Investigation on electrical and optical properties for different composition of Carbon Nanotube (CNT) in nanocomposite MEH-PPV: CNT

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Abstract- **Nanocomposites are created by blend host polymers with nanoparticles that typically have higher or lower refractive indices. The host polymer for this research is Poly [2-methoxy-5-(2'-ethyl-hexyloxy)-1, 4-phenylene vinylene] (MEH-PPV) and the nanoparticles is Carbon Nanotube (CNT) that has been doped with the Iodine. The nanocomposite MEH-PPV: CNT using Tetrahydrofuran (THF) as solvent was then deposited on substrates. The characterization of a nanocomposite MEH-PPV: CNT with different composition of CNT weight percent (0wt%, 30wt%, 40wt%, 50wt%, 60wt%, 70wt% and 80wt %) is investigated. The electrical property that is I-V characteristic was measured in dark and under illumination. From the current voltage characteristics it can be seen that there is an increment of current when composition of CNT weight percent increase in a sample. The highest conductivity is at 60 wt% concentration of CNT with 0.0832Sm -1. It also gives the highest value of absorption coeficient which is $1.1x10^5 m^{-1}$ and 2.12eV of bandgap energy for nanocomposite MEH-PPV: CNTs thin film.**

Keywords-Nanocomposite; CNT; MEH-PPV; **Weight Percent**

I. INTRODUCTION

Nanocomposite is a phase of material where it is used to get smaller filler size due to high surface to volume ratio.[1] In recent years, the research on organic solar cells systems based on nanocomposites containing conjugated polymers has lead to great attention with the aim or replacing conventional inorganic solar cells. These nanocomposites can be processed at lower cost, low weight and ease of synthesis with greater versatility than today's solar cell [2]. The properties of nanocomposite materials depend not only on the properties of their individual parents but also on their morphology and interfacial characteristics. Instead of that, there is certain issue of blending CNT into the MEH-PPV that is the dispersion properties where it undergoes difficulties in solubility of using CNTs as polymer composites. As a solution, CNT is stirred and then sonicated to ensure that it well dispersed in the MEH-PPV solution. Addition of CNTs into the polymer will give the same mechanism of absorption but the existence of the CNTs somehow will increase the absorption due the structure of the CNT. [3].

CNT can be defined as allotropes of carbon with a cylindrical structure [4].There are two type of CNT which are Single Wall Carbon Nanotube (SWCNT) and Multi Wall Carbon Nanotube (MWCNT). Since CNTs was found by Iijima in 1991, it has been regarded as the core of nano-technologies and referred to as "a material for the 21st century". This is due to its excellent electrical and mechanical properties [5]. CNTs are commonly used and can be adopted in various applications due to its advantages and excellent performance in electrical, thermal, strength and hardness. The suitable and advantages of CNTs make it to be used as a filer to increase potential of nanocomposite thin film.

Recently, organic semiconductors have been extensively used in electronic devices as active components [6]. Organic material are used in electronic device due to device performance can be achieve at low cost [7]. Conjugated polymers are recognized as organic semiconductors with electronic properties and they have found a wide application area in electronic technology. Poly [2-methoxy-5-(2'-ethyl-hexyloxy)-1, 4-phenylene vinylene] (MEH-PPV) is a highly luminescent p-transporter that possesses electron donating p-conjugated system, and excellent film-forming properties due to 'swallow-tailed' aliphatic side-chains. MEH-PPV act as hole transport material [8]. Because of low hole and electron mobility, it is known as P-type semiconductor polymer with a relatively conductivity. One of the advantages of this conjugated polymer is its solubility in common organic solvent and its ability to produce a good optical quality film through a simple processing technique such as spin coating [9].

The properties of MEH-PPV also depend directly on the solvent. Solvent that normally used are THF, toluene and chloroform. THF will cause the absorbance of MEH-PPV shift to shorter wavelength [10]. In this research, the solvent used to dissolve MEH-PPV is THF.The nanocomposite MEH-PPV: CNT is used as a thin film to investigate either it gave any suitable effect in form of electrical, optical and physical properties to be implement in the organic solar cell after the composition of CNT is varied.

