

The DC Electrical Properties of Polyvinyl Alcohol/ Multi-Walled Carbon Nanotube Composites

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Abstract—Polymer composites are intensively studied for the new properties which are given by the combination of the properties of the both polymer matrix and the filler respectively. When the concentration of the filler in the composite reaches the percolation value, the continuous bulk network structure is formed. If electrical conductive filler (Carbon black (CB)) is used, the composite properties can change from insulator to conductive ones. Electrical conductivity can change in the magnitude of several orders.

The combination of polymers with carbon nanotubes allows linking the properties of both materials to form new functional materials.

Samples were prepared in three steps. First, the solution samples were prepared by dissolving 1wt% sodium dodecyl sulfate (SDS) in distilled water using magnetic stirrer (corning hot plate stirrer PC-351) at 25°C for 1 hr. In the second step different weights of Multi-walled Carbon nanotube (CNT) in volume fraction (0.004, 0.009, 0.019, 0.029 and 0.038) were dispersed in the SDS/H₂O solutions by using a high power ultrasonic homogenizer at 0 °C for 20min. Finally, solutions were prepared by dissolving 8wt % of poly vinyl alcohol (PVA) in sonicated solutions by using a magnetic stirrer at 80°C for 2hr.

From the filler content (CNT) dependence of the electrical (DC) conductivity of PVA composites, we notice that in the case of very low filler concentration, the composites conductivity remain almost the same of that of the polymeric matrix. If the filler loading exceeds a certain critical value, however, a drastic rise in the composites conductivity by several orders of magnitude can occur.

The present study is aimed to study the effect of carbon nanotube (CNT) filler on physical properties of poly vinyl alcohol (PVA) loaded with different CNT- filler. In addition the effect of CNT filler on the DC electrical properties of PVA samples will be elucidated.

Keywords—Polyvinyl alcohol, multi-walled carbon nanotube, DC electrical properties

Introduction

In recent years, studies on the electrical and optical properties of polymers have attracted much attention in view of their applications in electronic and optical devices. The electrical properties are aimed to understand the nature of the charge transport prevalent in these materials while the optical properties are aimed to achieving better reflection, antireflection, and polarization properties. Electrical and optical properties of the polymers can be suitably modified by the addition of dopant depending on their reactivity with the host matrix.

Moreover the advantages of polymer materials such as high strength, good mold ability, and flexibility could be combined with the great properties of inorganic materials such as high strength, heat strength, heat stability, and chemical resistance through producing composite materials [1-3]. The wide range applications of nano-fillers such as filters, catalysis, tissue engineering, wound dressing, scaffold, and sensors could be extended with enhancing their mechanical, electrical, optical, thermal, and magnetic properties by incorporating inorganic and organic nanoparticles in their structures [4-6].

Conductive filler particles in an insulating matrix are able to lower the overall resistivity by several orders of magnitude when a network develops throughout the matrix. The transition from an insulating to a conducting composite as a function of filler concentration is known as percolation and the critical concentration at which this drop occurs is called percolation threshold.

Percolation is described by many theories using different approaches. Some of them take into account the dependence of the percolation threshold on the filler shape, size or aspect ratio, based upon excluded volume approach of infinitely thin particles. Another approach considers the dependency on the orientation of finitely thick sticks [7].

Experimental

PVA powder (M_w = 72000 g/mol, 98% hydrolyzed) as a polymer was obtained from Merck and MWCNT (purity = 95%, diameter ~ 10 nm, Length: 30 μm) were supplied from Neutrino Company. Sodium dodecyl

sulfate (SDS) was obtained from Sigma-Aldrich. The solvent used for dissolving PVA and PVA/SDS/CNT dispersion was distilled water. All reagents used were of analytical grade and were used as received without further purification.

a-) Preparation of Sample

Solutions were prepared in three steps. First, the solution samples were prepared by dissolving 1wt% SDS in distilled water using magnetic stirrer (corning hot plate stirrer PC-351) at 25 °C for 1 hr. In the second step; different weights of CNT were dispersed in the SDS/H₂O solutions by using a high power ultrasonic homogenizer (UP200, Germany) at room temperature for 20min. 8wt% of PVA in sonicated solutions by using a magnetic stirrer at 80°C for 2hr. The calculated CNTs concentrations in each composition of any sample are listed in Table 1.

