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ELECTRICAL CONDUCTIVITY AND DIELECTRIC CONSTANT OF HOT PRESSED MWCNTs/ CARBON NANO FIBRIL COMPOSITE PAPER

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ABSTRACT

Optimum electrospinning conditions by using response surface methodology (RSM) have been recalled from previous work to produce MWCNTs/PAN nanofibril composites. The as electrospun fabrics have been heat treated. SEM have been used to analyze the produced fabrics before and after heat treatment took place The presence of MWCNTs reduces the produced fiber in diameter from 190 nm to 180 nm. Also, the hot pressed sample showed a reduction in fiber diameter and dielectric properties improved by adding MWCNTs as well as by heat treatment. Dielectric constant of 330 and conductivity of 100 S/cm were reported for the flexible MWCNTs/carbon nanofibril composite fabrics at 25000 Hz. Analytical approach has been used to evaluate the electric properties of a single nanofiber and nanofibril composite as function in its fabrics. Calculations of single nanofiber and nanofibril composites showed an increase in it electrical conductivity.

KEY WORDS

Electrospinning, MWCNTs, Heat treatment, Dielectric, Conductivity.

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INTRODUCTION

Polymer nanofiber papers have been fabricated using an electrospinning process that produces nanofibers from an electrically charged jet of polymer solution or polymer melts. The nanofiber diameters range from 40 nm to 2 μm, depending on the polymer types, bias voltage, viscosity of the solution, and so on [1]. One advantage of nanofibers is the high specific surface area developed by creating pores on the nanofiber surface [2]. Mechanical strength of an individual nanofiber is also expected to be enhanced with decreasing diameters [3]. This material has been widely applied to filters [4], scaffolds [5], protective clothing [6], and sensors [7]. Polyacrylonitrile (PAN) has been widely used to fabricate nanofibers owing to their easy carbonization process. PAN nanofiber papers can be used directly for electrode materials after stabilization and carbonization, which cannot be realized in other types of polymers. Another advantage of the carbonized PAN nanofiber is that the nanofiber surface can be modified and functionalized by activation process under different ambient conditions [2]. G. Sui et al. [8] concluded that the Polypropylene (PP) nanocomposite containing 5 wt. % carbon nano fibers (CNF) exhibits a surprisingly high dielectric constant under wide sweep frequencies attended by low dielectric loss. Bal [9] showed an addition of 1 wt% of carbon nanofibers brought improvement in electrical properties of epoxy composite.

Spitalsky et al. [10] studied nanotube/ polymer composites in which the presence of interconnected nanotube network results in a dramatic increase of their electrical conductivity. Also, nanocomposites based on Polymethylmethacrylate (PMMA) and MWCNT as filler show a significant enhancement in the electrical conductivity. The multiwalled carbon nanotubes (MWCNTs)/ PAN (20/80) Wt% composite papers without carbonization possess electrical conductivities of up to 0.5 –1.0 S/cm at ambient temperature. However, the PAN-based carbon nanofibers are often required in many applications, which accompany inevitably stabilization and carbonization process. For instance, the PAN-based carbon nanofiber papers have been directly used for supercapacitor electrodes, where high capacitance of 173 F/g at 10 mA/g was obtained but the power density was poor due to large electrical resistivity of the PAN-based carbon nanofibers [11].

Higher electrical conductivity is always desired to have high capacitance and high power density in supercapacitors [12]. This is the main reason to introduce CNTs in PAN nanofibers. While CNT/ PAN nanofibers were prepared in organic solvent, CNT/poly(ethylene oxide) (PEO) was electrospinned in water with additional surfactant [13]. Dielectric properties vary with the compositions of iron (III) chloride dopant [14]. The permittivity behavior of the device at the frequency below 102 Hz shows the relaxation contribution along with the electrode polarization. Dielectric loss peak in loss tangent also confirms the presence of relaxing dipoles in TNFs. The AC conductance as a function of frequency confirms the semiconducting nature of TNFs and obeys Jonscher's power law except a small deviation in the low frequency region. DC conductivity increases with increase in temperature [15].

