Morphological, Mechanical and Electrical Properties of Thermally Stable CNT/Carbon Nano Fibril Composite Structures

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Introduction

Electrospun nano fibers are characterized by its high surface area; this characterization showed a different behavior than bulk, for the nano sized fibers such as super absorbent characteristics of electrospun PAM nano fibers [1] and a nano reinforcement size effect with carbon nano tubes [2] and graphite nano platelet [3] which has been correlated to the unusual behavior of molecular chains on the surface of nano scale fibers. It's well known that, atoms at a free surface experience a different local environment than do atoms in the bulk of a material. However, for nano-size materials such as nano fibers, the surface to volume ratio becomes significant, and so does the effect of surface free energy. Dingreville and et al [4] showed 20% increase in the axial Young's modulus for 4 nm diameter copper wire. Also, Nanda and et al [5] showed 5-6 times increase in material surface energy for Ag nano-particles relative to bulk. Also, He and et al [6] found a size effect in the elastic property of electrospun PAN nanofibers below 150 nm.

Nano diamond nucleation has been reported for carbon nanomaterials below the required pressure and temperature for similar bulk materials [7&8].

The present study is an attempt to continue a work that has been started by Ali AA and Rutledge GC [9] to use this high surface energy of the electrospun PAN nano fibers along with different carbon nano tube sizes as a cohesive bond to build a firm strong precursor carbon nano fibril composite fabrics. Also, to get the use of the high degree of entanglement inside the nano fibrous structure and carbon nano tubes to gain a higher degree of flexibility in the overall produced fabrics. Finally a heat treatment in nitrogen has been took place to improve the conductivity and to produce CNT/carbon nano fibril composite fabrics that can be used in many application aspects.

Experimental Work

Materials

Polyacrylonitrile (PAN) of 150000 g/mol molecular weight, dimethylformamide (DMF) with three different CNT sizes from Aldrich (CNT#!: O.D. =10-30 nm, I.D.= 3-10 nm, L=1-10 µm – CNT#2: O.D.= 30-50 nm, I.D.= 5-15 nm, L= 0.5-20 µm – CNT#3: O.D.= 40-60 nm, I.D.= 5-10 nm, L= 0.5-60 µm) have been electrospun by using High voltage source assisted with syringe pump.

A four different orifice inner diameter of metal tubes (0.254, 0.508, 0.762 and 1.016 mm) have been used to study the effect of spinneret diameter on the morphology of the produced fiber at 35kV of positive potential. A metal screen collector was centered vertically at a 30 cm distance away from the orifice of the metal tube

Hot-press

The electrospun mat was placed in between two aluminum plates. The mold with the mat in between was placed in a hot press set to reach 220°C with applying pressure of 1 metric ton for 3 hours period.

Carbonization

A CARBOLITE tube furnace of 75 mm diameter 600 mm effective length and 1100°C maximum temperature has been used at 750°C with nitrogen dynamic flow of 5 ml /min

Tensile Test

Five tensile samples of approximately 60 mm length and 5 mm width were cut from the hot-pressed nanofiber mat, each sample has been weighted to an accuracy of 3 digits. A UTM with 500 N maximum load cell and 1µN accuracy has been used with an optical extensometer set-up to investigate the tensile properties (strength, modulus and Poisson's ratio) of the hot-pressed nanofiber fabric. Also, Fracture patterns of the tensile samples have been investigated using an optical microscope.

Results and Discussion

Effect of spinneret diameter on electrospun fiber diameter

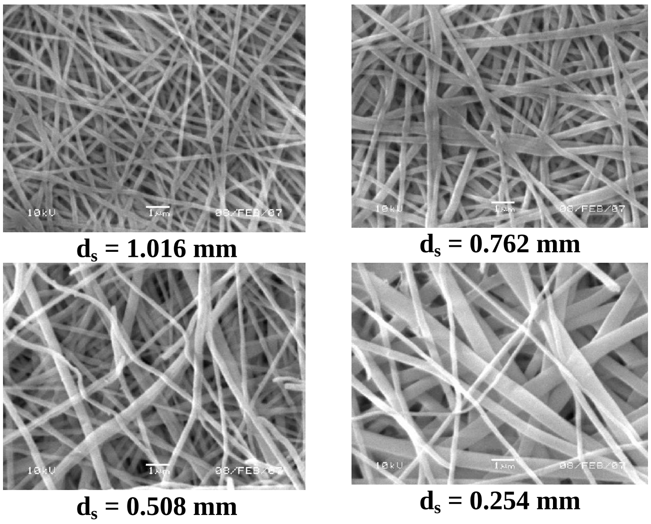


Fig. (1): SEM Images of hot-pressed electrospun PAN fabrics

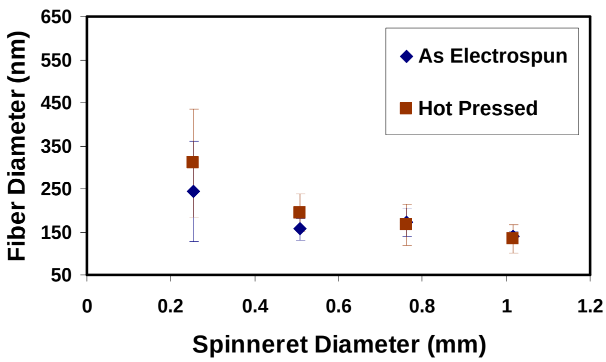


Fig. (2): Effect of spinneret diameter on the produced PAN fibers before and after hot-pressed

