Effect of NaCl Solution Addition on Improving Some of the Physical Properties of Nylon 6 Solutions used for Electro Spinning Purpose

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ABSTRACT:
Nylon 6 / (0.5, 1, 1.5, 2 and 2.5) wt. % NaCl solutions were prepared for electrospinning technique. The electrical conductivity of polymeric solution increases directly with NaCl concentration from 3.8 (mS/ cm) for pure nylon solution to 12.7 mS/cm at nylon 6/ 2.5 wt. % NaCl, and slight decreasing the viscosity and the surface tension of the solution . Increasing the polymeric solution conductivity cause more electrical charges carried by the electrospinning jet. Prepared films morphology tested by SEM and the average fibers diameters measured for each concentration. In this research, it was proved that the nanofibers film shows decreasing the average diameter by increasing NaCl concentration.
Keywords: Electro spinning , electrical conductivity.

INTRODUCTION

One-dimensional (1D) nanostructured materials such as nanowhiskers, nanorods , nanotubes and nanofibers have been intensively studied due to their technological applications in many areas. The wide range use of 1D nanostructures stems from their ability to precisely control their dimensions, chemical compositions, surface properties, phase purity, and crystal structure [1].

Nylon 6, a thermoplastic polymer [2], is considered as one of three major, synthetic polymers in the fiber industry, and is also widely used in film manufacturing .As shown in Figure 1, the molecular structure of nylon 6 consists of amide groups (CO–NH) separated by linear chains of methylene units [– $(CH_2)_5$ –], and all of the amide groups are oriented approximately perpendicular to the polymer-chain axis [3].

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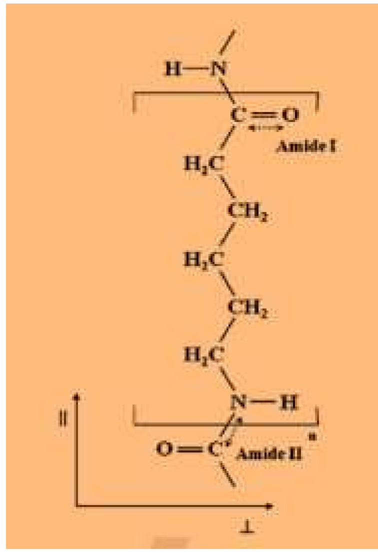

Figure(1):Chemical structure of nylon 6 [3]

Nanofibers have large number of current and potential future applications. These consist of automotive and aerospace, consumer, defense and security, electronics, energy, mechanical/chemical, medical, biological, sensors and instrumentation, and thermal and acoustic insulation. The largest segment of the market is mechanical and chemical products. The second and the third largest segments are energy and electronic products[4].

Electrospinning is a versatile process used to produce a wide range of polymers in the form of nano and micrometer-scale fibers. It is one of the simplest techniques used for obtaining polymer nano fibers characterizing by large surface area to volume ratio [5].

The principle of electrospinning operation is the use of high voltage electrostatic field to draw a jet from a polymer solution. When this jet travels toward the collector electrode, the solvent evaporates and a polymer fiber will be formed [6]as represented in fig. (2)[4].

In the earlier stages of the process, the droplet is held by its own surface tension, until it gets electrostatically charge.When the electric potential is overcome the polymeric solution surface tension, the droplet will have a cone shape before the jet formation called Taylor cone. After the formation of the Taylor cone,the liquid jet is ejected [7].

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].

