# Low percolation threshold of functionalized SWCNTs-polycarbonate nanocomposites

| | |
|---|---|
| Journal: | *Journal of Reinforced Plastics and Composites* |
| Manuscript ID: | JRP-12-0117.R2 |
| Manuscript Type: | Original Article |
| Date Submitted by the Author: | 12-Jun-2012 |
| Complete List of Authors: | Ayesh, Ayman; KFU, Physics<br>Ibrahim, Sobhy; KFU, Physics<br>Abu Abdeen, Mohamed; KFU, physics |
| Keyword: | polycarbonate, SWCNTs, nanocomposite, electrical, mechanical, percolation |
| Abstract: | A series of polycarbonate films loaded with different concentrations of UV-ozone (UVO) pretreated single walled carbon nanotubes (SWCNT) were prepared. The electrical and mechanical properties of these composites were investigated. The improvement of the SWCNTs dispersion in PC matrix leads to a dramatic enhancement in the electrical conductivity with low percolation threshold (0.5 wt. % of SWCNTs loading). Results obtained from the analysis of the dielectric parameters at room temperature and domain frequency range reveal that SWCNTs increases the dielectric constant, dielectric loss, and AC conductivity of the composites. The dielectric relaxation behavior of these composites is mostly due to polymer molecular relaxation when the SWCNTs content is below the percolation threshold whereas it is almost due to the charge conductivity relaxation above 0.8 wt% SWCNTs. The calculated values of the elastic modulus obtained from the stress-strain curves, also show a percolation behavior with a threshold of 0.08 wt % SWCNT. |
| | |

# Low percolation threshold of functionalized SWCNTs- polycarbonate nanocomposites

**Ayman S. Ayesh*[1], S.S. Ibrahim[1,2], and M. Abu-Abdeen[1,2]**

[1] Department of Physics, College of Science, King Faisal University, Al-Ahsa, KSA.
[2] Department of Physics, College of Science, Cairo University, Egypt.

## Abstract

A series of polycarbonate films loaded with different concentrations of UV-ozone (UVO) pretreated single walled carbon nanotubes (SWCNT) were prepared. The electrical and mechanical properties of these composites were investigated. The improvement of the SWCNTs dispersion in PC matrix leads to a dramatic enhancement in the electrical conductivity with low percolation threshold (0.5 wt. % of SWCNTs loading). Results obtained from the analysis of the dielectric parameters at room temperature and domain frequency range reveal that SWCNTs increases the dielectric constant, dielectric loss, and AC conductivity of the composites. The dielectric relaxation behavior of these composites is mostly due to polymer molecular relaxation when the SWCNTs content is below the percolation threshold whereas it is almost due to the charge conductivity relaxation above 0.8 wt% SWCNTs. The calculated values of the elastic modulus obtained from the stress-strain curves, also show a percolation behavior with a threshold of 0.08 wt % SWCNT.

**Keywords**
SWCNTs, polycarbonate, nanocomposites, percolation, electrical, mechanical.

*Corresponding author: Ayman S. Ayesh, Department of Physics, College of Science, King Faisal University, P.O. B 400, 31982 Al-Ahsa, KSA, Email: dr_ayesh67@yahoo.co.uk or assalem@kfu.edu.sa.

## Introduction

Electrically conducting polymer composites have gained popularity recently because of their light weight, resistance to corrosion, flexibility, and processing advantages[1-10]. Generally, electrical conductivity of a polymer nanocomposite material depends on many factors, including the filler's intrinsic conductivity, dielectric constant, and aspect ratio[3]. Thus, the small diameter, high aspect ratio, high conductivity, and mechanical strength of carbon nanotubes (CNTs), make them an excellent option for creating conductive composites at low filling[3, 11-18].

Extensive researches studied the electrical and mechanical properties of CNTs-polymer nanocomposites and they demonstrate that the electrical conductivity and mechanical properties highly depend on the dispersion of CNTs in the polymer matrix and also depend on the interfacial stress between the two components[2, 3, 19-23].

Due to the van der Waals attraction, nanotubes are held together as bundles and ropes. Thus they have very low solubility in solvents and tend to remain as entangled agglomerates. However, many techniques were used to overcome the difficulty of CNTs dispersion in polymer matrix, such as ultrasonication, high shear mixing, surfactant addition, melt blending and chemical modification through functionalization[1-4, 6-8, 12, 19-28]. The wet chemical functionalization of carbon nanotubes using different strong acids, generally, will introduce carboxylic groups at CNTs surface and consequently, this will improve CNTs dispersion in organic solvents or polymer matrix. At the same time, such a method will cause a morphological damages to CNTs. In addition, oxidation process with strong acids creates significant physical damages and causing severe degradation of the originally desirable properties of CNTs[29, 30]. On the other hand, dry oxidation such as ozone in the presence of ultraviolet (UV/$O_3$) have been an alternative treatment to resolve the issues associated with the wet oxidation[31-34]. Additionally, many researchers showed that UV-modified CNTs induced a higher electrical conductivity in polymer matrices and they reported that this method will not cause any morphological damages to CNTs[33, 34] .

Several studies investigated the effect of MWCNTs or SWCNTs on the electrical and mechanical properties of polycarbonate using different preparation techniques[2, 23, 35-37]. They reported that the percolation threshold in these composites was between 1.5 and 2.5 wt% CNTs[38]. Despite of these studies, present work, however, introduces interesting additions to CNT-PC nanocomposites.

The present work aims to prepare well dispersed SWCNTs-PC nanocomposites using UVO pretreatment. The electrical properties (DC and AC) of these nanocomposites are presented and discussed. The percolation threshold of SWCNTs in PC matrix is also presented and estimated. Finally, the correlations between structure, electrical and mechanical properties are discussed.

## Experimental

### *Materials*

Single walled carbon nanotubes (SWCNTs) was purchased from Aldrich company ( 704113) with outer diameter of 0.7-1.3 nm and average length of 800 nm. SWCNTs was functionalized with UVO using UV-ozone generator (Model # 42-220, Jelight Co.) in ambient laboratory air for a period up to 180 min. Bisphenol A polycarbonate resin PC (product by ACROS ORGANICS Company, New jersey (USA) , MW 64,000 ) was used as a matrix polymer and Dichloromethane (Aldrich) was used as solvent for PC polymer.

### *Sample preparation*

The SWCNTs was irradiated with UV-ozone (UVO 41 commercial lamp) at a distance of 6 mm from the lamp of power 28,000 W per $cm^2$ and wavelength of 254 nm. During the UV irradiation, the powder was stirred with a spatula at 10 min intervals to provide a uniform exposure up to 180 min. The pretreated SWCNTs was added to dichloromethane solvent and ultrasonicated for 30 min using UP 200S ultrasonicator (Hielsher Company-Ultrasonic Technology). The dispersion of SWCNTs in dichloromethane was observed at different UV exposure time with 30 min ultrasonication as shown in Figure 1A. It is clear that the dispersion of SWCNTs improved when the exposure time is 180 min.

Bisphenol A polycarbonate resin was dissolved in dichloromethane solvent and was stirred at 30 $^0$C by a magnetic stirrer for 24 hr. UV pretreated SWCNTs was first ultrasonicated in dichloromethane for 30 min and then mixed with polymer solution. The mixture was again stirred for 24 hr until the SWCNTs powder became highly dispersed in polycarbonate solution. This solution was casted in a glass petri dish (dia. of 10 cm). The solvent was evaporated at room temperature for 24 h. Samples with different SWCNTs-PC concentrations (0.05, 0.2, 0.4, 0.5, 0.8, 1, 2 and 3 SWCNTs wt%) were kept inside vacuumed dissector. The film thickness (~ 0.1 mm) was measured using digital micrometer (MOTOTOYO - China) with 0.001mm resolution.

### *Electrical measurements*

Electrical measurements with AC and DC applied electric fields were performed using 4200-SCS Semiconductor Characterization System (KEITHLEY Co.). Samples were shaped into circular discs of area 1.2 $cm^2$ and thickness of 0.1 mm. The DC electrical parameters (I-V and DC conductivity ($\sigma_{DC}$)) were measured at room temperature. Relative permitivity (ε'), dielectric loss (ε'') and AC conductivity ($\sigma_{AC}$) was calculated from the measured capacitance (C), and loss tangent (tan (δ)) data[13, 14, 16, 17] at room temperature and frequency range 1 KHz-10 MHz.

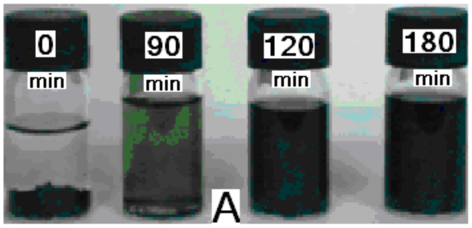
### *Tensile test*

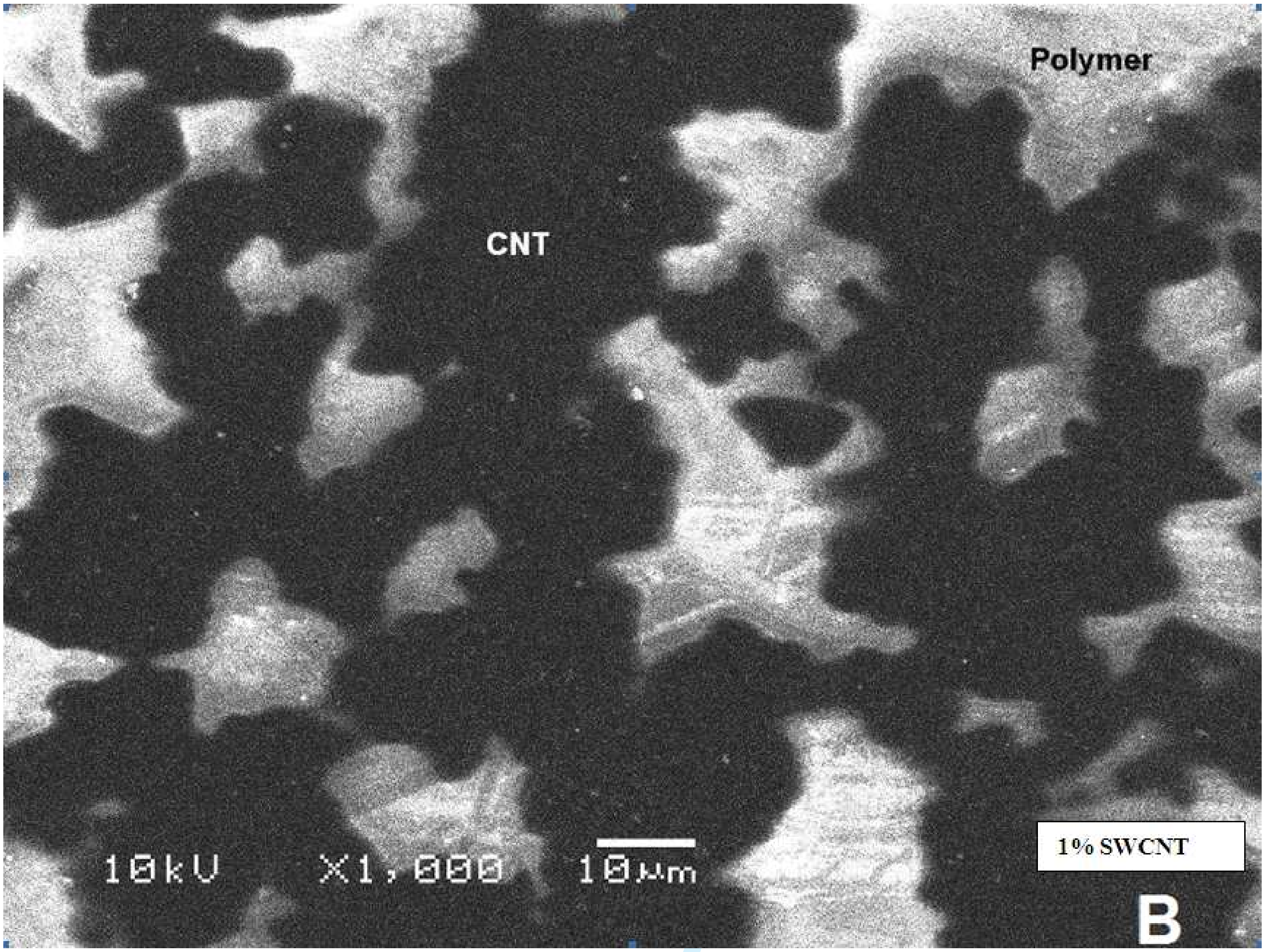
The tensile test were carried out on a dynamic mechanical analysis Q800 (TA Instruments LLC, Delaware, USA) instrument using the tension film clamping arrangement. Specimens in the form of films with dimensions 15 mm length, 4 mm width and 0.1 mm thick were used. The tensile test on film samples were carried out at 25 °C at a force rate of 3 N/min.

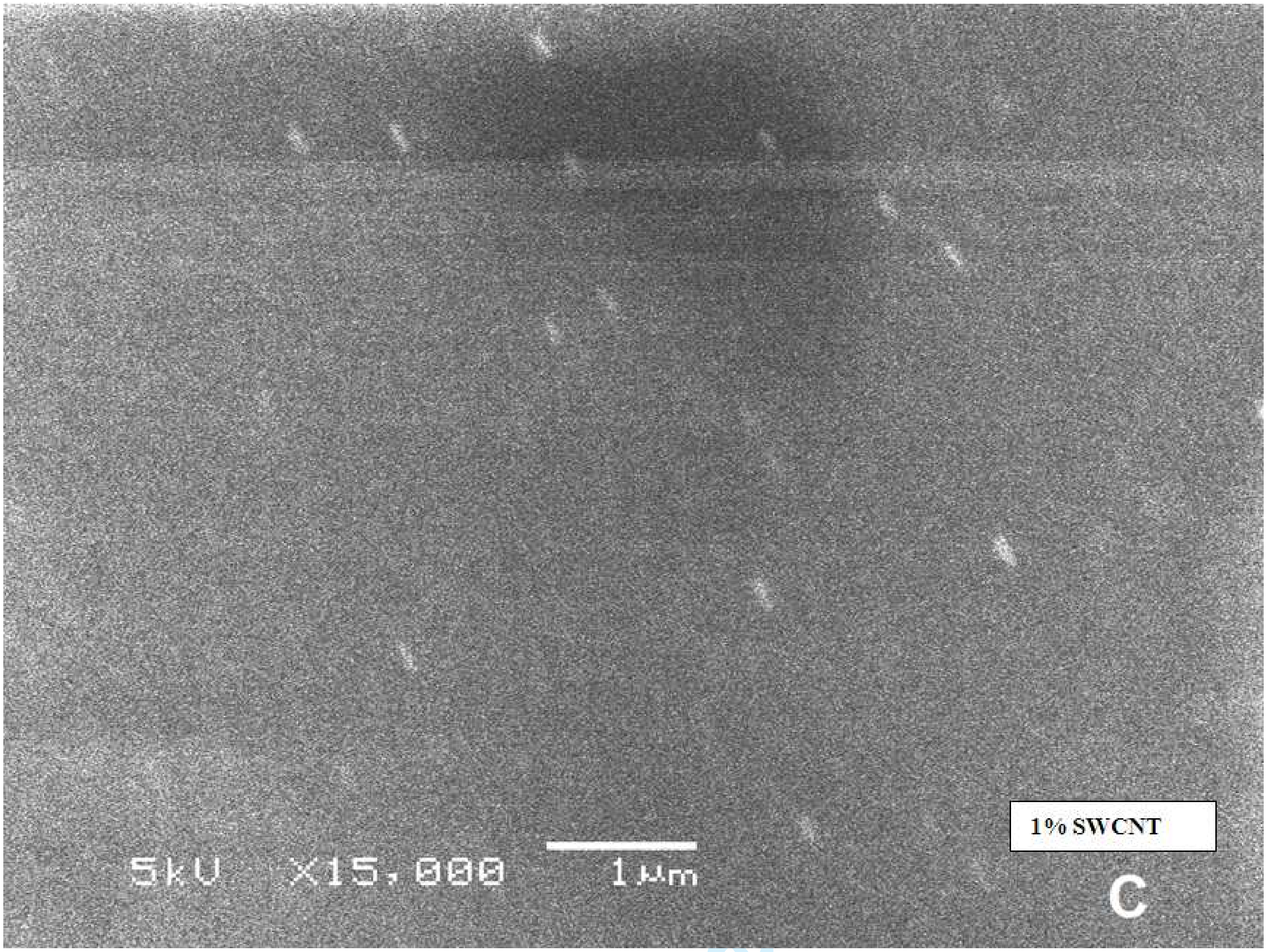
### *Scanning electron microscopy (SEM)*

The morphology of the prepared nanocomposites were examined using a Jeol scanning electron microscope (J.S.M. 6380 ) with low and high vacuum. The operation system controlled by IBM computer. Samples were coated with gold in automatic sputter coater (Polaron SC 500), and then transferred to the electron microscope to be examined. The electrical image shift of $\pm 50 \mu m$.

