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ORIGINAL ARTICLE

A novel 3-D graphite structure from thermally stabilized electrospun MWCNTs/PAN nanofibril composite fabrics

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Abstract Multiwall carbon nanotubes (MWCNTs) and nanofibers are characterized by their high surface energy. In this paper, such a cohesive energy was activated by using hot-pressing technique to build strong and flexible MWCNTs/carbon nanofibril hybrid fabrics. MWCNTs of three different diameters, and each with five different weight concentrations, were dispersed in 10 wt% polyacrylonitrile (PAN)/DMF polymer solution. PAN/DMF+MWCNT dispersions were electrospun under optimum electrospinning conditions, and the collected fabrics were thermally stabilized under a static pressure. They were then re-heat-treated in a tube furnace with a nitrogen flow. Strength of 70 MPa, modulus of 4 GP, and strain of 5 % were reported for the fabrics. Modulus of 100 GPa was reported for a single nanofibril composite. A novel 3-D graphite structure has been discovered as a result of the interaction between MWCNTs and stabilized PAN nanofibers during graphitization at much lower temperature and pressure. Fabrics were investigated by using SEM, HRTEM, AFM, and x-ray diffraction.

Keywords 3-D graphite · Carbon nanotubes · Carbon nanofibril composites · Flexible carbon fabrics · Mechanical properties · Electron microscopy

1 Introduction

Optimization of electrospinning process to produce minimum polymer fiber diameters has been studied for more than a decade. Most of these publications [1–6] were focusing on specified processing parameters such as Berry's number, charge density, spinning angle, spinneret diameter, and spinning distance as the most influencing processing parameters on the electrospun nanofiber diameters. Electrospun nanofibers are characterized by its high surface area; this characterization showed a different behavior for the nanosized fibers such as super absorbent characteristics for electrospun polyacrylamide (PAM) nanofibers [7]; in this paper, a fourfold increase in absorbent capacity has been reported for the processed PAM nanofibers more than original microsized particulate one. Also, nano reinforcement size effect has been reported for carbon nanotube-reinforced carbon nanofibers [8]. In this paper, it has been proved that fibril composites in nano level do not obey tradition physics and mechanics such as rule of mixture and hook's law. Also, the effect of graphite nanoplatelets as reinforcement nano materials with carbon nanofibers showed a nano size effect on the rule of mixture as well [9]. In these two papers [8, 9], nano reinforcement effect has been correlated to the unusual behavior of molecular chains (atoms) on the surface of nanoscale 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; as a result, the energy associated with these atoms will, in general, be different from that of the atoms in the bulk. The excess energy associated with surface atoms is called surface free energy. In traditional continuum mechanics, such surface free energy is typically neglected because it is associated with only a few layers of atoms near the surface and the ratio of the volume occupied by the surface atoms and the total volume of material of interest is extremely small. However, for nanosized materials such as nanofibers, the surface to volume ratio becomes significant, and so does the effect of surface free energy [10]. The effect of surface energy on the elastic behavior at the nano level has been studied in literature. For example, Dingreville et al. [11] showed 20 % increase in the axial Young's modulus for a 4-nm diameter copper wire. Also, Nanda et al. [12] showed five

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to six times increase in material surface energy for Ag nanoparticles relative to bulk. One important discovery by He et al. [13] is a size effect in the elastic property of electrospun polyacrylonitrile (PAN) nanofibers only below 150 nm that has been found. On the other hand, Nano diamond nucleation has been reported for carbon nanomaterials below the required pressure and temperature for similar bulk materials [14]. Sun et al. [15] showed a formation of Nanodiamond from carbon nanotube wires. In general, the last two papers [14, 15] proved that materials in nano level behave thermodynamically different than do materials in bulk.

