International Journal of Thin Films Science and Technology

http://dx.doi.org/10.18576/ijtfst/050205

Fabrication and Characterization of Nylon 6/ MWCNTs Conductive Polymer by Electrospinning Technique

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Received: 12 Feb. 2016, Revised: 12 Mar. 2016, Accepted: 13 Mar. 2016.
Published online: 1 May 2016.

Abstract: Nylon 6 / with (0, 0.1, 0.2, 0.4, 0.8, 1) wt. % Multiwall Carbon Nano Tubes MWCNTs films conductive polymers were prepared by electrospinning technique. Electrical conductivity for Polymeric solution were measure, increases from (3.8 x 10^{-3} S/cm) for pure nylon 6 solution and increase directly with MWCNTs concentration to (10.2 x 10^{-3} S/cm) at 1 % MWCNTs concentration. Prepared films morphology was tested by SEM and the average fibers diameters measure statically was 140 nm. The nanofibers film show enhancing the electrical conductivity by increase MWCNTs concentration, from (2.9 x 10^{-9} S/cm) for pure nylon 6 film ,increased to (1.042x10^{-6} S/cm) for 0.8 wt. % MWCNT . The solution of nylon 6 / 1% MWCNT cannot be electrospun due to low viscosity and high electrical conductivity associated with high percentage of MWCNT , So there is no produced film from this solution

Keywords: Conductive Polymer, Electrospnning, Nanofibers, Morphology.

1 Introduction

During the past few decades, a great deal of attention has been received to conductive polymers due to the importance of these materials in many important and versatile applications [1]. Conductive polymers can gathering between the electrical properties of metals and organic polymers properties such as the light weight, flexibility and resistance to corrosion in addition to low cost. The properties of conductive polymers can be tailored to get specific applications which considered to be very important criteria [2].

Some of the important applications of conductive polymers are light weight and rechargeable batteries, chemical and thermal sensors, super capacitors, light emitting diodes, organic solar cells and many other applications [3]. There are many methods used to produce conductive polymers like chemical, electrochemical, Hydrogels, composites and electrospinning processes [4]. Conductive polymers preparation by adding MWCNTs to host polymer attracted considerable importance resulting from structural characteristics as high aspect ratio, surface area, with electrical, thermal, and mechanical properties [5]. MWCNTs addition to the polymeric solution before electrospinning has many benefits like producing uniform fibers, fewer fibers diameters as well as less resistivity to electric current [6].

This article will focus on the effect of MWCNT addition firstly, on the properties of nylon 6 solution parameters such as viscosity, surface tension, electrical conductivity and secondly, on the electrical conductivity of films produced by electrospinning technique in different MWCNT wt. % at temperature ranging between 20-100 C°.

2 Electrospinning

Electrospinning is a versatile process used to produce a wide range of polymers in the form of nano- and micrometer-scale fibers. The principle of electrospinning operation is using a high-voltage electrostatic field to draw a jet from a polymer solution [7]. When this jet travels toward the collector electrode, the solvent evaporates and a polymer fiber will be formed. Electrospinning is used to produce the conductive polymers by combining additives with a spinnable polymer. The nanofiber is the ultra-fine solid fibers notable for owing a very small diameter which is lower than 100 nm Nanofibers have large surface area per unit mass as well as small pore size [8].

3 Solution Parameters Effect of Electrospinning Process

There are many solution parameters affecting the electrospinning process such as polymeric molecular weight, viscosity, conductivity and surface tension of the polymeric solution [8]. The effects of the solution parameters may be difficult to isolate because varying one parameter will generally affect other solution parameters,

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for example changing the conductivity of the solution can also change the viscosity [9]. Solution parameters are molecular weight, viscosity, electrical conductivity, and surface tension affects directly the fiber dimensions and morphology.

3.1 Molecular Weight

Increasing the polymeric molecular weight cause increasing the density of chain entanglements (in solution) at the same polymeric concentration. Consequently, the minimum concentration to produce polymeric nanofibers was lower for the highest molecular weight nylon 6 [10].

3.2 Viscosity

Viscosity is one of the most important solution parameters. Nano fibers can be obtained without beds when the polymer solution develops a minimum polymeric chain network in other words minimum entanglement concentration. In fact, both solution viscosity and concentration are closely related to each other [11].