Figures 1B, 1C and 1D show the SEM micrographs of 1% SWCNTs (Figures 1B and 1C) and 0.6% SWCNTs (Figure 1D) samples. These images show a good dispersion of CNTs with enhanced interfacial bonding between CNTs and PC matrix[39] in addition to the formation of CNTs network in the PC matrix.




Polymer
CNT
10kV X1,000 10µm
1% SWCNT
B


1% SWCNT
5kV X15,000 1μm
C

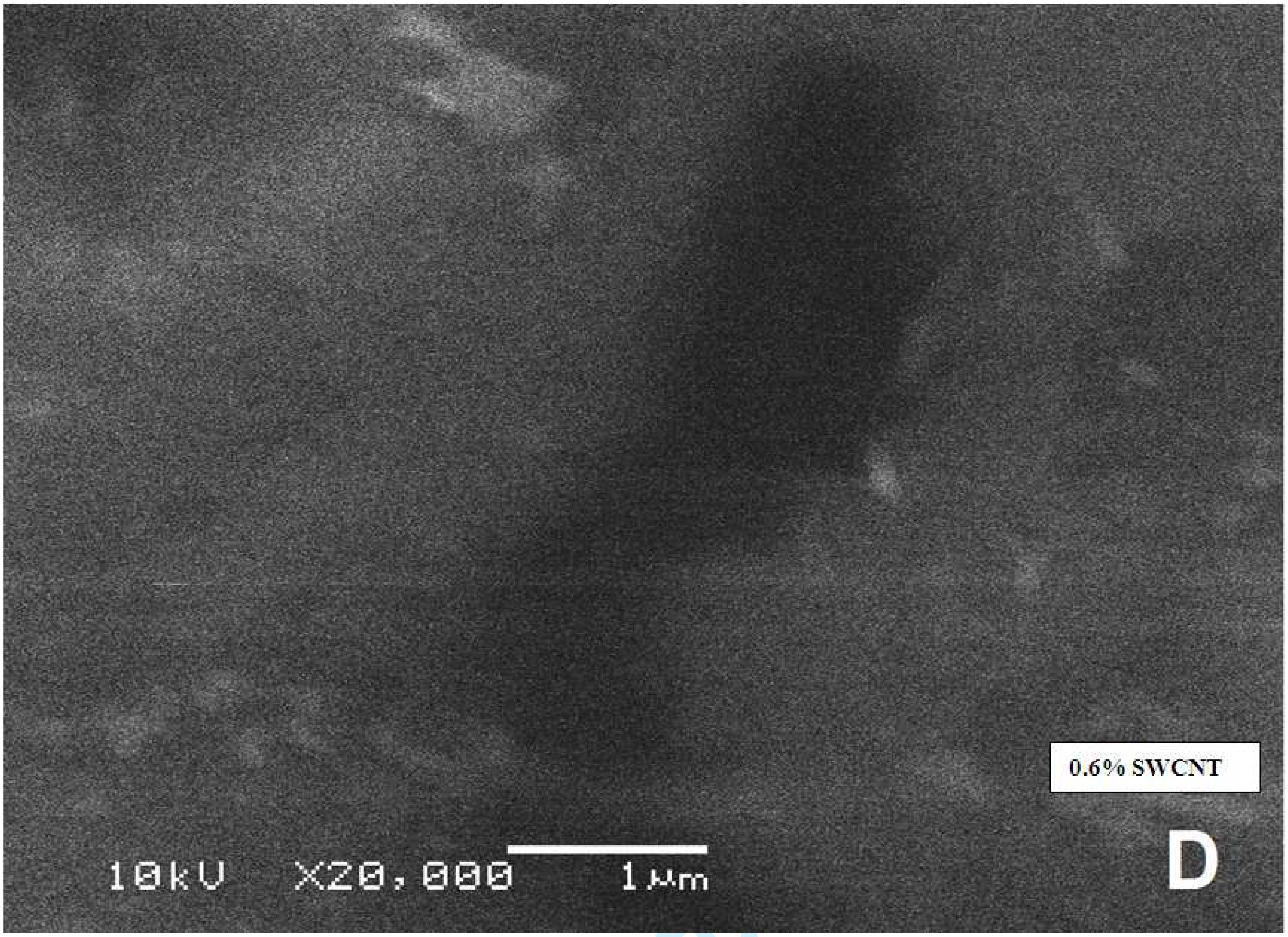


**Figure 1.** **(A)** Dispersion of UVO pretreated SWCNTs in dichloromethane, (B) to (D) SEM micrographs of SWCNTs-PC composites: (B)-(C) 1% SWCNTs and (D) 0.6% SWCNTs .

## Results and Discussion

### *Electrical Properties*

### *I-V characteristics and DC conductivity*

I-V characteristics of the pretreated SWCNTs-PC composites with different SWCNT loadings at room temperature are shown in Figure 2. These characteristics indicate that the current level in these composites increases with the addition of SWNTs. This is consistent with the fact that the conductivity of the composites increases as the SWNTs concentration increases and such a trend was also observed previously by many authors in SWCNTs-polymer composites[2, 3, 12, 40-46]. The charge transport mechanism based on the general power law model $I=KV^m$, where $K$ is a constant and $m$ is the exponent, has been widely used for the analysis of the conduction phenomenon in organic or polymeric materials[41,42]. The model is divided into three regimes, Ohmic (m=1), trap-free space charge limited (m=2), and trap charge limited (m>2)[44-46].

I-V characteristics on log-log scales reveal two distinct regions which can be fitted using the general power law model. The obtained results which are listed in Table (1) reveal that at lower voltages, the exponent $m_1$ is determined to be around 1, implying that the current varies linearly with voltage and hence the charge transport mechanism is governed by Ohm's law. At second voltages region (region II in Figure 2) , the exponent $m_2$ is around 2 which means that at this region the charge mechanism is due to the space charge limited current (SCLC) [40]. Generally, in the ohmic region the field due to the injected barriers is negligible compared to that due to the applied bias. This condition breaks down at the space charge limit when the injected carrier density becomes so large that the field due to the carriers themselves dominates over that of the applied bias[12, 21, 26, 27, 40, 43].

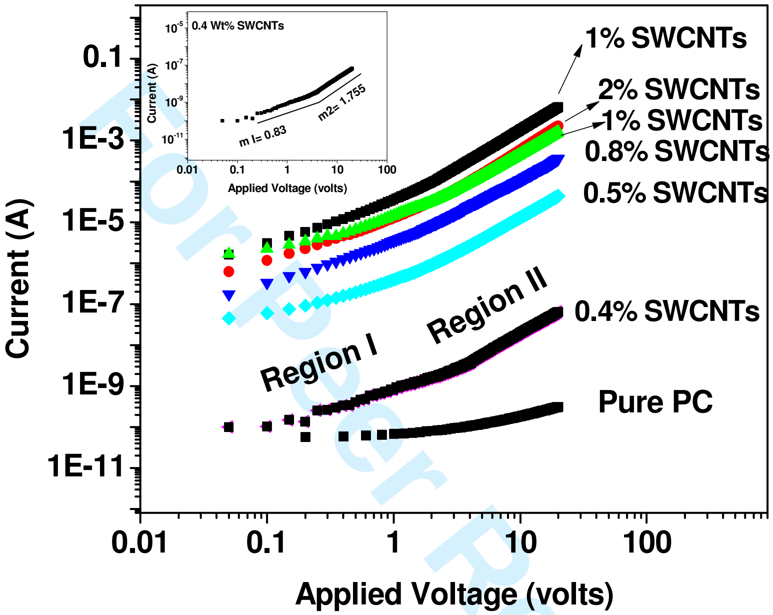


**Figure 2.** I-V characteristics of SWCNTs-PC nanocomposites**.**

**Table 1.** The calculated exponent values $m_1$ and $m_2$ of SWCNTs-PC nanocomposites.

| SWCNTs wt% | $m_1$ | $m_2$ |
|---|---|---|
| 0 | 0.65 | - |
| 0.4 | 0.83 | 1.75 |
| 0.5 | 0.77 | 1.74 |
| 0.8 | 1.01 | 1.64 |
| 1 | 0.75 | 1.77 |
| 2 | 1.01 | 1.93 |
| 3 | 1.04 | 1.86 |

Electrical conductivity depends on the polymer matrix and the filler materials. If the filler material is CNTs, it is decided by its purity, alignment, and the concentration. In such composites, the polymer layer in the internanotube connections presents highly resistive section in the electrical pathway, acting as a barrier to efficient carrier transport between the nanotubes and models fluctuation-induced tunneling for the conductivity[45-46]. However, the room temperature DC conductivity of SWCNTs-PC composites was calculated from the known current, area, and thickness values for each sample and was determined at 20 volt. The obtained results are presented in Figure 3 as a function of the weight fraction of SWCNTs in PC matrix. As shown in this figure, the SWCNT increases the conductivity of the composites by about six orders of magnitude. This result suggests the existence of other contributions in the electrical conduction process in addition to those mechanisms mentioned above that is the formation of network structure between nanotubes in the polymer matrix will facilitate the electron transport through tunneling throughout the polymer or by electron hopping along CNTs interconnects[44-46] .

In the case of CNTs-polymer composites, the polymer layer in the internanotube connections presents highly resistive section in the electrical pathway, acting as a barrier to efficient carrier transport between the nanotubes. When the distance between nanotubes becomes sufficiently small, the electrical response of the composites is then described by percolation theory. The CNTs concentration that marks this insulator-conductor transition is referred to as the percolation threshold (Pc). Additionally, direct connection and overlapping of the CNT is not necessary i.e. nanotubes do not need to physically touch each other for conductivity. Nanotubes can just be close enough to allow for a hopping/ tunneling electron effect; these mechanisms require the CNT- CNT distance to be less than 5nm. As a result, a higher volume fraction of CNTs filler is needed to achieve electrical percolation threshold[21]. However, one of the percolation theories has the following formula[44-46]:

$$\sigma = C\,[P - P_c]^t \qquad (1)$$

where σ is the composite conductivity, *P* the weight fraction of nanotubes in the composites, *C* is a constant, and *t* is a critical exponent. A successful fitting result was obtained when the experimental data (scatter curve) was fitted with Equation (1) (solid curve), see Figure 3. The obtained fitting parameters which are listed in Figure 3 reveal that the percolation threshold (Pc) of SWCNTs-PC is bout 0.5%. Compared with other researchers[2, 23, 35-38] in CNTs-PC composites, the obtained results in the present study show a dramatic improvements in the electrical conductivity with a low percolation threshold (0.5 wt.% of SWNT loading), by significantly improving the dispersion of SWNTs in polycarbonate matrix. Kim et al [38], reported that the percolation threshold of CNTs-PC is between 1.5 and 2.5 wt% CNTs. Moreover, present study shows that UV pretreatment of SWCNT up to 180 min will improve SWCNTs dispersion, enhance their interfacial bonding with polymer, and reduce the percolation threshold of SWCNTs-PC composites.

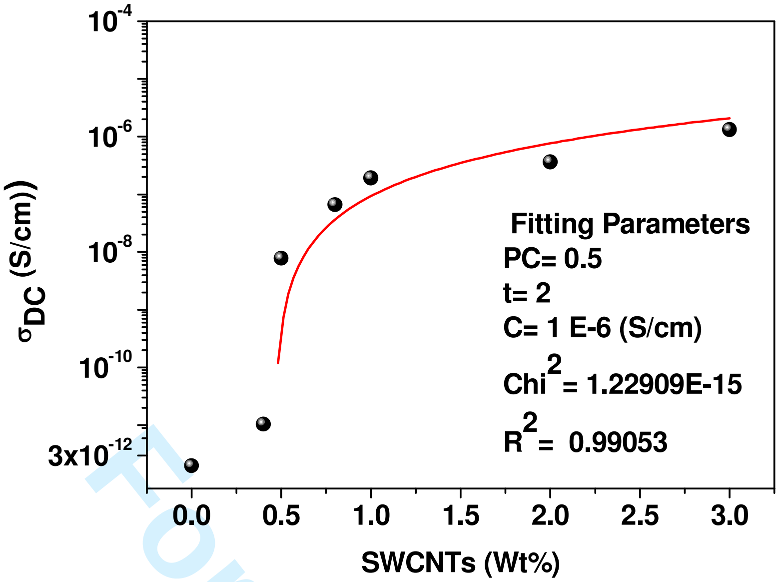


**Figure 3.** DC conductivity versus SWCNTs weight fraction for SWCNTs-PC nanocomposites**.** Scattered curve represent the experimental data while the solid one represent the fitted data.

### 3.1.2 Dielectric Relaxation and Ac Conductivity

AC dielectric parameters (relative permittivity $\varepsilon^{/}$, dielectric loss $\varepsilon^{//}$, and AC conductivity $\sigma_{AC}$) were determined from the obtained measured capacitance and loss tangent data for all SWCNTs-PC nanocomposites at room temperature and frequency range 1 KHz-10 MHz[13-17, 34]. The obtained results are presented graphically in Figures 4, 5, and 6 respectively. It is clear that relative permittivity, dielectric loss and AC conductivity are increased with increasing the loadings of SWCNTs in the PC matrix. Besides, the decrease of relative permittivity with frequency could be attributed to the insufficient time for dipoles to align before the field changes direction[13-17, 34]. Furthermore, the variations of relative permittivity, dielectric loss and AC conductivity with SWCNTs loadings could be attributed to the charge diffusions, chains orientation polarizations in addition to the contribution of Maxwell-Wagner polarization[13, 14, 17, 34, 46-47]. The AC conductivity versus SWCNTs loading is shown in Figure 7 at 1 KHz. AC conductivity also shows that the percolation threshold is almost around 0.5 wt% SWCNTs.

Generally, in all cases the relaxation behavior in these composites shows the existence of capacitor element. Moreover, the dielectric constant, dielectric loss, loss tangent and dielectric relaxation behavior of pure PC was previously measured and discussed by us [13, 16-18]. However, it will be very interested here if we consider the Argand plot between imaginary part (M'') versus real part (M') of electric modulus to recognize the relaxation behavior of SWCNTs-PC composites before and after the percolation threshold. It was reported previously[13, 15, 16, 34], if the Argand plot between imaginary part (M'') versus real part (M') of electric modulus has semicircular behavior then the relaxation is due to conductivity relaxation process, if not, then it is due to viscoelastic relaxation (or polymer molecular relaxation). In the present work, the values of $M^{/}$ and $M^{//}$ were determined from:

$$M^* = \frac{1}{\varepsilon^*} = \frac{1}{\varepsilon' - i\varepsilon''} = \frac{\varepsilon' + i\varepsilon''}{(\varepsilon' - i\varepsilon'')(\varepsilon' + i\varepsilon'')}$$

$$M^* = \frac{\varepsilon'}{(\varepsilon' - i\varepsilon'')(\varepsilon' + i\varepsilon'')} + i\frac{\varepsilon''}{(\varepsilon' - i\varepsilon'')(\varepsilon' + i\varepsilon'')}$$

$$M^* = \frac{\varepsilon'}{(\varepsilon'^2 + \varepsilon''^2)} + i\frac{\varepsilon''}{(\varepsilon'^2 + \varepsilon''^2)} = M' + iM'' \qquad (2)$$

Where $\square^{/}$ is the relative permittivity, $\square^{//}$ is the dielectric loss, $M^{/}$ is the electric modulus and $M^{//}$ is the electric loss modulus. The obtained results are presented graphically in Figures 8 and 9. It is clear that below the percolation threshold (0.4 Wt% SWCNTs), the plot does not follow semicircular behavior. This indicates that, at the domain frequency range, the relaxation process below the percolation threshold is mostly due to polymer molecular relaxation process. While above the percolation threshold (Figure 9), the relaxation behavior is mostly due to charge conductivity relaxation[13-16, 34]. Also it was reported[13, 14] that in case of charge relaxation, plots of log(M″) versus log(frequency) will reveal a slope value of 1. Figure 10 shows a plot graph of log(M”) versus log(frequency) for 0.8 , 1 , 2 , and 3 wt% SWCNTs samples. The slope values in case of 1 , 2 , and 3 wt% SWCNTs samples are around 1, while the slope value in the case 0.8 wt% SWCMTs sample is -0.35. This indicates that the charge conductivity relaxation appears when the SWCNTs content is above 0.8 wt% SWCNTs.