Ali [16-20] published a series of publications studying the characteristics of the electrospun PAN/DMF polymer solution in both wet and dry collectors before and after heat treatment as well as with and without nano reinforcements. The present study is an attempt to characterize the electrical and dielectric properties of the hot-

pressed MWCNTs/carbon nanofibril composite paper that can be used in advanced electronic devices. Moreover, it is meant to predict the electrical and dielectric properties of a single nanofiber.

EXPERIMENTAL WORK

Materials

Polyacrylonitrile (PAN) of 150000 g/mol molecular weight from Aldrich catalog no. (181315) was used with10% weight concentration in dimethylformamide (DMF) to form a polymer solution after hot stirring for 3 hrs at 60oC to ensure a complete solubility. MWCNTs size from Aldrich (MWCNT: O.D. = 40-60 nm, I.D. = 5-10 nm, L= 0.5-500μm) has been well dispersed (after 24 sonication hours) inside the PAN/DMF polymer solution within five different concentrations from 1% to 5% by weight.

Electrospinning

The PAN/DMF-CNT polymer solution was poured to fill a clean syringe of 10 ml volume. The syringe was connected to a metal tube of orifice inner diameter 0.9 mm. The metal tube was connected to the power supply at 25kV of positive potential. A metal screen collector of 15x15 cm dimensions was centered horizontal at a 20 cm distance away from the orifice of the metal tube and covered with aluminum foil. The electrospun fibers were collected for about 8 hours.

HEAT TREATMENT

Stabilization

About 2 cm from each side of the collected fiber mat was trimmed then the mat was placed in between two aluminum plates of 110x105 mm dimensions and 10 mm thickness after being covered with aluminum foil. The mold with the mat in between was placed in a hot press set to reach 220oC with no applying pressure for 1 hour until the plate's temperature reached the maximum set temperature. Then 1 metric ton was applied for another one hour. The hot press was then allowed to cool down for another 1 hour while keeping the pressure on until it reaches 100oC then the pressure was released completely from the fabric except the weight of the upper aluminum plate until it cooled down to room temperature. Also, the morphological behavior of the nano fibers before and after hot pressing has been investigated using SEM.

Carbonization

Hot pressed for 3 hour in between single plate and double aluminum foils with 5 Metric Tons at 380 ˚C pressure released after cool down to 100 ˚C.

CHARACTERIZATION

Electron microscopy

Scanning electron microscopy (SEM, JEOL JSM-5600LV) in the Central Laboratory for Elemental and Isotopic Analysis (Atomic Energy Authority Nuclear Research Center, Egypt) was used to characterize the fiber morphology, average diameter and its distribution of the resultant PAN/MWCNTs nanofibers.

Raman spectroscopy

The Raman spectra were recorded with a Raman spectrometer (FT/IR- 6300 type A), and the spectral resolution was 16 cm^{-1}. , Central Metallurgical Research and Development Institute (CMRDI), Egypt.

Dielectric Properties Measurements

Dielectric properties were measured in the frequency range from 50 Hz to 5 MHz at room temperature using H10K13532-50LCR meter at physics lab and electrical power lab at engineering Monofiya University Egypt.

RESULTS AND DISCUSSION

Morphology of nanofibers

SEM pictures Fig. 1 show the fiber diameters and pattern for the as electrospun PAN and the hot-pressed one. It has been found that the fiber kept its morphological behavior after the hot pressing. Also, the measured average fiber diameter for the as electrospun (Fig.1a) nano fibroses paper found to be 194 nm ± 34 nm and 140 nm ± 50 nm for the hot pressed one (Fig.1b). Also at (Fig. 1c) PAN/MWCNT nano fibroses paper found to be 183 nm ± 32 nm and 130 nm ± 32 nm for the hot pressed one (fig.1d).

Dielectric Properties

Dielectric constant (έ)

The dielectric constant showed the ability of a material to store electric potential energy under the influence of an alternative electric field. In (Fig. 2a &2b), at frequency 25000 Hz the effects of MWCNT loading on the dielectric constant (έ) under various heat treatments are shown. The addition of MWCNTs increases the dipole moments and charge carriers concentration. This leads to an increase in the polarizability of the nano-composite, and therefore, the dielectric constant increases.