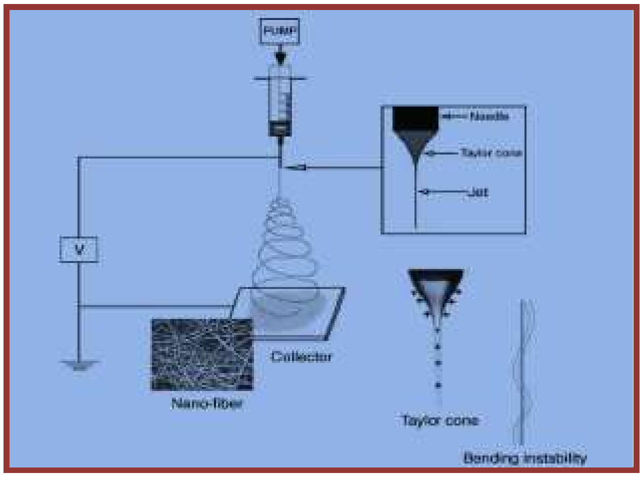

Figure (2): Schematic illustration of the conventional set-up for electrospinning [4].

There are many solution parameters affecting the electrospinning process such as polymeric molecular weight, viscosity, conductivity and surface tension of the polymeric solution [9]. The effects of the solution parameters may be difficult to isolate because varying one parameter will generally affect other solution parameters, for example changing the viscosity of the polymeric solution accompanied with changing the surface tension and conductivity .In fact, both solution viscosity and concentration are closely related to each other [10]. Solution parameters are molecular weight, viscosity, electrical conductivity, and surface tension. These parameters affect directly on the fiber dimensions and morphology. Increasing the polymeric molecular weight causes 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 ofnylon-6 [11]. Nano fibers can be obtained without beds when the polymer solution develops a minimum polymeric chain network, in other words minimum entanglement concentration [12]. 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 [13, 14]. 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 [15]. 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 [16].

Increasing the concentration of ionic salts additions to nylon 6 leads to decrease the viscosity and the surface tension of the produced solution due to reduced the polymeric content. The least viscosityand surface tension of the produced solution the thinnest and smoothest fiberdiameter [17].Decreasing the diameter of nanofibers is and producing smaller and more uniform fibers is also related to increasing the conductivity of polymeric solution as more charge density and more elongation forces imposed to the jet under the electrical field [18]. The electrical conductivity of polymeric solutions increased with increasing the salts additions which is responsible for increasing the number of ions in the produced solutions.

In this research,adding NaCl to nylon 6 solutions is to discussthe effectof NaCl on the electrical conductivity, the surface tension and viscosity of the polymeric solution and the morphology of resulted films

Experimental

Preparations of Solutions:

Nylon 6of high purity was purchased from SIGMA-ALDRICH CHEMINE Gmbh , USA . Nylon 6 solution was prepared at concentration 25% in formic acid solution at temperature (30-40) C°, Sodium chloride (purity 99%) was purchased from Edutek Chemicals Company, India. Solution of Sodium chloride of concentration 5% was prepared by dissolving the salt in formic acid. Thissolution were added separately to pure nylon solution, and the obtained solutions was continuously stirred for (3 hours) at room temperature to increase homogeneity. Nylon 6 / (0.5, 1, 1.5, 2 and 2.5) wt. % NaCl solutions were prepared, stirred for sufficient time to increase homogeneity.

Characterization of Prepared Solution Properties

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. The conductivity of solutions would be measured in mS /cm.

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 is 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.

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.The conductivity, surface Tension and viscosity tests were performed in polymers fibers technology laboratory, Materials Engineering Department, University of Technology.

Electrospinning Process

After stirring the polymeric solution at room temperature, the solution was electrospun by using electrospun device type (NaBond Technologies Co., China)in polymers fibers technology laboratory, Materials Engineering Department, University of Technology. 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 0.3 ml/hr. The electric field was generated using a high DChigh voltage powersupply of 0-50 kV. The anode was connected to the syringe needle and the collector plate was grounded. The needle end-collector distance was 15 cm and theelectrospinning process performs at room temperature.Films obtain from pure solution as well as solutions of (0.5, 1, 1.5, and 2) wt. %NaCl were obtained , except the solution of nylon / 2.5% NaClis unable toelectrospun, as a result of low viscosity and high electrical conductivity, so there is no film associated with this percentage .

Characterization of Electrospun Films .