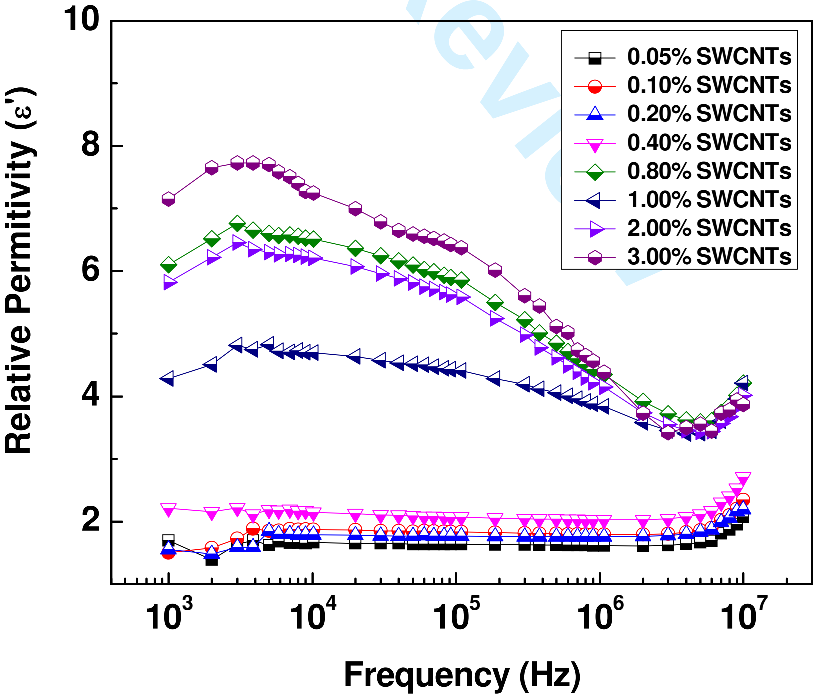


**Figure 4.** Relative dielectric permittivity versus frequency) for SWCNTs-PC composites.

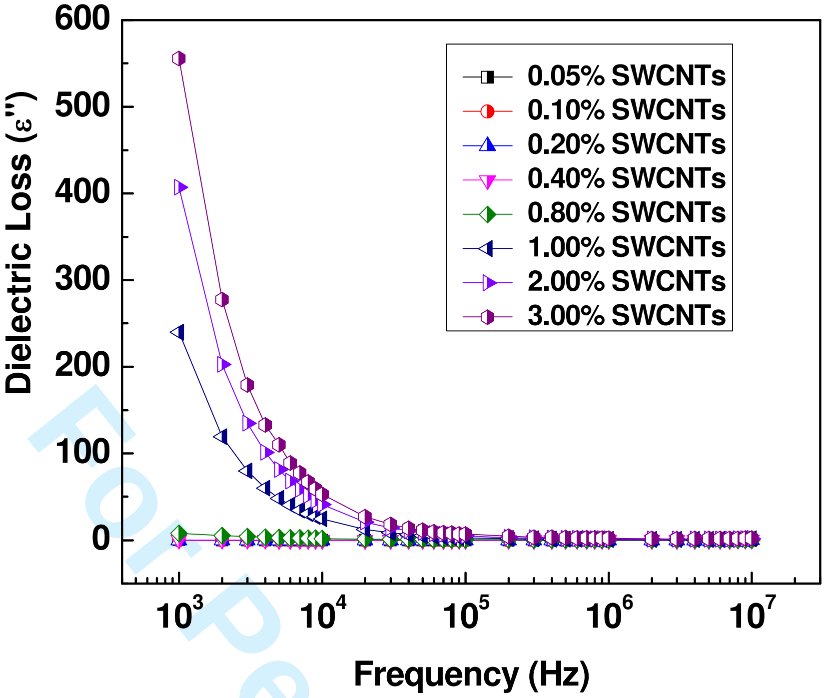


**Figure 5.** Dielectric loss versus  frequency) for SWCNTs-PC composites

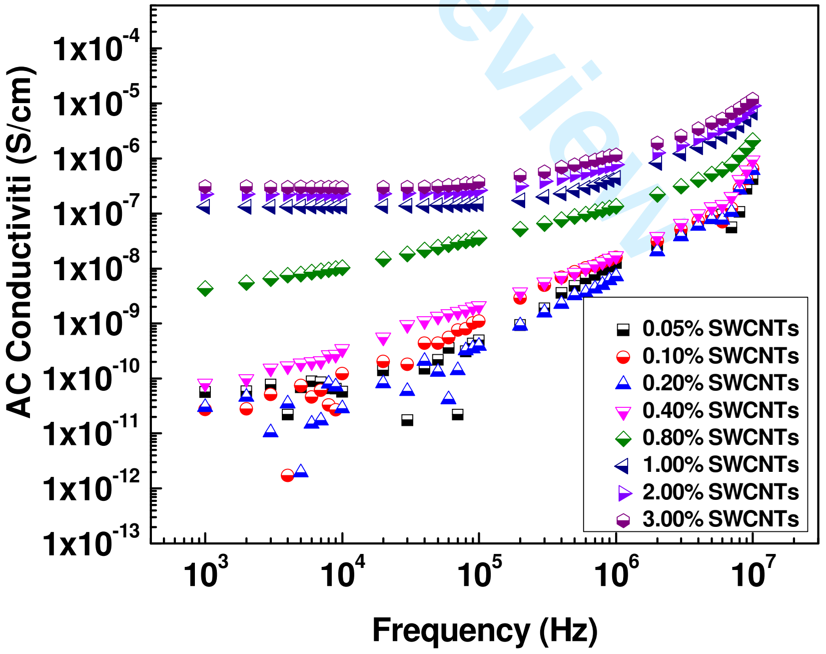


**Figure 6. The dependence of AC conductivity on frequency for SWCNTs-PC composites.**

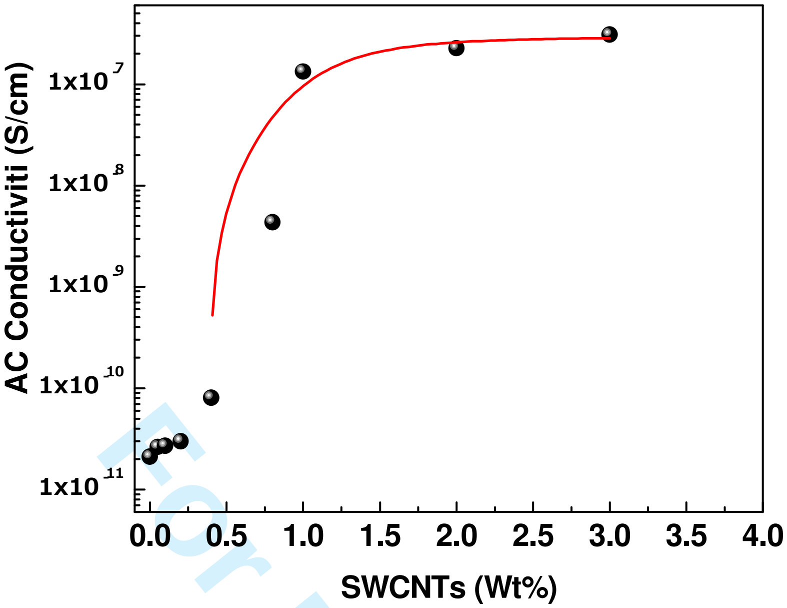


**Figure 7.** AC conductivity versus SWCNT concentration at 1 KHz.

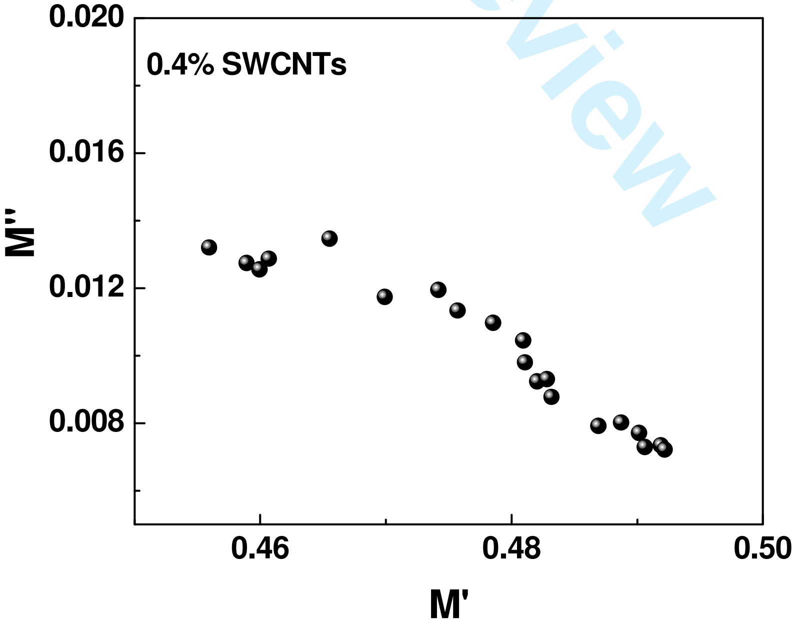


**Figure 8.** Argand plot below the percolation threshold .

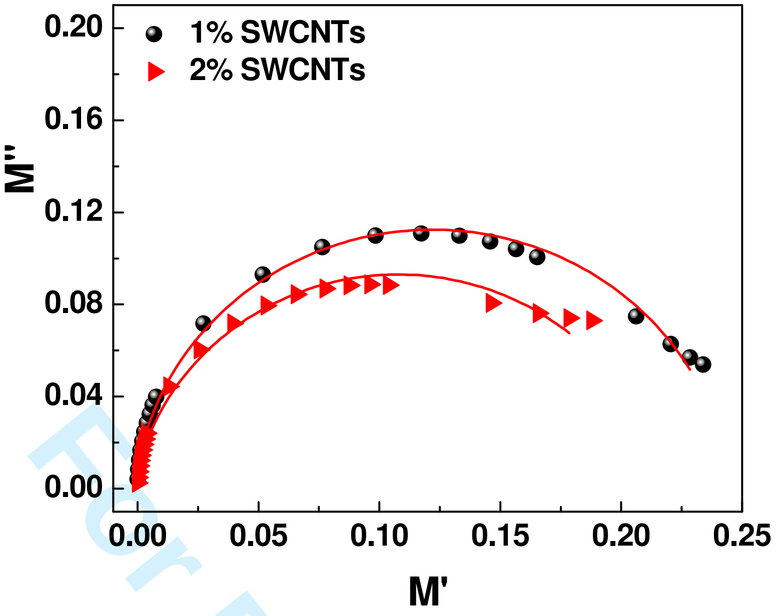


**Figure 9.** Argand plots above the percolation threshold.

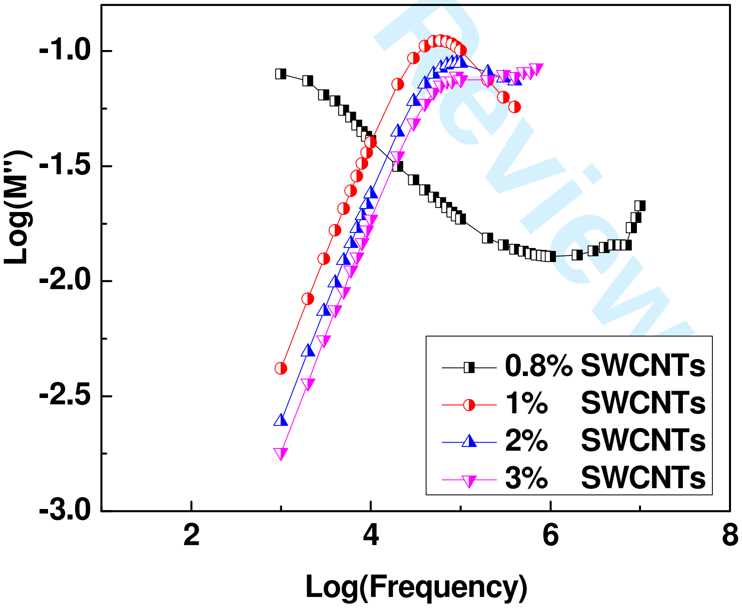


**Figure 10.** Log(M”) versus Log (Frequency) above the percolation threshold.

*Mechanical properties*

Figure 11 presents the stress–strain curves for PC loaded with 0, 0.2, 0.4, 0.8 and 2 wt % SWCNTs at constant temperature of 25 °C. The ultimate strength is not shown in this figure and this refers to the maximum stress available in the used instrument. However, all composites show at first straight lines relations between stress and strain in the studied range of stresses. This reflects the Hookean behavior for all composites at low strain values. The elastic modulus, E, was determined from the insert of the figure for all composites. The obtained values are presented in Figure 12 as a function of the weight content of SWCNTs. This dependence appears to have what is known as the mechanical percolation behavior[43] .

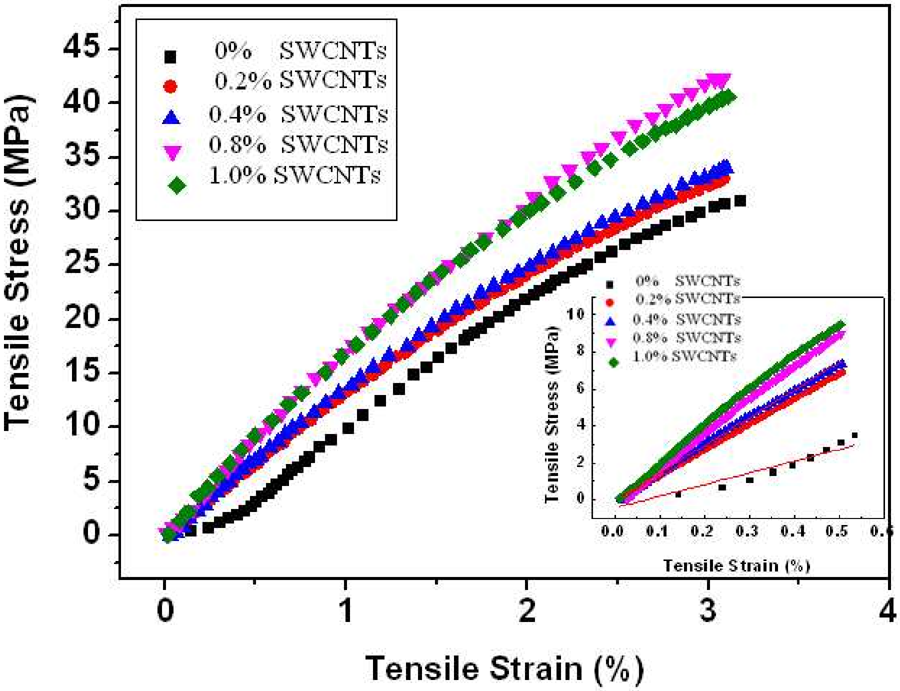


**Figure 11.** Stress-Strain curves of PC loaded with different SWCNTs loading at 25 °C.

To determine the mechanical percolation threshold of SWCNTs-PC composites, the relation between the elastic modulus (E) and loading of the filler in a medium (C) is drawn into a modified power law equation:

$$E \; □ \; (C - C_o)^a \qquad (3)$$

where C is the CNTs loading, $C_o$ is loading at the mechanical percolation threshold and ***a*** is a constant depending on the host material (PC).

