



# Synthesis and Characterization of Conducting Polymer Poly(O-Toluidine) - DBSA Blend with Poly(Ethylene Oxide) for Solar Cell Application

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## الخلاصة

بوليمر البولي اوتولودين (Poly (O-Toluidine) (POT) المشوب ذاتيا بحامض Dodecyl Benzene (DBSA) (Sulfonic Acid) والمحضر بطريقة البلمرة الكيميائية واستخدم الامونيوم بيرسلفايت (NH<sub>4</sub> 2S<sub>2</sub>O<sub>8</sub>) كعامل مؤكسد. حضرت الخلائط البوليمرية وذلك بخلط نسبتين وزنيتين (10% و80%) من بوليمر البولي اثلين اوكسايد (Poly (Ethylene Oxide) (PEO) مع البوليمر المحضر لانتاج الخلائط البوليمرية النانوية (PEO/POT-DBSA). حضرت الأغشية الرقيقة من الخلائط البوليمرية بطريقة الطلاء البرمي Spin Coating. التركيب الكيميائي للخلائط المحضرة شخّصت بواسطة الأشعة تحت الحمراء FTIR. طبيعة السطح وألأقطار تم دراستها باستخدام مجهر القوة الذرية (AFM). وأظهر التشخيص أن معدل القطر كان (85 nm) بتركيز 10%wt من PEO وازداد الى (120 nm) بزيادة تركيز PEO في الخليط الى (80%). في مجال التطبيقات الالكترونية للبوليمر المحضر جرى تضمين الخلائط البوليمرية في صناعة الخلايا الشمسية، لوحظ بأن تيار الدائرة المفتوحة J<sub>sc</sub> يزداد من (3-5.25) mA/cm<sup>2</sup> وان الكفاءة تزداد من (0.46) الى (1.58) عندما تزداد نسبة PEO في مزيج الطبقة الفعالة.

## الكلمات المفتاحية

الخلائط البوليمرية الموصلة، البولي اوتولودين (POT)، البولي اثلين اوكسايد (PEO)، الخلايا الشمسية.



### Abstract

Poly(O-Toluidine) (POT) doped with Dodecyl Benzene Sulfonic Acid (DBSA) was synthesized by chemical polymerization method using ammonium persulphate ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ) as oxidizing agent. This polymer blended with two different weight ratios (10%, 80%) of Poly (Ethylene Oxide) (PEO) by spin coating method to produce Nano conducting poly blend (POT-DBSA/PEO). The chemical structure of prepared polymers (POT-DBSA, PEO) were characterized by the FTIR spectra. Morphology and diameters were studied by Atomic Force Microscope (AFM). The average diameter was about 85nm for (10%wt PEO concentration) and increased with increasing concentration to (120) nm for 80%wt PEO concentration for solar cell application of (POT-DBSA/PEO). It is noted that the short circuit current density  $J_{sc}$  increased from (3-5.25)  $\text{mA}/\text{cm}^2$  and the efficiency also increased from (0.46) to (1.58) when the PEO ratio was increasing from 10% to 80% in the active layer mixture.

### Keywords

Conducting poly blend, Poly(O-Toluidine)(POT), Poly Ethylene Oxide (PEO), Solar Cell.



## 1. Introduction

Intrinsically conductive polymers (ICPs) have become an efficient alternative to inorganic conductors in many practical applications in the recent decade. Polyaniline has been an important member in the ICP family due to its ease of preparation, excellent environmental stability, various forms, interchangeable oxidation states, electrical, optical properties and economic cost [1-3]. It has various potential applications; in many high performance devices such as rechargeable batteries [4], chemical sensors [5], electrochemical and corrosion devices [6,7], organic light emitting diodes (OLEDs) [8], field-effect transistors (OFETs) [9]. And solar cells [10-12]. The common synthesizing method of conducting polymers, namely: chemical oxidative [13], or electrochemical polymerization [14].