3.3 Electrical Conductivity

It has been found that increasing the solution conductivity or charge density can be used to produce more uniform fibers with fewer beads and smaller fiber diameter. Increasing the of polymeric solution conductivity cause more electric charges carried by the electrospinning jet, this will result in higher elongation forces imposing to the jet under the electrical field. The overall tension will be depended on the self-repulsion of the excess charges on the jet. Thus, increasing the concentration of salts in the polymeric solution increases the charge density, so smaller and more spindles like beads [12, 13].

3.4 Surface Tension

Surface tension is the function of solvent compositions in the solution. It is an effective factor in electrospinning. It is found that different solvents cause different surface tensions. If the concentration of solution fixed, reducing the surface tension of the solution, leading to formation of smooth fibers [7]. It is important to mention that the surface tension control the formation of beads and the beaded fibers. Surface tension role is trying to make the surface area per unit mass smaller by changing the jets into spherical shapes [11].

4 Experimental

4.1 Preparations of Solutions

Nylon 6 solution was prepared at concentration 25% in formic acid solution at temperature (30-40) C°, added to MWCNT solution in formic acid , the mixed solution stirred for sufficient time to increase homogeneity ,then different solution compositions was prepared with different concentrations of MWCNT. Nylon 6 with (0.1, 0.2, 0.4, 0.6, 0.8, 1) wt. % MWCNT were prepared.

4.2 Characterization of Prepared Solution Properties.

4.2.1 Electrical Conductivity of Prepared Solutions

The electrical conductivity for the prepared solutions was measured by electrical conductivity device of type (C and 7110 inolab). The probe of the device was dipped in the polymeric solution and the values of conductivity will be appeared and read easily. The conductivity of solutions would be measured in S /cm.

4.2.2 The Surface Tension

The surface tension of the solutions measured by Surface Tensiometer Model (JYW-200A – LARYEE TECHNOLOGY CO) .The polymeric solution has been poured in a standard Petridish. The standard Petridish place on a stage inside the device where a lever with Platinum rings hanging freely. Firstly the ring must be lowered until it submerged inside the solution, and then the lever was raised gradually until it separate from the solution surface. The units of surface tension (mN /cm) would be displayed.

4.2.3 The Viscosity

The viscosity of the solutions measured by Viscometer of type (DV - II – Pro) Brook field. The top plate had been rotated with controlled rotation rate to provide the shear force on the solution. The value of solution viscosity would be measured by (cp) unit.

4.3 Electrospinning Process

After cooling to room temperature, the solution was electrospun by using electrospun device of type (NaBond Technologies Co.). The solution was applied through a (10 ml syringe needle with internal diameter of 0.6 mm) using a syringe pump of type (NaBond Technologies Co) at a flow rate 3 ml/hr. The electric field was generated using a high voltage supply of about 25 kV.

The positive end was connected to the syringe needle and the collector plate was grounded. The needle-collector distance was 15 cm and the process performs at room temperature. Films obtain from pure solution as well as solutions of (0.1 ,0.2, 0.4, 0.6, 0.8) wt. % MWCNT except the solution of nylon 6 / 1% MWCNT cannot be electrospun firstly , due to low viscosity resulting from increasing the solvent concentration and reducing the polymeric content and secondly , due to high electrical conductivity associated with high percentage of MWCNT.

4.4 Characterization of Electrospun Films.

4.4.1 Scanning Electron Microscopy (SEM)

Scanning electron microscope test is used to characterize the morphology of the electrospun fibers. This test is performed by (INSPECT S50). A small pieces (1×1) cm of the Electrospun films have been cut from the produced electrospun films and prepared for SEM testing. Firstly, the films have to be coated by gold using Fine Coating Ion Sputtering Device (Quorum-Q150R ES). Coating provides for (2) minutes to obtain 100 A^0 thickness.

4.4.2 EDX (Energy Dispersive X-Ray Spectroscopy)

Energy Dispersive X-Ray Spectroscopy was performed in the same test within SEM test to get information about the chemical content inside the nanofibers.

4.4.3 The thickness test:

Due to the big role of electrospun films thickness in the electrical conductivity measurements, it would be a necessary test for films. The thickness of electrospun films was tested by (COATING THICKNESS METER CM 8829S). The electrospun films were put on the devise substrate, and by standing the device probe vertically, touching the films slightly, the thickness will appear on the screen of the device in units (nm and µm).