The present study is an attempt to continue a work that has been started by Ali and et al. [10, 16] to utilize the high surface energy associated with the electrospun PAN nanofibers along with different carbon nanotube sizes and use it as a cohesive bond aiming to build a firm, strong, and flexible precursor carbon nanofibril hybrid fabrics and also to utilize the high degree of entanglement inside the electrospun nanofibril carbon/carbon nanotube structure to gain a higher degree of flexibility for such carbon/carbon hybrid fabrics. Finally, a heat treatment in nitrogen environment has been introduced to improve the fabric mechanical properties and to produce strong and flexible MWCNTs/carbon nanofibril hybrid fabrics which are a good and promised candidate for many important applications such as an inner layer between shaft and journal for wear application or as a reinforcement material for ballistic and aerospace materials (ongoing research work).

2 Experimental work

2.1 Materials

Polyacrylonitrile (PAN) of 150,000 g/mol molecular weight from Aldrich was used with 10 % weight concentration in dimethylformamide (DMF) to form a polymer solution after hot stirring for 3 h at 60 °C to ensure a complete solubility.

Fig. 1 Electrospinning set-up

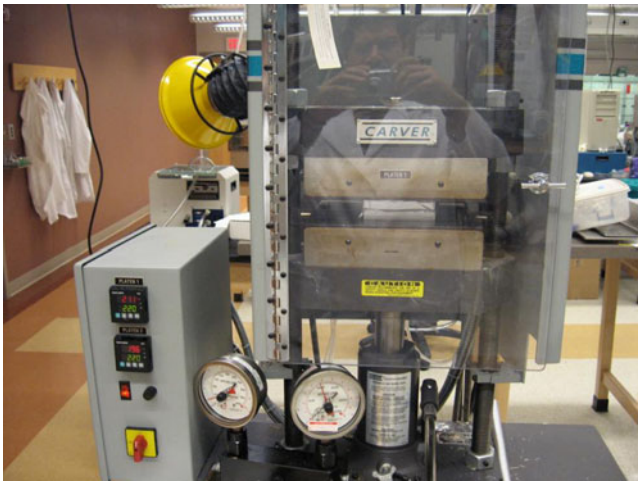


Fig. 2 Carver hot-press

Three different MWCNT sizes from Aldrich were identified as follows:

$$MWCNT\#1 : O.D. = 10{-}30\ nm, I.D. = 3{-}10\ nm, L = 1{-}10\ \ddot{E}m,$$
$$MWCNT\#2 : O.D. = 30{-}50\ nm, I.D. = 5{-}15\ nm, L = 0.5{-}200\ \ddot{E}m, and$$
$$MWCNT\#3 : O.D. = 40{-}60\ nm, I.D. = 5{-}10\ nm, L = 0.5{-}500\ \ddot{E}m.$$

SONOREX Digital 10P Bandel-model sonicator was used for 24 h to disperse MWCNT with different concentrations inside the polymer solution.

2.2 Electrospinning

PAN/DMF+MWCNT dispersions were poured to fill a clean syringe of 10 ml volume, and the syringe was placed in a controlled pump set to give a flow rate of 0.025 ml/min. The syringe was connected to a rubber tube of 30 cm length and 2 mm inner diameter, and the other side of the rubber tube was connected to a metal tube of 35 cm length and four different inner diameters: 0.254, 0.508, 0.762, and 1.016 mm The metal tube was placed in a hole drilled in a circular aluminum disc of 15 cm diameter and 1 cm thickness, the aluminum disc was connected to the power supply at approximately 35 kV of positive potential. A metal screen collector of 15×15 cm dimensions was centered vertically at a 30-cm distance away from the orifice of the metal tube and was covered with