POT polymer is a PANI derivatives which contains the –CH<sub>3</sub> group in the ortho position of the aniline monomer. Among the ring substituted PANi derivatives [15]. POT has been probably the most widely studied one. The chemical polymerization of (O-Toluidine) and its application in solar cell studied by author in the paper [16]. The electro polymerization method of (O-Toluidine) was studied by other authors using various electrolytes with different concentrations, These works revealed that POTs have interesting electro-optical properties and can be used as electrochromic and electronic devices [17]. While the polymerization of POT doping with DBSA by chemical

method which has not been reported thus far.

Many researches on polymer blends (mixed two or three polymers) were done to improve the physical properties of polymers [9,18]. One of these polymers is PEO which is used to obtain nano fiber conducting polymers [19]. These fibers have a high surface area to volume ratio, which is useful for many applications [20]. In the present work, synthesis of conducting polymer of POT-DBSA by chemical polymerization and study the effects of different wt% PEO on structure properties by Atomic Force Microscope (AFM). As for the electronic application of nano poly blend (POT-DBSA/PEO) in solar cell type (Indium Tin Oxide/Poly (3,4-Ethylene Dioxy Thiophene): Poly Styrene Sulfonate/ Poly(O-Toluidine)-Dodecyl Benene Sulfonic Acid-Poly(Ethylene Oxide):Indene - C<sub>60</sub> Bis Adduct/Aluminium) (ITO/PEDOT:PSS/POT-DBSA-PEO:ICBA/Al) were fabricated. The current-voltage characteristics are measured at light source of 100 mw/cm<sup>2</sup>. The solar cell parameter like open circuit voltage, short circuit current, fill factor, efficiency, shunt resistance and series resistance ( $V_{oc}$ ,  $J_{sc}$ , FF,  $\eta$ ,  $R_s$  and  $R_{sh}$ ) are calculated. The efficiency of solar cell measured at different ratios of PEO in POT-DBSA/PEO was calculated.

## 2. Experimental

### 2.1. Materials

The (O-Toluidine) monomer provided by fisher scientific company. Hydrochloric acid (HCl) provided by Fuka company. Dodecyl



Benzene Sulfonic Acid (DBSA) and Ammonium Persulfate ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ) provided by Aldrich Co., Poly (ethylene oxide) (PEO) provided by Alpha chemical. Indene- $\text{C}_{60}$  Bis Adduct (ICBA) provided by Sigma Aldrich company. Different solvents were used to process the solution such as chloroform, Acetone, Ethanol and methanol were purchased from Sigma Aldrich company. Poly (3,4Ethylene Dioxy Thiophene): Poly(Styrene Sulfonate) PEDOT:PSS provided by Sigma Aldrich company.

## 2.2. Preparation of The Polymer blend (POT-DBSA /PEO)

The Poly(O-Toluidine) (POT) doped with Dodecyl Benzene Sulfonic Acid (DBSA) was synthesized by the oxidative polymerization of monomer (O-Toluidine) in acidic media with the help of ammonium persulfate ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ) as oxidizing agent. We used three-necked flask armed with thermometer and stirrer. (2.4) gm from (O-Toluidine) monomer, was dissolved with (4) ml HCl. The solution was stirred for (1) hour and then (5.4) gm of (DBSA), which dissolved with (20.2) ml HCl and left on the stirring for (30) min and then a weighted (4.3) gm of Ammonium Persulfate ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ) as oxidizing agent, which dissolved with (24) ml HCl, it added slowly and carefully to the flask under the temperature cooled to (0)  $^\circ\text{C}$ . After that, the mixture was kept under constant stirring for (24) hours. The product of the greenish – black precipitate was filtered by using Vacuum Pump, then

after the resultant washed with distilled water and methanol, then dried in a vacuum oven at (80)  $^\circ\text{C}$  for (12) hours. The resultant was green powder (POT-DBSA). This polymer blend prepared by weight (1) mg from POT-DBSA was dissolved in (10) ml of chloroform ( $\text{CHCl}_3$ ) with stirring for (8-9) hours. Poly (Ethylene Oxide) PEO (200.000) Mw with different weight ratio added to POT-DBSA solution under stirring for (3) hours to produce Nano conducting poly blend (POT-DBSA/PEO). These blends were used to prepared thin films samples.

