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Multiwall Carbon Nanotube / Polyvinyl Alcohol Nanofibers Film, Electrical Conductivity Improvement

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K E Y W O R D S

Electrospun; Nanofiber; Electrical Conductivity; Activation Energy; PVA, MWCNT.

A B S T R A C T

Conductive polymer films were prepared of polyvinyl alcohol (PVA) with (0, 2, 4, 6, 8, and 10) wt. % multiwalled carbon nanotubes (MWCNTs) by electrospinning technique. The morphologies of the synthesized films were tested by scanning electron microscopy (SEM). Average fiber diameters gauged statically was (115nm) for (PVA/10 wt. % MWCNT film) while (170nm) for pure PVA electro spun film. Electrical conductivity (EC) of Polymeric nanofiber films improve by increasing MWCNT addition concentration from (3.69 × 10-7 S/ cm) for the pure (PVA) film to (1.24 ×10-2 S/cm) for the film with 10 wt. % MWCNT. The maximum stress of PVA film were increased by adding MWCNTs concentration, the modulus of elasticity was enhanced from 12.87 MPa for pure PVA to 49.89 MPa for PVA/8wt% MWCNT.

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1. Introduction

Great attention was directed to polymers conducting electricity current during the past few decades. This is due to specific properties as light weight, controlled conductivity and usage in high importance applications such as thermal sensors, fuel cells and so on [1,2]. Simply conductive polymers are polymers conduct electricity. They were produced by many methods [3,4]. Conductive polymers are characterized by intermediate electrical resistivity compare to conductor and classical semiconductors. Their special electronic structures are to monitor for their affect electron affinities [5], and thus conductive polymers are considered materials of the 21st century. Conductive polymers are often called synthetic metals [6] as they have organic characteristics and metal-like properties. They gathered electrical features of metals and semiconductors, with useful behavior of conventional polymers, such as Operating scalability, flexibility, the ability to operate, environmental stability, and low cost [7-10].

Conductive polymers prepared more by adding MWCNTs to host polymers attracted more attention due high surface ratio, electrical, thermal, and mechanical properties specialized to resultant nanofilms [11].

Due to the clear effect of van der Waals forces in MWCNTs structure, it is difficult to manufacture MWCNTs polymer composites with homogeneous dispersion and powerful interfacial adhesion between MWCNTs and the matrix [12]. The conduction pathway formed by MWCNTs allows electrons to move out of the composite structure of fibers. MWCNTs are composed of concentric tubes with one end capped; as a result, only the outer layer participates in electron transmission, resulting in the electrical properties of nanocomposites [13,14]. The interconnecting filler network of MWCNTs allows them to have uniform dispersion. Industrially, it is useful to have a small concentration of MWCNTs to insure enhancement in electrical conductivity [15].

