Author's Accepted Manuscript

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PII: S0167-577X(16)31430-6
DOI: http://dx.doi.org/10.1016/j.matlet.2016.08.125
Reference: MLBLUE21409

To appear in: *Materials Letters*

Received date: 24 May 2016
Revised date: 15 August 2016
Accepted date: 26 August 2016

Cite this article as: Pierre G. Ramos, Noé J. Morales, Silvia Goyanes, Roberto J Candal and Juan Rodríguez, Moisture-sensitive properties of multi-walled carbo nanotubes/polyvinyl alcohol nanofibers prepared by electrospinnin electrostatically modified method, *Materials Letters* http://dx.doi.org/10.1016/j.matlet.2016.08.125

Moisture-sensitive properties of multi-walled carbon nanotubes/polyvinyl alcohol nanofibers prepared by electrospinning electrostatically modified method

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Abstract

Polyvinyl alcohol (PVA) nanofibers reinforced with multi-walled carbon nanotubes (MWCNTs) were fabricated by electrospinning. MWCNTs were introduced into the PVA matrix through the application of an electric field. The morphology of the composite MWCNTs/PVA fibers was characterized by scanning electron microscopy. Results show that the nanofibers had a diameter between 48 and 103 nm and contained a variable amount of MWCNTs. The electrical properties of MWCNTs/PVA nanofibers were investigated by fabricating impedance-type sensors. The impedance and electrical conductivity of the samples were evaluated in the range 46% and 89% relative humidity.

Keywords: Electrospinning, multi-walled carbon nanotubes, nanocomposites, electrostatic, sensors, fiber technology

1. Introduction

In recent years, the development of moisture sensors has become a major branch of detection technology and an important part of modern material science [1]. Polyvinyl alcohol (PVA) is a highly hydrophilic, cheap nontoxic and biocompatible semicrystalline polymer with excellent properties such as strength, low water solubility, gas permeability and thermal characteristics [2]. All these characteristics and its conductivity make PVA a good choice for the synthesis of sensors and new materials, with wide application for the manufacture of supported or self-supported membranes [3]. For this purpose fibers have to be cross-linked, in order to acquire the appropriate mechanical resistance. One way to obtain a convenient PVA mesh, with spacing of the order of the nanometer, is through electrospinning. Electrospinning is a technique widely used to obtain polymer fibers using electrostatic forces [4,5]. The resulting fibers have a high area/volume ratio, making them good candidates for application in a variety of fields, such as sensor design, optoelectronics, tissue engineering and biomedicine [6,7]. The use of fillers can also improve some characteristics of these fibers, such as mechanical and electrical properties [8,9].

Carbon-based materials, because of their good physical, mechanical and electrical properties, have been used as fillers in the manufacture of carbon/polymer composites for many applications [10-12]. In particular, multi-walled carbon nanotubes (MWCNTs) are known exhibit a good response to humidity changes [13,14]. For this reason, it was decided to attempt the development of the present MWCNTs/PVA nanofiber composite.

There are different methods for functionalization of the MWCNTs wall [15-17]. However, some operations tend to damage the MWCNTs wall or being a costly and lengthy process. Here, a novel form of MWCNTs deposition onto surface of the polymer nanofiber is proposed, which uses the electrical field of the electrospinning technique. The MWCNTs/PVA nanofibers obtained by this method exhibiting the MWCNTs exclusively onto its surface have been evaluated by measuring their impedance and conductivity response to humidity changes.

2. Experimental

2.1. Materials

In this work, the MWCNTs used in all the experiments were synthesized in according to Morales et al. [18], while polyvinyl alcohol ($\overline{\mathrm{M}}_{\mathrm{w}} = 61{,}000$, Fluka), was used as a matrix.

2.2. Electrospinning process

The PVA solution was obtained by dissolving 8 g of PVA in 42 g of hot distilled water (close to boiling point) under constant stirring for 1 h (16 w/w PVA solution). This solution was loaded into a plastic syringe fitted with a 0.6 mm diameter hypodermic needle. The needle was connected to the positive terminal of a high-voltage generator while the negative terminal was connected to the fiber collector, a metal cylinder rotating at 120 rpm. The distance between collector and needle tip was 30 cm, the solution flow rate was controlled at 2 mL/h and the voltage between the terminals was set at 62 kV (Fig. 1). The electrospinning process was carried out during 5 hours.