II. METHODOLOGY

2.1 Flowchart of Methodology

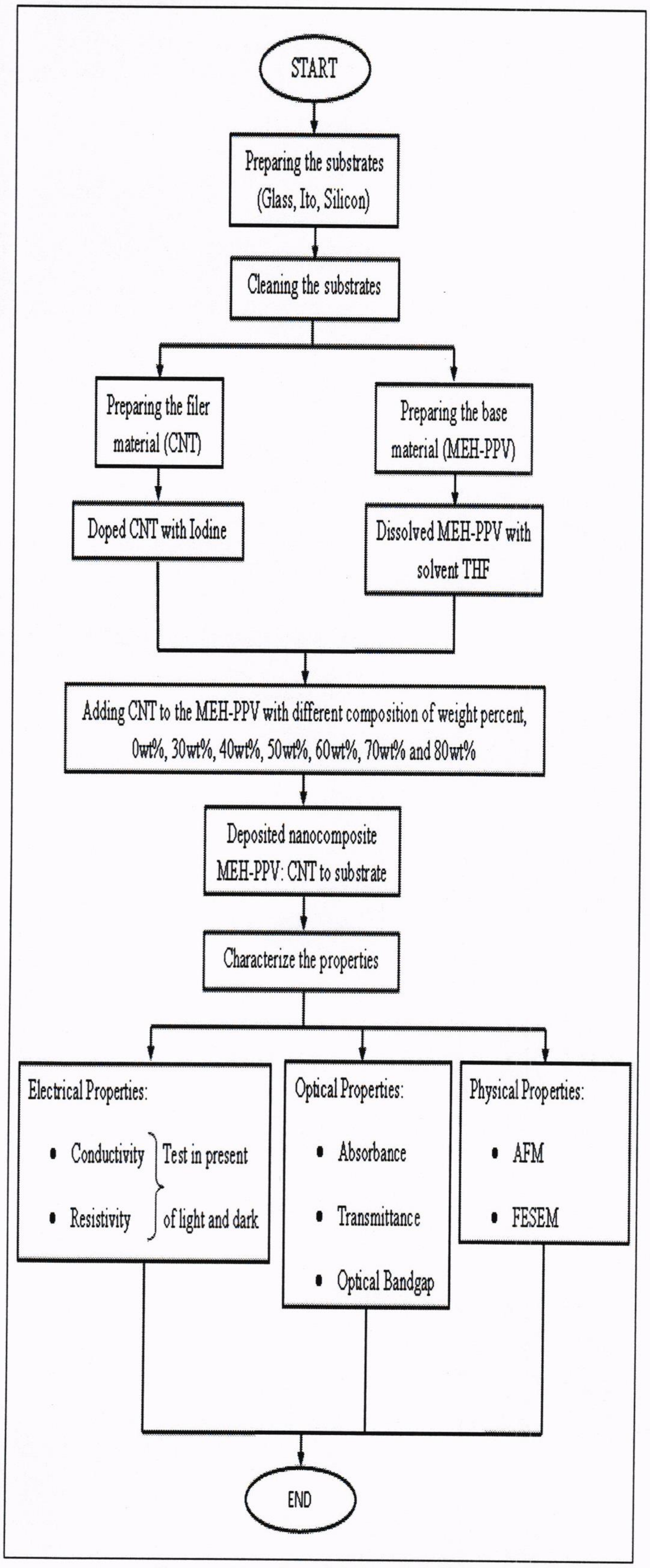

Figure 1: Flowchart of the methodology.

2.2 Cleaning the Substrate

All substrate surfaces should be considered contaminated, and must be cleaned prior to pressure sensitive material applications. All surfaces should be dry as well as clean. To make sure the substrate are totally clean, several chemical are used to clean it such as acetone, methanol and de-ionized (DI) water. The substrate is sonicated for 10 minutes for each chemical solution. Then dry the substrate by blowing Nitrogen gas to the substrate.

2.3 Preparation of Solution

In solution preparation, MEH-PPV and CNT that are basically in form of powder is weighing according to the amount needed. CNT that acts as filler were added to the MEH-PPV that acts as a base and stirred for 400rpm in duration of 48 hours. Earlier, the MEH-PPV powder is mix with the Tetrahydrofuran (THF) that acts as solvent to become a solution before adding the CNT. Before adding the CNT, the CNT is annealed and doped with the Iodine (I_2) using thermal chemical vapor deposition method. The complete solution will result in the nanocomposite MEH-PPV: CNT.

2.4 Thin Film Deposition and Metal Contact

Last but not least, the complete nanocomposite MEH-PPV: CNT solutions were deposited on a substrate (glass, ITO and Silicon). There are several ways of performed the deposition of thin films composed of chemical compounds. The method use in this research is spin coating. The substrates were spin for 2000rpm in 1 minute duration. During this spin process, 10 drops of nanocomposite MEH-PPV: CNT solution is drop in the middle of the substrates. Then, the substrates is heated for 5 minutes with 50°C to evaporate the residual solvent from the nanocomposite thin films. Then, the metal contacts were prepared using the EMITECH K550X Sputter Coater machine. The thickness is set at 60nm using 50mA current for 4 minute duration using gold as a masking layer.