Dielectric loss (ε˝)

The variation of dielectric loss (έ) with different concentrations MWCNTs at frequency 25000 Hz is as depicted in (Fig. 3a & 3b) the higher value of dielectric loss for the higher concentration of MWCNT can be understood in the terms of

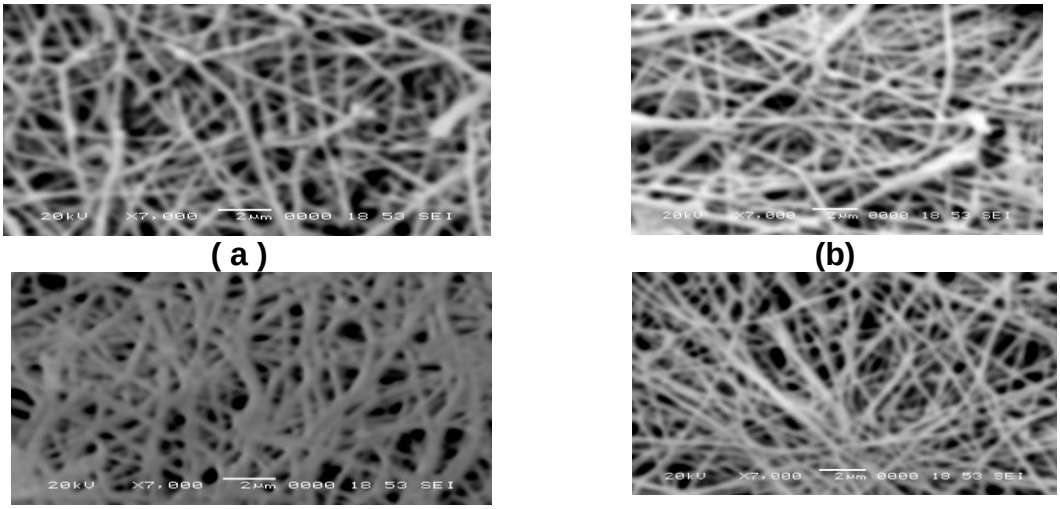


Fig.1. SEM micrographs of composites CNF: (a) Pure PAN As electrospun, (b) Pure PAN hot pressed, (C) 5% MWCNT in PAN As electrospun, (d) 5% MWCNT in PAN hot pressed.

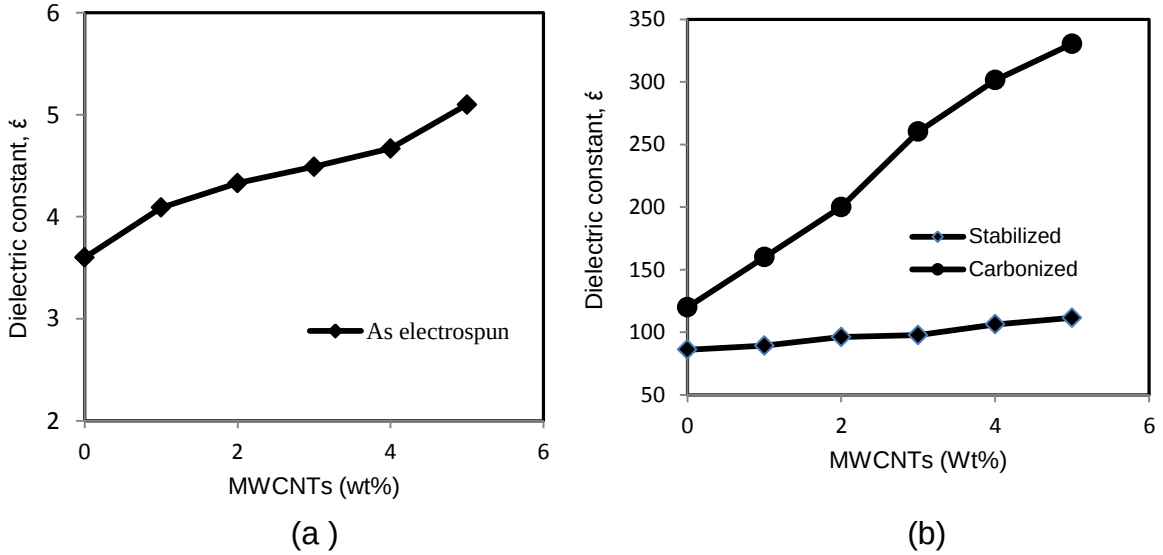
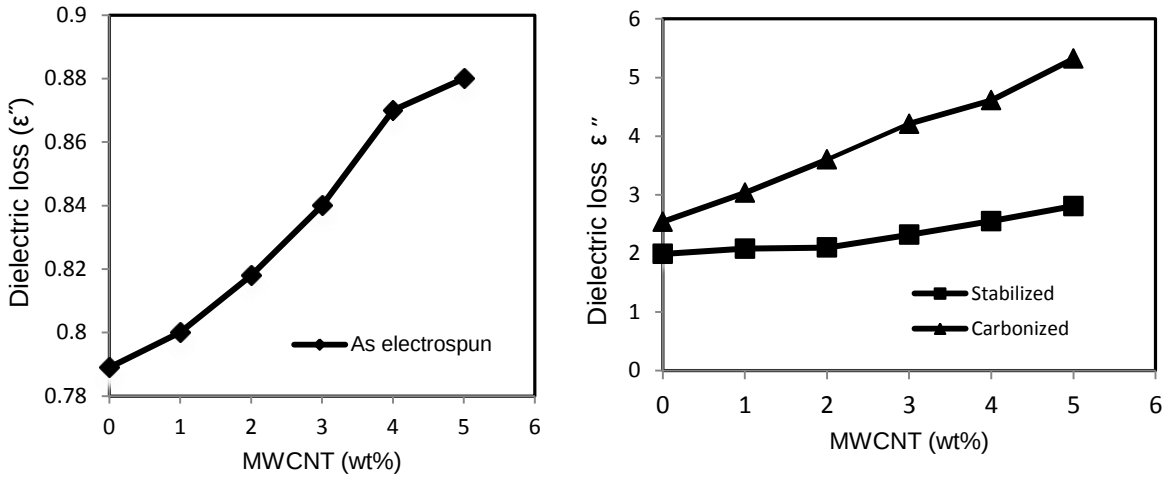