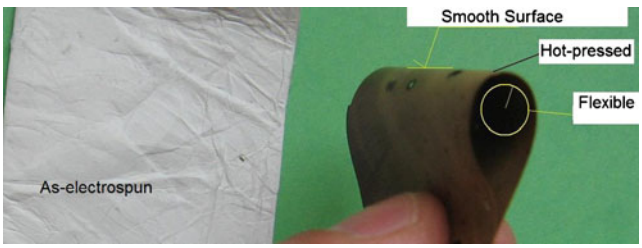


Fig. 3 As-electrospun vs. hot-pressed fabrics

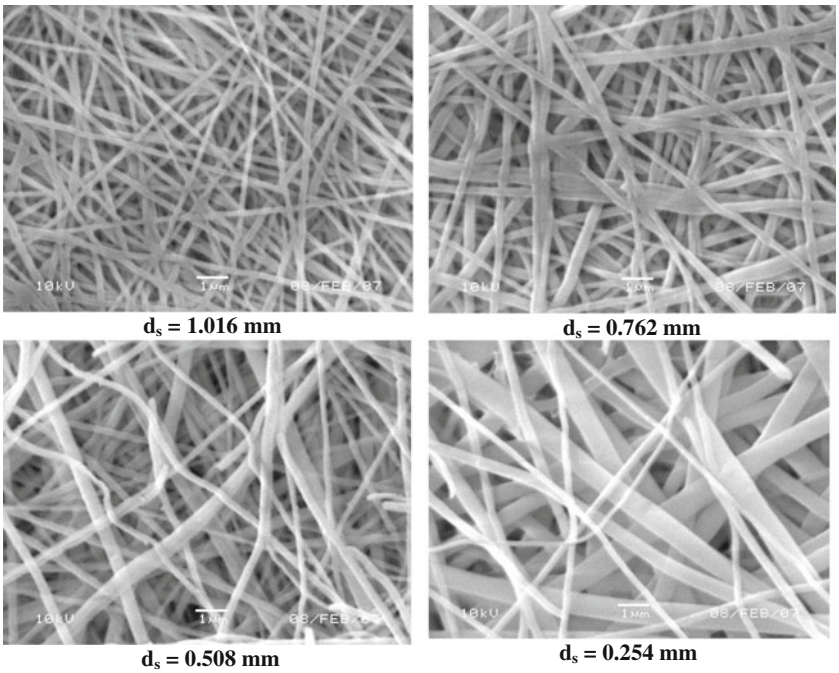


Fig. 4 SEM images of hot-pressed electrospun PAN fabrics

aluminum foil. The potential was applied first then the pump flow rate was increased to ensure no droplet accumulation on the metal screen collector which was covered with aluminum foil. The electrospun fibers were collected for about 8 h. Figure 1 shows the electrospinning set-up that has been used to produce the as-electrospun fabrics. This set-up is designed and approved by ISN, MIT, USA based on theoretical and experimental approaches. Also, the set-up has been proved its ability to produce uniform and small fibers in previous corresponding author's research publications [10, 16].

2.3 Hot-pressing

About 2 cm from each side of the collected fiber mat was trimmed, and then the mat was placed in between two aluminum plates of 110×105-mm dimensions and 10-mm thickness after it was covered with aluminum foil. The mold with the mat in between was placed in a hot press, Fig. 2, Carver hot-press USA model of maximum 10 metric tons and 500 °C, set to 220 °C with no applying pressure for 1 h until the plate's temperature reached the maximum set temperature. Then, 1 metric ton was applied for another 1 h. The hot-press was then allowed to cool down for another 1 h while keeping the pressure on until it reaches 100 °C then the pressure was released completely from the fabric except the weight of the upper aluminum plate until it cooled down to room temperature. The produced hot-pressed strong and flexible fabric is shown in Fig. 3 in comparison with the as-electrospun fabric. Also, structural characteristic of nanofibers before and after hot pressing has been investigated using scanning electron microscope (SEM) and high-resolution transmission electron microscope (HRTEM).

2.4 Carbonization

A CARBOLITE tube furnace of 75 mm inner diameter and 600 mm effective length with 1,100 °C maximum temperature was used at 750 °C with nitrogen dynamic flow of 5 ml/min.