## 2.3. The Solar cell devices

The thin films of POT-DBSA/PEO was synthesized by using spin coating method technique (4000 Electronic Microsystems Model) at speed (1000) for (20) sec deposited on glass substrate to study optical properties. As for electronic application of nano poly blend in solar cell type (ITO/PEDOT: PSS/POT-DBSA-PEO:ICBA/Al) were fabricated. The ITO coated glass slides cleaned in acetone, chloroform and distilled water for (10) min by using device of Ultrasonic Bath. The solution of PEDOT: PSS was prepared by mixing the weight ratios of (1:0.04) with Methoxyethanol (ME), which is known as P-type semiconductor polymer and used as a buffer layer in organic photovoltaic cells. The solution was stirred overnight without heating then filtered, then the product was kept in desiccator overnight in the dark. The PEDOT: PSS solution was spin coated onto ITO slides at speed of

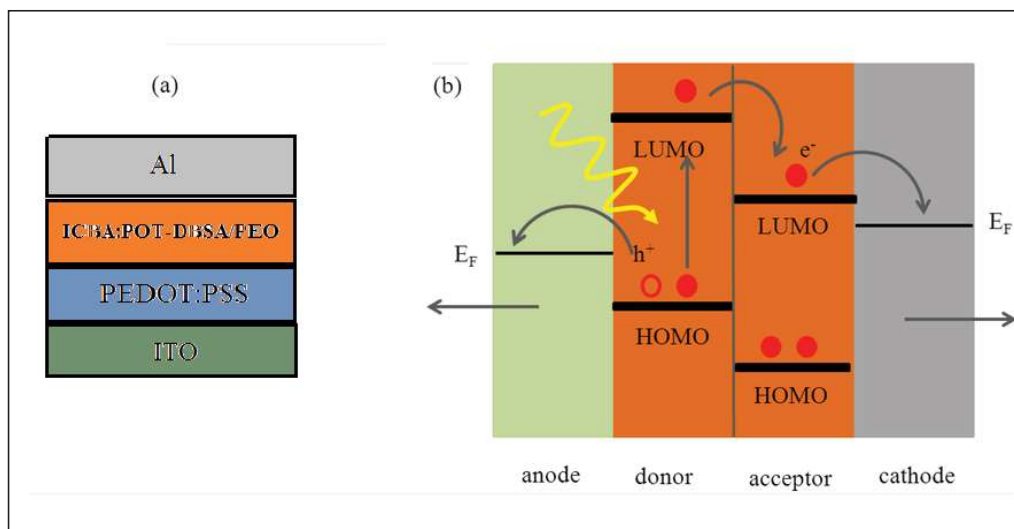


(2000) rpm for (30) sec then that annealing the sample in a furnace set up at (120) C° for (10) min. The active layer was prepared by mixing POT-DBSA/ PEO and ICBA materials as blends with the ratio 1:1 were dissolved in each solvent chloroform with change ratio PEO in the mixture. The solutions were stirred overnight at (45) C°, and then filtered. The product solution spin coated onto PEDOT: PSS (buffer layer)–coated ITO slides at speed

(1000) rpm for (40) sec. The films were then annealed on a hot plate at (130) C° for (10) min. A thin Al layer was finally deposited on the active layer for all samples with thickness of (70) nm under vacuum of ( $10^{-5}$ ) Torr using thermal vacuum evaporation. The devices names that has different ratios listed in Table (1). Fig.(1a) shows the devices structures for the organic solar cell and (b) Homo and Lumo energy levels diagram of the materials.