4.4.4 Preparation of the films for electrical conductivity measurement:

The electrodes used in DC measurement were made by making two squares of silver paste with the aid of mask foil. Figure (1) represents the foil template and the silver paste electrodes used in this research.

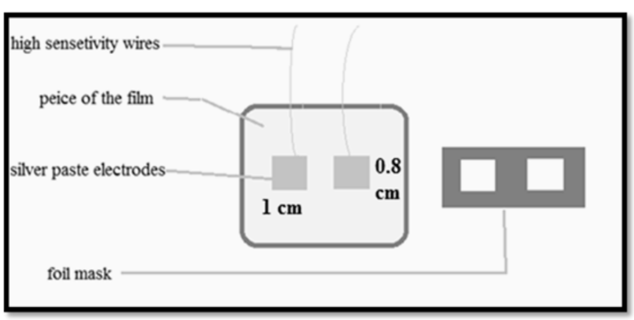

Figure 1: The foil template and the silver paste electrodes.

4.4.5 Electrical conductivity

The electrical resistance of the electrospun films has been measured as a function of temperature in the range (20 - 100) ^oC by making two silver paste electrodes and connecting these electrodes with a sensitive digital electrometer type KEITHLY 616 and electrical oven type memmert . The resistivity of the films can be calculated from the equation:

$$\rho = R.\ W.t / L \qquad (1)$$

Then the electrical conductivity can be calculated from equation:

$$\sigma = 1/\rho \qquad (2)$$

Where ρ: the resistivity of the films, R: the resistance, σ: the electrical conductivity, t: the thickness, W and L are dimensions of the electrodes.

5 Results and Discussion

5.1 solution properties

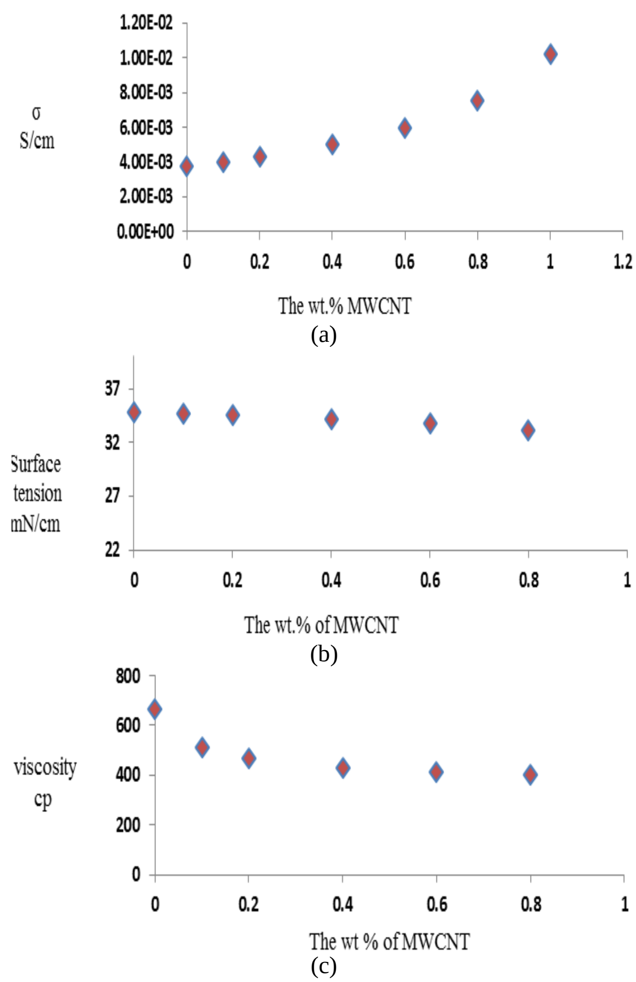

Figure 2: (a) MWCNT effect on the electrical conductivity of polymeric solution; (b): MWCNT effect on the surface tension of polymeric solution; and (c): MWCNT effect on the viscosity of polymeric solution.

The effect of MWCNT was increasing the electrical conductivity of the nylon 6 solution with increasing the wt. % of MWCNT. The electrical conductivity increases from (3.8×10^{-3} S/cm) for pure nylon (10.2×10^{-3} S/cm) for nylon 6 /1%MWCNT .This increasing in electrical conductivity is due to increasing the concentration of charge carriers in the solution. Adding MWCNT cause the formation of additional energy levels between the valance band and conduction band and thus these energy levels will decrease the band gab of the material and the increasing the electrical conductivity. The viscosity and the surface tension decreases with increasing the MWCNT wt.% in the solution duo to decreasing the polymeric content while increasing the solvent content in the resulted polymeric solutions .The effect of MWCNT on the polymeric solution properties represented in fig.2(a, b, c).

