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ELECTRICAL PROPERTIES OF NANOCOMPOSITE FIBERS UNDER VARIOUS LOADS
AND TEMPERATURES

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Abstract

Multi-wall carbon nanotube (MWCNT) based nanocomposite fibers were fabricated using electrospinning method, and their electrical properties were investigated under various loads and temperatures. MWCNTs were initially dispersed into polyvinylpyrrolidone (PVP) and electrospun at various spinning conditions, including DC voltage, pump speed, concentration and distance. When the mechanical load was applied to a film of PVP nanocomposite fibers, the contact resistance, separation between sites and jumping distance of the charge carriers were gradually reduced, thus likely enhancing the electrical conduction. Additionally, as the temperature increased from 20 to 90 °C, the electrical resistance drastically decreased. These behaviors may be a consequence of conductivity and polarization effects of the nanoscale inclusions in the fibers.

Keywords: Electrospinning, PVP Nanocomposite Fibers, Load, Temperature, Electrical Resistance.

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1. INTRODUCTION

Electrospinning is relatively an easy and direct method of fabricating a non-woven mat of polymeric fibers compared to the conventional methods, such as melt spinning, wet spinning, and extrusion molding. Electrospinning uses an electrical charge to form a mat of micro and nanosize polymeric fibers (Figure 1) [1,2]. The polymer solutions dissolved in appropriate solvents are placed in a plastic syringe, and then attached to a syringe pump, generating a constant pressure and flow of the fluid through the tip of the syringe needle. The driving force is provided by a DC electric source through a conductive wire immersed in the polymer

solution. When the intensity of the electric field is increased, the hemispherical surface of the fluid at the tip of the capillary tube elongates to form a conically shaped Taylor cone. The repulsive electrostatic force overcomes the surface tension, and a charged jet of fluid is ejected from the tip of the Taylor cone. The jet of the discharged polymer solution undergoes a drying process in the air, whereupon the solvent evaporates, leaving behind polymeric micro and nanofibers, which lay themselves randomly (non-woven) on a grounded, collecting metal screen. At the end of the spinning process, the discharged jet completely solidifies in two hours, and is then collected on the grounded surface. Adjusting the flow of the fluid, distance, and magnitude of the electric field primarily controls the spinning rate, size, and morphology of the fiber [1-4].

In the electrospinning process, a polymeric solution is held by its surface tension at the end of the capillary tube. The liquid meniscus emanating from the capillary (capillary stress) has a stress of the order of γ/r , where γ is the surface tension of the polymeric solution and r is the radius of the meniscus. The driving force for electrospinning is the electrostatic field. In this case, Maxwell stress can be used to calculate the stresses induced by the electromagnetic field. The Maxwell stress can be given as [1]:

$$\sigma = \epsilon V^2 / H^2 \quad (1)$$

where ϵ is the permittivity, V is the applied voltage and H is the distance between capillary and collection screen. Other forces, such as inertia, viscoelastic and hydrostatic can be neglected in comparison to that due to the high electrostatic field. By balancing the two stresses, the critical spinning voltage can be estimated [1]:

$$V_C = \sqrt{\frac{\gamma H^2}{r \epsilon}} \quad (2)$$

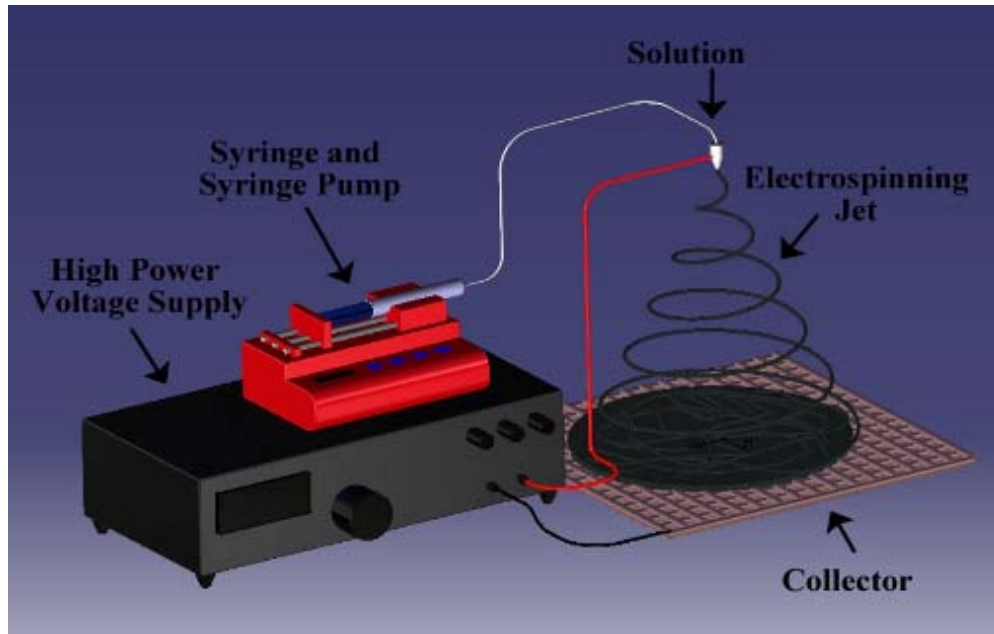


Figure 1: Schematic illustration of an electrospinning process to produce electrospun fibers.

Most of the polymers are insulators with their resistance usually of the order of 10^9 ohm-m. That is why they have potential application in areas where high resistance is required. Load and temperature have direct relationship with the resistance of fibers. When the load is applied on a film of fibers, the molecules of polymer can come closer, heat conduction can become easy, and resistance eventually can decrease.

Polyvinylpyrrolidone (PVP) is a good insulator. When the load is applied on a film of PVP fibers, both the contact resistance and the separation between hopping sites can decrease; therefore, the jumping distance of the charge carriers can decrease, which in turn makes the conduction easier. As the temperature increases on a film of PVP fibers held in a furnace, the resistance decreases drastically. This is because of the fact that at high temperatures molecules vibrate and can transfer translational and rotational energy to neighboring molecules, so the mobility of charge can increase. The rate of decreasing resistance is increased by the addition of MWCNTs. MWCNTs have good electrical and thermal properties, and they can help change the physical properties of the PVP fibers.

2. EXPERIMENTAL

Unless otherwise specified, all chemicals used in the present studies were purchased from Sigma - Aldrich and are all reagent grades. PVP with a molecular weight of 130,000 and ethanol were directly used without further purification or modifications. MWCNTs (Fisher Scientific) have an average diameter of 140 (+/- 30) nm and a length of 7 (+/- 2) μm . PVP was initially dissolved in ethanol and then different percentages (0, 1, 2 and 4%) of MWCNTs were added. After sonicating 30 minutes and then mixing for two hours, the dispersions were electrospun to produce nanocomposite PVP fibers. Figure 2 shows the photographs of the electrospinning unit utilized in the present study. Scanning electron microscope (SEM) was used to determine the fiber diameter and morphology. Figure 3 shows the SEM images of 0 and 2% of MWCNT nanocomposite fibers. The fibers were then placed in a hydraulic press, heated to the specified temperature and loaded up to 9 tons during the electrical resistance measurements. At least, five readings were taken and the results were averaged for each point.



Figure 2: Photograph showing the electrospun nanofibers on the grounded collector.