2.5 Characterization of the Properties

There are three properties that are being characterized which are electrical, optical and physical properties. For the electrical properties, the I-V characteristic was measured under illumination and dark condition. From the I-V characteristic, the conductivity is calculated. In optical properties, there are three measurements that being measured that is absorbance, transmittance and the band gap which is calculated from the Tauc's plot formula. The absorbance and transmittance is measured using JASCO 670 UV-Vis-NIR spectrophotometer. The thickness of thin film is measured using Dektak 150 Stylus Surface Profiler. Lastly, in physical properties, there are two measurements that need to be measured that are roughness using Atomic Force Microscopy (AFM) and surface morphology using JOEL JSM -7600F Field Emission Scanning Electron Microscopy (FESEM).

III. RESULT AND DISCUSSION

3.1. Electrical Properties

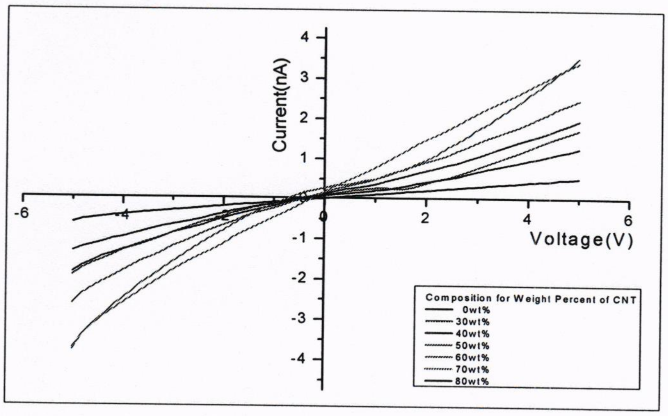

Figure 2: I-V characteristic of MEH-PPV: CNT nanocomposited in dark.

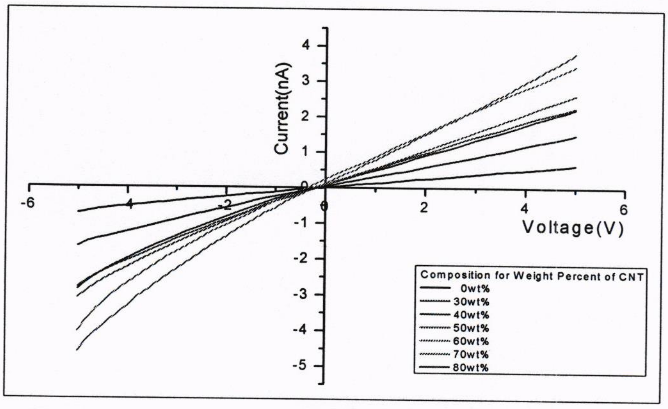

Figure 3: I-V characteristic of MEH-PPV: CNT nanocomposited under illumination.

In electrical properties, the current voltage characteristic (IV) for nanocomposite MEH-PPV: CNT is measure d by two probed point method using the Solar Simulator machine in two condition that is in dark and under illumination. From the IV characterization, graph current versus voltage for both condition are plotted which is shown in Figure 2 and Figure 3. The current measurements between the different compositions of CNT weight percent are compared. It shows an enhancement in current value as the number of weight percent increase from 0wt% to 60wt% but slowly decrease for 70wt% and 80wt%. From the I-V graphs it can be seen that the highest value of the current is obtained at 60wt% of CNT composition either in dark or under illumination condition. Furthermore, for both condition, it can be seen that current show an increment with the addition of CNTs. The reason is that carbon nanotubes have the unique electrical characteristic of utilizing a diffusive process resulting in electron scattering [1]. Electrons travel down to the axis of the tube because the nanotubes prohibit electrons from diffusing through the wall. Therefore, it will generate a very rapid and efficient charge transport system [11]. The current increased when the CNTs are well dispersed in the MEH-PPV solution. The reason is that it is easier to form electrical paths due to the relatively homogeneous dispersion of particles [12]. Other than that, the doped process of CNT with Iodine also contributed to the current enhancement. In particular, intercalation into the hollow space of CNT results in stable doping, in contrast to interstitial doping which is not stable[13]. This will result to the current enhancement.