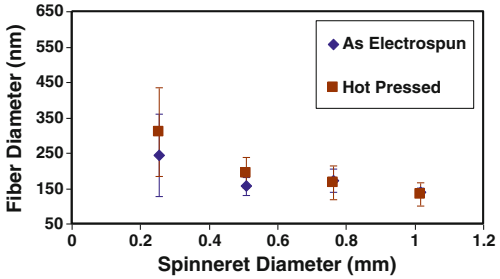


Fig. 5 Effect of spinneret diameter on the produced PAN fibers before and after hot-pressed

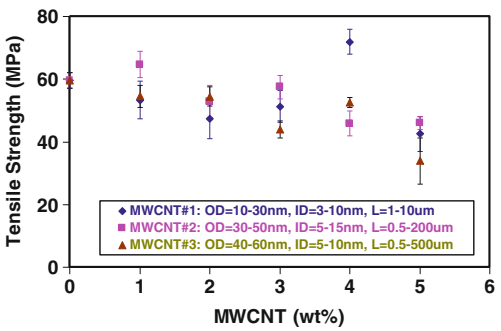


Fig. 6 Tensile strength of hot-pressed MWCNTs/PAN nanofibril composite fabrics

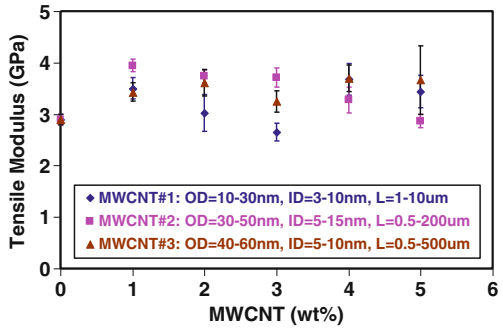


Fig. 7 Tensile modulus of hot-pressed MWCNTs/PAN nanofibril composite fabrics

Samples were placed in ceramic boats for 1 h under the specified condition.

2.5 Tensile test

Five tensile samples of 60 mm length and 5 mm width were cut from the hot-pressed nanofibril hybrid fabrics. Each sample has been weighted to an accuracy of three digits. A Zwick machine with 500 N load cell and 1 μN accuracy has been used with an optical extensometer set-up to investigate the tensile properties (strength and modulus) of the thermally stabilized nanofibril hybrid samples.

3 Results and discussion

3.1 Effect of spinneret diameter on electrospun fiber diameter

As shown in Fig. 4, images of collected electrospun PAN for different spinneret diameters were taken before and after stabilization by using SEM to study the effect of the spinneret diameter on both thermally stabilized and as-electrospun PAN nanofibers. Each was divided into four quarters, and then, ten readings were collected randomly from each quarter in an accurate computerized method. The correlation between fiber diameter and spinneret diameter for both as-electrospun and stabilized PAN nanofibers is presented as shown in Fig. 5; the spinneret diameter of 1.016 mm was found to produce the minimum fiber diameter of 134±32 nm for as-electrospun and 139±12 nm for hot-pressed.

The spinneret inner diameter of 1.016 mm has been recommended to be used to study the effect of MWCNT sizes on the mechanical behaviors of hot-pressed electrospun MWCNT/PAN nanofibril hybrid fabrics within the same other used electrospinning conditions.

3.2 Tensile properties

The stress–strain behavior of hot-pressed MWCNT/PAN samples was similar to the behavior of many tradition materials such as metals and polymers and was not similar to the behavior of commercial in-plane random fiber mats that were usually behaved according to the orientation of their fibers in the applied force direction. However, such a behavior indicates the absence of the single nanofiber role in stress–strain correlation. MWCNT effects on the strength and modulus values were not at the positive side for all concentrations or/and MWCNT sizes. As shown in Fig. 6, there was no clear effect for MWCNTs' weight percent on the strength values; it had almost equally the same value with the control one, or in some cases, it was even decreased. On the other hand, as shown in Fig. 7, adding more MWCNTs increases the modulus of the hot-pressed nanofibril hybrid fabrics compared to the control one. Increases in modulus values could be explained as follows: MWCNTs were acted as a reinforcement for the stabilized PAN fibers; on the other hand, the difference in lengths between the electrospun fibers and MWCNTs (ranged from 0.5 to 500 μm) as well as the effect of both bond and orientation between both of them resulted in a noticeable decrease in the strength of the whole nanofibril hybrid fabrics especially at 5 wt%. The reported maximum strength and modulus values, as shown from Figs. 6