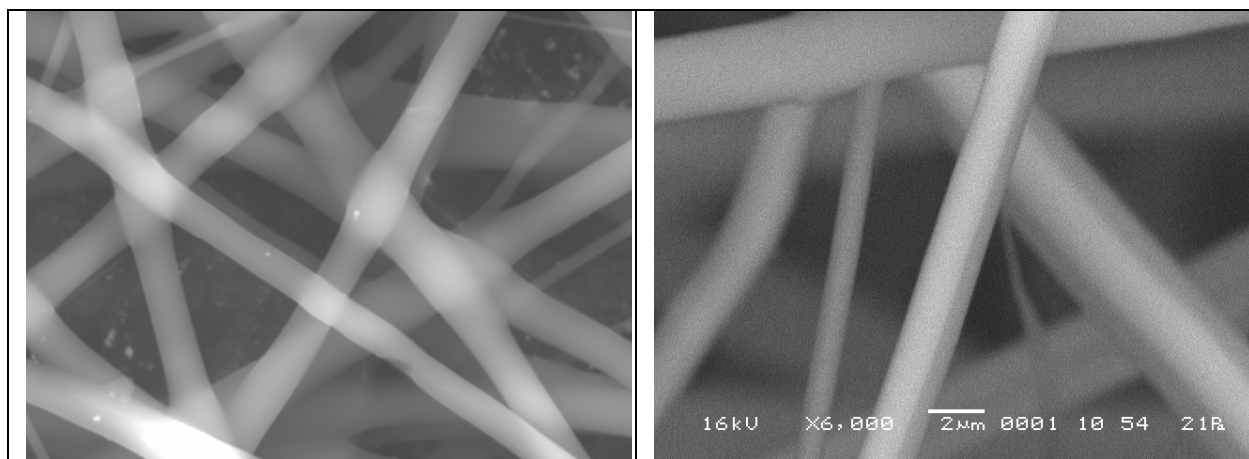


Figure 3: SEM images showing the 0 (left) and 2% MWCNT nanocomposite fibers.

3. RESULTS AND DISCUSSION

3.1 Loading Effects on Electrical Resistance

Figure 4 shows the electrical resistance of PVP fiber films with various MWCNTs and external mechanical loadings. The resistance was measured using the two props (with circular cross section of diameter 2.5 cm) technique and the readings were recorded by a highly sensitive multi-meter while changing loads from 0 to 10 tons. Five loading cycles were conducted for each set of the sample. Generally, for all the samples and cycles, as expected, the resistance decreases with load. This behavior could be explained in view of the well known relation, $R = \rho L/A$, where ρ , L , and A are the resistivity, thickness and the cross section area of the sample, respectively. As the load increases, there are three effects. First, the thickness of the sample reduces to decrease the resistance, second, the hopping length of the charge carriers decreases causing a decrease in the resistivity of the material and thus the resistance

reduces. Finally, as the load increases the contact area between the sample, which is fiber, and the electrode increases, which cause a reduction in resistance. At 0 % MWCNTs (Figure 4a), fiber film resistance is the highest at 0 ton, and gradually reduced at higher loadings. This may be due to the porosity effect at lower loadings. When the number of loading cycle increases, the electrical resistance drastically increases, which may be caused by molecular-level damages on the polymer chains. At 1% (Figure 4b) and 2% (Figure 4c) of MWCNTs in the PVP fibers, the similar behavior could be seen, but the resistance changes are more drastic (higher slopes) especially between 0 and 2 tons of load. After four tons, all resistance curves overlap. In addition to the level of molecular changes, MWCNTs in fibers may be broken at higher mechanical loadings, which generate the observed elevated resistance with the number of measuring cycles. Apparently, as the content of MWCNTs increases, porosity and

resistance may be decreased, due to increased polarizability and concentration of charge carries. At 4% of MWCNTs (Figure 4d), all these effects disappear due to the higher concentration of

MWCNTs. Increasing the content of MWCNTs increases the thermal conductivity of the fibers, as well. The data are not presented here.