Polyvinyl alcohol (PVA) a very common and useful in high applications because of the excellent chemical resistance in addition to the physical [16]. PVA shows ability to form films and adhesives; it is also resistant to solvents, greases, and oils. PVA is odorless, non-toxic, and high oxygen and aroma barrier [17]. Pure PVA is very high electrical resistivity and can be modified by doping with appropriate concentrations of doping materials like Ag, Ni, Cu, C, and Fe ions, where it is incorporated within the polymeric system, thus conductivity can be enhanced [18]. A wide range of polymers can be produced as fibers with nano and micrometer scales by electrospinning process. This technique is simple and used to obtain polymer nanofibers characterized by large surface area to volume ratio [19]. High-voltage electrostatic field is the principle on which the electrospinning process depends to spray a jet of polymer solution. Polymer fibers are formed by solvent evaporation when the jet travels into the collector electrode. Conductive polymers are produced by combining additives with a spinnable polymer using electrospinning [20]. Produced nanofibers can have diameters less than 100 nm in addition to small pores and large surface areas per unit mass. The electrospinning process for polymer solution is affected by several parameters such as its molecular weight, viscosity, electrical conductivity, and surface tension [21]. Changing one of the parameters will be affected on other parameters. A difference in the electrical conductivity of the solution, for example, will result from increasing MWCNTs solution added to the polymeric solution due to reduction in viscosity and surface tension [22]. These parameters will affect not only fiber dimensions but also fiber morphology. Changing the conductivity of the solution can also change the viscosity. Solution parameters are molecular weight, viscosity, electrical conductivity, and surface tension affects directly the fiber dimensions and morphology [23]. Producing fibers with little beads and small diameters could be done by decreasing the resistivity or increase charge carrier number in the solution. More electric charges loaded by an electrospinning jet will increases conductivity of polymeric solution [24,25]. Surface tension is a function of solvent constituents in the solution, act as active factor in electrospinning. Smoother fibers were formed, with fixing other parameters, when surface tension of solution is reduced [16,26- 28]. Following the results of previous works by the Authors, improving the physical properties of nylon with MWCNTs [6,23], nylon with NaCl additive [26] and with polyaniline [19] where additives in general increase conductivity and decrees activation energy. In this paper, we propose the use MWCNTs with excellent physical properties and conductivity as addition to polymer to improve electrical and mechanical properties of polyvinyl alcohol films produced by electrospinning. Electrical conductivity (DC), activation energy, and tensile strength of (PVA) films with different concentrations of MWCNTs were studied.

2. Experimental

I. Preparation of solutions

PVA was purchased from (Gerhard Buchmann KG Tuttlingen / Germany). The molecular weight for repeat unit was equal to (44.0g/mol) while the total molecular weight was (79000 g/mol) 7wt% PVA dissolve in DW for 6 hr. at 80°C solution was prepared, which was added to MWCNT dispersion solution in formic acid. MWCNTs were from (Nanosheel LLC) as tubes with average radius (20 – 60 nm). To increase the homogeneity of the solution, it was stirred for a sufficient period, then solution combinations were prepared with various concentrations of MWCNTs. PVA / (2, 4, 6, 8, and 10) wt. % MWCNT solutions were prepared.

II. Characterization of solutions before electrospinning process

Electrical conductivities of the prepared solutions were measured via an electrical conductivity instrument (C & 7110 inolab). The conductivity values were taken when the probe of the device was immersed in polymer solution. The conductivity was measured in S/cm.

Viscosities of solutions were measured using a Brookfield viscometer. Solution viscosity was determined in cP.
PVA/MWCNTs solutions surface tension value were performed using tensiometer model (JYW − 200A Laree Tec). Petri dish containing the polymer solution was put on device stage, and a loose Pt ring was immersed in the solution by lowering the lever. The value of surface tension in mN.cm-1 was measured at lever gradually point raised to separate the ring from the solution.

III. Electrospinning process

Cooled prepare PVA /MWCNT solution was it for electrospinning via utilizing an electrospun/ electrospray device (ESB-200). A 5 ml injection needle with interior diameter 0.7mm was used to inject the solution at flow rate 5mL.h-1using an injection pump. The electric potential was created by employing applied voltage of about 25KV. Metallic needle of the syringe was linked to the anode end while the Al collect plate is grounded. Needle end to-collector distance was (140 mm) and the electrospinning was performed at RT. Films were prepared from pure polymer solutions with the addition of solutions of (0.2, 4, 6, 8, and 10) wt% MWCNTs.

IV. Characterization of electrospun films

1. Scanning electron microscopy And Energy dispersive spectroscopy:
The structure of the intended sample was analyzed using (SEM) technique to determine fibers diameter distribution and smoothness using VEGA3 LM SEM. The prepared film was cut and ultrafine Au coating utilizing Fine coat device with of 150 Å thickness. Chemical components of the electrospun films is obtain using EDX to confirm the presence of MWCNTs in (PVA/MWCNTs) film.