In percolated systems one can observe a drastic change of the elastic modulus for a given concentration of the filler. This indicates that the SWCNTs-PC composite reaches a mechanical percolation threshold at which the nanotubes block the motion of the polymer molecules [43]. The power law Equation (3) was used to determine the value of the mechanical percolation threshold. The function was fitted to the experimental data points of E at C > Co. The scaling parameters were found by incrementally varying C until the best linear fit to the data points was obtained. The mechanical percolation threshold ($C_o$) was found to be at 0.08 wt% SWCNT. The scaling exponent *a* is found to equal 1.85. The low mechanical percolation threshold obtained in this study (0.08 wt%) is attributed to the high aspect ratio of the CNTs filler and also indicates a homogenous dispersion of SWCNTs within PC matrix. Comparing with electrical and structure results, there is a good agreement between mechanical and electrical results, both analysis shows improvement in the electrical and mechanical properties with low percolation threshold value. Additionally, the increase of the elastic modulus with CNTs support the SEM conclusion that there is good interfacial bonding between CNTs and polymer matrix.

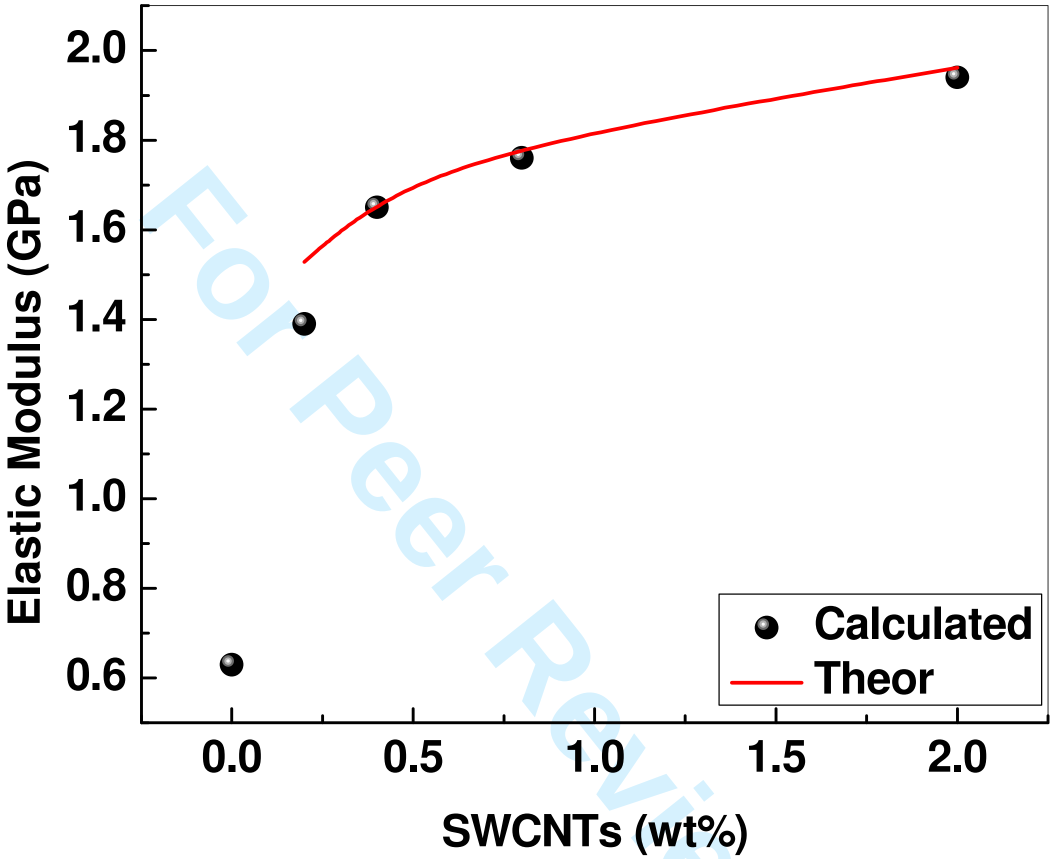


**Figure 12.** The dependence of the elastic modulus of PC on the SWCNTs loading at 25 $^{o}$C.

## Conclusions

This study shows that UVO Functionalized SWCNTs up to 180 min will improve SWCNTs dispersion and will initiate CNTs network with low SWCNTs fraction. Electrical results show that the electrical conductivity increases up to six order of magnitudes after the percolation threshold (0.5 wt% SWCNTs) and the conduction mechanisms that appear in these samples are Ohmic and Space Charge Limited mechanisms at low and high applied electric field respectively. Generally, SWCNTs increase the dielectric constant and dielectric loss of PC matrix. The dielectric relaxation behavior, in general, indicates the existence of capacitor element. At the same time, the analysis of the relaxation behavior before and after the percolation threshold, reveal that the relaxation behavior is mostly due to polymer chain relaxation at low SWCNTs content. While at high level of SWCNTs fraction ( above 0.8 wt% SWCNTs) , the relaxation behavior appears to be mostly due to charge conductivity relaxation. Finally, the elastic modulus results show a percolation behavior with a threshold of 0.08 wt. %

SWCNT and the increase of the elastic modulus with CNTs support the SEM conclusion that there is a good interfacial bonding between CNTs and polymer matrix.

## Acknowledgements

The authors would like to thank the Deanship of Scientific Research at King Faisal University, Al-Ahsa, KSA, for the financial support for this research, which has a project ID number: 120049.

## References

1. Barrau S, Demont P, Peigney A, Laurent C and Lacabanne C. DC and AC conductivity of carbon nanotubes-polyepoxy composites. *Macromolecules*. 2003; 36: 5187-94.
2. Hornbostel B, Pötschke P, Kotz J and Roth S. Single‐walled carbon nanotubes/polycarbonate composites: basic electrical and mechanical properties. *physica status solidi (b)*. 2006; 243: 3445-51.
3. Huang Y, Li N, Ma Y, et al. The influence of single-walled carbon nanotube structure on the electromagnetic interference shielding efficiency of its epoxy composites. *Carbon*. 2007; 45: 1614-21.
4. Jung YJ, Kar S, Talapatra S, et al. Aligned carbon nanotube-polymer hybrid architectures for diverse flexible electronic applications. *Nano letters*. 2006; 6: 413-8.
5. Li N, Huang Y, Du F, et al. Electromagnetic interference (EMI) shielding of single-walled carbon nanotube epoxy composites. *Nano letters*. 2006; 6: 1141-5.
6. Moniruzzaman M and Winey KI. Polymer nanocomposites containing carbon nanotubes. *Macromolecules*. 2006; 39: 5194-205.
7. Ramasubramaniam R, Chen J and Liu H. Homogeneous carbon nanotube/polymer composites for electrical applications. *Applied physics letters*. 2003; 83: 2928-30.
8. Spitalsky Z, Tasis D, Papagelis K and Galiotis C. Carbon nanotube-polymer composites: Chemistry, processing, mechanical and electrical properties. *Progress in Polymer Science*. 2010; 35: 357-401.
9. Aljaafari A, Ibrahim S and El-Brolossy T. Thermophysical and electrical characterization of PVC–SWNT nanocomposites. *Composites Part A: Applied Science and Manufacturing*. 2011; 42: 394-9.
10. Ibrahim S. Low Percolation Behaviour of Polystyrene Carbon Nanoparticles (PS/CNPs) Composite. . *J. Mater. Environ. Sci.*. 2011; 2(2): 118-127.
11. Singh V, Mohan S, Singh G, Pandey P and Prakash R. Synthesis and characterization of polyaniline–carboxylated PVC composites: Application in development of ammonia sensor. *Sensors and Actuators B: Chemical*. 2008; 132: 99-106.
12. Bryning MB, Islam MF, Kikkawa JM and Yodh AG. Very Low Conductivity Threshold in Bulk Isotropic Single‐Walled Carbon Nanotube–Epoxy Composites. *Advanced materials*. 2005; 17: 1186-91.
13. Ayesh A. Dielectric relaxation and thermal stability of polycarbonate doped with MnCl2 salt. *Journal of Thermoplastic Composite Materials*. 2008; 21: 309-22.
14. Ayesh AS. Dielectric Properties of Polyethylene Oxide Doped with NH4I Salt. *Polymer journal*. 2009; 41: 616-21.

15. Ayesh AS. Electrical and optical characterization of PMMA doped with Y 0.0025 Si 0.025 Ba 0.9725 (Ti (0.9) Sn 0.1) O 3 ceramic. *Chinese Journal of Polymer Science*. 2010; 28: 537-46.

16. Ayesh AS and Abdel-Rahem R. Effect of Ba (Ti (0.9) Sn 0.1) O 3 ceramic doping on optical, thermal and dielectric properties of polycarbonate host. *Bulletin of Materials Science*. 2010; 33: 589-95.

17. Ayesh AS and Abdel-Rahem RA. Optical and electrical properties of polycarbonate/MnCl2 composite films. *Journal of Plastic Film and Sheeting*. 2008; 24: 109.

18. Ibrahim S, Al Jaafari AA and Ayesh AS. Physical characterizations of three phase polycarbonate nanocomposites. *Journal of Plastic Film and Sheeting*. 2011; 27: 275-91.

19. Gupta V and Miura N. Polyaniline/single-wall carbon nanotube (PANI/SWCNT) composites for high performance supercapacitors. *Electrochimica acta*. 2006; 52: 1721-6.

20. Sun L, Warren G, O'reilly J, et al. Mechanical properties of surface-functionalized SWCNT/epoxy composites. *Carbon*. 2008; 46: 320-8.

21. Bauhofer W and Kovacs JZ. A review and analysis of electrical percolation in carbon nanotube polymer composites. *Composites Science and Technology*. 2009; 69: 1486-98.

22. Chen L, Pang XJ and Yu ZL. Study on polycarbonate/multi-walled carbon nanotubes composite produced by melt processing. *Materials Science and Engineering: A*. 2007; 457: 287-91.

23. Hornbostel B, Pötschke P, Kotz J and Roth S. Mechanical properties of triple composites of polycarbonate, single-walled carbon nanotubes and carbon fibres. *Physica E: Low-dimensional Systems and Nanostructures*. 2008; 40: 2434-9.

24. Barrau S, Demont P, Perez E, Peigney A, Laurent C and Lacabanne C. Effect of palmitic acid on the electrical conductivity of carbon nanotubes-epoxy resin composites. *Macromolecules*. 2003; 36: 9678-80.

25. Chen ZK, Yang JP, Ni QQ, Fu SY and Huang YG. Reinforcement of epoxy resins with multi-walled carbon nanotubes for enhancing cryogenic mechanical properties. *Polymer*. 2009; 50: 4753-9.

26. Sandler J, Kirk J, Kinloch I, Shaffer M and Windle A. Ultra-low electrical percolation threshold in carbon-nanotube-epoxy composites. *Polymer*. 2003; 44: 5893-9.

27. Song YS and Youn JR. Influence of dispersion states of carbon nanotubes on physical properties of epoxy nanocomposites. *Carbon*. 2005; 43: 1378-85.

28. Tseng CH, Wang CC and Chen CY. Functionalizing carbon nanotubes by plasma modification for the preparation of covalent-integrated epoxy composites. *Chemistry of materials*. 2007; 19: 308-15.

29. Kim SD, Kim JW, Im JS, Kim YH and Lee YS. A comparative study on properties of multi-walled carbon nanotubes (MWCNTs) modified with acids and oxyfluorination. *Journal of fluorine chemistry*. 2007; 128: 60-4.

30. Meng H, Sui G, Fang P and Yang R. Effects of acid-and diamine-modified MWNTs on the mechanical properties and crystallization behavior of polyamide 6. *Polymer*. 2008; 49: 610-20.

31. Najafi E, Kim JY, Han SH and Shin K. UV-ozone treatment of multi-walled carbon nanotubes for enhanced organic solvent dispersion. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2006; 284: 373-8.

32. Sham ML and Kim JK. Surface functionalities of multi-wall carbon nanotubes after UV/Ozone and TETA treatments. *Carbon*. 2006; 44: 768-77.

33. Najafi E, Kim J-Y, Han S-H and Shin K. UV-ozone treatment of multi-walled carbon nanotubes for enhanced organic solvent dispersion. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2006; 284-285: 373-8.

34. Najafi E and Shin K. Radiation resistant polymer–carbon nanotube nanocomposite thin films. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2005; 257-258: 333-7.

35. Yu JG, Huang KL, Yang Q and Liu YF. Solubilizing polycarbonate-modified single-walled carbon nanotubes by simultaneously attaching octadecylamine. *Physica E: Low-dimensional Systems and Nanostructures*. 2009; 41: 771-4.

36. Kim GM, Michler G and Pötschke P. Deformation processes of ultrahigh porous multiwalled carbon nanotubes/polycarbonate composite fibers prepared by electrospinning. *Polymer*. 2005; 46: 7346-51.

37. Ding W, Eitan A, Fisher F, et al. Direct observation of polymer sheathing in carbon nanotube-polycarbonate composites. *Nano letters*. 2003; 3: 1593-7.

38. Kum CK, Sung YT, Han MS, et al. Effects of morphology on the electrical and mechanical properties of the polycarbonate/multi-walled carbon nanotube composites. *Macromolecular Research*. 2006; 14: 456-60.

39. Ibrahim S, Ayesh A and Shoaibi AA. Optoelectrical properties of ferroelectric PC/ceramic composites. *Journal of Thermoplastic Composite Materials*. 2009; 22: 335-48.

40. Bunakov A, Lachinov A and Salikhov R. Current□voltage characteristics of thin poly (biphenyl□4□ylphthalide) films. Wiley Online Library, 2004, p. 387-92.

41. Burrows P, Bulovic V, Forrest S, Sapochak L, McCarty D and Thompson M. Reliability and degradation of organic light emitting devices. *Applied physics letters*. 1994; 65: 2922-4.

42. Musa I, Eccleston W and Higgins S. Further analysis of space-charge-limited currents in polybenzo [c] thiophene films. *Journal of applied physics*. 1998; 83: 5558.

43. Abu□Abdeen M. Investigation of the rheological, dynamic mechanical, and tensile properties of single□walled carbon nanotubes reinforced poly (vinyl chloride). *Journal of Applied Polymer Science*, DOI: 10.1002/app.35061

44. Koizhaiganova RB, Kim HJ, Vasudevan T and Lee MS. Double-walled carbon nanotube (DWCNT)-poly (3-octylthiophene)(P3OT) composites: Electrical, optical and structural investigations. *Synthetic Metals*. 2009; 159: 2437-42.

45. López-Mata C, Nicho M, Hu H, Cadenas-Pliego G and García-Hernández E. Optical and morphological properties of chemically synthesized poly3-octylthiophene thin films. *Thin solid films*. 2005; 490: 189-95.

**46. Abu-Abdeen M, Ayesh AS and Al Jaafari AA. Physical characterizations of semi-conducting conjugated polymer-CNTs nanocomposites. *Journal of Polymer Research*. 2012; 19: 1-9.**

**47. Li Y, Tjong S and Li R. Dielectric properties of binary polyvinylidene fluoride/barium titanate nanocomposites and their nanographite doped hybrids. *Express Polymer Letters*. 2011; 5: 526-34.**

# Low percolation threshold of functionalized SWCNTs- polycarbonate nanocomposites

**Ayman S. Ayesh*[1], S.S. Ibrahim[1,2], and M. Abu-Abdeen[1,2]**

[1] Department of Physics, College of Science, King Faisal University, Al-Ahsa, KSA.
[2] Department of Physics, College of Science, Cairo University, Egypt.