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 type (Quorum-Q150R ES). Coating provides for (2) minutes to obtain 100 A^0 thickness. Both of INSPECT S50 and Quorum-Q150R ES in Al - Nahren University, Department of Physics, Collage of Science .

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 composition inside the nanofibers.

Results and discussion:

Solution properties

The effect of NaCl on nylon 6 solution was increasing the electrical conductivity of the solution with increasing the wt. % of NaCl. The electrical conductivity increases from 3.8 mS/cm for pure solution to 12.7 mS/cm for nylon 6 / 2.5 % NaCl. This increasing in electrical conductivity is due to increasing the concentration of charge carriers in the solution .Increasing the percentage of salt addation results in increasing the number of ions in prepared nylon / salt solution, which are responsible ofthe electrical conductivity increasing. This explanation agrees with Funda **C.** [19] who explicated increasing the electrical conductivity of PVA solution with the addition of NaCl because the ions of the salts act as charge carriers in a static electric field.

The viscosity and the surface tension decreases with increasing the NaCl wt.% in the solution due to decreasing the polymeric content and in the same time , increasing the solvent content in the resulted polymeric solutions .The effect of NaCl on the conductivity of polymeric solution represented in fig.(3).It has been observed that the viscosity of the (nylon /NaCl) solution decreases with increasing NaCl ratio due to reducing the polymeric content. The effect of NaCl addition on the viscosity of nylon / NaCl solution is shown in fig.(4).The small decreasing in the surface tension for NaCl /nylon solution represented in fig .(5) .The increase in the additive percentage in solution will not lead to increase the additive ratio only , but also lead to reduce the polymeric content which reduces the surface tension of solutions with increasing the additives .

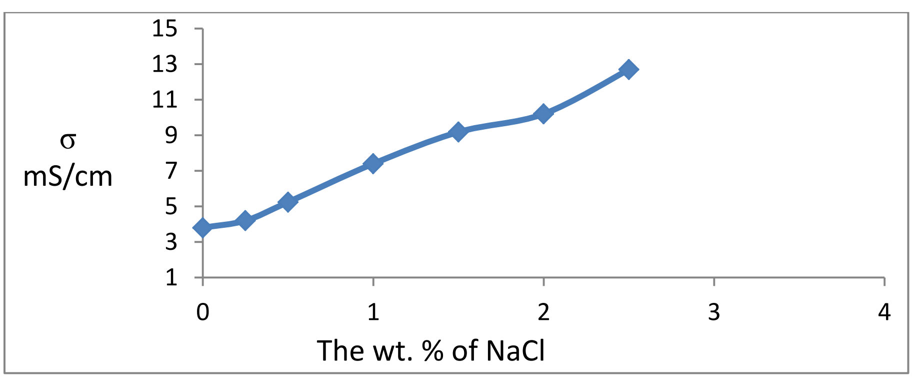

Figure (3): NaCl effect on the electrical conductivity of polymeric solution.