2) Thickness measurement:
Prepared films thickness was obtained using coating thickness- meter 9 (CM 8839S. Films thickness value will use later to find electric conductivity and activation energy.
3) Films electrical conductivity:
The electrical measurements included DC conductivities of the electrospun films. The electrodes utilized were made by making a pair of circles of silver paste assisted by a foil template. Figure 1 clarifies Ag electrodes point and mask used in sample preparation.
Film resistance can be determined using the following equation:

$$\rho=(R.w.t)/L \quad (1)$$

and EC determined as:

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

Such that:
ρ: film resistivity (Ωcm-1)
R: resistance (Ω)
σ: electric conductance (S/cm)
t: thickness (cm), w and L: electrodes dimensions (cm)

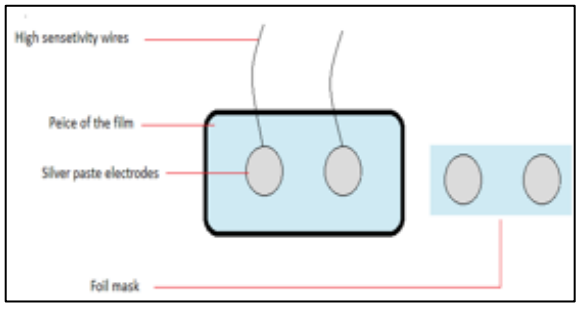

Figure 1: Ag paste electrodes with mask

4) Conductivity measurement:
The temperature function was used to measure the electrical resistances of the electrospun films in the range of (30–100) ºC using a close circuit with sensitive digital nanovoltmeter type (KEITHLY 6517B) and electric oven used to measure the conductivity.

3. Results and discussion

I. Solution properties

Electric conductivity of polymeric solution increased with increasing MWCNT addition. Increasing the wt % of MWCNT led to the production of more conductive pathways in PVA. This increased the mobility and density of charge carriers, which led to a rise in EC. EC for pure PVA solution was (1.047) mS/cm, which rise to (6.18) mS/cm for PVA /10wt%MWCNT, as represented in Figure 2. These results agree with the previous works [25].
Surface tension of PVA/MWCNT solutions reducing with increase MWCNT addition amount, cause in turn decreasing the viscosity of the solution, as represented in Figure 3.
Viscosity of polymeric Solutions decreased with increasing MWCNT concentration amount because of reduction in the polymeric content, as represented in Figure 4 and agree with [6,25].

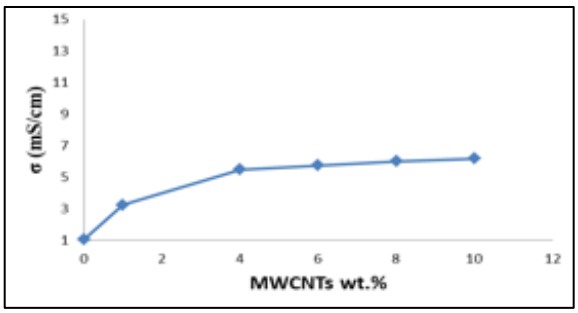

Figure 2: Influence of the addition of (MWCNT) on EC of PVA/ (MWCNT) solutions

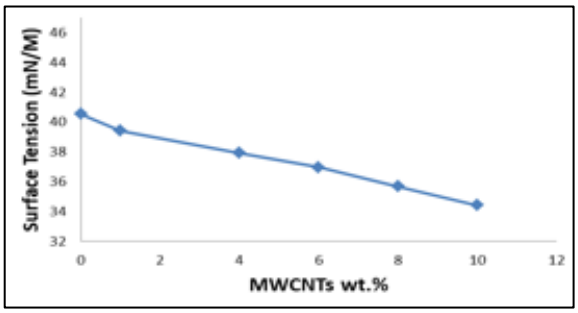

Figure 3: Influence of the addition of (MWCNT) on surface tension of PVA/ (MWCNT) solutions.