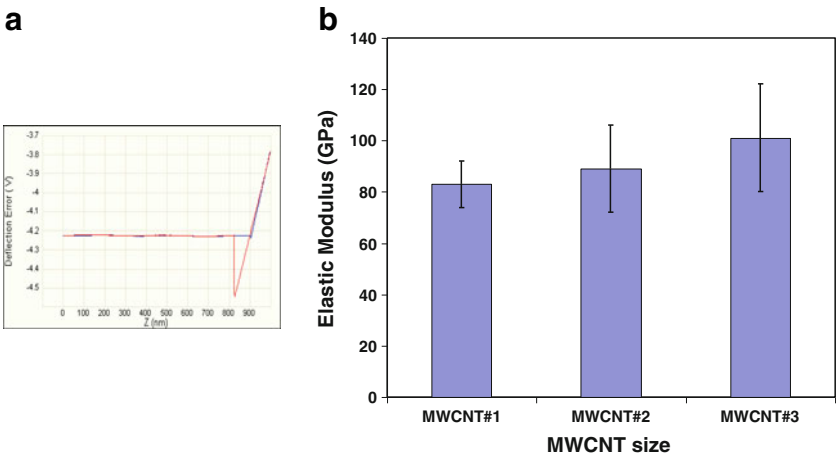


Fig. 8 Effect of MWCNTs sizes on the modulus of single nanofibril composite **a** AFM load–displacement retracted curve. **b** Modulus vs. MWCNTs#

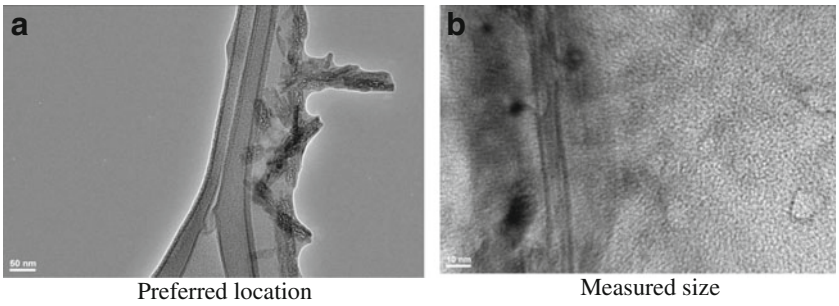


Fig. 9 MWCNTs#1 (hot-pressed samples)

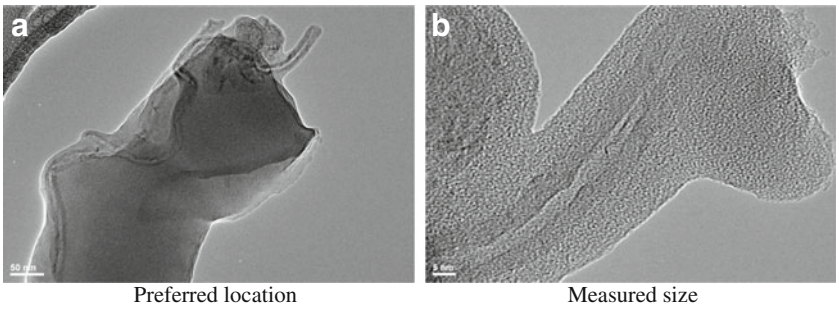


Fig. 10 MWCNTs#2 (hot-pressed samples)