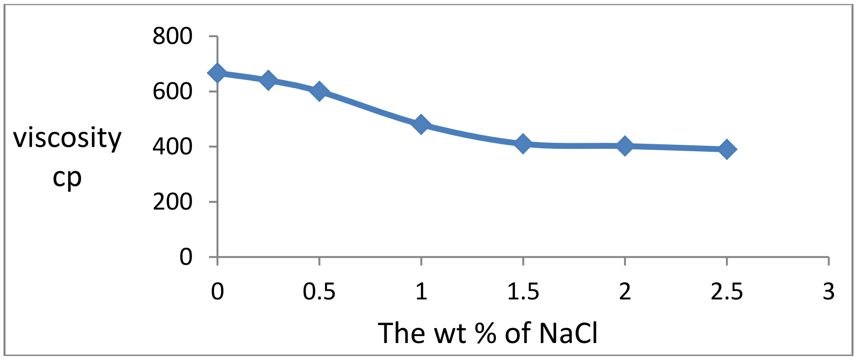

Figure (4): NaCl effect on the viscosity of polymeric solution

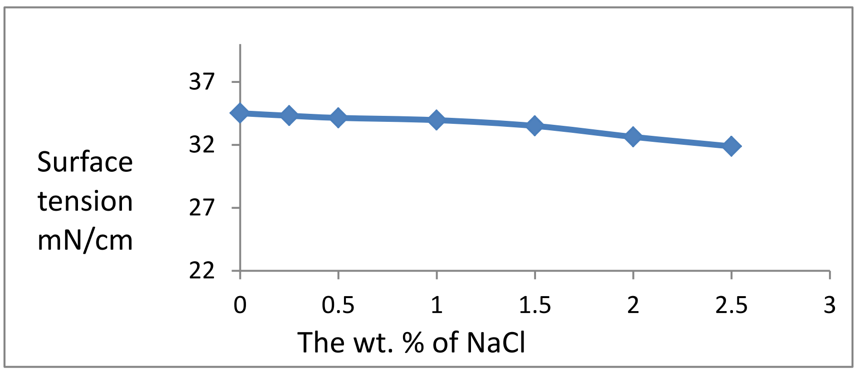

Figure (5): NaCl effect on the surface tension of polymeric solution.

SEM and EDX Results

The SEM image for the pure nylon electrospun film represents fig (6.A). The average fiber diameter of the pure Nylon film is 180 nm as shown in fig. (6.B).The EDX spectrum analysis of the pure electrospun film is shown in fig. (6.C). The EDX spectra were collected with SEM zoomed into the nanofiber only. The EDX spectra for pure nylon 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 . Figure (7.A) represented the SEM image for nylon / 0.5wt % NaCl. This image shows the presence of slight swelling inside the smooth nanofiber, these bulges indicate the presence of ionic salts inside the fiber that illustrated in EDX Analysis later. As shown in the fig. (7.B) , the average fiber diameter is (88 nm). EDX spectra for nylon / 0.5wt, % NaCl electrospun film , represented in fig. (7.C), suggest that the chemical composition consists of C (Carbon) , Na (Sodium) and Cl (Chlorine) peaks due to adding NaCl as an additive that decomposed in electrospinning process to Na and Cl ions .

Fig. (8.A) represents the SEM for nylon /1wt. % NaCl electrospun film and this image shows the presence of slight swelling inside the nanofiber. These bulges appeared clearer than image of the nylon / 0.5wt % NaCl film due to increasing salt percentage. The average fiber diameter was 60 nm, as shown in fig. (8.B) .

Figure (9.A) represents the SEM image for nylon / 2wt.% NaCl film which shows more slight swelling presence inside the smooth nanofiber. The average fiber diameter was 14 nm, as shown from fig. (9.B) .

In comparison between the results of nylon / NaCl films, the smallest fiber diameter was 14 nm for nylon / 2wt. % NaCl. This is due to more proportion of the added salt that leads to more charge density in the polymeric solution, and thus more elongation forces are imposed to the jet under the electrical field, leading to produce smaller diameter and more uniform smooth nanofibers. As it is clear from SEM images, with increasing the NaCl wt. % in the polymeric solution the viscosity and surface tension will decrease, thus smaller fiber diameter will be obtained.

Figure (10) illustrates the effect of increasing the proportion of added NaCl on the diameters of nanofibers. With increasing the proportion of the added salt, smaller fiber diameter will obtained. When the proportion of the added salt increase, more charge density in the polymeric solution will be formed and thus more elongation forces are imposed to the jet under the electrical field, leading to produce smaller diameter and more uniform smooth nanofibers.