## Abstract

A series of polycarbonate films loaded with different concentrations of UV-ozone (UVO) pretreated single walled carbon nanotubes (SWCNT) were prepared. The electrical and mechanical properties of these composites were investigated. The improvement of the SWCNTs dispersion in PC matrix leads to a dramatic enhancement in the electrical conductivity with low percolation threshold (0.5 wt. % of SWCNTs loading). Results obtained from the analysis of the dielectric parameters at room temperature and domain frequency range reveal that SWCNTs increases the dielectric constant, dielectric loss, and AC conductivity of the composites. The dielectric relaxation behavior of these composites is mostly due to polymer molecular relaxation when the SWCNTs content is below the percolation threshold whereas it is almost due to the charge conductivity relaxation above 0.8 wt% SWCNTs. The calculated values of the elastic modulus obtained from the stress-strain curves, also show a percolation behavior with a threshold of 0.08 wt % SWCNT.

**Keywords**
SWCNTs, polycarbonate, nanocomposites, percolation, electrical, mechanical.

*Corresponding author: Ayman S. Ayesh, Department of Physics, College of Science, King Faisal University, P.O. B 400, 31982 Al-Ahsa, KSA, Email: dr_ayesh67@yahoo.co.uk or assalem@kfu.edu.sa.

## Introduction

Electrically conducting polymer composites have gained popularity recently because of their light weight, resistance to corrosion, flexibility, and processing advantages[1-10]. Generally, electrical conductivity of a polymer nanocomposite material depends on many factors, including the filler's intrinsic conductivity, dielectric constant, and aspect ratio[3]. Thus, the small diameter, high aspect ratio, high conductivity, and mechanical strength of carbon nanotubes (CNTs), make them an excellent option for creating conductive composites at low filling[3, 11-18].

Extensive researches studied the electrical and mechanical properties of CNTs-polymer nanocomposites and they demonstrate that the electrical conductivity and mechanical properties highly depend on the dispersion of CNTs in the polymer matrix and also depend on the interfacial stress between the two components[2, 3, 19-23].

Due to the van der Waals attraction, nanotubes are held together as bundles and ropes. Thus they have very low solubility in solvents and tend to remain as entangled agglomerates. However, many techniques were used to overcome the difficulty of CNTs dispersion in polymer matrix, such as ultrasonication, high shear mixing, surfactant addition, melt blending and chemical modification through functionalization[1-4, 6-8, 12, 19-28]. The wet chemical functionalization of carbon nanotubes using different strong acids, generally, will introduce carboxylic groups at CNTs surface and consequently, this will improve CNTs dispersion in organic solvents or polymer matrix. At the same time, such a method will cause a morphological damages to CNTs. In addition, oxidation process with strong acids creates significant physical damages and causing severe degradation of the originally desirable properties of CNTs[29, 30]. On the other hand, dry oxidation such as ozone in the presence of ultraviolet (UV/$O_3$) have been an alternative treatment to resolve the issues associated with the wet oxidation[31-34]. Additionally, many researchers showed that UV-modified CNTs induced a higher electrical conductivity in polymer matrices and they reported that this method will not cause any morphological damages to CNTs[33, 34] .

Several studies investigated the effect of MWCNTs or SWCNTs on the electrical and mechanical properties of polycarbonate using different preparation techniques[2, 23, 35-37]. They reported that the percolation threshold in these composites was between 1.5 and 2.5 wt% CNTs[38]. Despite of these studies, present work, however, introduces interesting additions to CNT-PC nanocomposites.

The present work aims to prepare well dispersed SWCNTs-PC nanocomposites using UVO pretreatment. The electrical properties (DC and AC) of these nanocomposites are presented and discussed. The percolation threshold of SWCNTs in PC matrix is also presented and estimated. Finally, the correlations between structure, electrical and mechanical properties are discussed.

## Experimental

### *Materials*

Single walled carbon nanotubes (SWCNTs) was purchased from Aldrich company ( 704113) with outer diameter of 0.7-1.3 nm and average length of 800 nm. SWCNTs was functionalized with UVO using UV-ozone generator (Model # 42-220, Jelight Co.) in ambient laboratory air for a period up to 180 min. Bisphenol A polycarbonate resin PC (product by ACROS ORGANICS Company, New jersey (USA) , MW 64,000 ) was used as a matrix polymer and Dichloromethane (Aldrich) was used as solvent for PC polymer.

### *Sample preparation*

The SWCNTs was irradiated with UV-ozone (UVO 41 commercial lamp) at a distance of 6 mm from the lamp of power 28,000 W per $cm^2$ and wavelength of 254 nm. During the UV irradiation, the powder was stirred with a spatula at 10 min intervals to provide a uniform exposure up to 180 min. The pretreated SWCNTs was added to dichloromethane solvent and ultrasonicated for 30 min using UP 200S ultrasonicator (Hielsher Company-Ultrasonic Technology). The dispersion of SWCNTs in dichloromethane was observed at different UV exposure time with 30 min ultrasonication as shown in Figure 1A. It is clear that the dispersion of SWCNTs improved when the exposure time is 180 min.

Bisphenol A polycarbonate resin was dissolved in dichloromethane solvent and was stirred at 30 $^0$C by a magnetic stirrer for 24 hr. UV pretreated SWCNTs was first ultrasonicated in dichloromethane for 30 min and then mixed with polymer solution. The mixture was again stirred for 24 hr until the SWCNTs powder became highly dispersed in polycarbonate solution. This solution was casted in a glass petri dish (dia. of 10 cm). The solvent was evaporated at room temperature for 24 h. Samples with different SWCNTs-PC concentrations (0.05, 0.2, 0.4, 0.5, 0.8, 1, 2 and 3 SWCNTs wt%) were kept inside vacuumed dissector. The film thickness (~ 0.1 mm) was measured using digital micrometer (MOTOTOYO - China) with 0.001mm resolution.

### *Electrical measurements*

Electrical measurements with AC and DC applied electric fields were performed using 4200-SCS Semiconductor Characterization System (KEITHLEY Co.). Samples were shaped into circular discs of area 1.2 $cm^2$ and thickness of 0.1 mm. The DC electrical parameters (I-V and DC conductivity ($\sigma_{DC}$)) were measured at room temperature. Relative permitivity (ε'), dielectric loss (ε'') and AC conductivity ($\sigma_{AC}$) was calculated from the measured capacitance (C), and loss tangent (tan (δ)) data[13, 14, 16, 17] at room temperature and frequency range 1 KHz-10 MHz.

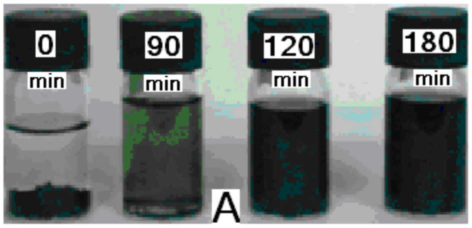
### *Tensile test*

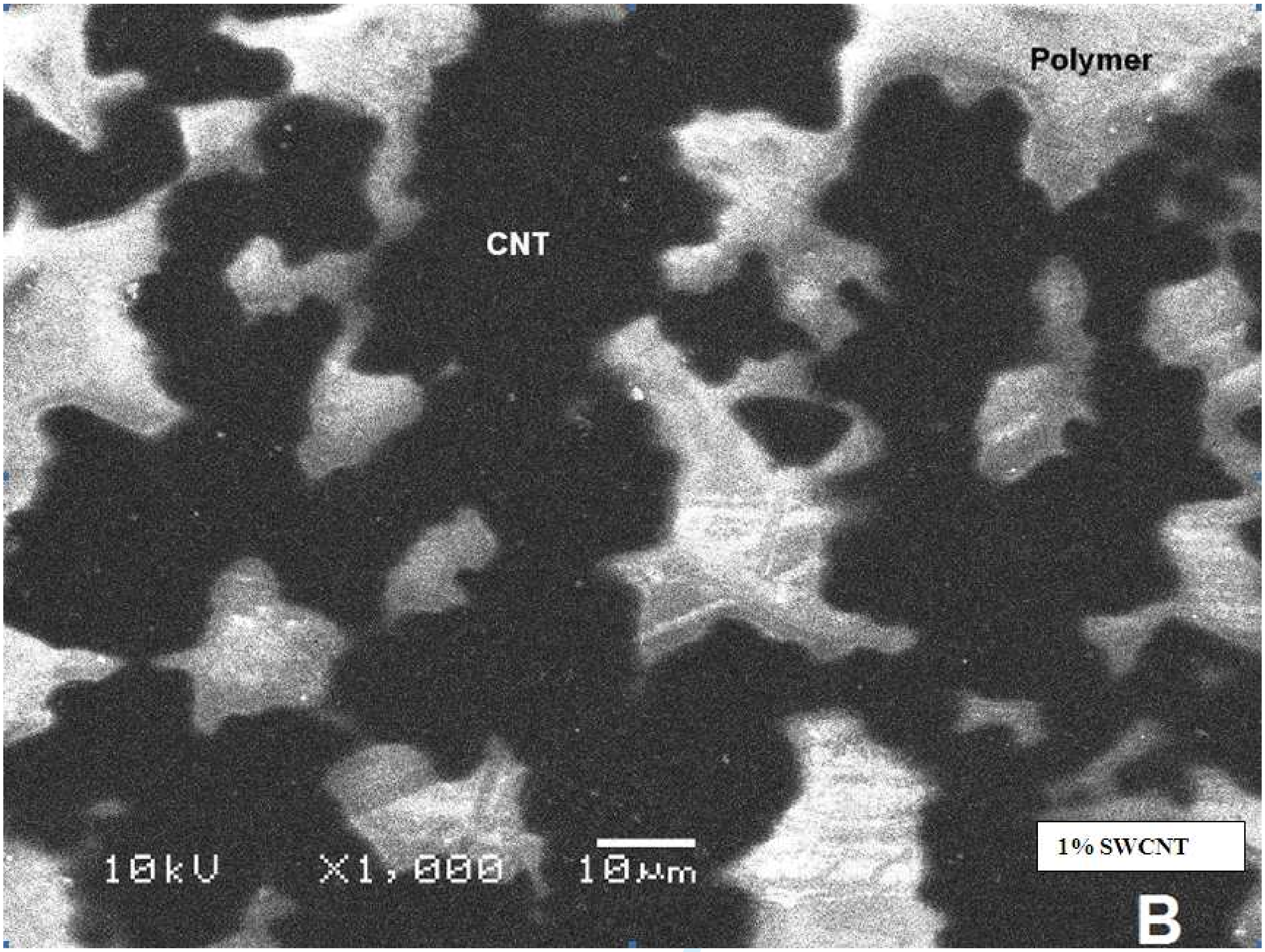
The tensile test were carried out on a dynamic mechanical analysis Q800 (TA Instruments LLC, Delaware, USA) instrument using the tension film clamping arrangement. Specimens in the form of films with dimensions 15 mm length, 4 mm width and 0.1 mm thick were used. The tensile test on film samples were carried out at 25 °C at a force rate of 3 N/min.

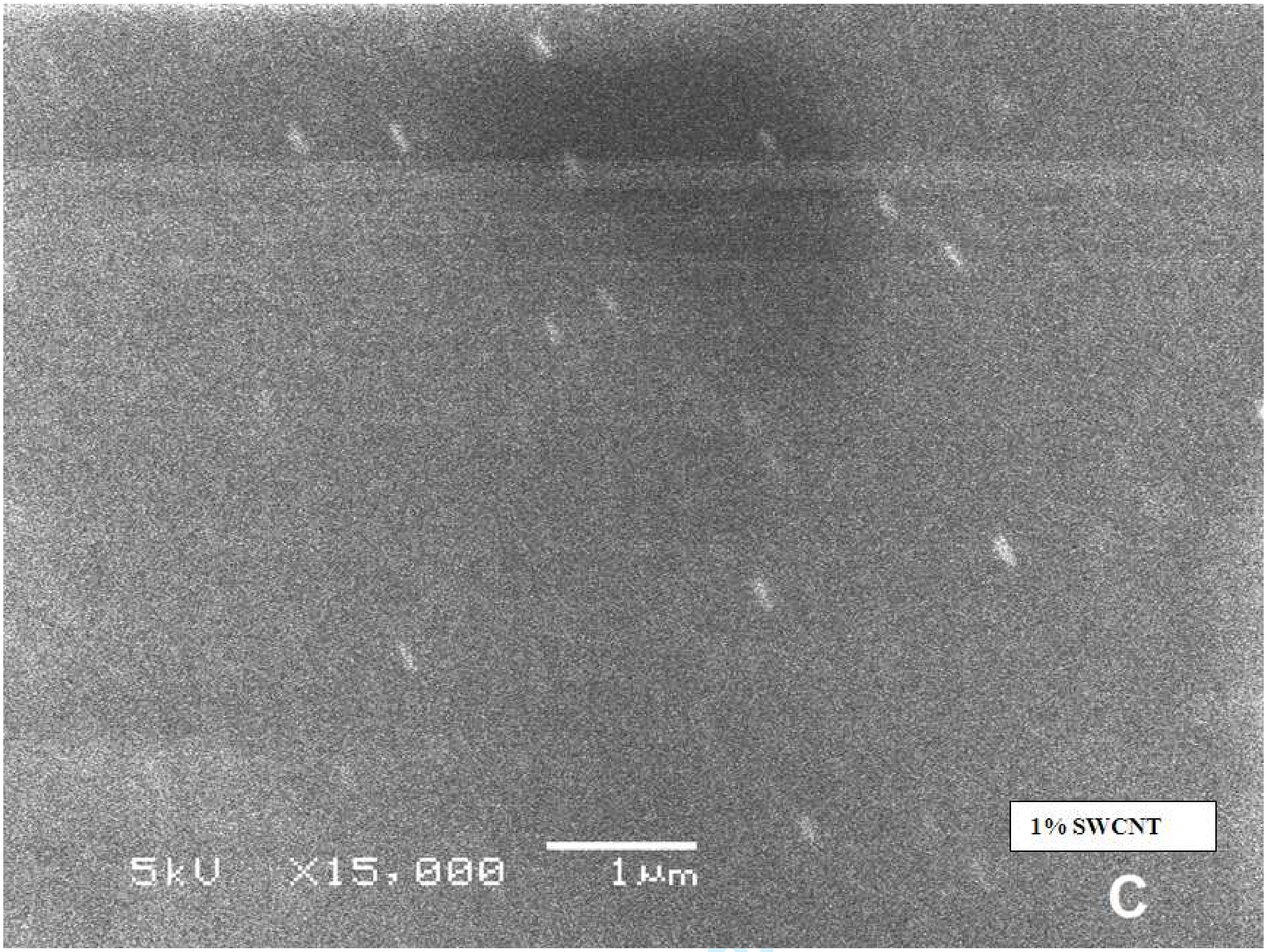
### *Scanning electron microscopy (SEM)*

The morphology of the prepared nanocomposites were examined using a Jeol scanning electron microscope (J.S.M. 6380 ) with low and high vacuum. The operation system controlled by IBM computer. Samples were coated with gold in automatic sputter coater (Polaron SC 500), and then transferred to the electron microscope to be examined. The electrical image shift of $\pm 50\mu m$.

Figures 1B, 1C and 1D show the SEM micrographs of 1% SWCNTs (Figures 1B and 1C) and 0.6% SWCNTs (Figure 1D) samples. These images show a good dispersion of CNTs with enhanced interfacial bonding between CNTs and PC matrix[39] in addition to the formation of CNTs network in the PC matrix.