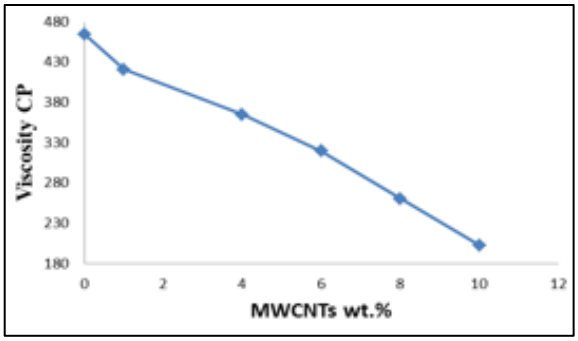

Figure 4: (MWCNT) affect viscosity of PVA/ (MWCNT) solutions

II. Fibers diameters distribution and morphology

Figure 5-A represents the microscopic image of pure PVA electrospin film that appeared to be smooth nanofibers, with 170 nm average diameter and a few microfibers had diameters of about 0.8 – 2.1 µm in the background of the nanofiber films which caused by to fast flow at earlier step of the electrospinning process, showing in Figure 5-B. The chemical component of pure PVA film is appear in Figure 5-C. The (EDS) analysis of pure PVA electrospun film explained the component, which included C in polymer backbone, O, and Au crests, which showed up due to of fine coat ion sputter by gold required for inspecting a specimen using SEM.

The SEM image of PVA / 10 wt% MWCNT film is represented in Figure 6-A. Disorder in the structure of the produced nanofiber network and the small swelling showing up into the fibers demonstrated the presence of MWCNTs inside. The average fiber diameter of PVA / 10 wt. % MWCNT film was 115nm, as in Figure 6-B. These results agree with the results of previous works by the Authors [6, 23, 19, & 26]. Figure 6-C shows the (EDX) spectrum analysis of PVA/10 wt% MWCNTs film, which suggested that the chemical composition consisted of C (carbon), O (oxygen), and Au (gold; because of the process of coating the sample with gold for SEM and EDX).

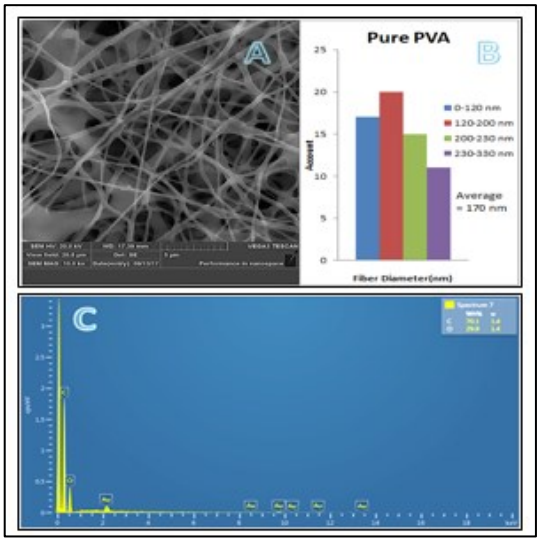

Figure 5: Pure PVA electrospun film (A) electron microscopy picture, (B) fibers dia. histogram, (C) chemical component

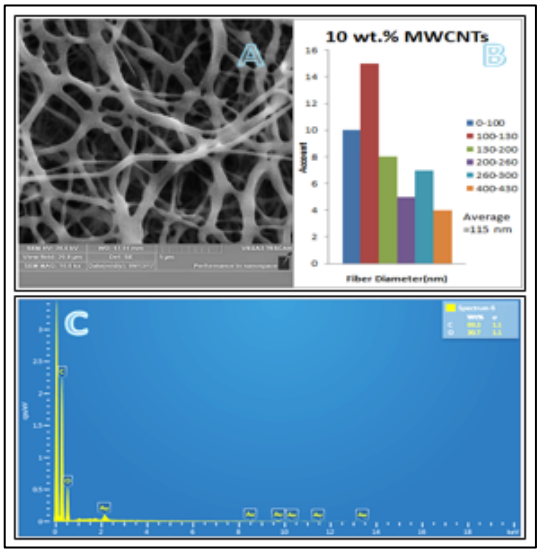

Figure 6: PVA /10 wt% MWCNT electrospun film (A) electron microscopy picture, (B) fibers dia. histogram, and (C) chemical component.