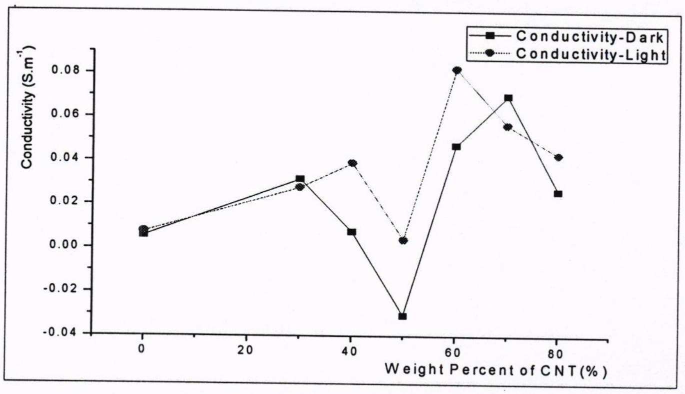

Figure 4: Conductivity of MEH-PPV: CNT nanocomposited

Figure 4 show the conductivity for nanocomposite MEH-PPV: CNT in dark and under illumination condition. The conductivity under illumination condition is higher when compared to dark. This is due to the energy that has been absorbed from photon. The response in photoconductivity could be explained by photon excitation of electron from highest occupied molecular orbital, HUMO to lowest unoccupied molecular orbital, LUMO. When the thin films are illuminated under white light, the photon energy which has a higher band gap than MEH-PPV is being absorbed and thus gives enough energy to the electrons in the thin films to excite from highest occupied molecular orbital, HUMO to the lowest unoccupied molecular orbital, LUMO [14].This will result the increment of current when compared to dark condition.

3.2. Optical Properties

In the optical properties, the characterizations involve are the absorbance and transmittance measurement. The absorbance and transmittance are shown in Figure 5 and Figure 6 which is in the range of wavelength from 250nm -800nm. For both absorbance and transmittance, the highest value was obtained for 60wt% composition of CNT. The absorption of thin film is expected to increase as composition of CNTs is increases. This is due to CNTs absorb light in the infrared (IR) region of the solar spectrum while semiconducting polymer absorb light in the ultra-violet (UV) and visible region [15]. Other than that, there is also a longer peak shifting occurred at 80wt% sample that contributed to lower band gap. This is shown in Figure 9 that the band gap for 80wt% is low than 70wt% sampled. This is due to the distribution of energy levels corresponding to the π-π* transition [16]. The solvent in which the absorbing species is dissolved also has an effect on the spectrum of the species. Peaks resulting from n-π^* transitions are shifted to longer wavelengths (red *shift*) with increasing solvent polarity. This is caused by attractive polarisation forces between the solvent and the absorber, which lower the energy levels of both the excited and unexcited states. This effect is greater for the excited state, and so the energy difference between the excited and unexcited states is slightly reduced - resulting in a small red shift. This effect also influences n-π^* transitions but is overshadowed by the blue shift resulting from solvation of lone pairs.

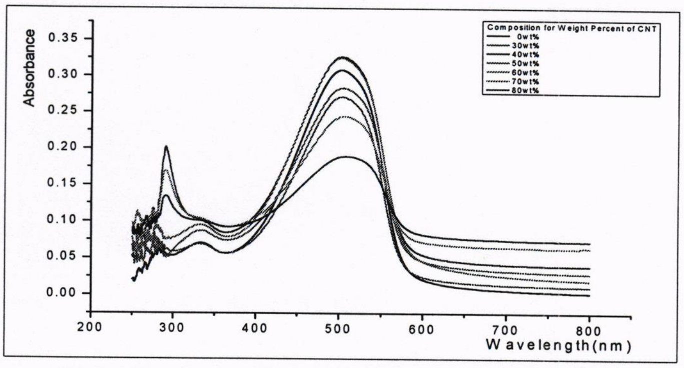

Figure 5: Absorbance measurement of MEH-PPV: CNT nanocomposited.

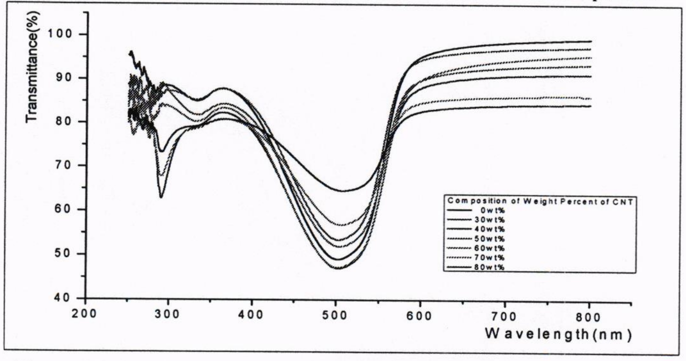

Figure 6: Transmittance measurement of MEH-PPV: CNT nanocomposited.

From the transmittance spectra, the absorption coefficient of MEH-PPV: CNT nanocomposite thin film with different number of deposition can be calculated using Lambert's Law as shown in Equation (1):

$$\alpha = (1/t)\ln(100/T) \qquad (1)$$

where α is the absorption coefficient, t is the film thickness and T is the transmittance of the film. The absorption spectra, α of nanocomposited MEH- PPV: CNTs also in the range of wavelength from 200 nm - 800 nm which is presented in Figure 7. The edge in the spectrum approximately at 500 nm originates from band-gap absorption in polymer MEH-PPV.