Polymer
CNT
10kV X1,000 10μm
1% SWCNT
B


1% SWCNT
5kV X15,000 1μm
C

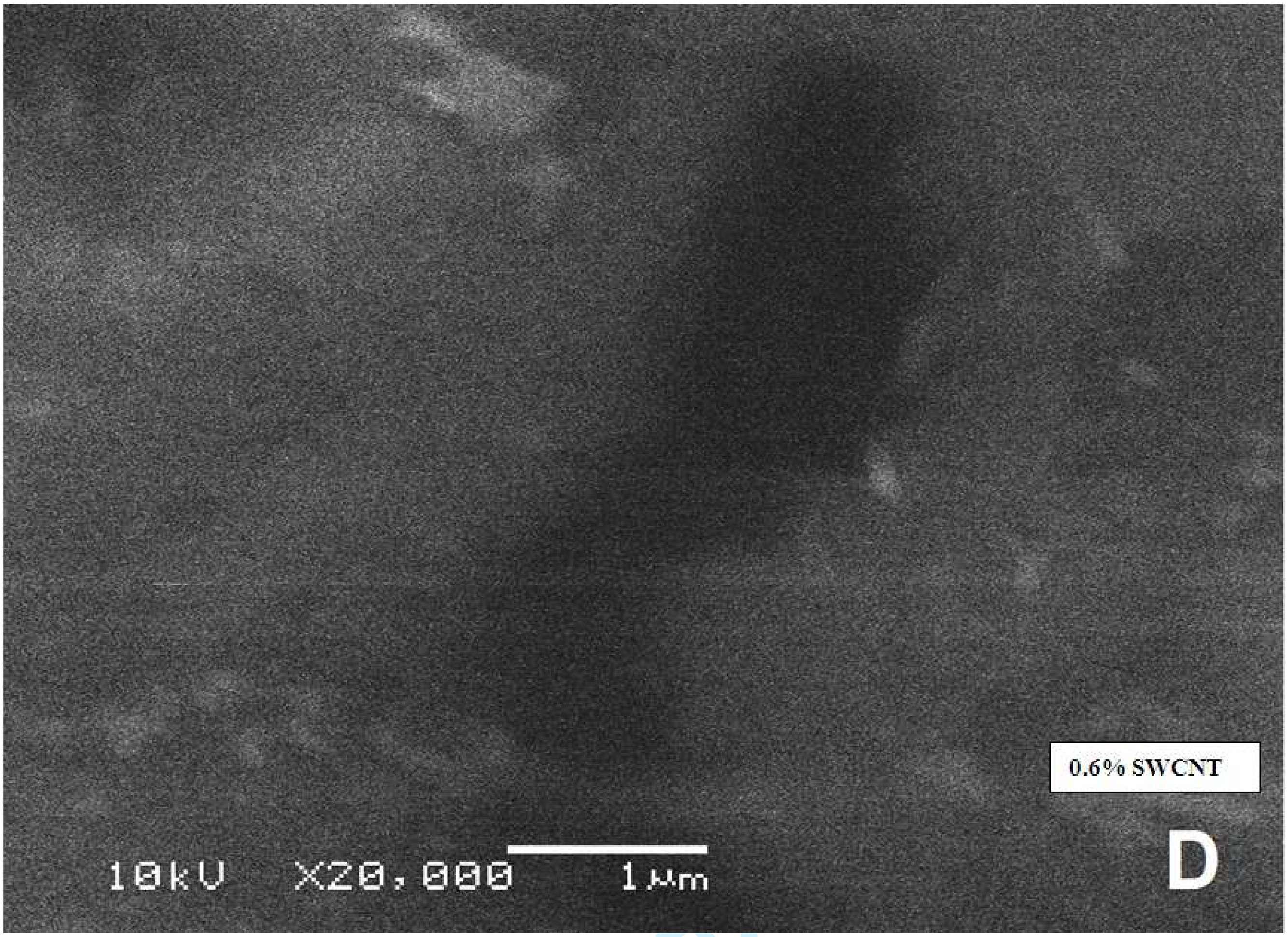


**Figure 1. (A)** Dispersion of UVO pretreated SWCNTs in dichloromethane, (B) to (D) SEM micrographs of SWCNTs-PC composites: (B)-(C) 1% SWCNTs and (D) 0.6% SWCNTs .

## Results and Discussion

### *Electrical Properties*

### *I-V characteristics and DC conductivity*

I-V characteristics of the pretreated SWCNTs-PC composites with different SWCNT loadings at room temperature are shown in Figure 2. These characteristics indicate that the current level in these composites increases with the addition of SWNTs. This is consistent with the fact that the conductivity of the composites increases as the SWNTs concentration increases and such a trend was also observed previously by many authors in SWCNTs-polymer composites[2, 3, 12, 40-46]. The charge transport mechanism based on the general power law model $I=KV^m$, where $K$ is a constant and $m$ is the exponent, has been widely used for the analysis of the conduction phenomenon in organic or polymeric materials[41,42]. The model is divided into three regimes, Ohmic (m=1), trap-free space charge limited (m=2), and trap charge limited (m>2)[44-46].

I-V characteristics on log-log scales reveal two distinct regions which can be fitted using the general power law model. The obtained results which are listed in Table (1) reveal that at lower voltages, the exponent $m_1$ is determined to be around 1, implying that the current varies linearly with voltage and hence the charge transport mechanism is governed by Ohm's law. At second voltages region (region II in Figure 2) , the exponent $m_2$ is around 2 which means that at this region the charge mechanism is due to the space charge limited current (SCLC) [40]. Generally, in the ohmic region the field due to the injected barriers is negligible compared to that due to the applied bias. This condition breaks down at the space charge limit when the injected carrier density becomes so large that the field due to the carriers themselves dominates over that of the applied bias[12, 21, 26, 27, 40, 43].

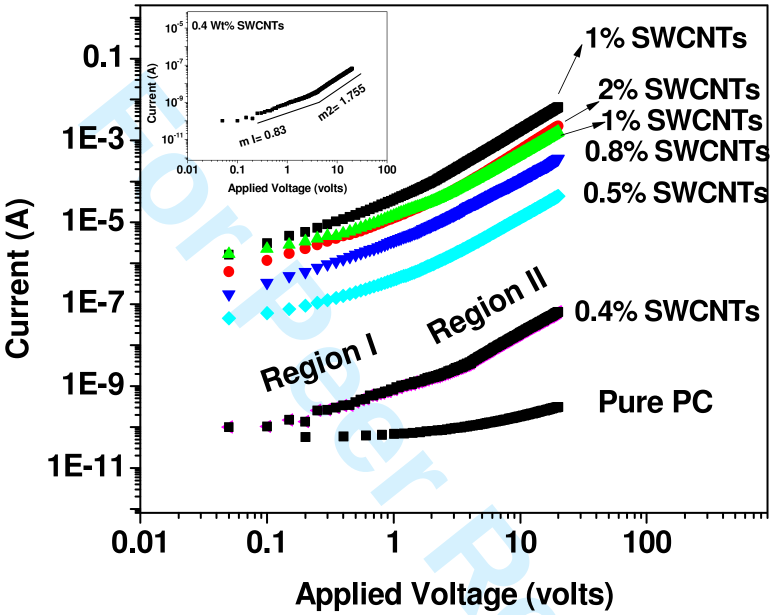


**Figure 2.** I-V characteristics of SWCNTs-PC nanocomposites**.**

**Table 1.** The calculated exponent values $m_1$ and $m_2$ of SWCNTs-PC nanocomposites.

| SWCNTs wt% | $m_1$ | $m_2$ |
|---|---|---|
| 0 | 0.65 | - |
| 0.4 | 0.83 | 1.75 |
| 0.5 | 0.77 | 1.74 |
| 0.8 | 1.01 | 1.64 |
| 1 | 0.75 | 1.77 |
| 2 | 1.01 | 1.93 |
| 3 | 1.04 | 1.86 |

Electrical conductivity depends on the polymer matrix and the filler materials. If the filler material is CNTs, it is decided by its purity, alignment, and the concentration. In such composites, the polymer layer in the internanotube connections presents highly resistive section in the electrical pathway, acting as a barrier to efficient carrier transport between the nanotubes and models fluctuation-induced tunneling for the conductivity[45-46]. However, the room temperature DC conductivity of SWCNTs-PC composites was calculated from the known current, area, and thickness values for each sample and was determined at 20 volt. The obtained results are presented in Figure 3 as a function of the weight fraction of SWCNTs in PC matrix. As shown in this figure, the SWCNT increases the conductivity of the composites by about six orders of magnitude. This result suggests the existence of other contributions in the electrical conduction process in addition to those mechanisms mentioned above that is the formation of network structure between nanotubes in the polymer matrix will facilitate the electron transport through tunneling throughout the polymer or by electron hopping along CNTs interconnects[44-46] .

In the case of CNTs-polymer composites, the polymer layer in the internanotube connections presents highly resistive section in the electrical pathway, acting as a barrier to efficient carrier transport between the nanotubes. When the distance between nanotubes becomes sufficiently small, the electrical response of the composites is then described by percolation theory. The CNTs concentration that marks this insulator-conductor transition is referred to as the percolation threshold (Pc). Additionally, direct connection and overlapping of the CNT is not necessary i.e. nanotubes do not need to physically touch each other for conductivity. Nanotubes can just be close enough to allow for a hopping/ tunneling electron effect; these mechanisms require the CNT- CNT distance to be less than 5nm. As a result, a higher volume fraction of CNTs filler is needed to achieve electrical percolation threshold[21]**.** However, one of the percolation theories has the following formula[44-46]:

$$\sigma = C\,[P - P_c]^t \qquad (1)$$

where σ is the composite conductivity, *P* the weight fraction of nanotubes in the composites, *C* is a constant, and *t* is a critical exponent. A successful fitting result was obtained when the experimental data (scatter curve) was fitted with Equation (1) (solid curve), see Figure 3. The obtained fitting parameters which are listed in Figure 3 reveal that the percolation threshold (Pc) of SWCNTs-PC is bout 0.5%. Compared with other researchers[2, 23, 35-38] in CNTs-PC composites, the obtained results in the present study show a dramatic improvements in the electrical conductivity with a low percolation threshold (0.5 wt.% of SWNT loading), by significantly improving the dispersion of SWNTs in polycarbonate matrix. Kim et al [38], reported that the percolation threshold of CNTs-PC is between 1.5 and 2.5 wt% CNTs. Moreover, present study shows that UV pretreatment of SWCNT up to 180 min will improve SWCNTs dispersion, enhance their interfacial bonding with polymer, and reduce the percolation threshold of SWCNTs-PC composites.

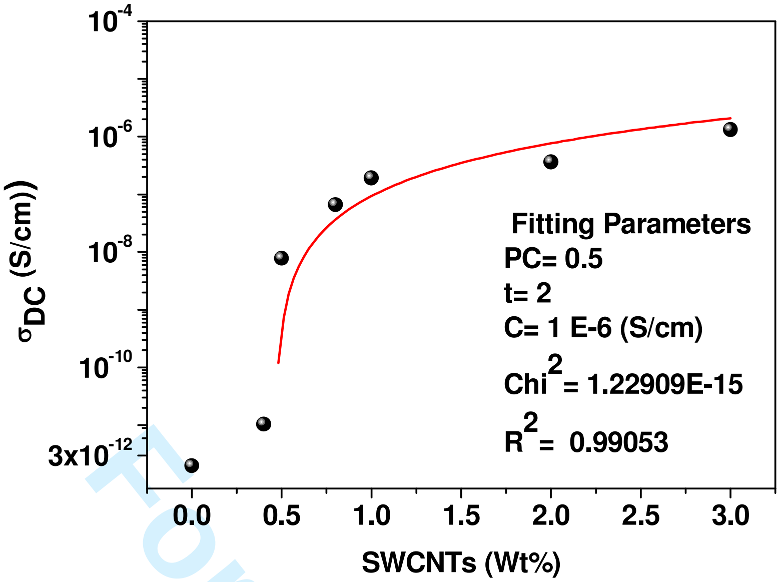


**Figure 3.** DC conductivity versus SWCNTs weight fraction for SWCNTs-PC nanocomposites**.** Scattered curve represent the experimental data while the solid one represent the fitted data.

### 3.1.2 Dielectric Relaxation and Ac Conductivity

AC dielectric parameters (relative permittivity $\varepsilon^{/}$, dielectric loss $\varepsilon^{//}$, and AC conductivity $\sigma_{AC}$) were determined from the obtained measured capacitance and loss tangent data for all SWCNTs-PC nanocomposites at room temperature and frequency range 1 KHz-10 MHz[13-17, 34]. The obtained results are presented graphically in Figures 4, 5, and 6 respectively. It is clear that relative permittivity, dielectric loss and AC conductivity are increased with increasing the loadings of SWCNTs in the PC matrix. Besides, the decrease of relative permittivity with frequency could be attributed to the insufficient time for dipoles to align before the field changes direction[13-17, 34]. Furthermore, the variations of relative permittivity, dielectric loss and AC conductivity with SWCNTs loadings could be attributed to the charge diffusions, chains orientation polarizations in addition to the contribution of Maxwell-Wagner polarization[13, 14, 17, 34, 46-47]. The AC conductivity versus SWCNTs loading is shown in Figure 7 at 1 KHz. AC conductivity also shows that the percolation threshold is almost around 0.5 wt% SWCNTs.

Generally, in all cases the relaxation behavior in these composites shows the existence of capacitor element. Moreover, the dielectric constant, dielectric loss, loss tangent and dielectric relaxation behavior of pure PC was previously measured and discussed by us [13, 16-18]. However, it will be very interested here if we consider the Argand plot between imaginary part (M") versus real part (M') of electric modulus to recognize the relaxation behavior of SWCNTs-PC composites before and after the percolation threshold. It was reported previously[13, 15, 16, 34], if the Argand plot between imaginary part (M") versus real part (M') of electric modulus has semicircular behavior then the relaxation is due to conductivity relaxation process, if not, then it is due to viscoelastic relaxation (or polymer molecular relaxation). In the present work, the values of $M^{/}$ and $M^{//}$ were determined from:

$$M^* = \frac{1}{\varepsilon^*} = \frac{1}{\varepsilon' - i\varepsilon''} = \frac{\varepsilon' + i\varepsilon''}{(\varepsilon' - i\varepsilon'')(\varepsilon' + i\varepsilon'')}$$

$$M^* = \frac{\varepsilon'}{(\varepsilon' - i\varepsilon'')(\varepsilon' + i\varepsilon'')} + i\frac{\varepsilon''}{(\varepsilon' - i\varepsilon'')(\varepsilon' + i\varepsilon'')}$$

$$M^* = \frac{\varepsilon'}{(\varepsilon'^2 + \varepsilon''^2)} + i\frac{\varepsilon''}{(\varepsilon'^2 + \varepsilon''^2)} = M' + iM'' \qquad (2)$$

Where □′ is the relative permittivity, □″ is the dielectric loss, *M*′ is the electric modulus and *M*″ is the electric loss modulus. The obtained results are presented graphically in Figures 8 and 9. It is clear that below the percolation threshold (0.4 Wt% SWCNTs), the plot does not follow semicircular behavior. This indicates that, at the domain frequency range, the relaxation process below the percolation threshold is mostly due to polymer molecular relaxation process. While above the percolation threshold (Figure 9), the relaxation behavior is mostly due to charge conductivity relaxation[13-16, 34]. Also it was reported[13, 14] that in case of charge relaxation, plots of log(M″) versus log(frequency) will reveal a slope value of 1. Figure 10 shows a plot graph of log(M") versus log(frequency) for 0.8 , 1 , 2 , and 3 wt% SWCNTs samples. The slope values in case of 1 , 2 , and 3 wt% SWCNTs samples are around 1, while the slope value in the case 0.8 wt% SWCMTs sample is -0.35. This indicates that the charge conductivity relaxation appears when the SWCNTs content is above 0.8 wt% SWCNTs.