Table 1: Concentrations of CNT, SDS, and PVA in the mixed solutions

	Mass in 100ml H ₂ O			CNT Mass ratio (wt%)
	PVA(mg)	SDS(mg)	CNT(mg)	
CNT-0	8000	920	0	0
CNT-1	8000	920	90	1
CNT-2	8000	920	180	2
CNT-4	8000	920	360	4
CNT-6	8000	920	540	6
CNT-8	8000	920	720	8

b-) Measurement and Characterization

The dc measurements were calculated using PASCO scientific model 1030A HIGH VOLTAGE SUPPLY and KEITHLY model 614 ELECTROMETER (Figure 1).

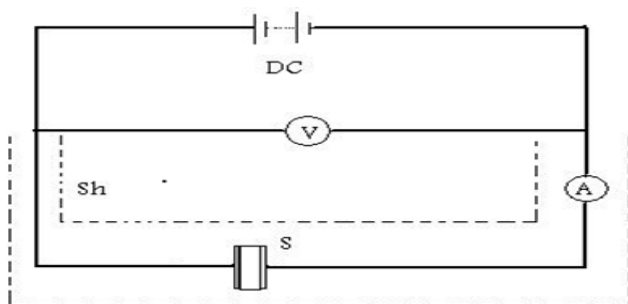


Figure (1): Diagram of the circuit used for the measurements of the DC electrical conductivity.

D.C.: power supply (up to 1 KV), S: Sample, Sh: Metallic shield, A: D.C. Electrometer, V: D.C. Voltmeter.

Results and discussion

Electrical properties of PVA – loaded Carbon nanotube Composites

a- Carbon black loading [8]

As a member of the functional composite materials family, an electrically conductive polymer composite comprised of conductive fillers (e.g. graphite, metal powder or carbon black) and an insulating polymer matrix plays an important role in modern industries owing to its advantages of light weight, good process ability, chemical stability, cost, effectiveness and easy regulation of electrical conductivity and mechanical performance within a wide range [9,10].

With respect to the mechanism of conductivity, usually two considerations must be made. One deals with the formation of electrical paths through the composite, and the other looks into movement details of electrons along the electrical paths. Both mechanisms are highly dependent on the filler content [8].

Figure (2) represents the filler content (carbon nanotube) dependence of the electrical (dc) conductivity of PVA composites. In the case of very low filler concentration, the composites conductivity remains almost the same as that of the polymeric matrix.

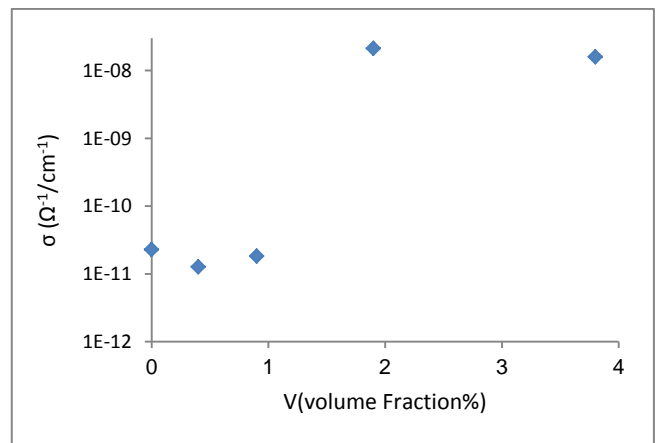


Figure (2): Filler content (CNT) dependence of the electrical (dc) conductivity of PVA composites.

If the filler loading exceeds a certain critical value, however, a drastic rise in the composites conductivity by several orders of magnitude can occur (Figure 2)). Meaning that at least one conductive network is formed. The subsequent change in electrical conductivity with a further increase in filler volume fraction takes place again rather slowly.