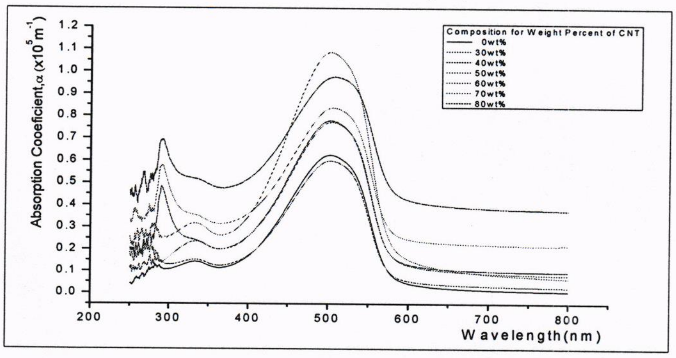

Figure 7: Absorbtion Coefficient, α of MEH-PPV: CNT nanocomposited.

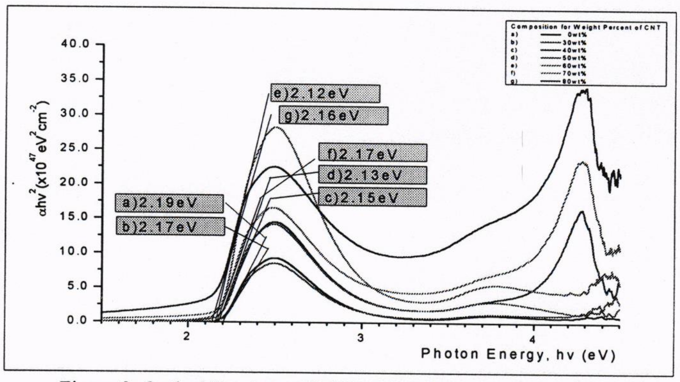

Figure 8: Optical Bandgap of MEH-PPV: CNT nanocomposited.

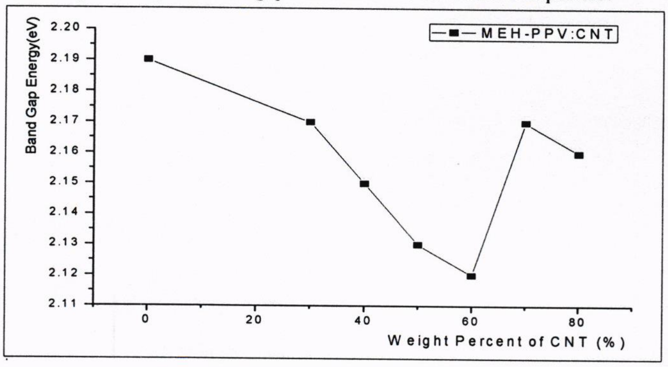

Figure 9: Band gap Energy of MEH-PPV: CNT nanocomposited.

The optical band gap, Eg can be obtained by plotting the graph using Tauc's Plot formula as shown in Equation (2):

$$(\alpha hv)^2 = B(hv - E_g) \qquad (2)$$

where α is the absorption coefficient and hv is the photonic energy. This is shown in Figure 8. From the Tauc's plot the optical band gap can be found by the extrapolation of the linear region of absorption edge to the hv axis as shown in Figure 9. The results showed the optical band gap is found to be 2.19eV, 2.17eV, 2.15eV, 2.13eV, 2.12eV, 2.17eV and 2.16eV for 0wt%, 30wt%, 40wt% 50wt%, 60wt%, 70wt% and 80wt% of CNT composition. The optimum and low optical band gap of thin film is important as with the lower band gap, it is much easier for the electron to excites from the highest occupied molecular orbital, HUMO to the lowest unoccupied molecular orbital, LUMO and thus give a better performance to the device[14].

3.3. Physical Properties

In the physical properties, there are two characterization involves that is FE-SEM and AFM. The FE-SEM method is to see the dispersion of CNT filling towards MEH-PPV matrix particles. The dispersion property becomes more important when nanotubes are blended into the polymer. Nanotubes tend to remain as entangled agglomerates, and homogeneous dispersion is not easily obtained [17]. This is due to the high surface-to- mass ratio of CNTs, molecular scale forces and interactions should be considered among CNTs. Van der Waals forces usually promote agglomeration of CNTs [18], whilst electrostatic charges lead to a stabilization of the dispersion through repulsive forces. As a consequence, by considering the nature of percolating network formed by very fine filler, in this paper CNTs, the balance of the two factors above should be taken into account. For this paper, when the weight percent concentration of CNT increased, the dispersion of CNT in filling MEH-PPV particle is obtained which is shown in Figure 11.

