THE AFFECT OF NANOTUBE REINFORCEMENTS ON CARBON FIBERS FROM PITCH REINFORCEMENTS

J.C. Withers, J. Webb, W. Kowbel, B. Safadi and R.O. Loutfy
Materials & Electrochemical Research (MER) Corporation
7960 South Kolb Road
Tucson, Arizona 85706, USA

Introduction

Carbon/graphite nanotubes represent a near ideal reinforcement for micron size fibers since the nanotube's size is a few nanometers in diameter with exemplary strengths and stiffness coupled with very light weight. Initial attempts to utilize the various nanotube architectures of single wall (SWNT), double wall (DWNT) and multi wall (MWNT) have resulted in disappointing composite properties that extracted virtually none of the nanotube inherent properties. A major barrier to the fabrication of nanotube reinforced materials and particularly composite micron size fibers has been the effective and efficient dispersion of the nanotubes in the host matrix.

Since nanotubes possess a carbon structure, there is good reason to believe nanotubes would be a good reinforcement for a carbon/graphite fiber. Also, a published report [1] of 5% SWNT increased the tensile strength of an isotropic pitch based carbon fiber from 450 to 855 MPA, elastic modulus from 32.5GPa to 80GPa and electrical conductivity by 340%. Pitch is one of the major precursors from which carbon/graphite fibers are produced. Therefore, the goal was to disperse nanotubes into pitch and spin into fibers to determine the affect of nanotubes as reinforcements for carbon/graphite fibers.

Experimental

Coal-tar pitch with a softing point of 120ºC was utilized as the precursor. It was dissolved in boiling 1-methyl-2-pyrol-iodine (NMP), and filtered to remove the insoluble ashes and any other insoluble carboneous materials. MWNT in a concentration to provide 5%, were suspended in dichloromethane using ultrasonication. The pitch NMP and MWNT dichloromethane were mixed with stirring and continuous heating to remove both the dichloromethane and NMP. With continued stirring the pitch was heated to yield a softing point of 200ºC. The pitch was transferred to a spinning system and fibers spun at 230ºC. The green spun pitch fibers were oxidized in air at a heating rate of 0.5ºC/min to 200ºC, the 0.1ºC/min to 250ºC and hold for 8 hours. The oxidized fibers were then pyrolized/carbonized to 1800ºC.

Results and Discussions

Two separate batches of fibers were spun from the initial preparation of coal-tar pitch containing 5% MWNT's. This was compared to fibers spun from an identical batch of fibers without the MWNT additions. The fibers diameter was 15µ in one case and 18µ in the second case. The strength of the unreinforced carbon fibers was 2.8GPa. The strength of the first batch of MWNT reinforced fibers was 3.4GPa which was a 21% increase which can be attributed to the MWNT reinforcements. The strength of the second batch of MWNT reinforced fibers was 4.2GPa which is a 24% increase. In the second case the modulus increased from 96GPa to 155GPa which is a 61% increase. Of significance is the fact that strength was increased in both cases about the same amount with a significant increase in modulus. While the strength enhancement was not the same percentage as reported by others [1] the basic strength is significantly higher which results in fiber with useable commercial values.

Functionalizing nanotubes can have a marked effect on dispersion in solvents, which are then dispersed in the pitch precursor for spinning fibers. The nanotubes are functionalized by first opening the ends, by high power sonication in solution. In this case, the nanotubes were treated with sodium hypochlorite a aqueous solution followed by acid treatment. After opening the nanotubes, which were verified by TEM, different substituents were added to the oxidized open ended nanotubes to facilitate the dispersion process and increase the reactivity of the nanotubes. The reaction sequence is as follows;

NT $\xrightarrow[\text{Oxidation}]{\text{Chemical}}$ HO–NT–OH Y–R–X–NT-X–R-Y

Where R = Alkyl Acyl or aromatic,

X = O or N, Y = H, OH or NH_2

FTIR was utilized to confirm the functionalization of the MWNT's. After functionalization the nanotubes were readily dispersed in dichloromethane solvent. The functionalized nanotubes are ready to be added to pitch for fiber synthesis to determine the comparative effect of carbon fiber properties versus the unfunctionalized nanotubes.

Conclusions

Multi walled nanotubes (MWNT's) have been added to coal-tar pitch and carbon fibers produced which exhibited a 21 to 24% increased strength over the same carbon fiber without nanotube reinforcement. The nanotube reinforced carbon fiber exhibited strength up to 4.2GPa. Nanotubes have been functionalized for comparative evaluation to enhance the strength of fibers.