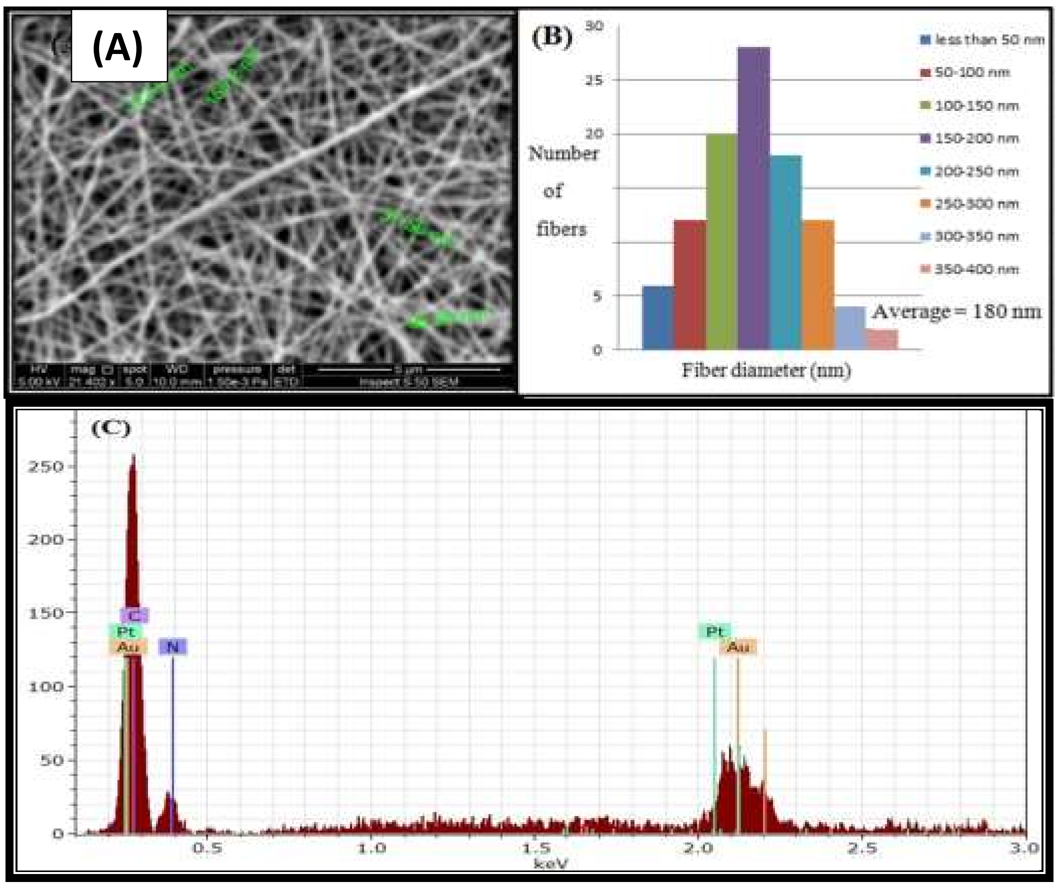

Figure (6): Pure nylon Electrospun film(A): SEM image (B): Fibers diameter distribution (C): EDX spectrum.