Fig. 2. (a) Dielectric constant as electrospun and (b) Dielectric constant satablization and carbonization for avs. MWCNTs (Wt %) at frequency 25000 Hz.

conductivity, which is associated with the dielectric loss. At Fig. (3b), it was founded that the dielectric losses increases at carbonization larger than stabilization this is due to the graphitic structure might be formed thus the material became having a lot of conductivity.

Conductivity of PAN/MWCNT Paper

One of the potential applications of MWCNT/PAN nanofiber paper as an electrode of supercapacitors and fuel cells, carbonization process is prerequisite prior to



(a) (b)

Fig. 3. (a) Dielectric loss PAN nanofiber as electrospun and (b) stabilization and carbonization PAN nanofiber for avs. MWCNTs (wt %) at frequency 25000 Hz.

applications. Carbonized pure PAN nanofiber papers have in general electrical conductivity of a few S/cm, much larger than that (a few μS/cm) of polymer nanofibers without carbonization [23]. Since MWCNTs have superb electrical properties, we expect a better electrical conductivity in MWCNT/PAN nanofibers. The electrical conductivity of the pure nanofiber paper as electrospun, stabilization, carbonization respectively is 10^{-9}, 4.8 and14.8 S/m as shown in (Fig 4a &4b). As shown in Fig. 4. Carbonization increased the electrical conductivity due to the reduction of sp^3 bonds. No significant conductivity change between perpendicular and parallel directions (Fig. 4a &4c) was observed in pure PAN nanofibers in spite of some preferential alignment along the electrospun direction. The electrical conductivity as a function of MWCNT concentration in terms of carbonization is also shown in (Fig. 4b&4d). The electrical conductivity of the MWCNT/PAN nanofiber papers was enhanced more appreciably at carbonization with increasing MWCNT concentration. This is strongly correlated with Raman spectra, where the relative ratio of graphitic sp^2 (corresponding G-band in Raman spectra) to the insulating sp^3 (D-band) was increased with increasing carbonization temperature and MWCNT concentration. Since MWCNTs are aligned preferentially along the nanofiber_axis and provide good conducting pathways, we expect a higher conductivity along the nanofiber axis. The gradual increase of the conductivity in both directions suggests that the percolation limit was not reached even at 5 wt% of MWCNT concentration. This value is relatively larger than the typical CNT concentration for percolation limit of the bulk polymer [24]. This could be attributed to the insufficient dispersion of MWCNTs in our sample or a characteristic of nanofibers. The parallel component of the electrical conductivity of the MWCNT/PAN nanofiber paper was significantly larger than that of perpendicular component by a factor of about three, regardless of the MWCNT concentration.