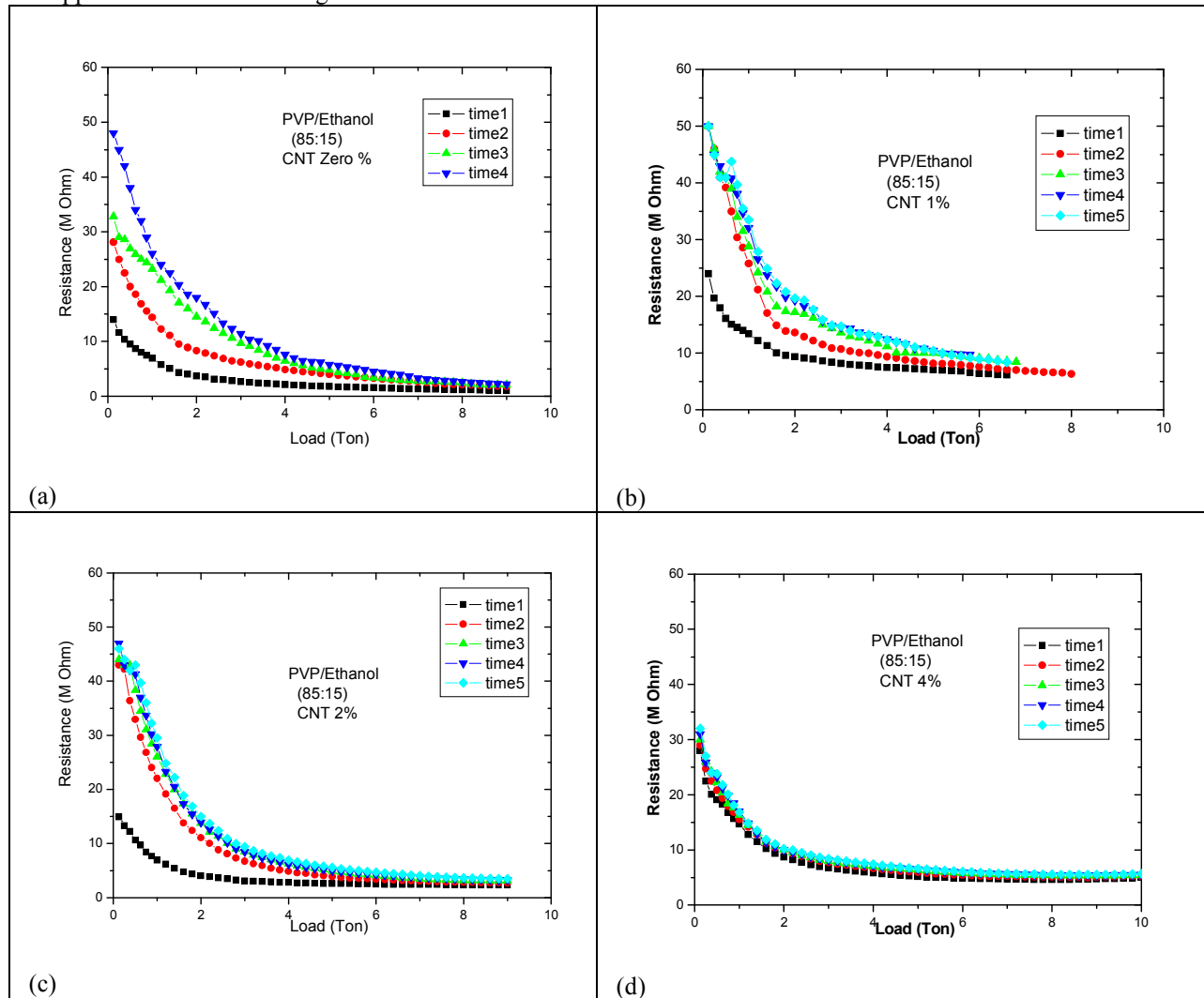


Figure 4: External loading dependence of electrical resistance of PVP fiber films with various MWCNTs concentration.

3.2 Temperature Effect on Electrical Resistance and DSC analysis

Figure 5 shows the electrical resistance values of PVP fiber films at various load, MWCNTs and temperature. At 0, 2 and 4% of MWCNT, the electrical resistance values are quite similar, overlapping on top of each other. It is clear that as the temperature increases, the resistance of all samples decrease. The relation between the temperature and the resistivity for conducting polymers composites, metal oxides and semiconducting materials is governed by the following the equation [14]

$$\rho = \rho_o e^{-\left(\frac{E_p}{KT}\right)} \quad (3)$$

where ρ is the resistivity at temperature T (K), E_p is the conduction activation energy, K is Boltzmann's constant and ρ_o is a temperature independent constant. However, at 1% of MWCNT and 0 ton loading, electrical resistance of the fibers loading differs a little, which may be related to electron charge blockage and release.