**Table (1): The devices names**

Device name	Wt% PEO in POT-DBSA/PEO
A1	0%
A2	10%
A3	80%



**Fig. (1): The structure of Solar cell**



## 2.4. Characterization

UV-Visible spectra (Spectro SC from Labomed, Inc. USA) at wavelengths of (300-1100) nm was used to record the spectra of the active layer POT-DBSA/PEO:ICBA blends which were spin coated onto glass substrates. The thickness of thin films (60-100) nm were measured using M2000 (J. A. Woollam Co., Inc.) spectroscopic ellipsometer operating in the wavelength range of (370-1000) nm. Furthermore, the blended structures were investigated by Fourier Transform Infra-Red (FT-IR). Morphology and diameters of the nano poly blend were studied by Atomic Force Microscope (AFM). The DC electrical properties were studied using (4200) Keithley semiconductor characterization system and the photo current was generated under AM 1.5 solar simulator generated source of (100) mWcm<sup>-2</sup>. The fill factor (FF) and the overall light to electrical conversion efficiency ( $\eta$ ) of the solar cell were calculated according to the following equations[21]:

$$\eta(\%) = \frac{J_{Max}V_{Max}}{P_{in}} \times 100\% = FF \frac{J_{sc}V_{oc}}{P_{in}} \times 100\% \quad (1)$$

and fill factor FF is given by:

$$FF = \frac{J_{Max}V_{Max}}{J_{sc}V_{oc}} \quad (2)$$

Where  $J_{sc}$  is the short circuit current density (mAcm<sup>-2</sup>),  $V_{oc}$  is the open circuit voltage (V),  $P_{in}$  is the incident light power and  $J_{max}$  (mAcm<sup>-2</sup>) and  $V_{max}$  (V) are the current density and voltage at the point of maximum power output in the J-V curves.

## 3. Results and Discussion

### 3.1. Structure analysis

The polymers were characterized by Fourier Transform Infra-Red (FT-IR) as a powder. The FTIR spectra of POT doped with DBSA are shown in the Fig.2 (a, b, c) at different the weight ratios from PEO (10%, 80%) in the mixture. The IR spectra Fig.(2-a1) showed the location of the most important peaks of spectrum of the POT-DBSA such as, the band at (3460) cm<sup>-1</sup> related to hydrogen bonding (NH). The two bands appeared at (1035,1008) cm<sup>-1</sup> corresponding to the SO<sup>-3</sup>. These bands are considered as from the important peaks indication on the doping the polymer POT in the DBSA[22]. The bands at (2854, 2956) cm<sup>-1</sup> is corresponding to the stretching vibration C-H<sub>2</sub> group, while band at (1600) cm<sup>-1</sup> is corresponding to the stretching vibration of quinoid. The band at (1456) cm<sup>-1</sup> is due to the CH<sub>2</sub> scissor. The two bands appearing at (1211, 1126) cm<sup>-1</sup> were attributed to (C-N) mode and the plane (C-H) vibration of quinoid rings. The effect of blending PEO in ratios (10%, 80%) with the POT-DBSA on the FT-IR spectrum is shown in figures 2(b, c). The change in the wave number values increases or decreases indicates to a common mixture. It can be seen from the figure that increase in the intensity for SO<sup>-3</sup> from (1035 -1059) cm<sup>-1</sup>. The hydrogen bonding (NH) in POT-DBSA compared with its value in the case of mixing with PEO, Where it is observed to decrease in the intensity from (3460-3041) cm<sup>-1</sup> as PEO ratio increases in the mixture[23]. The characteristic bands for the functional groups are listed in Table (2).





Table (2): The location peaks of FT-IR spectrum of the devices.

Functional groups	A1 ( $\text{cm}^{-1}$ )	A2 ( $\text{cm}^{-1}$ )	A3 ( $\text{cm}^{-1}$ )
Hydrogen-bonded(N-H)	3460	3041 ,3215	
Stretching Vibration of the methyl (-CH <sub>3</sub> )		2918	2919
C-H <sub>2</sub> Group	2854 ,2956	2953, 2849	2855 ,2873
Quinoid C=C	1600	1547 ,1599	1599
Benzenoid		1493	
CH <sub>2</sub> scissor	1456	1457	1465
vibration C-N	1211		1240 ,1278
Vibration C-H	1126	1124 ,1163	1103 ,1144
C-H bland out plan		1345 ,1397	1392 ,1358
C-O-C vibration		950	945 ,961
C-H bland in plan		831	840
SO <sup>-3</sup>	1008 ,1035	1006 ,1032	1032 ,1059
C-O-C bend		518	528