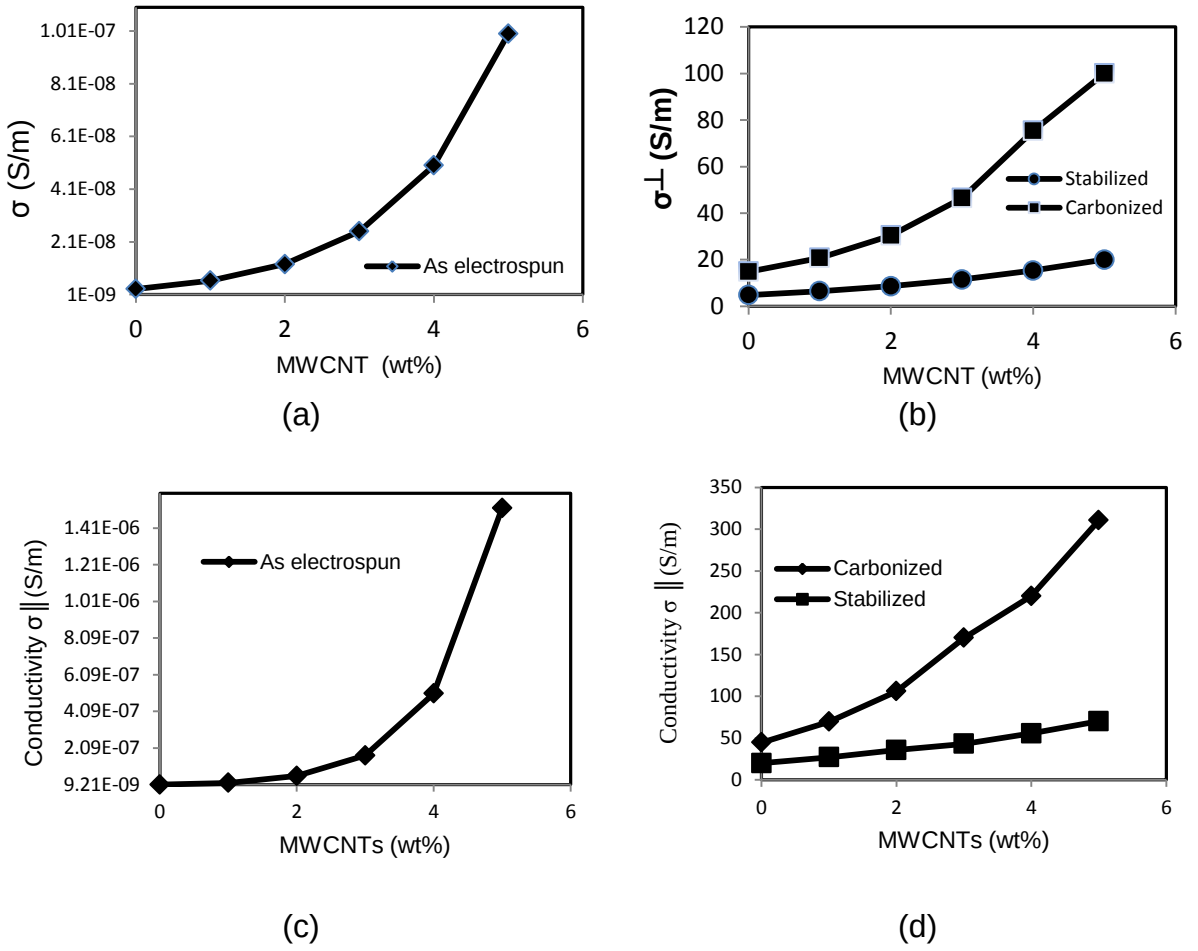


Fig.4. Electrical conductivity of nanofiber fabric as a function of MWCNT concentration in terms of heat treatment (a) vertical component as electrospinning; (b) vertical component at stabilization and carbonization; (c) parallel direction As electrospun and(d) parallel component at stabilization and carbonization.