The adhesion of MWCNTs to the PVA nanofibers was achieved by depositing MWCNTs on a metal plate situated at a distance d_0 of the cylindrical collector, as shown in Fig. 1. An amount of 1.7 mg of MWCNT, optimized after running a series of experiment, was deposited at the beginning and after each hour on this plate. The MWCNTs remaining at the end of the process on the metal plate was weighted, so as to obtain the quantity of MWCNTs incorporated into the fibers. Samples were processed with d_0 values of 1.0, 1.5 and 2.0 cm (Table 1).

2.3. Characterization

The morphology of the nanofibers was studied using a scanning electron microscope (SEM, Zeiss Supra 40). Humidity sensors were fabricated using FTO glass conductive plates, where 10 mg of the electro-spun nanofibers were deposited in a section area of 1 cm x 2 cm. The behavior of the samples as humidity sensor was studied between 46% and 89% relative humidity by measuring their impedance under a potential difference of 7.7 V. The relative humidity was measured with a calibrated thermo-hygrometer (Radioshack, mean accuracy: ± 0.5% RH at 22 °C).

3. Results and discussion

3.1. Characterization

Fig.2 shows SEM images for the electrospun MWCNTs/PVA fibers at different d_0 values. It could be seen that MWCNTs/PVA at d_0= 1 cm exhibited smaller diameter (48 ± 8 nm) than PVA (103 ± 10 nm) sample (Fig. 2a and 2b) and some beads in the fiber structure. On the other hand, as d_0 decreased, the diameter of MWCNTs/PVA fibers became thinner (64 ± 14 nm for PVA15 and 98 ± 9 nm for PVA20). Moreover, the quantity of beads in fiber structures diminishes (Fig 2b-d). This is due to the fact that as the plate and the cylindrical collector get closer to each other, they behave like a single structure and therefore increase the stretching of the nanofibers. According to reference [5] an increase in the electrical conductivity of the precursor solution results in a significant decrease of fiber diameter due to increased electric force for stretching the polymer. In accordance with the results, we can infer that the good electrical conductivity of MWCNTs which were incorporated in the PVA nanofiber during electrospinning, reduce the electrostatic potential and thus gives a smaller diameter of fibers during electrospinning.

3.2. Humidity sensor properties

Fig. 3a-d shows the variation of impedance with humidity for the MWCNTs/PVA-based sensor. The decrease in impedance with an increase in humidity is due to the absorption by the PVA nanofibers, of water molecules which gradually fill the pores [19,20].

Since the adhesion of MWCNTs to the electrospun PVA nanofibers improves their electrical properties [21], increasing the amount of MWCNTs also caused a decrease in impedance (Fig. 3b, 3c and 3d), following the same trend that the observed one for pure PVA [20], but with up the three orders of magnitude lower impedance depending on the amount of the MWCNTs within the composite, showing that the MWCNTs contributes positively to reduce it.

Throughout the humidity range studied, the logarithm of the conductivity was directly proportional to the moisture content and the amount of MWCNTs deposited on the nanofibers. This relationship is shown in Fig. 3e for the four types of sensors based on MWCNTs/PVA nanofibers. As shown in the figure, for the PVA20 the conductivity increases from 1.7 x 10^{-4} ms^{-1} to 7.2 x 10^{-2} ms^{-1}, for the PVA15 from 3 x 10^{-2} ms^{-1} to 1.4 ms^{-1} and finally for the PVA10 from 1.7 x 10^{-1} ms^{-1} to 7.7 ms^{-1}. Obtained results also shown that the swelling of the matrix with increasing humidity does not affect the observed trend of conductivity as it does in references [21,22]. This important fact is likely due to the different distribution of MWCNT in the PVA nanofibers. In this work, MWCNTs were placed on the surface of the fiber. The swelling of the PVA mesh with the increasing humidity diminished the space between the MWCNTs, leading to an increment in the mesh conductivity.

4. Conclusions

Different kinds of MWCNTs/PVA fibers were synthesized by electrospinning modified new method. The diameter and morphology of the MWCNTs/PVA fibers were influenced by the d_0 value. The conductivity of nanofibers was the result of MWCNTs addition and it increases with the MWCNTs content. The conductivity of the meshes formed with MWCNTs/PVA nanofibers was sensitive to the relative humidity of the environment. Based on the results obtained, MWCNTs/PVA nanofibers seem to constitute good candidates for application in the field of humidity sensors.

Acknowledgements

This work was supported by INNOVATE-PERU Project No 140-FINCYT-IB-2013, Project No 223, CONCYTEC-2015, the Peruvian-Argentinean 2011–02-CONCYTEC OAJ Project and MINCYT-CONCYTEC PE/11/02, CONICET-PIP 112–200801–02533, UBACYT Nos. 20020100100350 and 20020090100297. RJC and SG are members of CONICET.