5.2 SEM and EDX Results

The SEM image for the pure nylon 6 electrospun film represents fig (3-a). The average fiber diameter of the pure nylon 6 film is 180 nm as shown in fig. (3.b).

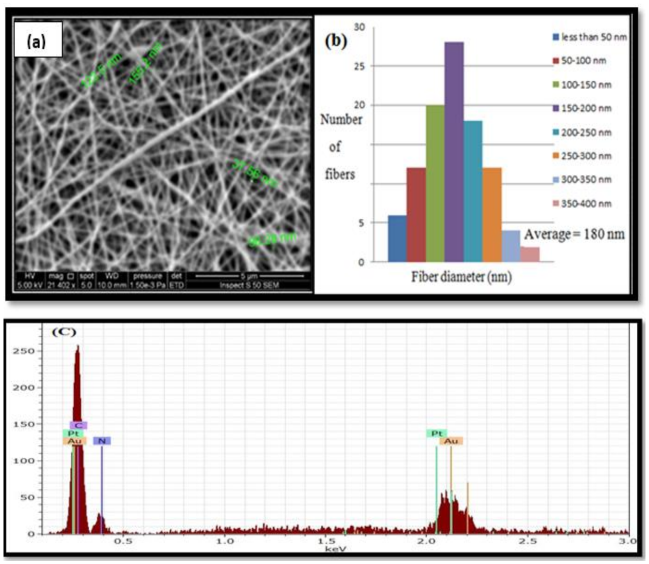

Figure 3: (a) SEM image for pure nylon 6 (b) fiber diameter distribution (c) EDX.

The EDX spectrum analysis of the pure electrospun film as shown in fig. (3.c). The EDX spectra were collected with SEM zoomed into the nanofiber only. The EDX spectra for pure nylon 6 electrospun film suggest the chemical composition which consist of C(Carbon) , N(Nitrogen) , Pt and Au (the platinum and Gold) peaks appear due to coating process required for electrical conductivity of the tested specimen for SEM test. The SEM image for nylon 6 / 0.4wt. % MWCNT film represents in fig (4.a) and the swelling appearing inside the fibers indicates the presence of MWCNT inside the fiber. The average fiber diameter for the nylon 6/ 0.4wt. % MWCNT film is 140 nm as shown in fig. (4.b). Figure (4.c) represents the EDX spectrum analysis of the nylon 6 / 0.4wt.% MWCNT film which suggest the chemical composition consist of C(Carbon),N(Nitrogen) ,O (Oxygen) and Au(Gold) as a result of sample coating process by Au for SEM and EDX.

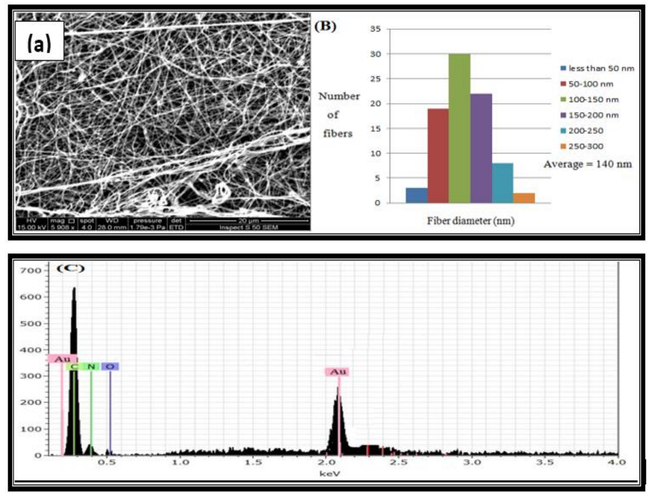

Figure 4: (a) SEM image for nylon 6/ 0.4 % MWCNT (b) fiber diameter distribution (c) EDX spectroscopy.

The diameter of nanofibers was 180 nm for the pure nylon 6 while 140 nm for nylon 6 / 0.4% MWCNT. Decreasing the diameter of nanofibers related to the increasing the conductivity of polymeric solution leading to more charge density and more elongation forces imposed to the jet under the electrical field , so smaller diameter and more uniform smooth nanofiber are produced. From EDX spectrum fig (4.c), it is clear increasing the intensity of carbon peaks inside the nanofiber as compared to carbon peaks in the pure sample spectrum.