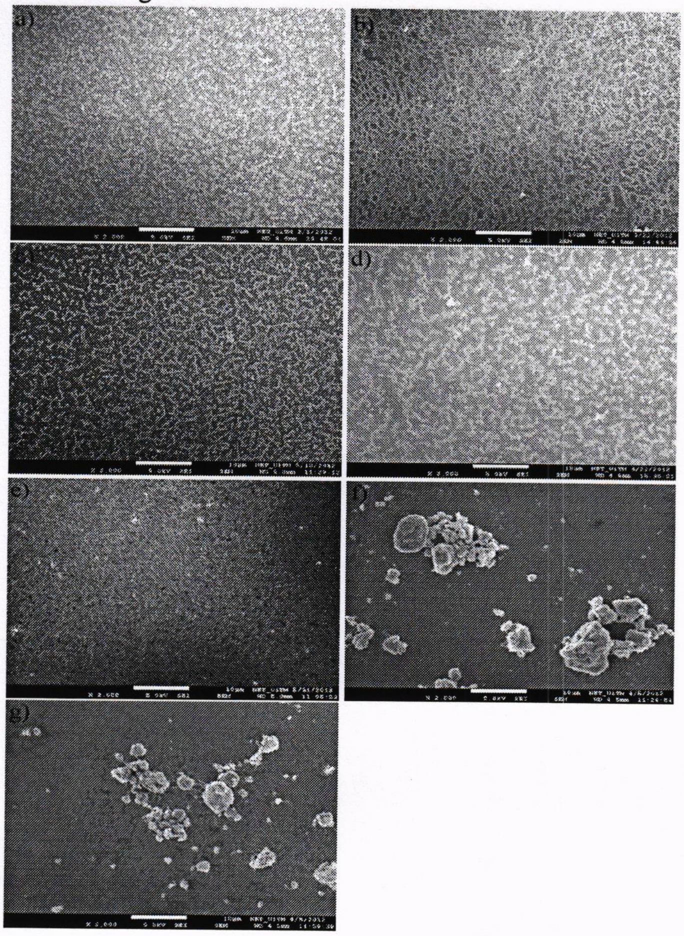

Figure 11: FESEM image of (a) 0wt %, (b)30wt%,(c) 40wt%,(d) 50wt%,(e)60wt%,(f)70wt%,(g) 80wt% of weight percent of CNT with 5kV voltage and zoom at 2000 magnification.

From Figure 11, the CNT powder dispersed well when the composition increase except for 70wt% and 80wt%. This is due to the large amount of CNT that make it to agglomerate and did not dispersed well. When there is a large amount of CNT, the nanocomposite MEH-PPV: CNT solution becomes saturated because CNT has been fully diffuse into the MEH-PPV particles. The remaining undiffused CNT particles will agglomerate and cause to the bad dispersion. The dispersion play an important role because the undispersed CNTs tend to disable the light to be absorbed efficiently due to light scattered when it hit the agglomerate CNTs. Collision of light with the agglomeration of CNTs cause the light absorption to be less[13].

Table 2: Surface roughness of MEH-PPV: CNT thin film.

Weight Percent of CNT (%)	0	30	40	50	60	70	80
Surface Roughness(nm)	17.327	24.713	24.852	24.946	40.011	18.072	11.706