III. Thickness measurement result

It was observed that under constant conditions of the electrospinning process, the thickness of electro spun film decreased with increase in the additive ratio. This was because electrical conductivity of PVA with MWCNTs solution was increased with increase in the MWCNTs addition. When high voltage (during electrospinning) was applied to solutions with higher electrical conductivity, these solutions had larger additives amount, larger solvent means in polymeric solutions. Thus, volatiles dissolved during electrospinning process will cause reduction in the volume and quantity of gathered fibres for the produced films, as represented in Figure 7.

IV. Films electrical conductivity

Polyvinyl alcohol is a known as high insulator -material with DC electric-conductivity of (10-11) S/cm [29], while obtained (3.69× 10-7) S/cm for PVA electrospun film without addition. Utilizing the electrospinning process for preparing pure PVA as thin films improve EC by 10000 greater than solid pure PVA. Indicating that the fabrication method as fibers and thickness of the samples were vital in increasing EC since backbone of a conducting polymer consists of highly delocalized electrons. Activation energy employ means influence on resistance versus temperature, and may be comprehended by the of the nanocomposite fibers according to Arrhenius' equation:

$$\sigma=\sigma_0 \exp(Ea/(K_B T)) \quad (3)$$

Where:

Ea.: activation energy in electron volt (correspond to ((Eg)/2) for intrinsically EC)

T= absolute temperature

kB=Boltzmann constant = (13.8×10-22 Joel/ °K),divided by the electron charge (e= 0.862×10-4 eV).

σ: = Minimum EC at 0°K [22-24].

The electric conductivity (σdc) and Ea of PVA films were measured with variable amount of MWCNTs at different temperatures (303 – 373) °K, as appear in Table 1 and Figure 8 showing (lnσdc) vs. (1000T-1) for those films.

Film Sample	Ea (eV)	σ d.c (S/cm) at 303K
Pure PVA	0.188	3.6
PVA/2wt% MWCNT	0.1275	3.3
PVA/4wt% MWCNT	0.1028	4.1
PVA/6wt% MWCNT	0.0643	7.1
PVA/8wt% MWCNT	0.0343	9.2
PVA/10wt% MWCNT	0.1288	1.2

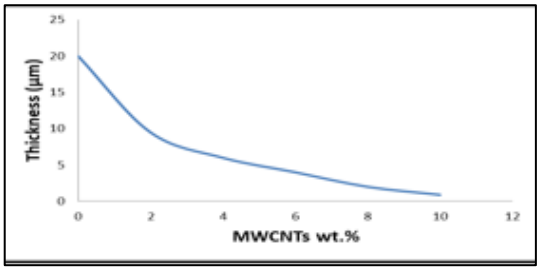

Figure 7: The effect of adding MWCNTs on the thickness prepared films

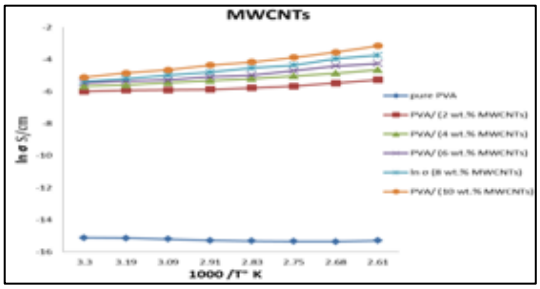

Figure 8: ln σ against (1000/T) of P V A / MWCNT electrospin films

Table 1: Ea and σd.c for prepared PVA / MWCNT films

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PVA/10wt% MWCNT	0.1288	1.2

The DC electric-conductive rose from- (3.69 × 10-7) S/cm for PVA without addition electro spun film up to (3.34×10-3) S/cm for PVA/2 wt.% MWCNTs and (1.24 × 10-2) S/cm for PVA/ 10wt% MWCNTs at 303 K. EC (σd.c) increased about 10000 times with PVA /2% MWCNTs and 100000 times with PVA /10 wt.% MWCNTs.