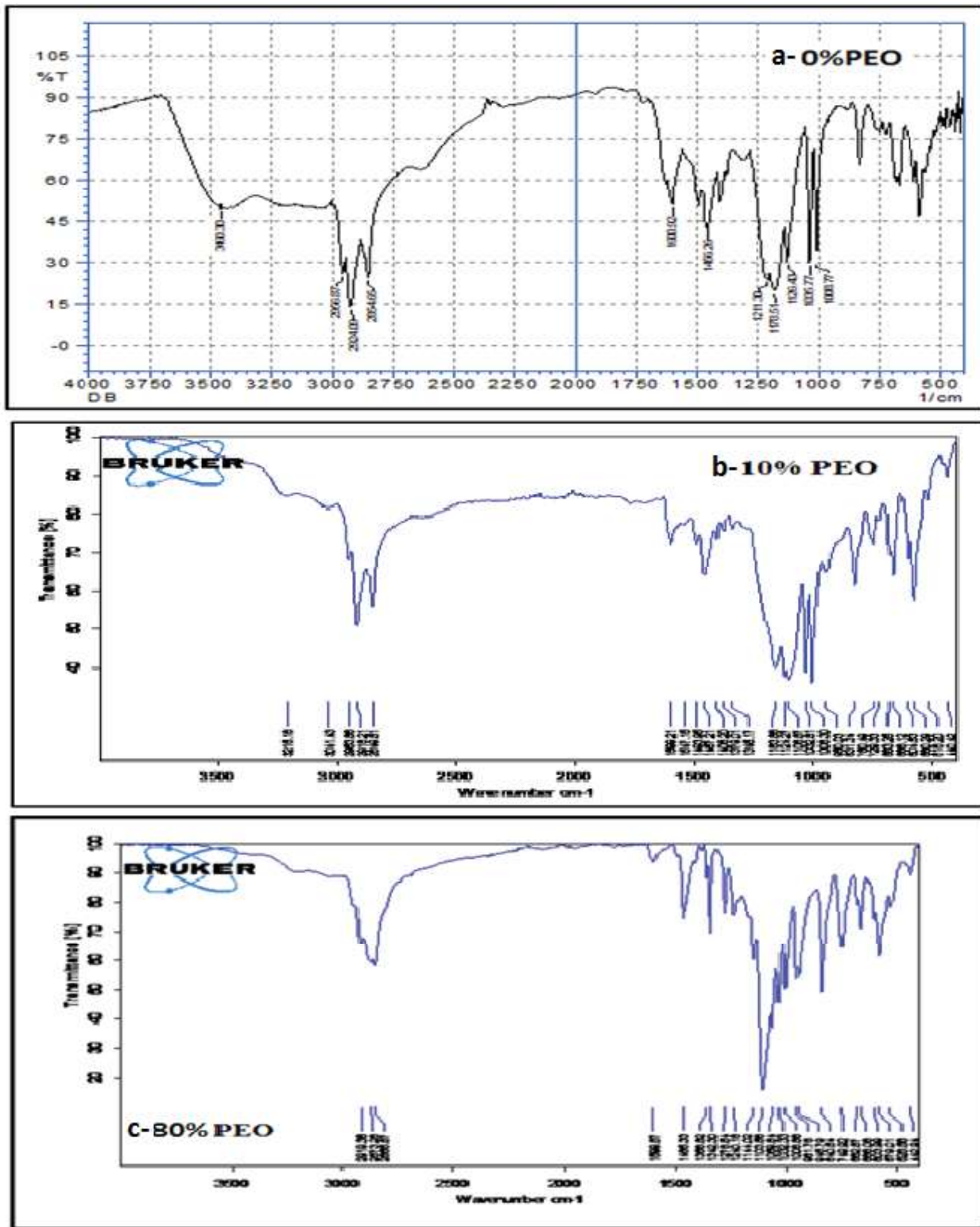


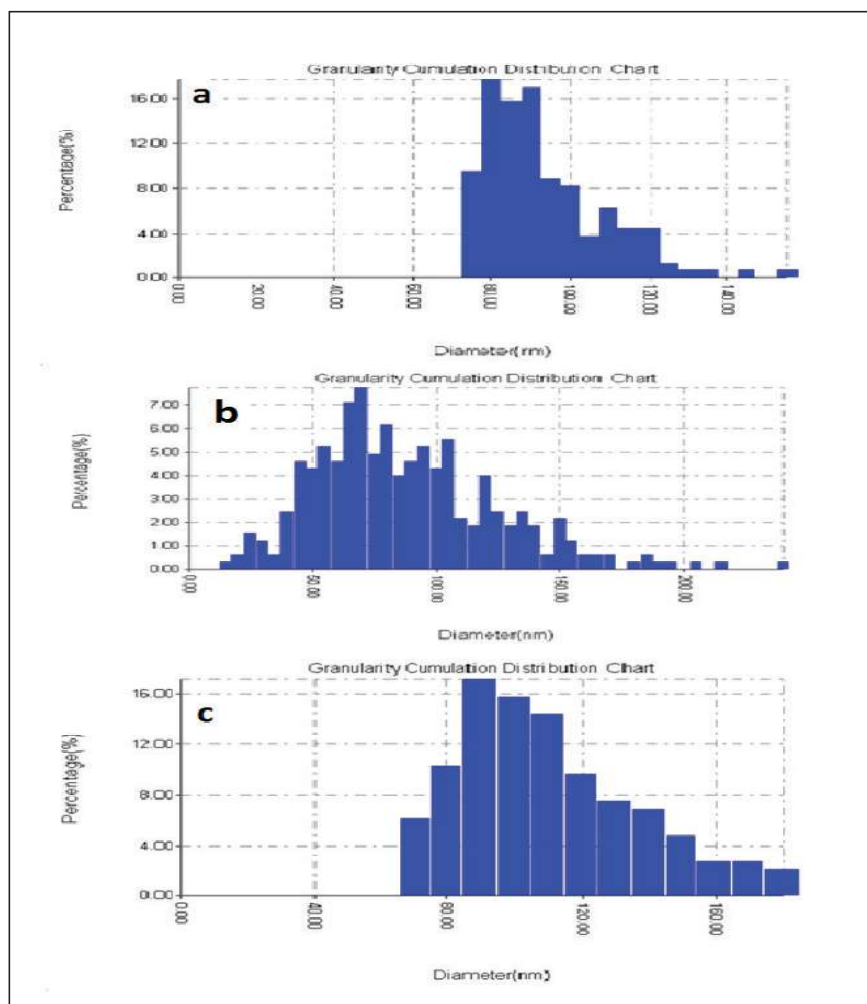
Fig. (2): FT-IR spectra of the POT-DBSA with different ratio of PEO in the blend (a) 0%PEO (b) 10% PEO (c)80% PEO





The morphology of the POT-BDSA and POT-DBSA/PEO blend were examined using AFM. The histograms diameters distributions of the above samples are displayed in Fig. (3). AFM images of pure POT-DBSA and the other sets of POT-DBSA /PEO blends with weight ratios concentrations of (10%, 80%) wt PEO are shown in Fig. (4). As it can be seen, the diameters distributions were obtained close to the Gaussian distribution. The average diameters were significantly reduced with decreasing the concentration of PEO. The average di-

ameter of nano polyblend was about (85) nm at (10%) wt PEO concentration and increased with increasing concentration to (120) nm at (80%) wt PEO concentration. To sum up, we could see from the Fig. (3), it is possible to know the type of diameters distributions as well as the number of grains and as for Fig. (4), we can conclude that increasing the PEO ratio in the mixture reduces the surface roughness and the granules are grouped together to form nanofibers, so the number of granules decreases.