In order to model such an S- shaped conductivity versus filler content curve, many theoretical treatments have been proposed; in all of these cases the critical filler volume fraction necessary to support a continuous electrical path in the composite received special attention [11].

It can be concluded from the literature, (as suggested by M.Q. Zhang [8]), that a model which is able to describe the electrical conductivity of a composite might be at least of the form:

$$\sigma = f(V, \sigma_0, \text{"filler arrangement"}) \quad (1)$$

Where V the filler volume fraction and σ_0 the filler conductivity.

By considering the electrical conduction model, a two-phase composite system is employed and its electrical conductivity is written as:

$$\sigma = \sigma_p^G \sigma_s^{1-G} \quad (2)$$

With

$$\sigma_p = V \sigma_0 + (1 - V) \sigma_m \quad (3)$$

$$\sigma_s = [V / \sigma_0 + (1 - V) / \sigma_m]^{-1} \quad (4)$$

Where σ_m denotes the matrix conductivity, σ_p and σ_s are the conductivity of the composite in the limiting cases of parallel and series concentration, respectively, and G is a distribution function that has the value of (1) for the parallel and (0) for the serial model Figure (3).

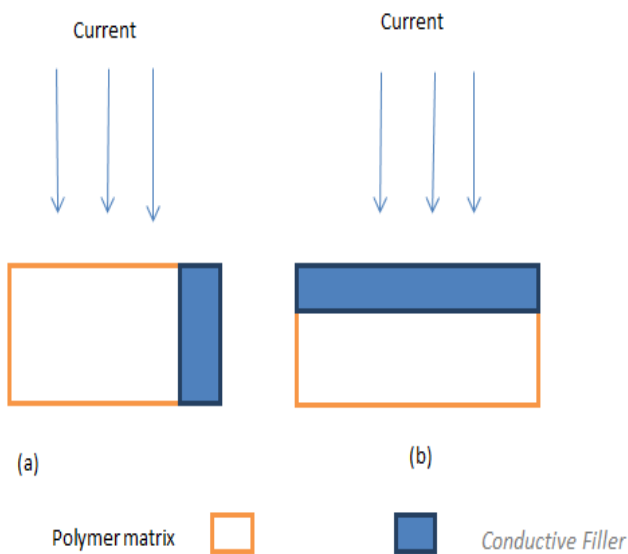


Figure (3): The electrical conduction model proposed for a two-phase composite: (a) Parallel model, (b) Serial model.

It is clear that G reflects the contact probability of fillers to form conductive networks, and it concerns the relative filler arrangement as well as other microscopic details of the composite. As long as the measure of G is obtained, the composite electrical conductivity can be deduced from equation (3), which coincides factually with the same function form as proposed by equation (1).

For the convenience of evaluation, the fillers are assumed to be spherical particles of identical diameter, D , distributing in the matrix in the form of a face centered cubic (fcc) structure Figure (4a).

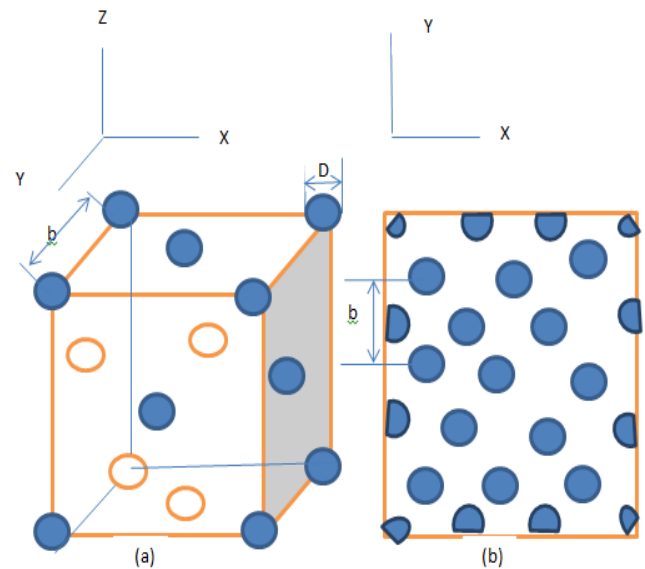


Figure (4): The fillers are assumed to be spherical particles of identical diameter D , (a) distributing in the matrix in the form of a face centered cubic (fcc) structure, (b) a cross-section of the composites randomly in the x-y plane.