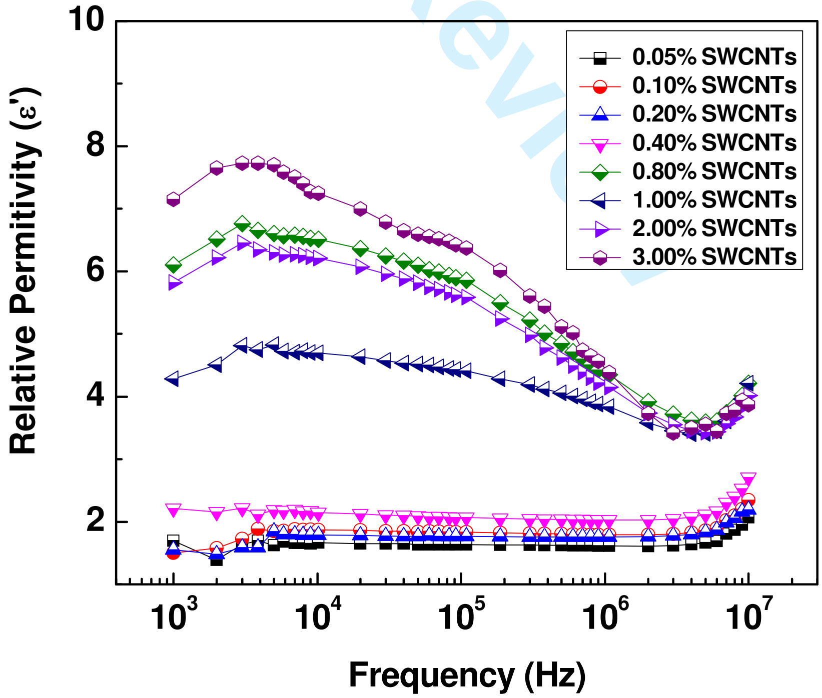


**Figure 4.** Relative dielectric permittivity versus frequency) for SWCNTs-PC composites.

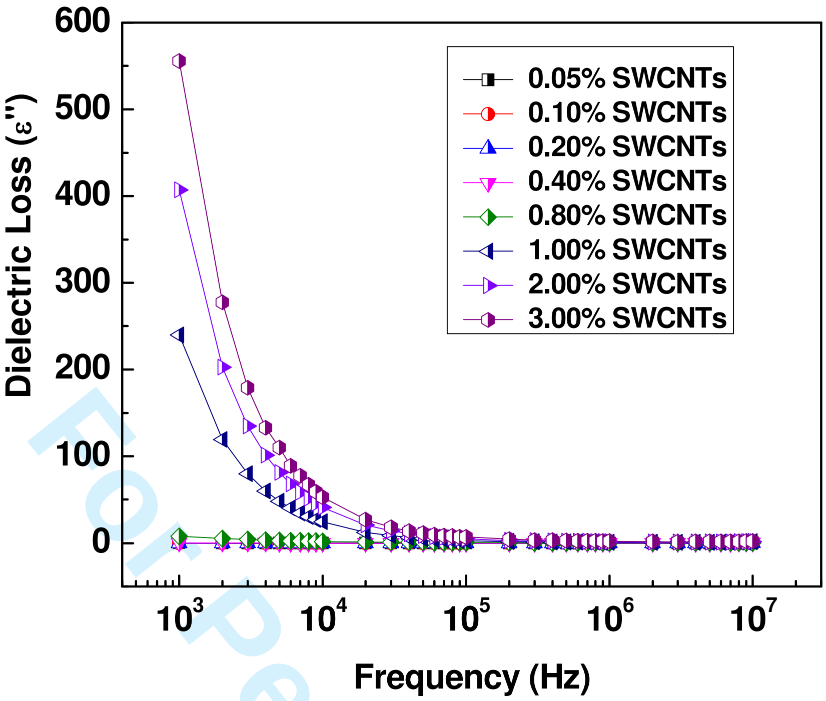


**Figure 5.** Dielectric loss versus  frequency) for SWCNTs-PC composites

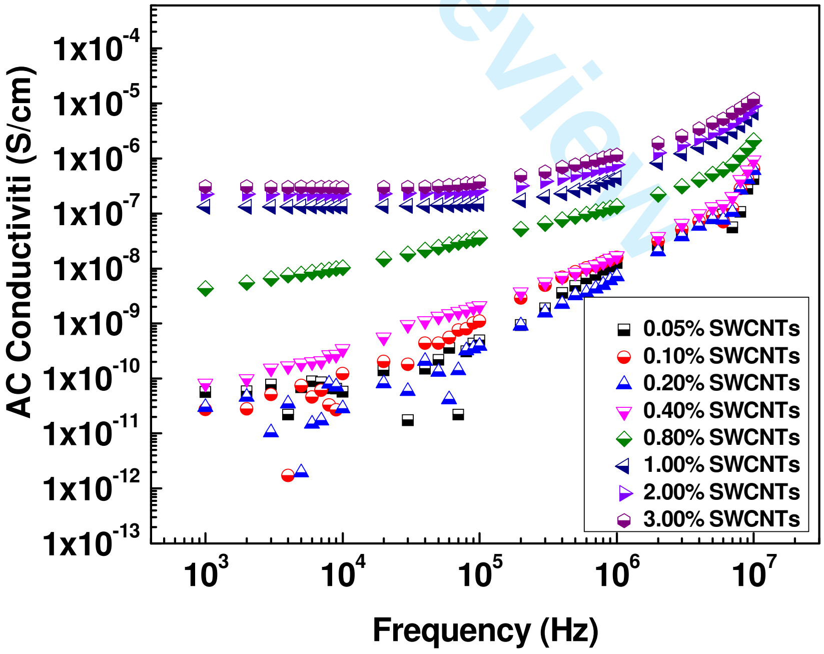


**Figure 6. The dependence of AC conductivity on frequency for SWCNTs-PC composites.**

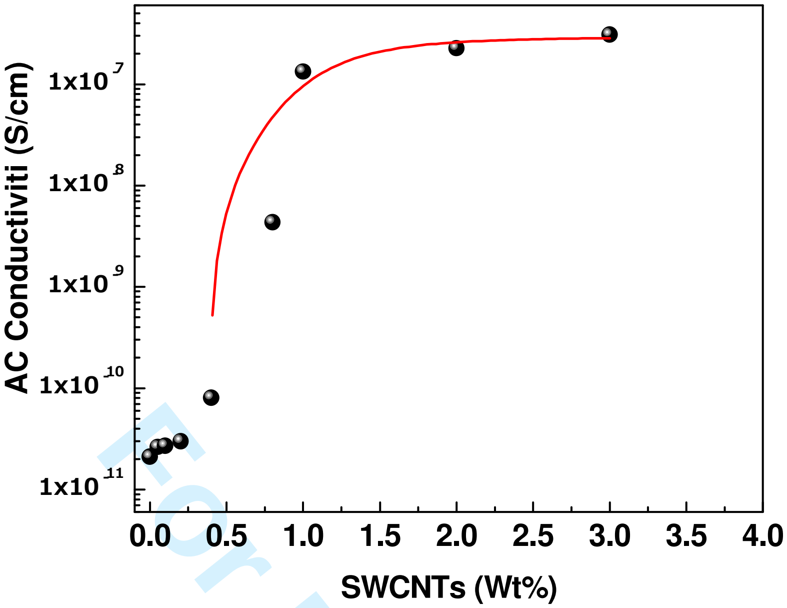


**Figure 7.** AC conductivity versus SWCNT concentration at 1 KHz.

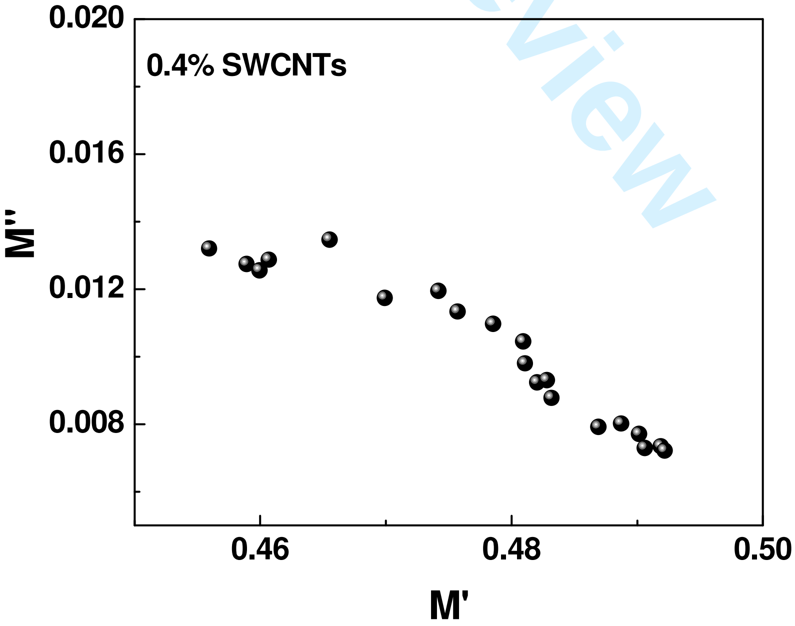


**Figure 8.** Argand plot below the percolation threshold .

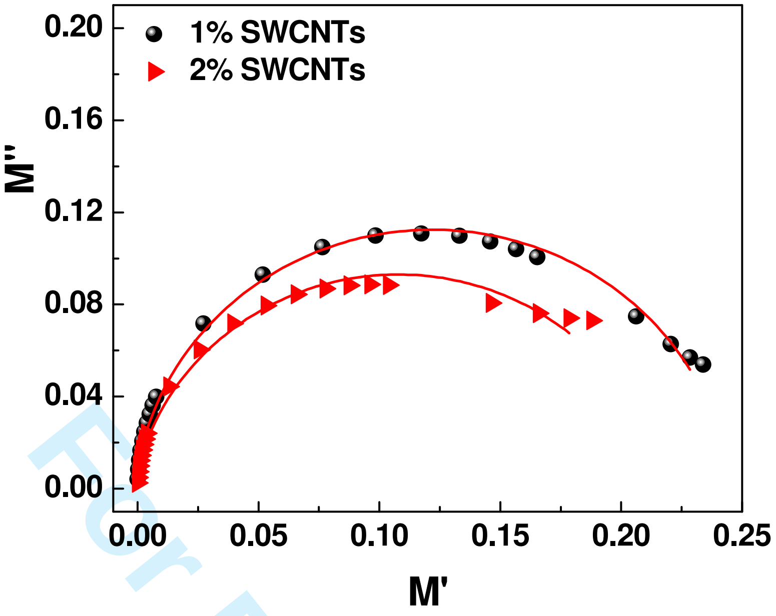


**Figure 9.** Argand plots above the percolation threshold.

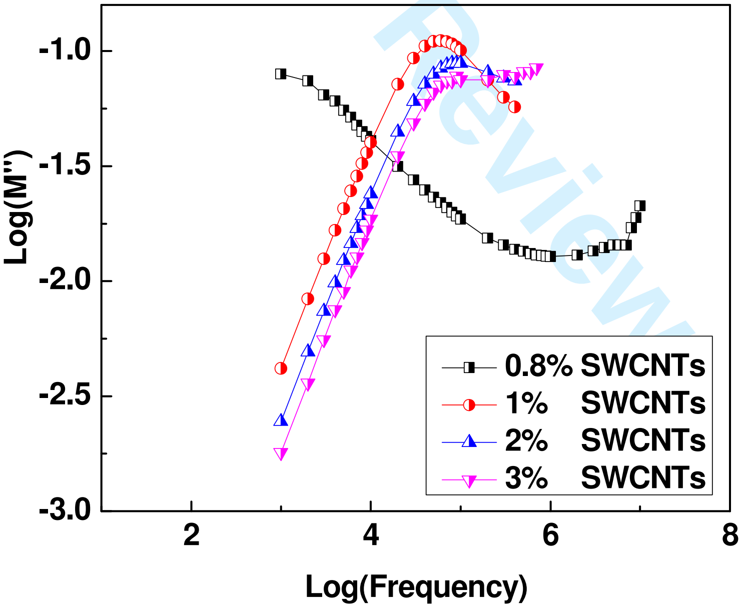


**Figure 10.** Log(M”) versus Log (Frequency) above the percolation threshold.

### *Mechanical properties*

Figure 11 presents the stress–strain curves for PC loaded with 0, 0.2, 0.4, 0.8 and 2 wt % SWCNTs at constant temperature of 25 °C. The ultimate strength is not shown in this figure and this refers to the maximum stress available in the used instrument. However, all composites show at first straight lines relations between stress and strain in the studied range of stresses. This reflects the Hookean behavior for all composites at low strain values. The elastic modulus, E, was determined from the insert of the figure for all composites. The obtained values are presented in Figure 12 as a function of the weight content of SWCNTs. This dependence appears to have what is known as the mechanical percolation behavior[43] .

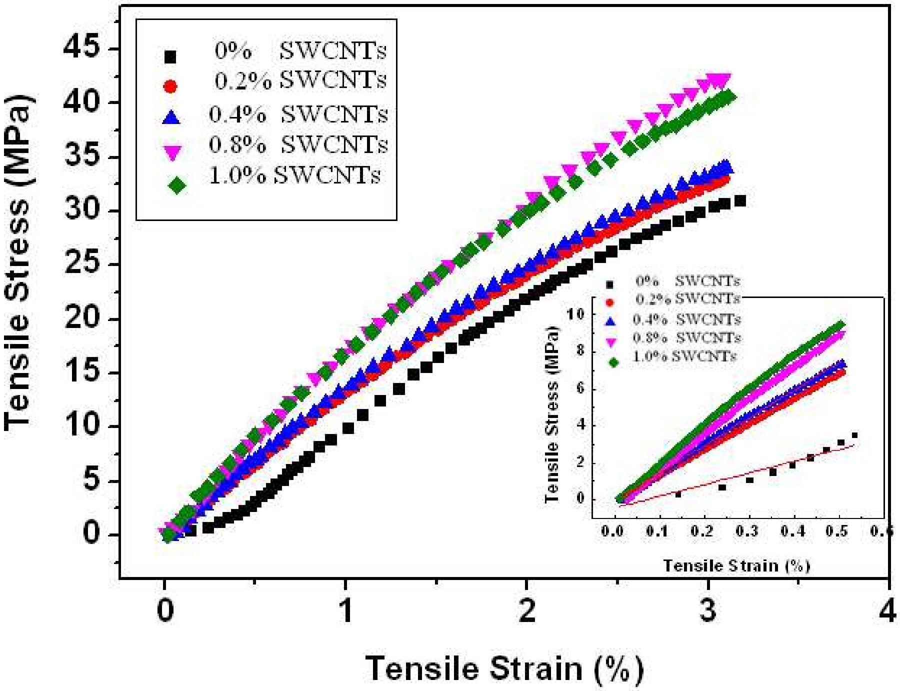


**Figure 11.** Stress-Strain curves of PC loaded with different SWCNTs loading at 25 °C.

To determine the mechanical percolation threshold of SWCNTs-PC composites, the relation between the elastic modulus (E) and loading of the filler in a medium (C) is drawn into a modified power law equation:

$$E \propto (C - C_o)^a \qquad (3)$$

where C is the CNTs loading, $C_o$ is loading at the mechanical percolation threshold and ***a*** is a constant depending on the host material (PC).

In percolated systems one can observe a drastic change of the elastic modulus for a given concentration of the filler. This indicates that the SWCNTs-PC composite reaches a mechanical percolation threshold at which the nanotubes block the motion of the polymer molecules [43]. The power law Equation (3) was used to determine the value of the mechanical percolation threshold. The function was fitted to the experimental data points of E at C > Co. The scaling parameters were found by incrementally varying C until the best linear fit to the data points was obtained. The mechanical percolation threshold ($C_o$) was found to be at 0.08 wt% SWCNT. The scaling exponent *a* is found to equal 1.85. The low mechanical percolation threshold obtained in this study (0.08 wt%) is attributed to the high aspect ratio of the CNTs filler and also indicates a homogenous dispersion of SWCNTs within PC matrix. Comparing with electrical and structure results, there is a good agreement between mechanical and electrical results, both analysis shows improvement in the electrical and mechanical properties with low percolation threshold value. Additionally, the increase of the elastic modulus with CNTs support the SEM conclusion that there is good interfacial bonding between CNTs and polymer matrix.