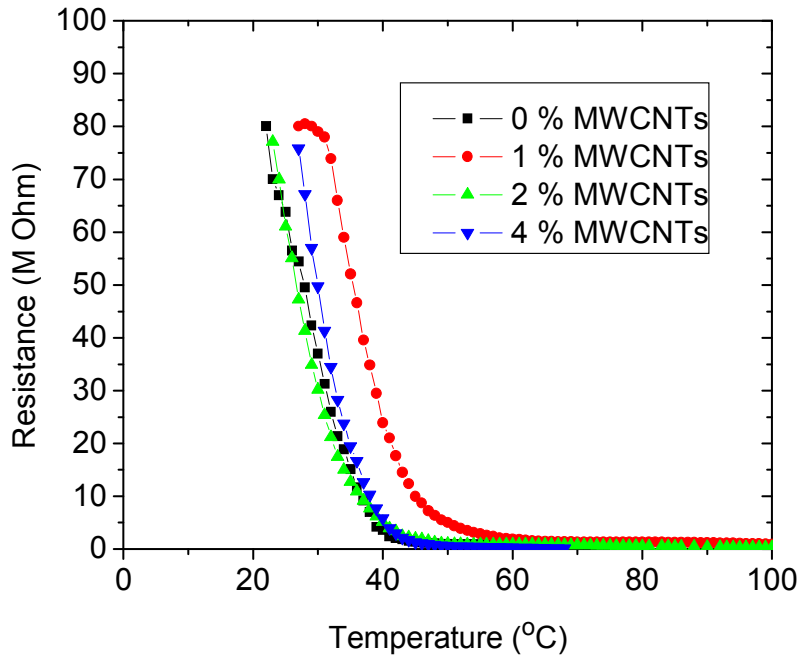


Figure 5: Temperature dependence of electrical resistance of PVP fiber films with various MWCNTs concentration.

As is known, most of the polymers are insulators. Unlike in semiconductors where, the charge carriers occupy states in wide energy bands, the charge carriers in insulators are localized at the atoms of polymer chains. Also, the valence band is almost fully occupied by valence electrons and the very narrow conduction band is practically unoccupied by conduction electrons, with a large band gap in between. It is well known that the localized electrons in ionic insulator do not participate in electrical conduction. However, in random ordering, due to the vibrations, it is possible that the surrounding of ion core, at which the electron is trapped, becomes identical with that of nearest ion core. At this time, the electron hops from the former site to the other. This can be considered as a diffusion of the trapped electron through the material. This mechanism may be the thermally activated hopping conduction. The main feature of that mechanism is the exponential temperature dependence of the charge carrier mobilities. For the process of jumping of electrons or holes, the drift mobility is governed by the following equation [15].

$$\mu = \mu_0 e^{-\left(\frac{E_\mu}{KT}\right)} \quad (4)$$

where μ is the mobility at temperature T (K), E_μ is the mobility activation energy, K is Boltzmann's constant and μ_0 is a temperature independent constant. The Equation (4) indicates that charge mobility is an exponential function of temperature.

Conduction is possible if the electrons in valence band have enough thermal energy to be excited to the conduction band. This can be achieved by heating the polymer fibers, providing enough thermal energy to cause valence electrons to jump to conduction band and may cause electrical conduction. Electrons are transferred from one band to another band by a carrier generation and mobility of carriers. Since the mechanisms of thermally-induced resistance variation are not completely established, more studies will be conducted on the materials to find out the real mechanisms of this variation [14].