A cross-section of the composite is randomly sampled in the X-Y plane Figure (4b), the section is divided into small grids (about one-tenth the particle diameter in size) in accordance with the sand box method, in order to measure the fractal dimension [12]. As a simplified but effective method, it is usually possible to obtain information on a complicated system through investigation of a generalized unit cell. In order to relate the macroscopic performance to the filler content and the fractal dimensions, Pitchumani and Yao [12] constructed the polygonal Wigner-Seitz cells of different sites around each fiber in a composite section [12,13]. Which were then represented by an equivalent rectangular cell having the same behavior.

Finally, they yielded a dimensionless generalized unit cell which was only the function of filler volume fraction and relative filler arrangement. Applying their results to the case here, a simplified description of the generalized filler fraction of dimensionless diameter D can be expressed as follows:

$$L = \left(\frac{\pi}{4V}\right)^{\frac{1}{2}} D \quad (5)$$

With

$$D = \left(\frac{4V}{\pi}\right)^{\frac{d}{(2d-2)}} \quad (6)$$

Where L is the size of the square generalized unit cell (Figure 5)

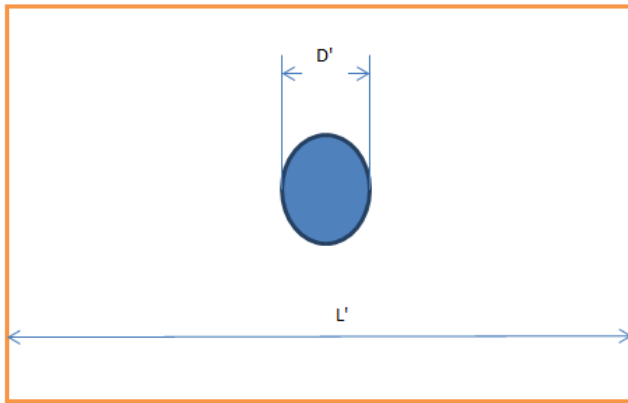


Figure (5): The size of the square unit cell

From the above equation (5), one could observe that, for a given volume fraction the total filler amount in a composite filled with small particles is always larger than in one filled with large particles, usually meaning that the contact possibility of the larger properties is rarer.

An important enlightenment is that the probability of the conductive network formation might be exponentially related to the filler content.

Considering the meaning of L implied by Figure (5), the expression for G appearing in equation (2) is written as:

$$G = V^{aL} \quad (7)$$

Where "a" is defined as a material factor that will be suggested as a value which give a best fit with the experimental value.

The dependence of the composite's conductivity on filler volume fraction can be evaluated from equation (2) as long as proper value of "a" is known.

The previous model will be examined with our measured results with suitable choice for the fitting parameter e.g

$$\sigma (\text{CNT}) = 10^4 \Omega^{-1} \text{Cm}^{-1}, \sigma (\text{polymer}) = 10^{-15} \Omega^{-1} \text{Cm}^{-1} \text{ and filler diameter} = 10 \text{ nm.}$$

Using equation (2) and the above data, the numerical expression of composite conductivity can be obtained. On the trial basis, 0.2 is found to be an approximate value of the material factor "a" in equation (7).

Figure (6) shows the results of CNT filler/PVA composites. The critical volume fraction, V_c is determined by the conventional method i.e the peak position of $\frac{d \log \sigma}{dV}$ in the drastically increasing regime.

It becomes evident, that the $\sigma - V$ curves describe the known S shaped relation very well.