Tensile Properties (Strength and Modulus)

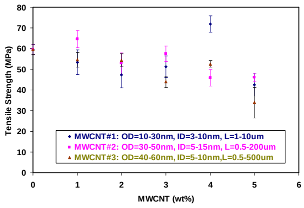


Fig. (3): Tensile strength of hot-pressed samples

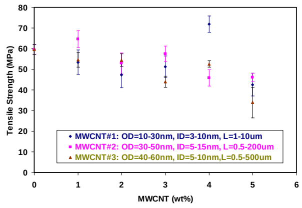
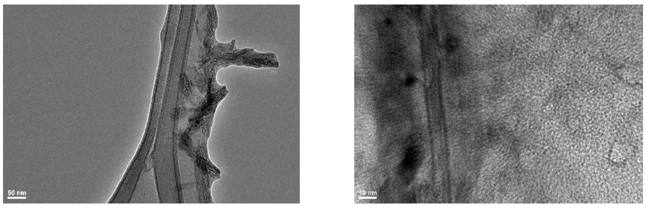


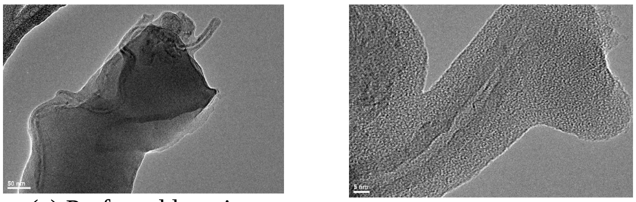
Fig. (4): Tensile modulus of hot-pressed samples

TEM Analysis (CNT location and size)



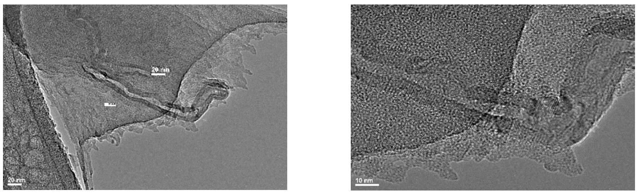
(a) Preferred location (b) Measured size

Fig (5): CNT#1 (hot-pressed samples)



(a) Preferred location (b) Measured size

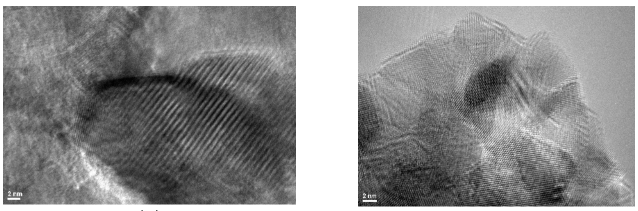
Fig (6): CNT#2 (hot-pressed samples)



(a) Preferred location (b) Measured size

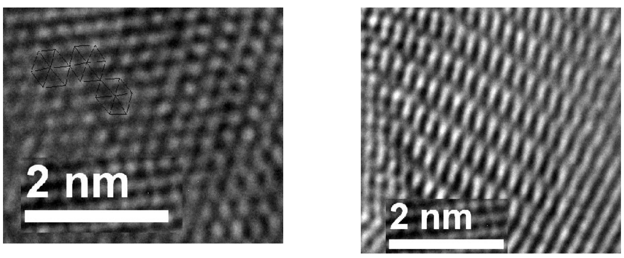
Fig (7): CNT#3 (hot-pressed samples)

TEM Analysis (2-D vs. 3-D Graphite structure)



(a) (b)

Fig. (8): Formation of 0.334 nm graphite lamellas (a & b) vs. 3-D graphite lamellas (b) (reheat treated samples)



3-D Graphite (Diamond Like) Pattern

Fig. (9): Close look for reheat treated hot-pressed samples

Conclusions

1. Hot-pressed electrospun CNT/PAN nano fibril composite fabrics showed an elastic characteristics with firm and strong behavior of around 60 MPa fabric strength (property of single nano fibril composite is under investigation).
2. Measurement of modulus of elasticity of a single nano fibril composite using AFM technique showed an average values of 83±9, 89±17 and 101±21 GPa for the 3% wt for CNT#3 to #1 samples respectively which indicates that, the measured modulus values (found to be in the range ~ 3-4 GPa) for the hot-pressed nano fibril composite fabrics is the measure of the physical bond between nano fibers and/or CNT and not the measure of single nano fiber modulus.
3. TEM images proved a formation of graphite lamellas for hot-pressed samples and 3-D graphite (Diamond Like) structures for the reheat treated hot-pressed samples which essentially required Raman spectroscopy analysis to identify the structure type (on going work)
4. Preliminary measurements for the electrical resistivity of the hot pressed samples by using micro-ohm meter and 4-point probing surface measurements system showed values of approximately 10^{-3} to 10^{3} Ohm .m) which is in between the tabulated values of commercial graphite (10^{-6} Ohm .m), PAN based carbon fibers (10^{-4} Ohm .m) and synthetic diamond (10^{9} Ohm .m). It should be noticed that these large ranged measured values is much lower than the tabulated values for PAN fibers (10^{14} Ohm .m) also, more experimental measurements are essentially required to conclude the effect of CNT on the resistivity of the single nano fibril composite structures as well as a direct conductivity measurement technique for single nano fiber.

Acknowledgment

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