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Figures caption

Fig. 1. Diagram of the electrospinning system producing PVA and MWCNTs/PVA nanofibers.

Fig. 2. SEM images of electrospun nanofibers: (a) PVA (d_0 = 0); (b) PVA10 (d_0 = 1 cm); (c) PVA15 (d_0 = 1.5 cm); (d) PVA20 (d_0 = 2 cm); (e) PVA10 with MWCNTs agglomerates; and (f) PVA10 with MWCNTs in the polymer matrix. Where “d_o“ is the distance of MWCNTs to the cylindrical collector. The fiber diameters distributions with corresponding standard deviation (SD) are shown as inserts in (a),(b), (c) and (d).

Fig. 3. The exponential relationship between impedance and RH shift of sensor based on (a) PVA; (b) PVA10; (c) PVA15 and (d) PVA20 nanofibers and (e) Relationship between conductivity and RH for the four types of sensor.

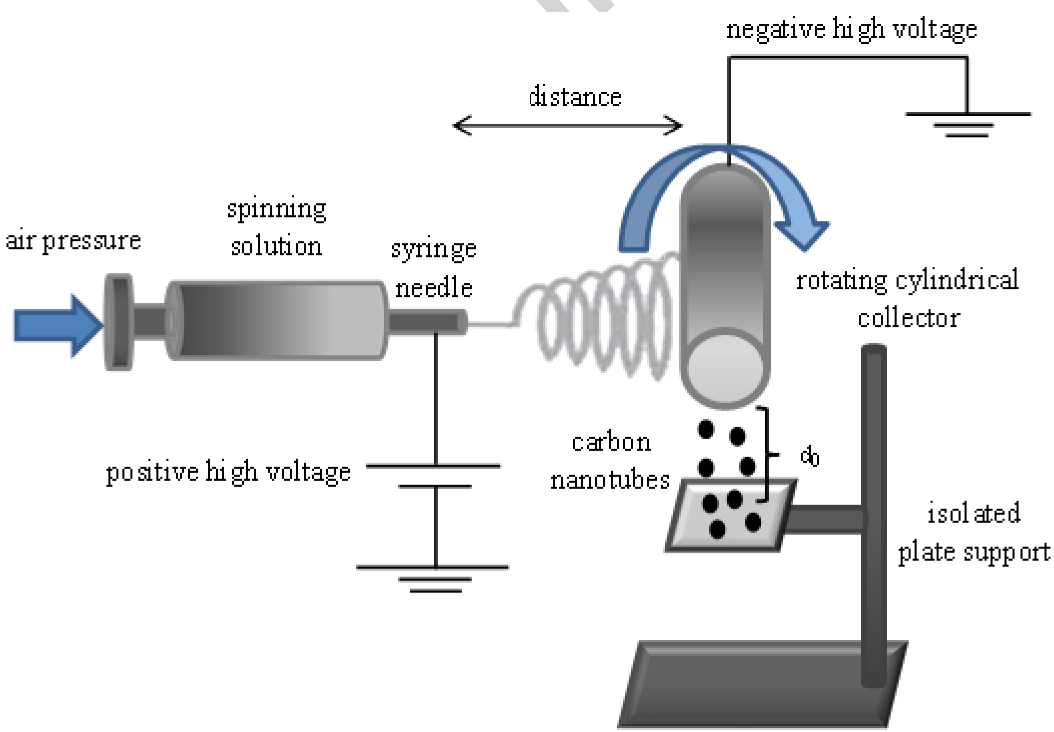