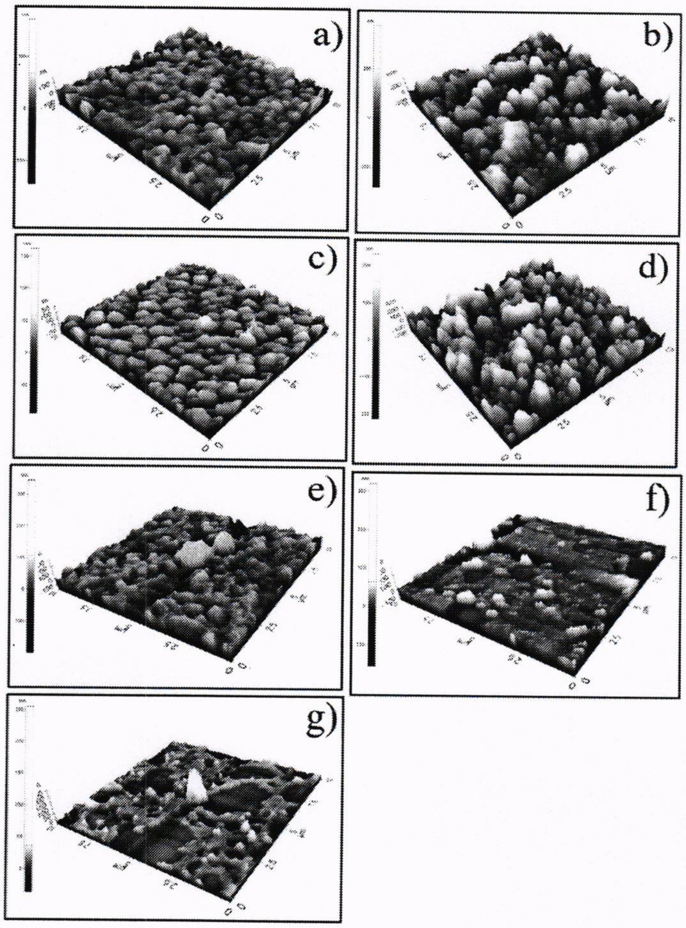

Figure 12: AFM image of (a) 0wt %, (b) 30wt%,(c) 40wt%,(d) 50wt%,(e) 60wt%,(f)70wt%,(g) 80wt% of weight percent of CNT.

In Atomic Force Microscopy (AFM) characterization, the very important point is to see the uniformity and surfaces morphology of the nanocomposites MEH-PPV: CNT thin film. This is shown in the Table 2 that the average roughness, Ra increases from low to high concentration of weight percent of CNT. From the Figure 12 above, it can see that the nanocomposites MEH-PPV: CNT is distributed uniformly from 0wt% to 60wt% of sample except for 70wt% and 80wt% of sample. This is supported by the FE-SEM images that show the agglomeration of the CNT powder. From the theory, when the composition for weight percent concentration of CNT higher, the surfaces roughness also increases. This is due to CNT has a large surface area and hollow structure [19]. Other than that, the doped Iodine-CNTs also contributed to this phenomenon. The iodine just adsorbed on the surface of all multi-walled nanotubes [20].This will increase the surfaces roughness. The increasing of surfaces roughness is important because it will increase the surface area. This will contribute to an increment of photon absorption due to large area. This mechanism will somehow increase the current and give optimal value of conductivity that suitable for organic solar cell application.

Other than that, thickness also plays an important role for thin film properties in absorbing light. The thickness for nanocomposite MEH-PPV: CNT decrease from low concentration to high concentration of weight percent of CNT. This was shown in the Table 1 below. As the thin film gets thicker, it will yield low carrier mobility. Low carrier mobility will occur in thick thin film due to collision of electrons. Very thick thin film will also decrease the conductivity of a thin film [14].

Table 1: Thickness of MEH-PPV: CNT thin film.

Weight Percent of CNT (%)	0	30	40	50	60	70	80
Thickness of Thin Film (nm)	114.033	104.593	96.760	82.740	69.073	67.48	44.813

CONCLUSION

From this research, it can be said that adding CNTs to the MEH-PPV solution with different concentration of weight percent give an electron movement in the structure by showing there is an increasing of current from 0 wt% to 60 wt%. However, when the amount is increased more than 60 wt% of CNTs, the CNTs tends to agglomerate that caused the I-V and optical showed a decreasing in their properties respectively. Moreover, all the electrical, optical and physical properties of 60 wt% sample supported each other which showed the highest value compared to the other weight percent parameters. The highest conductivity is $0.0832Sm^{-1}$ supported by highest absorbtion cooeficient, $1.1x105m^{-1}$ and lower bandgap of 2.12eV. Meanwhile, the conductivity increase when it absorbs light compared to dark condition. This prove that the photoconductivity of the nanocomposite thin film MEHPPV thin film was successful obtained for application of organic solar cell for 60wt% composition of CNT sample.

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REFERENCES

[1] M.S.P. Sarah[1*], M.Z. Musa[1], A.B. Suriani[2], N.S. Jumali[3], Z.Shaameri[3], A.S Hamzah[3], M. Rusop[1, 2], "Study on Existence of CNT in Nanocomposite CNT/MEH-PPV Thin Film", ICSE2010 Proc. 2010, Melaka, Malaysia.

[2] Gur, N. A. Fromer, C.-P. Chen, A. G. Kanaras, and A. P. Alivisatos, "Hybrid Solar Cells with Prescribed Nanoscale Morphologies Based on Hyperbranched Semiconductor Nanocrystals," *Nano Letters,* vol. 7, pp. 409-414, 2006.

[3] Q. Zhang, S. Rastogi, D. Chen, D. Lippits, and P. J. Lemstra, "Low percolation threshold in single-walled carbon nanotube/high density polyethylene composites prepared by melt processing technique," *Carbon,* vol. 44, pp. 778-785, 2006.