In fact, the conductive behavior of a composite material manufactured by a given processing technique is basically controlled by two types of factors:

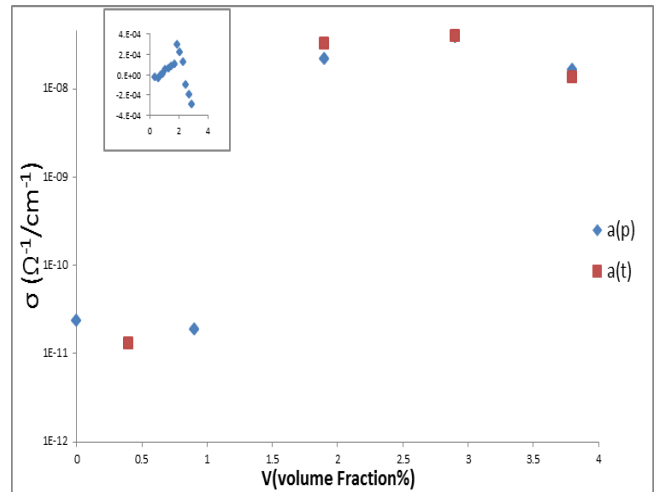


Figure (6): The results of CNT filler/PVA composites.

The critical volume fraction, V_c is determined by the conventional method.

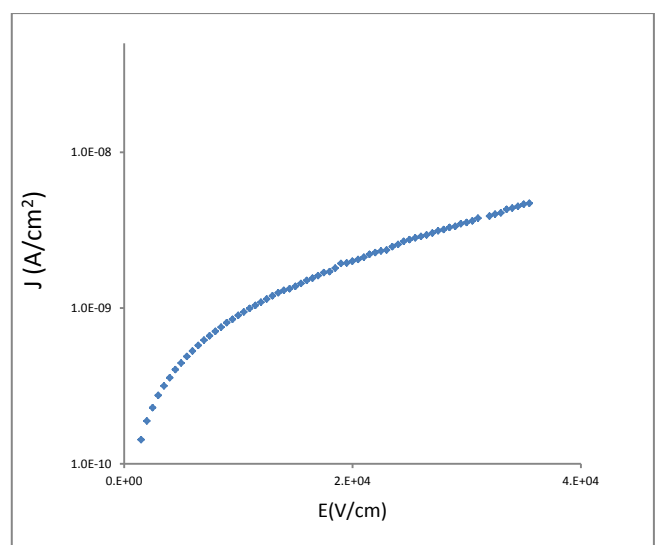
(1) A geometrical factor (including filler dimension, morphology, packing density and relative arrangement).

(2) A material factor (accounting for the filler and matrix species, macroscopic and microscopic properties, filler- matrix compatibility).

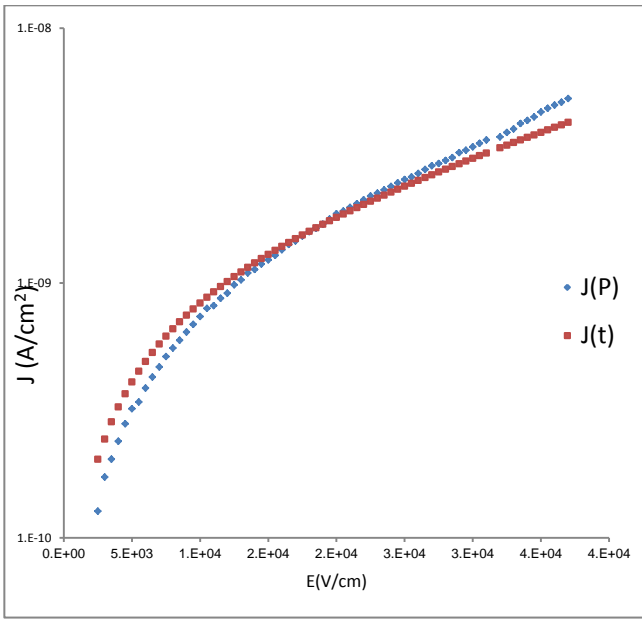
Both of these factors are related to and affect each other. This explains why some composites filled with different species of conductive particles of similar dimensions have quite different critical volume fractions.