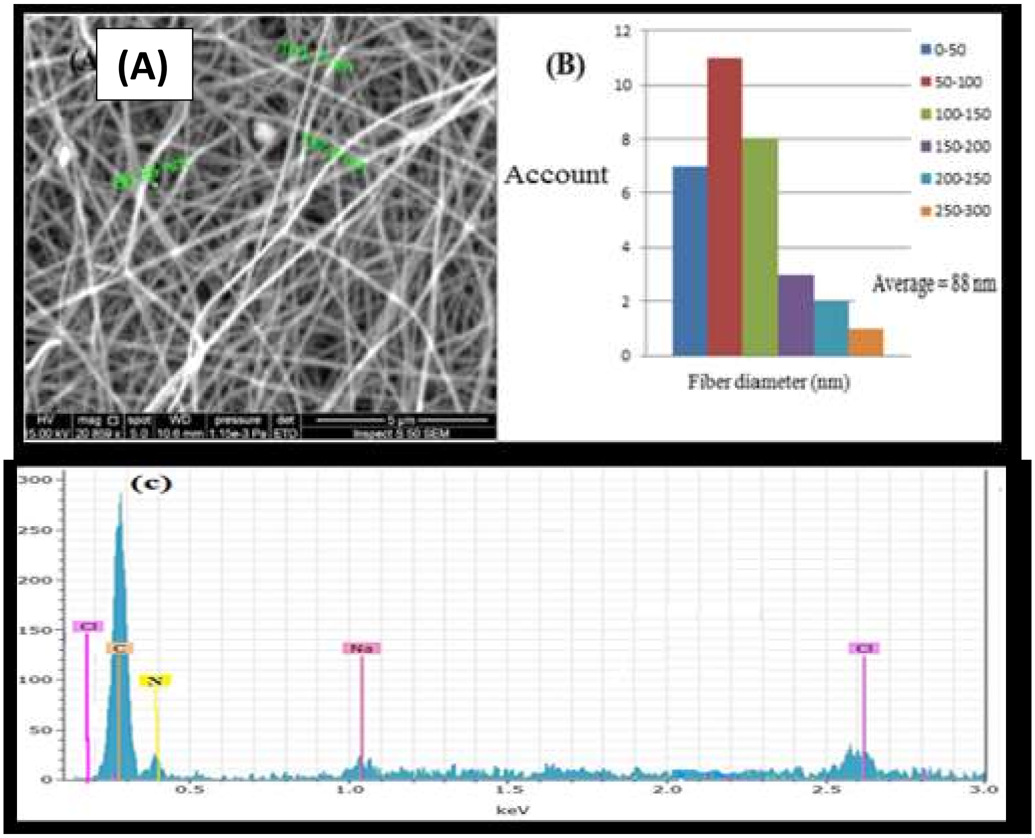

Figure (7) : Nylon / 0.5 wt. % NaCl film (A): SEM image (B): Fibers diameter distribution (C): EDX spectrum.

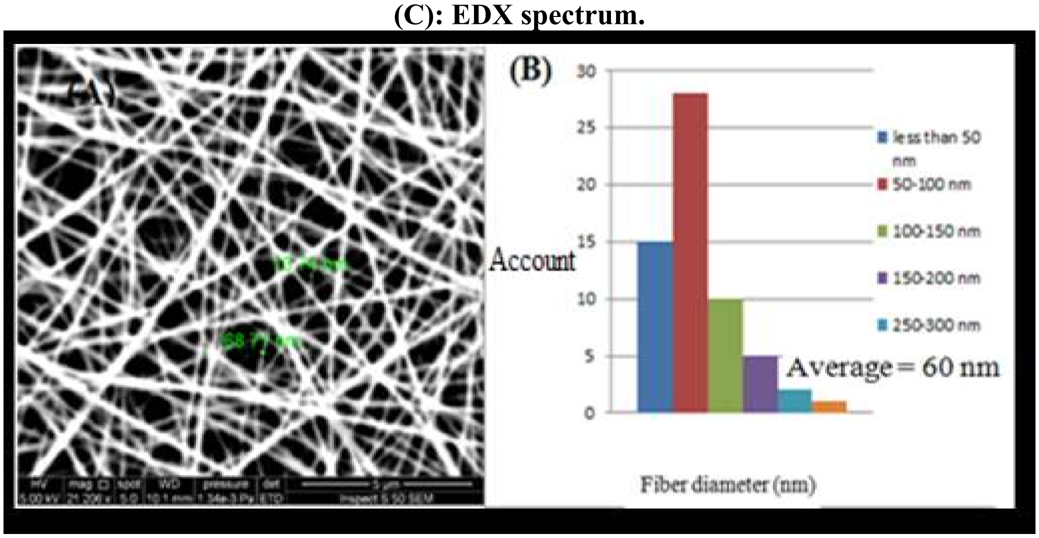

Figure (8) : Nylon / 1wt. % NaCl (A): SEM image (B): Fiber diameter distribution.