Conductivity Measurements

The mixing rule is a logical form for estimation of conductivity of composites. The most appropriate form of mixing rule can be written as:

$$\sigma^{\alpha} = (1 - V_f)\sigma_M^{\alpha} + V_f \sigma_A^{\alpha} \quad (1)$$

where σ_M, σ_A conductivity of the individual phase M and A, a constant depends on the morphology of composite, V_f volume Fraction

Conductivity of MWCNTs/carbon single Nanofibril Composite:

$$\boldsymbol{\sigma_{SNFC} = (1 - V_f)\sigma_{CNF} + V_f \sigma_{MWCNT}} \quad (2)$$

where σ_{SNFC} conductivity of single nanofibril composite, σ_{CNF} conductivity of carbon nanofiber, σ_{MWCNTs} conductivity of MWCNTs, V_f MWCNTs volume fraction, it has

been taken as function in Wf% by using the following relationship V_f% has been correlated to W_f% by using the density of MWCNTs = 1.7 g/cm3 and density of carbon nanofiber = 2 g/cm3. α = -1 values of a depends on the configuration between the two materials, for parallel arrangement = 1, for series arrangement = -1 and in random arrangement between -1/3 and 2/3, as MWCNTs is found to be in parallel with the nanofiber as it has been captured α assumed to be equal -1 [25]. From equation (2) we have calculated electrical conductivity for MWCNTs founded equal 4156 (S/m) this result compared with the purified MWCNTs from literature is 1000 (S/m), was founded to be.

Conductivity of MWCNTs/carbon nanofibril composite nonwoven fabrics:

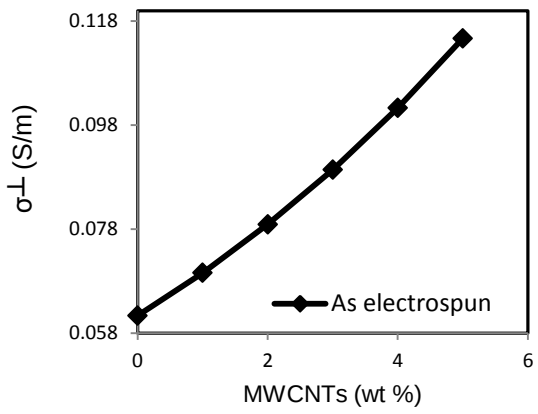
$$\boldsymbol{\sigma_F} = \boldsymbol{(1 - V_f)\sigma_0 + V_f \sigma_{SNF}} \quad (3)$$

where $\boldsymbol{\sigma_F}$ conductivity of the fabric, $\boldsymbol{\sigma_0}$ conductivity of vacuum, $\boldsymbol{\sigma_{SNF}}$ conductivity of single nanofibril composite

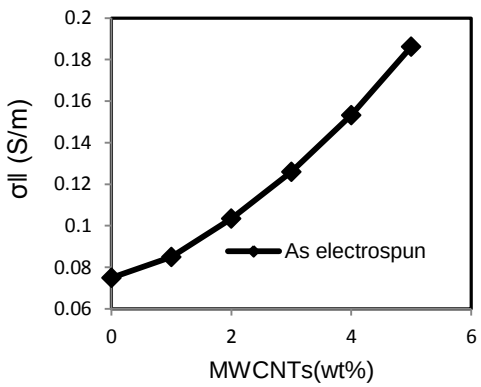
$$\boldsymbol{\alpha = \alpha_1(1 - V_f) + V_f \alpha_2} \quad (4)$$

where $\boldsymbol{\alpha_1}$ and $\boldsymbol{\alpha_2}$ constant depends on the morphology of composite, in random mixture the values of conductivity are limited by upper and lower bound, based on that $\boldsymbol{\alpha_1}$ and $\boldsymbol{\alpha_2}$ values will be as follows: $\boldsymbol{\alpha_1}$ = -1/3, $\boldsymbol{\alpha_2}$ = 2/3. Then $\boldsymbol{\alpha}$ = 0.186 for $\boldsymbol{V_f}$ = 0.508 (fiber to whole fabric volume fraction) counted from randomly selected SEM images by using simple graphical soft ware (Fig.5).