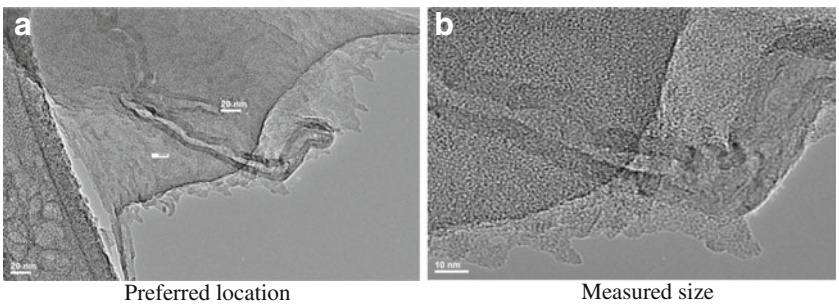


Fig. 11 MWCNTs#3 (hot-pressed samples)

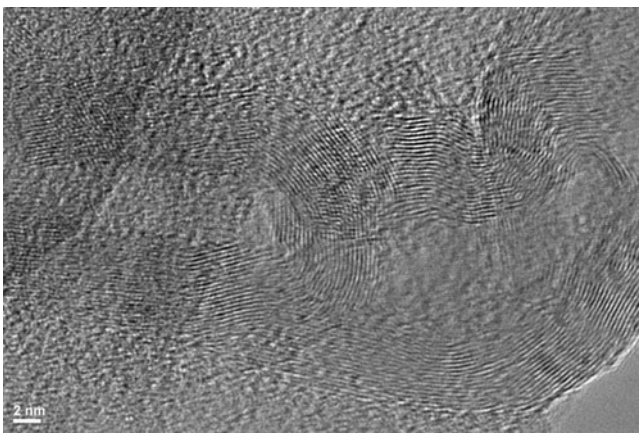
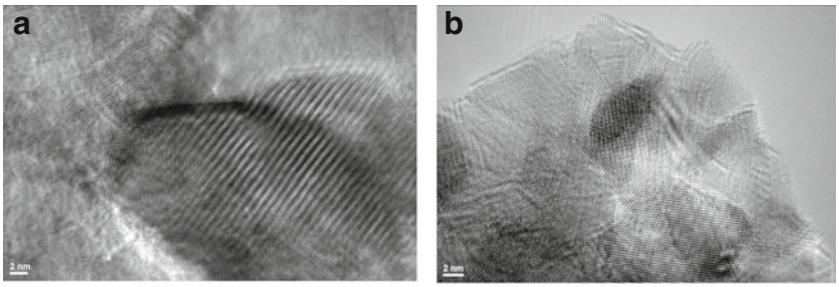


Fig. 12 Formation of 0.333-nm graphite lamellas for hot-pressed samples

and 7, were found to be equal to 71.92 MPa for MWCNT#1 at 4 wt% and 3.95 GPa for MWCNT#2 at 1 wt%, respectively. Based on the reported values shown in Figs. 3 and 7, no solid conclusion could be extracted to describe the effect of MWCNT sizes on both modulus and strength of the fabrics. However, more investigation on the level of single nanofibril hybrid by using an atomic force microscope (AFM) may discover such an unexplained behavior.

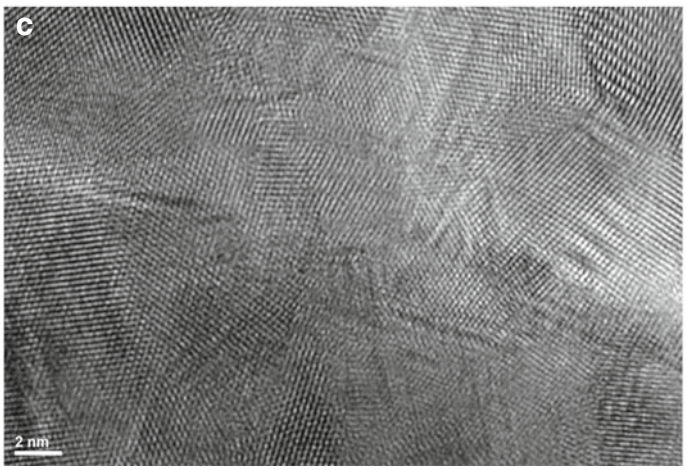
3.3 AFM analysis and single nanofibril composite modulus