Electrical conductivity of the produced films increased with increase wt.% of MWCNTs and increase in temperature. This happened as more conductive pathways were produced, leading to increase in the mobility and density of charge carriers. This agrees with Aghelinejad and Leung [29], who observed that both surface and bulk electrical-conductivity increased when the amount of MWCNTs increased. This phenomenon was described by the presence of more MWCNT conductive networks, and thereby a higher number of conductive paths throughout the insulating PVA matrix.

The activation energy of PVA / 10 wt.% MWCNT increased more than that of pure PVA film, while the electrical conductivity of this film was higher than those of other films. This behaviour was due to the greater electrical conductivity of MWCNs and MWCNTs agglomeration due to the higher concentration of MWCNTs in PVA solution. During DC conductivity measurement, when the test temperature increased to more than 343 °K, the activation energy of PVA / 10 wt.% MWCNTs changed. This was due to the formation of new electronic states between the LUMO and HOMO [18]. These results agree with the results of previous works by the Authors. Figure 9 represents the effect of MWCNTs adding on Ea.

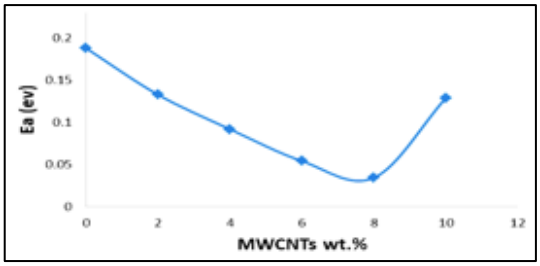

Figure 9: MWCNTs addition effect of on Ea.

V. Tensile behaviour

Tensile behaviour for PVA (without addition) and PVA /8 wt.% MWCNT) is shown in Figure 10. The maximum stress for pure PVA was (1.360) MPa, which increased to (5.748) MPa with the addition of 8wt% MWCNTs. The modulus of elasticity was (12.87) MPa, which increased to (49.89) MPa by adding 8wt% MWCNTs. The maximum strain decreased from 38.98% for pure PVA to 15.28% for PVA/8wt% MWCNTs. This meant that MWCNTs addition to a PVA made the specimens more strength since the nanoparticles of MWCNTs restraining polymer chain mobility, making the electro spin films more strength.

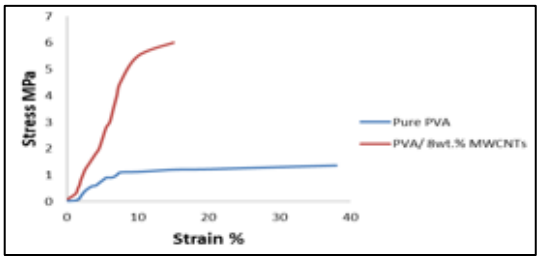

Figure 10: Tensile behavior of PVA and PVA/ 8 % MWCNT films.

4. Conclusion

MWCNT has a significant impact on the electrical properties and electro spun films of (PVA) solution. The quantity of MWCNT was directly proportional to the solution's electrical conductivity, and inversely proportional to surface tension and viscosity. The resistivity of the electro-spun film was inversely proportional to the temperature; PVA films thus possessed the behaviour of semiconductors. The (DC) electrical conductivity rises by four orders between the bulk PVA and electro spun films, while it rises five to six orders between pure electro spun and doped electro-spun films. The mechanical properties and the modulus of elasticity increased by adding MWCNTs.

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