[4] M.S.P Sarah, M.Z. Musa1, A.B. Suriani, N.S Jumali, Z.Shaameri[3], A.S Hamzah[3], M.Rusop *"Photoconductivity of Nanocomposite MEH-PPV: CNTs Thin Film for Organic Solar Cells Application"* 2009.

[5] R. Khare and S. Bose, "Carbon Nanotube Based Composites- A Review," *Journal of Minerals & Materials Characterization & Engineering,* vol. 4, pp. 31-46, 2005.

[6] F. Yakuphanoglu, "Electrical conductivity, optical and metal-semiconductor contact properties of organic semiconductor based on MEH-PPV/fullerene blend," *Journal of Physics and Chemistry of Solids,* vol. 69, pp. 949-954, 2008.

[7] A. Sertap Kavasoglu, F. Yakuphanoglu, N. Kavasoglu, O. Pakma, O. Birgi, and S. Oktik, "The analysis of the charge transport mechanism of n-Si/MEH-PPV device structure using forward bias I-V-T characteristics," *Journal of Alloys and Compounds,* vol. 492, pp. 421- 426, 2009.

[8] Anto Regis Inigo[a,b], Hsiang-Chih Chiu[a,b], Wunshain Fann[a,b,*], Ying-Sheng Huang[c], U.S. Jeng[d], C.H. Hsu[d], Kang-Yung Peng[e], Show-An Chen[e]. *"Structure and charge transport properties in MEH-PPV".*

[9] N. Juhari, A. Majid, and Z. Ibrahim, "Degradation of Single Layer MEH-PPV Organic Light Emitting Diode (OLED)," 2006, pp. 112-115.

[10] J. P. Ferrance, K. E. Meissner, and J. W. Pettit, "Solvent effects on the electrical and optical properties of composite carbon nanotube/MEHPPV films," 2009.

[11] Richard Elkins, Nathan Fierro, Erin Flanagan, Adam Haughton, Michael Kasser, Matthew Stair, and ScottWilson, "Utilizing Carbon Nanotubes to Improve Efficiency of Organic Solar Cells."

[12] H. H. So, J. W. Cho, and N. G. Sahoo, "Effect of carbon nanotubes on mechanical and electrical properties of polyimide/carbon nanotubes nanocomposites," *European Polymer Journal,* vol. 43, pp. 3750-3756, 2007.

[13] Sejung Ahn and Yukyung Kim, Youngwoo Nam, Honam Yoo, Jihyun Park, and Yungwoo Park, Zhiyong Wang and Zujin Shi, Zhaoxia Jin "Magnetotransport in iodine-doped single-walled carbon nanotubes",Physical Review B 80, 165426(2009)

[14] F.S.S. Zahid[1,*], M.S.P. Sarah[1*], M. Rusop[1, 2,*] "Effect of Thickness on the Electrical and Optical Properties of MEH-PPV: TiO2 Nanocomposite for Organic Solar Cell Application", IEEE Student Conference on Research and Development, 2011.

[15] E. Kymakis and G. Amaratunga, "Single-wall carbonnanotube/conjugated polymer photovoltaic devices," *Applied Physics Letters,* vol. 80, p. 112, 2002.

[16] NURUL Zayana Yahya[1,a] and MOHAMAD Rusop[1,2,b] "Optical and Structural Properties of MEH-PPV: ZnO Nanocomposites" Advanced Materials Research Vol. 364 (2012)

[17] Jiang Zhu, JongDae Kim, J. L. M. Haiqing Peng, a. Valery N. Khabashesku, and Enrique V. Barrera, "Improving the Dispersion and Integration of Single Walled Carbon Nanotubes in Epoxy Composites through Functionalization," *Nano Letter,* vol. 3, pp. 1107-1113, 2003.

[18] E. Kymakis, I. Alexandrou, and G. Amaratunga, "High open-circuit voltage photovoltaic devices from carbon-nanotube-polymer composites," *Journal of Applied Physics,* vol. 93, p. 1764, 2003.

[19] M.S.P.Sarah, R. Yaacob, F.S. Zahid, U.M.Noor and M.Rusop, "Photoconductivity of Nanocomposited MEH-PPV: CNTs Thin Film for Organic Solar Cells Application", International Conference on Electronic Devices, System and Application (ICEDSA) 2011.

[20] T. Michel, L. Alvarez, J.-L. Sauvajol, R. Almairac, R. Aznar, O. Mathon, J.-L. Bantignies and E. Flahaut, "Structural selective charge transfer in iodine doped carbon Nanotubes", Centre Interuniversitaire de Recherche et d' ingénierie des matériaux (IMR CNRS 5085), Iniversité Paul Sabatier, 31602 ToulouseCedex4,France.