The load–displacement retracted curve for AFM taping mode (Fig. 8a) was used to calculate the modulus of elasticity of a single MWCNT/carbon nanofibril hybrid fabric for only three hot-pressed samples at 3 wt% of MWCNT#1, 2, and 3 in order to study the effect of MWCNT sizes on the modulus values.



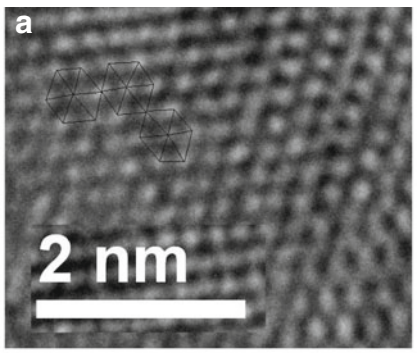
2-D graphitic structure

3-D graphitic structure

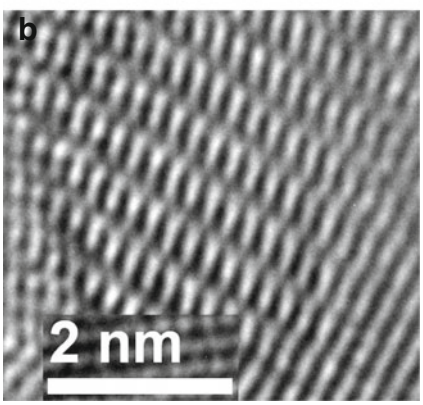


Interaction between MWCNTs and 2-D graphitic structures

Fig. 13 Formation of 0.333-nm graphite lamellas (**a** and **b**) vs. 3-D graphite lamellas (**b** and **c**) (reheat-treated samples)



Graphite Patterns



3-D Graphite Pattern

Fig. 14 Re-heat-treated hot-pressed samples

Ten measurements were taken from each sample, and the average modulus calculated values are found to be as follows: MWCNT#1 = 83 ± 9 GPa, MWCNT#2 = 89 ± 17, and MWCNT#3 = 101 ± 21, which indicates (up to that level of study) that MWCNT outside diameter has an effect on the modulus of single nanofibril hybrid value. As shown in Fig. 8b as MWCNT outside diameter and its attached fiber diameter are relatively close to each other a better nano reinforcement effect, might be due to better bonding, could be achieved and a higher modulus was reported. However, the difference between the measured modulus values for the fabrics versus its single nanofibril hybrid was found to be consistent with previous values that have been reported in literature.

3.4 TEM analysis

The following TEM images show the preferred location of dispersed MWCNT and its measured sizes. As shown from Figs. 9a, 10a, and 11a, MWCNTs are located inside the fiber with stick-out phenomenon of a free end; accordingly, the interaction between MWCNTs and stabilized PAN nanofibers was studied by using TEM with focusing on these locations as a desire of forming 3-D graphitic structure due to the direct interaction between MWCNT and graphitized PAN nanofibers.