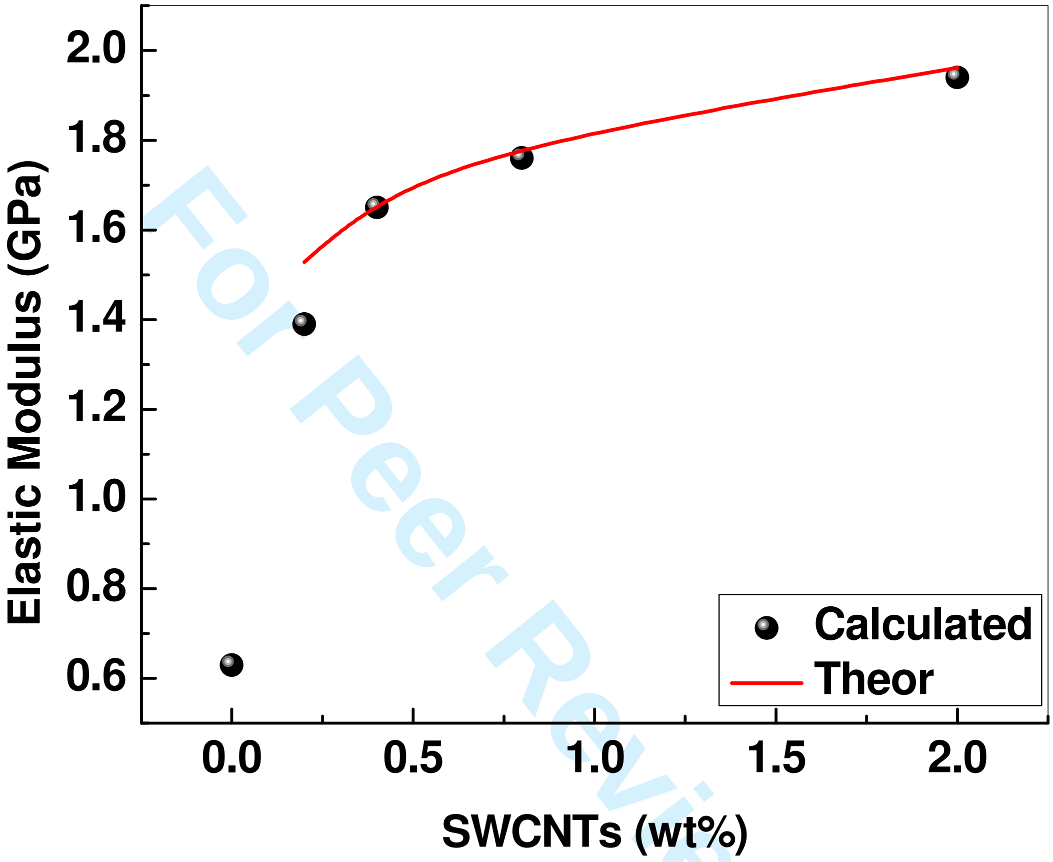


**Figure 12.** The dependence of the elastic modulus of PC on the SWCNTs loading at 25 $^{o}$C.

## Conclusions

This study shows that UVO Functionalized SWCNTs up to 180 min will improve SWCNTs dispersion and will initiate CNTs network with low SWCNTs fraction. Electrical results show that the electrical conductivity increases up to six order of magnitudes after the percolation threshold (0.5 wt% SWCNTs) and the conduction mechanisms that appear in these samples are Ohmic and Space Charge Limited mechanisms at low and high applied electric field respectively. Generally, SWCNTs increase the dielectric constant and dielectric loss of PC matrix. The dielectric relaxation behavior, in general, indicates the existence of capacitor element. At the same time, the analysis of the relaxation behavior before and after the percolation threshold, reveal that the relaxation behavior is mostly due to polymer chain relaxation at low SWCNTs content. While at high level of SWCNTs fraction ( above 0.8 wt% SWCNTs) , the relaxation behavior appears to be mostly due to charge conductivity relaxation. Finally, the elastic modulus results show a percolation behavior with a threshold of 0.08 wt. %

SWCNT and the increase of the elastic modulus with CNTs support the SEM conclusion that there is a good interfacial bonding between CNTs and polymer matrix.

## Acknowledgements

The authors would like to thank the Deanship of Scientific Research at King Faisal University, Al-Ahsa, KSA, for the financial support for this research, which has a project ID number: 120049.

## References

1. Barrau S, Demont P, Peigney A, Laurent C and Lacabanne C. DC and AC conductivity of carbon nanotubes-polyepoxy composites. *Macromolecules*. 2003; 36: 5187-94.
2. Hornbostel B, Pötschke P, Kotz J and Roth S. Single□walled carbon nanotubes/polycarbonate composites: basic electrical and mechanical properties. *physica status solidi (b)*. 2006; 243: 3445-51.
3. Huang Y, Li N, Ma Y, et al. The influence of single-walled carbon nanotube structure on the electromagnetic interference shielding efficiency of its epoxy composites. *Carbon*. 2007; 45: 1614-21.
4. Jung YJ, Kar S, Talapatra S, et al. Aligned carbon nanotube-polymer hybrid architectures for diverse flexible electronic applications. *Nano letters*. 2006; 6: 413-8.
5. Li N, Huang Y, Du F, et al. Electromagnetic interference (EMI) shielding of single-walled carbon nanotube epoxy composites. *Nano letters*. 2006; 6: 1141-5.
6. Moniruzzaman M and Winey KI. Polymer nanocomposites containing carbon nanotubes. *Macromolecules*. 2006; 39: 5194-205.
7. Ramasubramaniam R, Chen J and Liu H. Homogeneous carbon nanotube/polymer composites for electrical applications. *Applied physics letters*. 2003; 83: 2928-30.
8. Spitalsky Z, Tasis D, Papagelis K and Galiotis C. Carbon nanotube-polymer composites: Chemistry, processing, mechanical and electrical properties. *Progress in Polymer Science*. 2010; 35: 357-401.
9. Aljaafari A, Ibrahim S and El-Brolossy T. Thermophysical and electrical characterization of PVC–SWNT nanocomposites. *Composites Part A: Applied Science and Manufacturing*. 2011; 42: 394-9.
10. Ibrahim S. Low Percolation Behaviour of Polystyrene Carbon Nanoparticles (PS/CNPs) Composite. . *J. Mater. Environ. Sci.*. 2011; 2(2): 118-127.
11. Singh V, Mohan S, Singh G, Pandey P and Prakash R. Synthesis and characterization of polyaniline–carboxylated PVC composites: Application in development of ammonia sensor. *Sensors and Actuators B: Chemical*. 2008; 132: 99-106.
12. Bryning MB, Islam MF, Kikkawa JM and Yodh AG. Very Low Conductivity Threshold in Bulk Isotropic Single□Walled Carbon Nanotube–Epoxy Composites. *Advanced materials*. 2005; 17: 1186-91.
13. Ayesh A. Dielectric relaxation and thermal stability of polycarbonate doped with MnCl2 salt. *Journal of Thermoplastic Composite Materials*. 2008; 21: 309-22.
14. Ayesh AS. Dielectric Properties of Polyethylene Oxide Doped with NH4I Salt. *Polymer journal*. 2009; 41: 616-21.

15. Ayesh AS. Electrical and optical characterization of PMMA doped with Y 0.0025 Si 0.025 Ba 0.9725 (Ti (0.9) Sn 0.1) O 3 ceramic. *Chinese Journal of Polymer Science*. 2010; 28: 537-46.

16. Ayesh AS and Abdel-Rahem R. Effect of Ba (Ti (0.9) Sn 0.1) O 3 ceramic doping on optical, thermal and dielectric properties of polycarbonate host. *Bulletin of Materials Science*. 2010; 33: 589-95.

17. Ayesh AS and Abdel-Rahem RA. Optical and electrical properties of polycarbonate/MnCl2 composite films. *Journal of Plastic Film and Sheeting*. 2008; 24: 109.

18. Ibrahim S, Al Jaafari AA and Ayesh AS. Physical characterizations of three phase polycarbonate nanocomposites. *Journal of Plastic Film and Sheeting*. 2011; 27: 275-91.

19. Gupta V and Miura N. Polyaniline/single-wall carbon nanotube (PANI/SWCNT) composites for high performance supercapacitors. *Electrochimica acta*. 2006; 52: 1721-6.

20. Sun L, Warren G, O'reilly J, et al. Mechanical properties of surface-functionalized SWCNT/epoxy composites. *Carbon*. 2008; 46: 320-8.

21. Bauhofer W and Kovacs JZ. A review and analysis of electrical percolation in carbon nanotube polymer composites. *Composites Science and Technology*. 2009; 69: 1486-98.

22. Chen L, Pang XJ and Yu ZL. Study on polycarbonate/multi-walled carbon nanotubes composite produced by melt processing. *Materials Science and Engineering: A*. 2007; 457: 287-91.

23. Hornbostel B, Pötschke P, Kotz J and Roth S. Mechanical properties of triple composites of polycarbonate, single-walled carbon nanotubes and carbon fibres. *Physica E: Low-dimensional Systems and Nanostructures*. 2008; 40: 2434-9.

24. Barrau S, Demont P, Perez E, Peigney A, Laurent C and Lacabanne C. Effect of palmitic acid on the electrical conductivity of carbon nanotubes-epoxy resin composites. *Macromolecules*. 2003; 36: 9678-80.

25. Chen ZK, Yang JP, Ni QQ, Fu SY and Huang YG. Reinforcement of epoxy resins with multi-walled carbon nanotubes for enhancing cryogenic mechanical properties. *Polymer*. 2009; 50: 4753-9.

26. Sandler J, Kirk J, Kinloch I, Shaffer M and Windle A. Ultra-low electrical percolation threshold in carbon-nanotube-epoxy composites. *Polymer*. 2003; 44: 5893-9.

27. Song YS and Youn JR. Influence of dispersion states of carbon nanotubes on physical properties of epoxy nanocomposites. *Carbon*. 2005; 43: 1378-85.

28. Tseng CH, Wang CC and Chen CY. Functionalizing carbon nanotubes by plasma modification for the preparation of covalent-integrated epoxy composites. *Chemistry of materials*. 2007; 19: 308-15.

29. Kim SD, Kim JW, Im JS, Kim YH and Lee YS. A comparative study on properties of multi-walled carbon nanotubes (MWCNTs) modified with acids and oxyfluorination. *Journal of fluorine chemistry*. 2007; 128: 60-4.

30. Meng H, Sui G, Fang P and Yang R. Effects of acid-and diamine-modified MWNTs on the mechanical properties and crystallization behavior of polyamide 6. *Polymer*. 2008; 49: 610-20.

31. Najafi E, Kim JY, Han SH and Shin K. UV-ozone treatment of multi-walled carbon nanotubes for enhanced organic solvent dispersion. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2006; 284: 373-8.

32. Sham ML and Kim JK. Surface functionalities of multi-wall carbon nanotubes after UV/Ozone and TETA treatments. *Carbon*. 2006; 44: 768-77.

33. Najafi E, Kim J-Y, Han S-H and Shin K. UV-ozone treatment of multi-walled carbon nanotubes for enhanced organic solvent dispersion. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2006; 284-285: 373-8.

34. Najafi E and Shin K. Radiation resistant polymer–carbon nanotube nanocomposite thin films. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2005; 257-258: 333-7.

35. Yu JG, Huang KL, Yang Q and Liu YF. Solubilizing polycarbonate-modified single-walled carbon nanotubes by simultaneously attaching octadecylamine. *Physica E: Low-dimensional Systems and Nanostructures*. 2009; 41: 771-4.

36. Kim GM, Michler G and Pötschke P. Deformation processes of ultrahigh porous multiwalled carbon nanotubes/polycarbonate composite fibers prepared by electrospinning. *Polymer*. 2005; 46: 7346-51.

37. Ding W, Eitan A, Fisher F, et al. Direct observation of polymer sheathing in carbon nanotube-polycarbonate composites. *Nano letters*. 2003; 3: 1593-7.

38. Kum CK, Sung YT, Han MS, et al. Effects of morphology on the electrical and mechanical properties of the polycarbonate/multi-walled carbon nanotube composites. *Macromolecular Research*. 2006; 14: 456-60.

39. Ibrahim S, Ayesh A and Shoaibi AA. Optoelectrical properties of ferroelectric PC/ceramic composites. *Journal of Thermoplastic Composite Materials*. 2009; 22: 335-48.

40. Bunakov A, Lachinov A and Salikhov R. Current□voltage characteristics of thin poly (biphenyl□4□ylphthalide) films. Wiley Online Library, 2004, p. 387-92.

41. Burrows P, Bulovic V, Forrest S, Sapochak L, McCarty D and Thompson M. Reliability and degradation of organic light emitting devices. *Applied physics letters*. 1994; 65: 2922-4.

42. Musa I, Eccleston W and Higgins S. Further analysis of space-charge-limited currents in polybenzo [c] thiophene films. *Journal of applied physics*. 1998; 83: 5558.

43. Abu□Abdeen M. Investigation of the rheological, dynamic mechanical, and tensile properties of single□walled carbon nanotubes reinforced poly (vinyl chloride). *Journal of Applied Polymer Science*, DOI: 10.1002/app.35061

44. Koizhaiganova RB, Kim HJ, Vasudevan T and Lee MS. Double-walled carbon nanotube (DWCNT)-poly (3-octylthiophene)(P3OT) composites: Electrical, optical and structural investigations. *Synthetic Metals*. 2009; 159: 2437-42.

45. López-Mata C, Nicho M, Hu H, Cadenas-Pliego G and García-Hernández E. Optical and morphological properties of chemically synthesized poly3-octylthiophene thin films. *Thin solid films*. 2005; 490: 189-95.

46. Abu-Abdeen M, Ayesh AS and Al Jaafari AA. Physical characterizations of semi-conducting conjugated polymer-CNTs nanocomposites. *Journal of Polymer Research*. 2012; 19: 1-9.

47. Li Y, Tjong S and Li R. Dielectric properties of binary polyvinylidene fluoride/barium titanate nanocomposites and their nanographite doped hybrids. *Express Polymer Letters*. 2011; 5: 526-34.

***Dear Editor***

We would like to thank you again for the very useful additional comments. All corrections were performed step by step according to reviewer(s) All corrections and also additions are indicated by red text in the manuscript. Our response to reviewer comments us shown below.
Regards
Authors

## ***Revision No. 2***

## ***Authors Response to Reviewer(s) Comments:***

**Reviewer(s)' Comments to Author:**

**Reviewer: 1**

Comments to the Author
I can not suggest publication of the present paper, as it contains no new, valuable information. Moreover, results in Fig. 4 show that dielectric constant increases with increasing frequency, both at low and high frequencies. This contradicts basic physical laws. The fact that the authors ignore that, showing several experimental points and curves with this behavior, raises questions, among others, about the reliability of the rest of experimental data. Support to that is provided also by the much lower values of dielectric constant than dielectric loss. There are also many other points of concern, but there is no reason to continue with them.

***Answer: First of all our used instrument already Auto-measure the average of 5 readings per run. Accordingly our readings represent the average of 5 readings. As a part of the obtained results, the dielectric relaxation behavior of these composite. However, it is well known that dielectric loss increases as polymer composite becomes more conductor, this can be simply concluded from the AC conductivity at which it depends on dielectric loss. Additionally, the relaxation behavior of***

***different polymer composites were previously studied by us [9-10, 13-18, 46 ], so the dielectric parameters such as dielectric constant, dielectric loss tangent, …etc and relaxation behavior depend on polymer host, fillers, morphology and many other factors in addition to the experimental conditions. However, this article includes very interesting results in the AC and DC electrical properties in addition to the electrical and mechanical percolation threshold.***

**Reviewer:2 to the Author**
Revised manuscript has been significantly improved. Two minor points for review:
1). Concerning "Ohmic charge transport" point 3 of the initial report. Strictly speaking, ohmic behavior means that the current density is proportional to the field's intensity. Following the authors' response conduction at this region is due to contacts of impurities and CNTs, and the nature of the occurring conduction mechanism is supported via unmentioned refs. Initial question is still open, and the existence of conductivity does not report for the physical origin of the conduction mechanisms. Further, is the "ohmic behavior" limited at very low fields?
2). It is a matter of academic ethics to give the appropriate refs. There are several textbooks and review papers for conductivity and percolation theory, moreover in the case of polymer matrix-conductive filler composites. These should be given. Part of the scientists' responsibility is to "teach" young researchers to follow ethics and to recognize the contribution of previous works.

Concluding, the present manuscript could be accepted for publication after some further revision.

***Answer: The above notes are considered , text and some refs. were added, see red text.***

**Reviewer:3 3**
The background should be better disclosed - why not consider for example the following works:
Expr. Polym. Lett. 5(6), 2011,

***Answer: Considered and added.***