b. Current Density – Electric field Characteristics

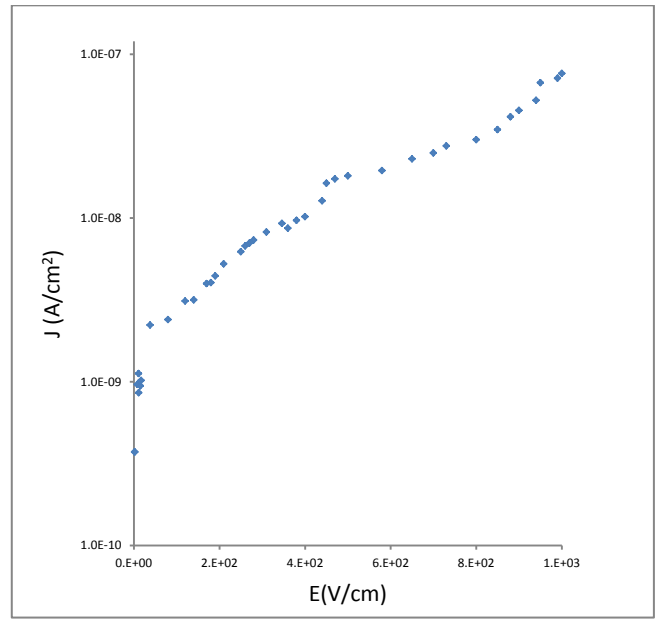
Figure (7) represent the current density "J" as a function of the applied electric field, E, measured for nano- filler carbon black loaded PVA vulcanizes.



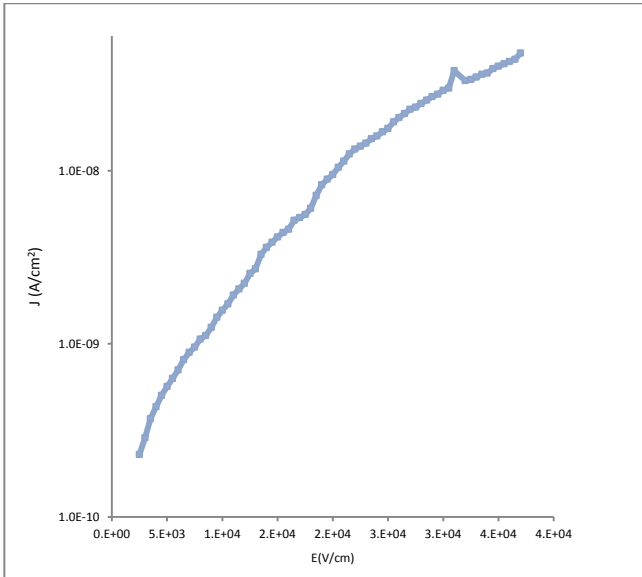
(a)



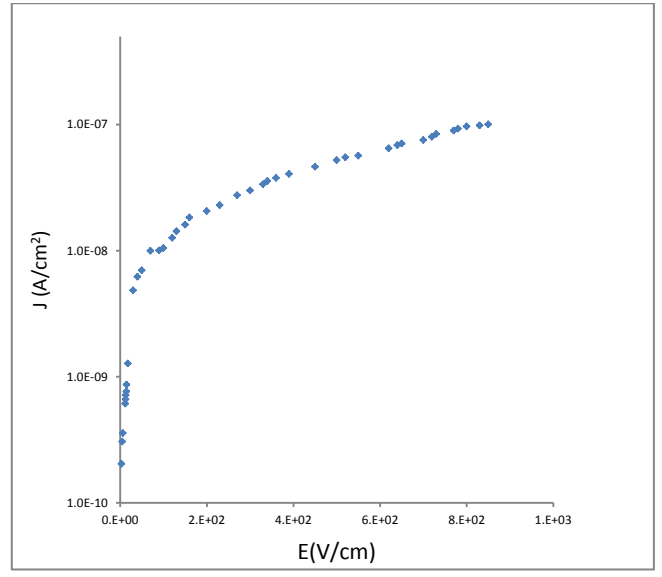
(b)



