration of 0.5 wt% MWNT/nylon. A 15 wt% polymer solution was cast onto a glass slide and placed in a 100 ml high pressure vessel held at 35°C. The rate of addition of carbon dioxide was controlled using a high pressure syringe pump. After reaching the desired pressure (typically less than 140 bar), a thirty minute hold time was used to ensure membrane formation. A solvent-free membrane was obtained following system depressurization.

The properties of the 50 to 250 mm-thick semicrystalline membranes obtained by this process were examined by

SEM and compared to membranes prepared in the absence of nanotubes, and membranes prepared by traditional phase inversion techniques. The membrane formed by supercritical extraction has a significantly different morphology than traditionally cast membranes, appearing to be highly porous, exhibiting a three-dimensional crystallite or 'snowflake' like structure. In continuing work, we will examine the properties of these membranes and study the ability to achieve unique composite morphologies using the tunable solvent strength of a near-critical fluid as a process variable.

Acknowledgments

The authors wish to acknowledge financial support from the NSF MRSEC grant DMR – 9809686.

References

1. Andrews R, Jacques D, Rao AM, Derbyshire F, Qian D, Fan X, Dickey EC, Chen J. Continuous Production of Aligned Carbon Nanotubes: A Step Closer to Commercial Realization. *Chem Phys Lett.*, 1999; 16 April.

Table 1. Properties of Polystyrene Films

Sample	Electrical Conductivity $\Omega^{-1} \text{ cm}^{-1}$	Tensile Strength MPa	Elastic Modulus GPa	Yield Strain %
Blank	0	13	1.2	1.3
1 wt% MWNT	$7.1 \cdot 10^{-2}$	16	1.6	1.4

Table 2. Properties of Polyfurfural Resin

Sample	Electrical Conductivity $\Omega^{-1} \text{ cm}^{-1}$	Flexural Strength MPa	Flexural Modulus GPa	Yield Strain %
Blank	0	30.2	1.65	1.86
0.5 wt% MWNT	$1.3 \cdot 10^{-2}$	6.7	0.23	2.75