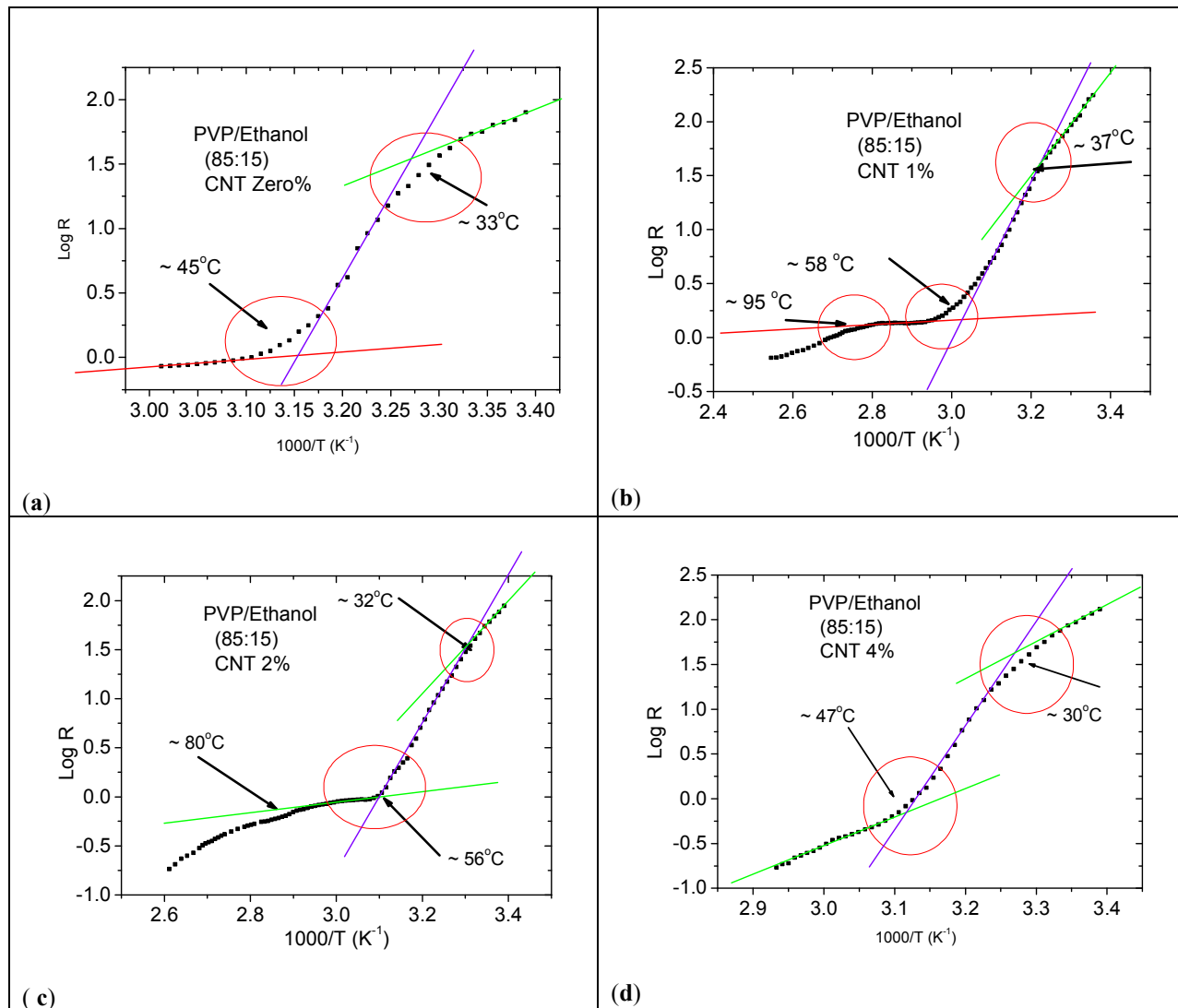


Figure 6: Plots showing $\text{Log } R$ vs. $1000/T$ of PVP fiber films containing 0% (a), 1% (b), 2% (c) and 4% (d) of MWCNTs.