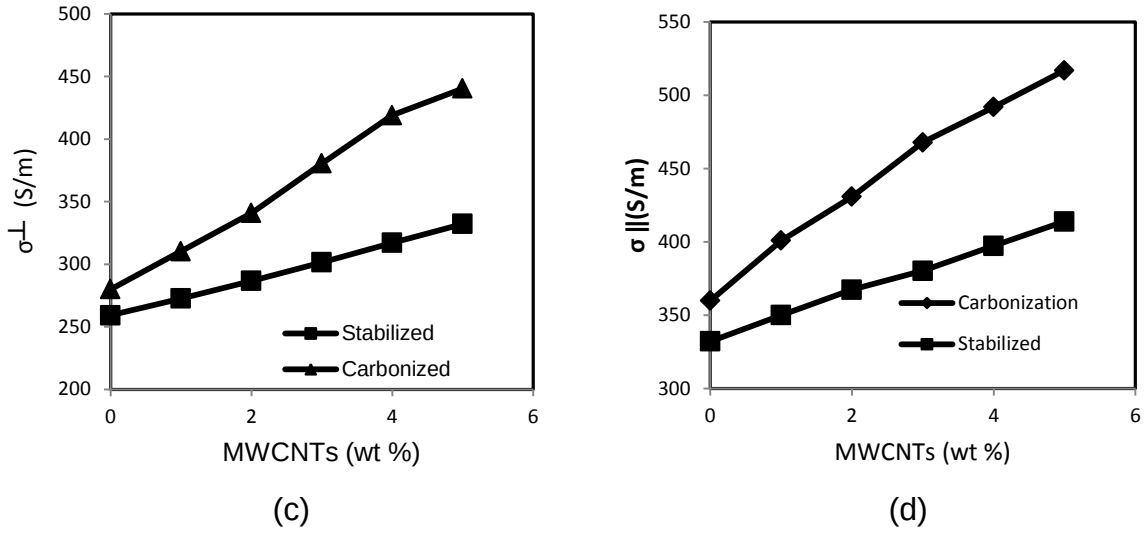
No significant conductivity change between perpendicular and parallel directions (Fig. 5) was observed in pure PAN nanofibers in spite of some preferential alignment along direction. The electrical conductivity as a function of MWCNT concentration in terms of carbonization temperature is also shown in Fig. 5. The electrical conductivity of the MWCNT/PAN nanofiber papers was enhanced more appreciably at higher carbonization temperature with increasing MWCNT concentration. We also found that the electrical conductivity of the carbonized MWCNT/PAN nanofiber papers is highly anisotropic, i.e., the conductivity parallel to the winding direction is about three times higher than that perpendicular to the winding direction at 2 wt% of MWCNT concentration.



(a)



(b)



(c) (d)

Fig.5. Electrical conductivity of MWCNTs/carbon single nanofibril composites in terms of heat treatment (a) vertical component as electrospinning; (b) parallel direction As electrospun; (c) vertical component at stabilization and carbonization and (d) parallel component at stabilization and carbonization.

CONCLUSIONS

Adding MWCNTs to PAN decreased its electrospun fiber diameter from 194±34 nm to 183 ± 32 nm as electrospun. Hot pressing of As-electrospun papers decreased its fiber diameter from 183 ±32 nm to 130 ± 32 nm. We have prepared MWCNT/PAN nanofiber papers by using electrospinning method. The paper was further stabilized and carbonized at different temperatures. We found that the diameters of MWCNT/PAN nanofibers decreased with increasing MWCNT concentration, which was attributed to the enhanced electrical conductivity of the polymer solution at high MWCNT concentration. We also found that the electrical conductivity of the carbonized MWCNT/PAN nanofiber papers is highly anisotropic, i.e., the conductivity parallel to the winding direction is about three times higher than that perpendicular to the electrospinning direction at 5 wt% of MWCNT concentration. The largest dielectric constant of 330 is obtained in the PAN/MWCNTs nanofibrile compoite at 25000 kHz. This ability to control the electrical properties of the composite carbon nanofibers over a wide range, together with their easy integration onto an underlying MEMS structure, should position them as a versatile advanced material for numerous electronic, sensors and inter-connect applications. More detailed investigations concerning the mechanism of CNT catalyzed graphitization in PAN and other carbonizable polymers is an interesting area for future investigations.

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