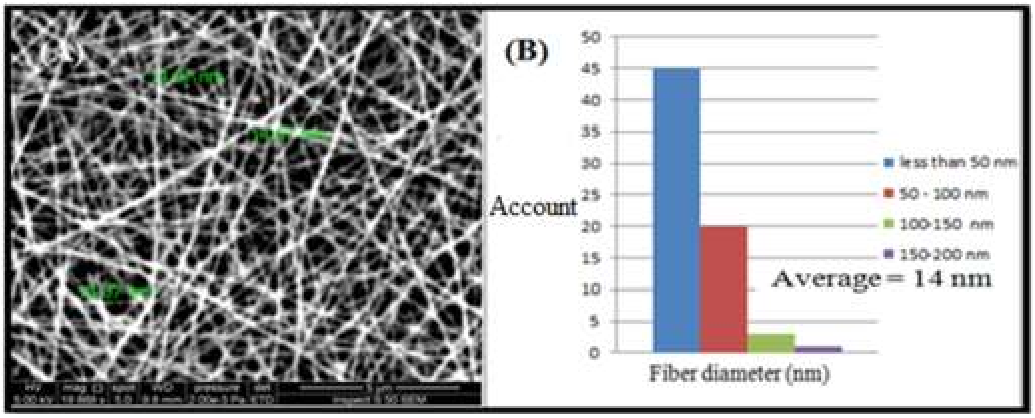

Figure (9) : Nylon /2wt. % NaCl (A): SEM image (B): Fibers diameter distribution.

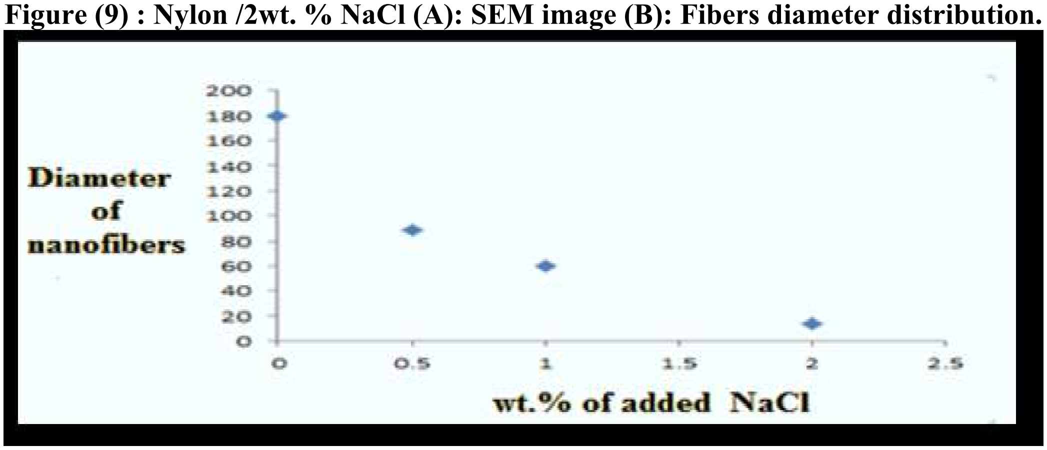

Figure (10): The effect of added NaCl on the diameters of nanofibers.

CONCLUSIONS

NaCl addition has great effect on the morphological properties of nylon 6 electrospun films. Electrical conductivity of the resulted polymeric solution increases with increasing the NaCl wt. % in the solutionas a result of increasing the number of ions in prepared nylon / salt solution.

More proportion of the added salt leads to more charge density in the polymeric solution, and thus more elongation forces are imposed to the jet under the electrical field, leading to produce smaller diameter and more uniform smooth nanofibers. The viscosity and the surface tension of nylon 6 solution decreases with increasing the NaCl wt.% in the solution . With increasing the proportion of NaCl, smaller fiber diameter will be obtained. Increasing the addition of NaCl decreases the polymeric content, reduces the viscosity and surface tension and thus, the fiber diameter decreases from 180 nm for pure nylon 6 film to 14 nm for nylon 6 / 2 wt. % NaCl.

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