5.3 Thickness measuring test results

It has been noted that with constant conditions of electrospinning process, the thickness of electrospun films decreases with increasing the wt. % of additives. The reason is the electrical conductivity of nylon 6 / additive solution will be increased with increasing the wt. % of the additives. When the electrospinning high voltage is applied to the higher electrical conductive solutions (these solution have higher additives content and higher solvent liquid in the polymeric solutions), increasing the solvent content mean reducing the surface tension. This may reduce the quantity and size of the collected fibers on the collectors thus the produced films will be thinner and less thickness, as it is clear from fig. (5)

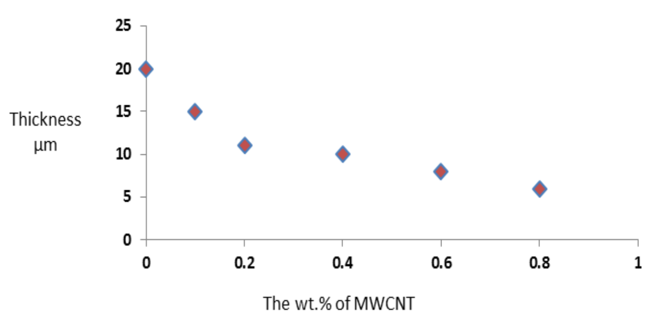

Figure (5): The effect of addition MWCNT on the thickness of nylon 6/ MWCNT electrospun films

5.4 Results of electrical Conductivity Measurements

Nylon 6 is one of the known insulating materials; the electrical conductivity of bulk pure nylon 6 is 10^{-14} S/cm. It is known that the conductivity of known semiconductors as silicon and germanium increased with increasing temperature, this is because of the increasing of charge carriers in the conduction band [14]. The results of this test show decreasing the electric resistance (increase in the electrical conductivity) with increasing the temperature from 25 to 100 C° in a behavior similar to that of semiconductors.

While the pure nylon 6 electrospun film has electrical conductivity equal to 2.9 x 10^{-9} S/cm (due to electrical conductivity results). In general, using the electrospinning process to prepare pure nylon 6 films increase the electrical conductivity five orders than bulk pure nylon 6, this means that the process and dimension of the prepared samples are important in increasing the electrical conductivity. The electrical conductivity of (0.1, 0.2, 0.4, 0.6, 0.8) wt. % are (1.05x10^{-7}, 1.28 x10^{-7} , 3.049x$10^{-7,}$ 4.484x10^{-7} , 1.042x10^{-6}) S/cm respectively. The electrical conductivity increasing due to increasing the density and mobility of charge carriers. Increasing the electrical conductivity with increasing the wt. % of MWCNT .The maximum electrical conductivity resulted with 0.8 wt. % of MWCNT which represented the maximum addition. Fig. (6) Represents increasing the electrical conductivity with MWCNT wt. %.

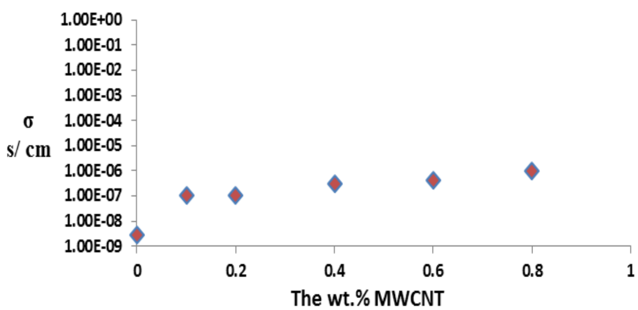

Figure (6): Increasing the electrical conductivity of the produced films with increasing MWCNT wt. %.

6 Conclusion

MWCNT has great effect on the electrical properties of nylon 6 solution and electrospun films. Electrical conductivity of the resulted polymeric solution increases with increasing the MWCNT wt. % in the solution while viscosity and surface tension reduces .The resistance of the electrospun films decreases (the electrical conductivity increases) with increasing the temperature and so the nylon 6 electrospun films exhibit semiconductor behavior. The electrical conductivity increases five orders between the bulk nylon 6 and the electrospun films while increased three orders between pure and doped electrospun films.

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