**Fig. (3): Size distribution of diameter in POT-DBSA with different ratio of PEO in the blend (a) 0%PEO (b) 10% PEO (C)80% PEO**

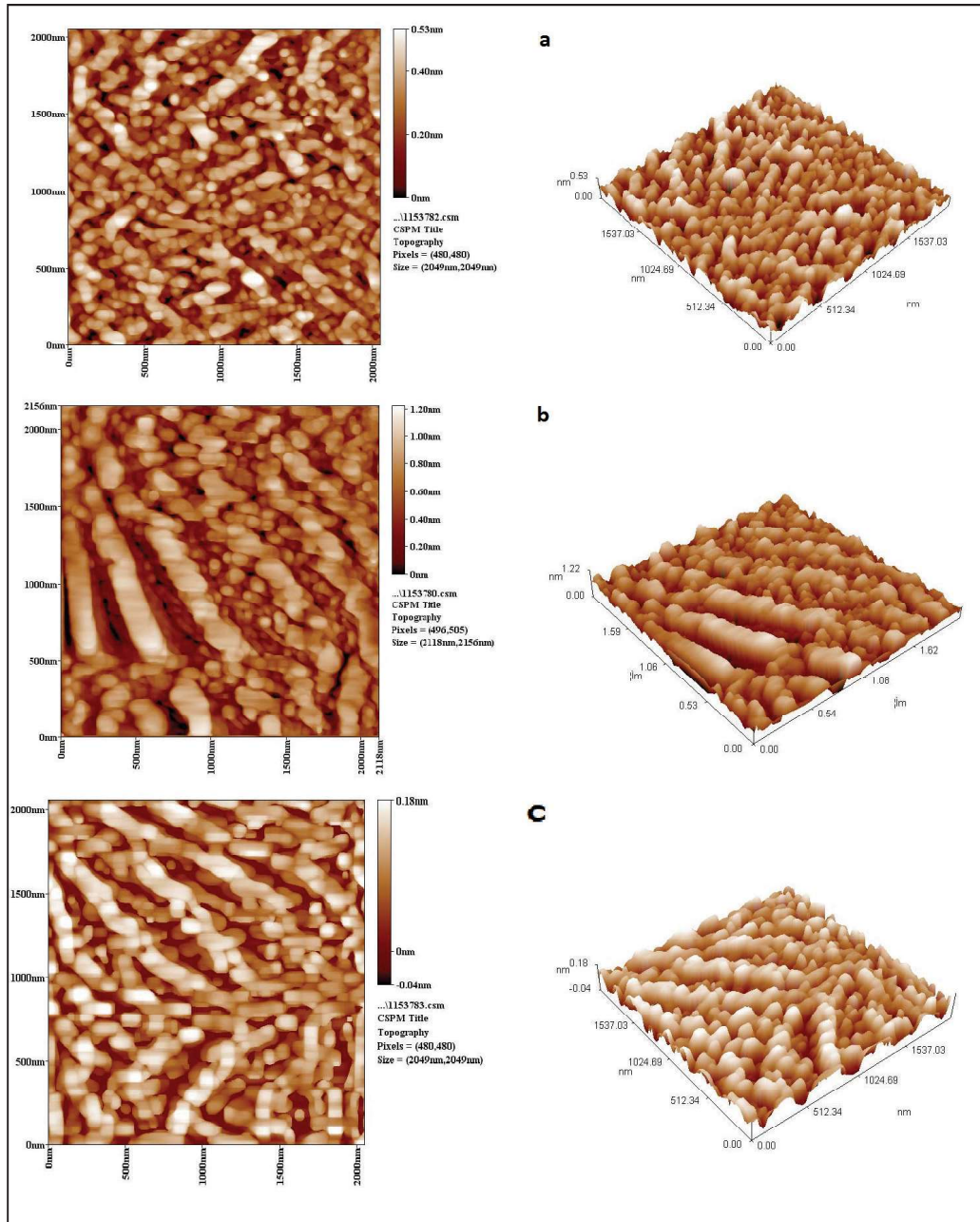


Fig. (4): AFM of the POT-DBSA with different ratio of PEO in the blend (a) 0%PEO (b) 10% PEO (C)80% PEO

### 3.2. Optical characterization

Optical characterization of samples gives information about other physical properties, e.g. band gap energy and band structure, optically active defects etc. and therefore that may be of permanent interest for several different

applications. Fig.(5) shows the absorption spectra of the blended active layers shown in A1, A2, A3. It is well known that P3HT:ICBA blends exhibit spectral absorption in the range of 400-650nm [24]. The measured spectra fall in the range starting at (~700) nm down



to (~300) nm for all samples with different weight ratios (0,10,80) % of PEO. In our research, we replaced the material P3HT with the prepared poly blend POT-DBSA/PEO.