Figure 6 shows the plots of $\text{Log } R$ vs. $1000/T$ for various MWCNTs contents in the electrospun fibers. The plots reveal linear behaviors in three distinct zones as indicated by green, blue and red lines. In the first zone (between 25 and 37 $^\circ\text{C}$), the conduction could be attributed to the impurities [16, 17]. In the second zone, the slopes of the lines (expressing the conduction activation energy) are larger than that of the first zone. This is due to that, hopping conduction in the second zone requires more energy than that required to move the charge carriers from the near impurity levels to the bands. The transition between the second and third zones is attributed to a phase transition which was happened in the nano-composites. This explanation is confirmed by the thermal analysis. Figure 7 shows

the Differential Scanning Calorimetry (DSC) study for the samples with 0, 1 and 4% MWCNTs. It is clear from both the heat flow and the derivative of heat flow that, there is a phase transition, which is a second order, takes place in the temperature rang (39-57 $^\circ\text{C}$). This coincidence with the fact that, the glass transition temperature, T_g , of these polymers around 50 $^\circ\text{C}$, and melting points of the polymeric nano-composite fibers (between 80 and 95 $^\circ\text{C}$). In the first and second zone, the activation energy is high, whereas in the third zone the activation energy is low. Insulators have their outer shell completely filled by valence electrons and therefore, a relatively higher energy is required to liberate some of the electrons from valence band. That is why the activation energy is high in the first and second zone. Once the electrons are freed from the shells,

conduction becomes easy and therefore, activation energy reduces to lower values in the third zone. Additionally, in the first and second zone, the slope is

steeper, while in the third zone, it is shallow, which also indicates the activation energy is high in the first and second zones.

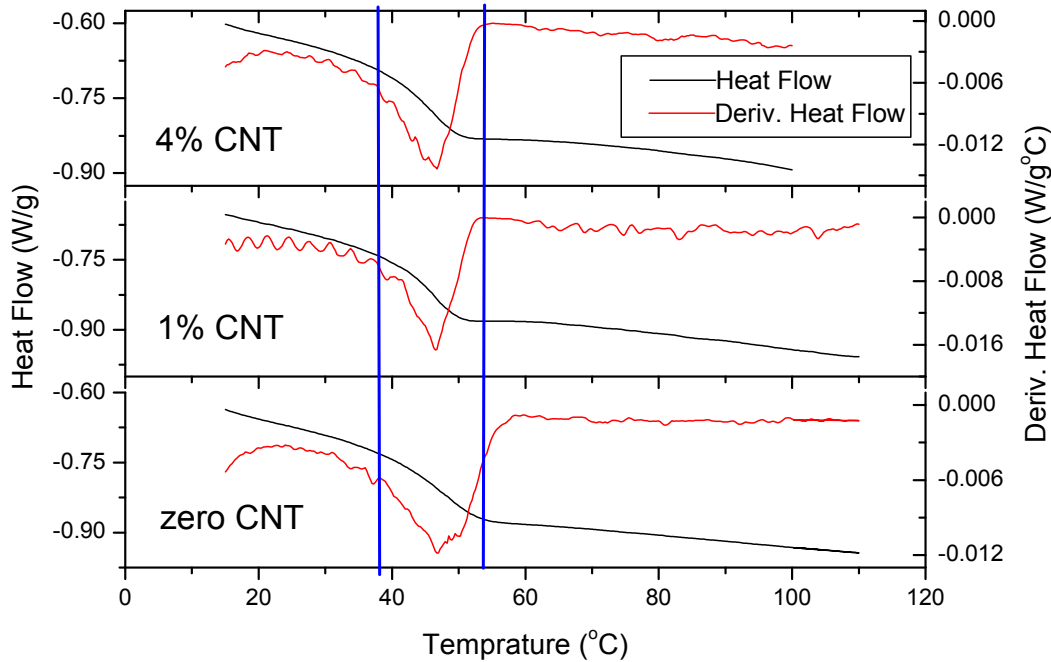


Figure 7: Differential Scanning Calorimetry (DSC) for the samples with 0, 1 and 4% MWCNTs

4. CONCLUSION

In this study, electrospun PVP nanocomposite fibers were produced by adding MWCNTs into the polymeric solution and their electrical properties were measured at various conditions. It can be concluded that mechanical loading and temperature drastically affect the electrical properties of the nanocomposite fibers. As a results, these studies help clarify the behavior of the nanostructured materials at different testing conditions.

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