Table caption

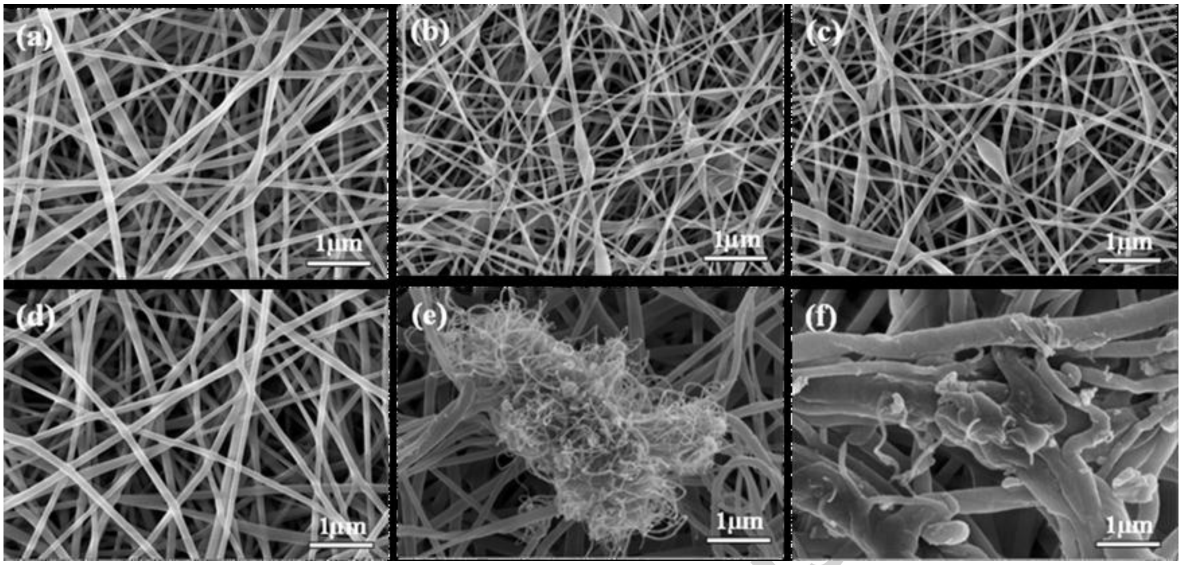
Table 1 - Types of samples obtained

Sample	d_0 (cm)	MWCNTs deposited (%)
PVA	-	0
PVA10	1.0	44.32
PVA15	1.5	18.42
PVA20	2.0	7.38

Highlights

- CNTs / PVA fibers fabricated by electrospinning modified method
- CNTs deposited onto the surface of PVA nanofibers by using an electric field
- CNTs / PVA nanofibers of 52-107 nm in diameter used to sense humidity in air




(a)
1μm
(b)
1μm
(c)
1μm
(d)
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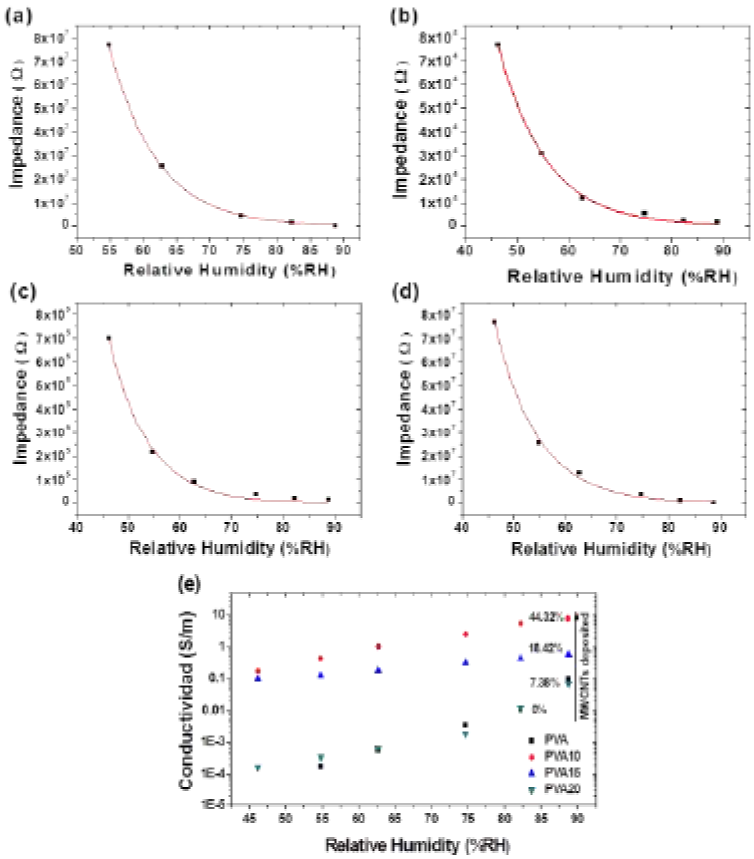
1μm


(a)
Impedance (Ω)
Relative Humidity (%RH)
(b)
Impedance (Ω)
Relative Humidity (%RH)
(c)
Impedance (Ω)
Relative Humidity (%RH)
(d)
Impedance (Ω)
Relative Humidity (%RH)
(e)
Conductividad (S/m)
Relative Humidity (%RH)
44.32%
18.42%
7.38%
0%
MWCNTs deposited
PVA
PVA10
PVA15
PVA20

Graphical abstract