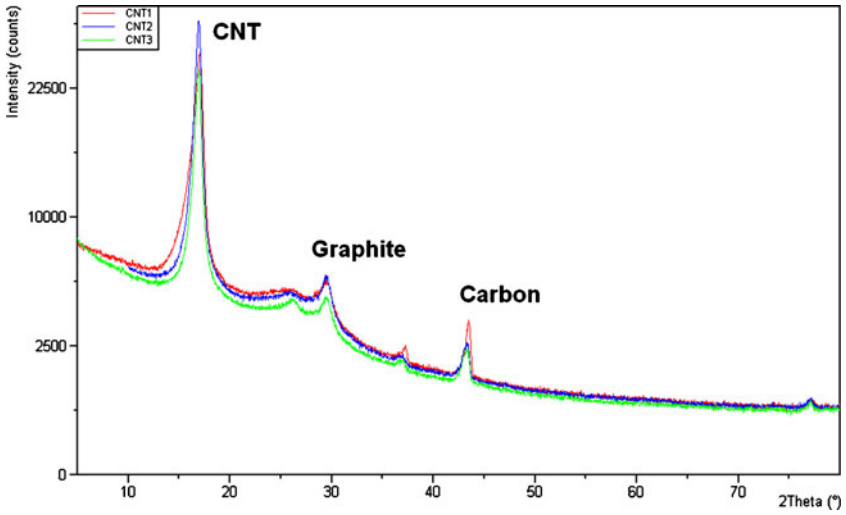


Fig. 15 X-ray shifts for hot-pressed electrospun MWCNTs/PAN samples

The formation of 2-D graphitic structures with 0.333 nm thickness was found as shown in Fig. 12 as a result for the hot-pressed electrospun PAN nanofiber samples. The following high-resolution TEM images shown in Fig. 13 describe a formation of 3-D structures versus 2-D structure, as shown in Fig. 13b and c 3-D structure mostly were found at the far ends, which is consistent with the preferred location that has been reported for MWCNTs for the hot-pressed electrospun MWCNT/PAN nanofibril hybrid fabrics, such structure was formed after carbonization took place for the hot-pressed samples. These thermally stable MWCNT/carbon nanofibril hybrid structures shown in Fig. 13b, c require more discussion for such different 3-D structure to investigate whether it forms due to the interaction of stabilized PAN nanofibers with MWCNTs during carbonization or it is a type of nano diamond nucleation for the MWCNT/carbon nanofibril hybrids due to the effect of both pressure and temperature for materials in nano level.

A close look at 2-D and 3-D graphite lamellas has been taken trying to explain the reason of forming such different two structures, as shown in Fig. 14a and b there are two types of graphitic structures; 2-D as shown in Fig. 14a was formed due to the effect of graphitization of PAN nanofibers only, while 3-D shown in Fig. 14b was formed, up to the best of my speculation, due to the interactions between MWCNTs and PAN nanofibers during graphitization.

3.5 X-ray diffraction analysis

Three samples of MWCNT#1, 2, and 3 at 3 wt% were used after thermally stabilized and graphitized to show the formation of two types of graphitic structures (two shifts). Four identical shifts were reported for the three samples and were identified as shown in Fig. 15 as follows: the first shift identifies the presence of MWCNTs, second shift indicates the discovered 3-D graphitic structure then the one in between the carbon (amorphous), and the 3-D graphitic (crystalline) is the 2-D graphitic structure that has been identified before. More investigation by using Raman spectroscopy is essential to get a clear idea about the discovered 3-D graphitic structure (ongoing research work).

4 Conclusions

Conclusions may be summarized in the following points:

1. Thermally stable and flexible electrospun MWCNTs/carbon nanofibril hybrid fabrics showed an elastic characteristic with a firm, strong, and flexible behavior of 72 MPa strength, 4 GPa modulus, and 5 % maximum strain.
2. The measurement of modulus of elasticity of a single nanofibril hybrid by using AFM technique showed an average value of 83, 89, and 101 GPa for the 3 wt% of MWCNT#1, #2, and #3, respectively.
3. The measured modulus values for flexible nanofibril hybrid fabrics by using UTM (found to be as maximum as 4 GPa) were the measure of the physical bond between MWCNTs and nanofiber and were not the measure of a single nanofibril hybrid elastic property.
4. A novel 3-D like graphite structures for the re-heat-treated samples was discovered by using HRTEM and x-ray diffraction which requires more analysis to identify the exact structure type (whether it is diamond like or another form of graphite structure) as well as its potential application (ongoing research work).

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