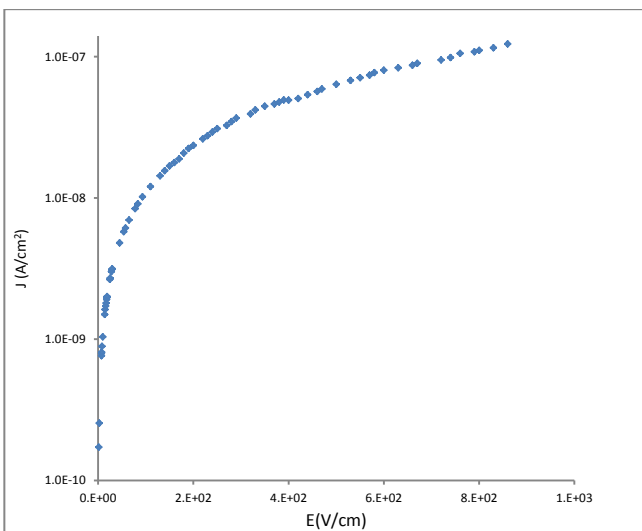
(e)



(c)



(f)



(d)

Figure (7a-f): The current density, J, as a function of the applied electric field, E, measured for nano- filler carbon black loaded PVA vulcanizes.(a=(pure), b=(0.004), c=(0.009), d=(0.019), e=(0.029), f=(0.038))

All the J-E curves exhibit linear current voltage relation at low current density ranges, the J-E curves deviate from the linear relation and the current density shows saturation – such behavior could be fitted by an empirical equation of the form:

$$J = J_0 \sinh\left(\frac{beE}{2KT}\right) \tag{8}$$

Where J_0 is a fitting parameter, its value depends on the concentration of the carbon nanotube, e is the effective electronic charge, K is Boltzman' constant, T is the ambient temperature and b is the average distance between two adjacent potential wells which

represent conducting particles separated by an insulating layer.

An approximate estimate of the values of the separation distance, b , can be obtained by the iterative method from figure (7) and are represented in Figure (8).

An example of the fitting empirical equation (8) was represented to PVA sample loaded with (0.009) CNT (cf. Figure 7).

Table (2) illustrates the dependence of the separation distance on carbon nano- filler concentration. It is noticed that, the interspacing separation distance, b , decreases with carbon contents and has the inverse behavior of the dc conductivity with carbon contents which confirm the data measured [cf. Figure (8)].

Table (2): The dependence of the separation distance on carbon nano- filler concentration.

Content of CNT (%)	b (μm)
0	40
1	20
2	6.0
4	2.0
6	1.1
8	1.0

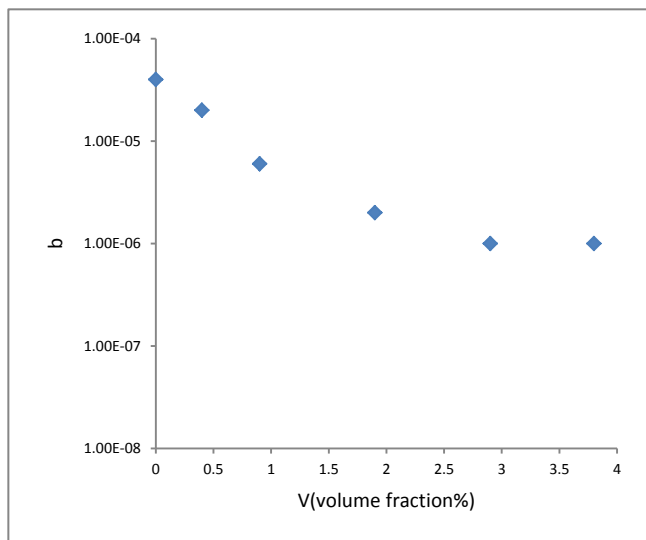


Figure (8): The dependence of the separation distance on carbon nano- filler concentration

Conclusion

From the forgoing results and discussion we may conclude the following:

The electrical conductivity of polymer composites is due to the formation of continuous networks by conducting carbon nano-tube fillers in the insulating polymer (PVA) matrix. Percolation limit was found to be around 0.019 volume fraction of CNT filler. Zhang model was tested to model the S- shaped conductivity versus filler content curve which gave a good fitting with the experimental values. The interspacing distance between CNT particles was found to decrease with CNT contents.

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