We observed that it absorbs light at the same wavelengths of P3HT and concluded the blends was good for the formation of solar cell as well as absorbed in the visible area .

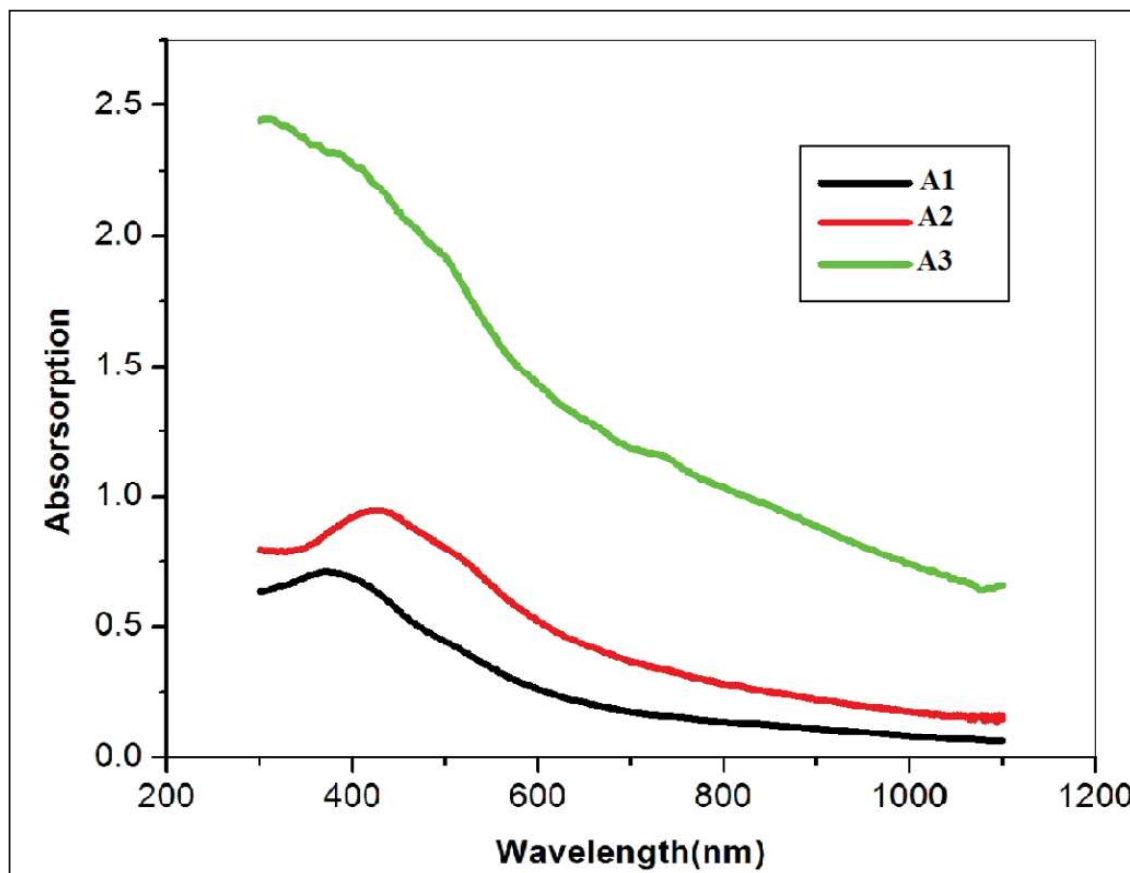


Fig. (5): The absorption spectra of the blended active layers for the Solar cell

### 3.3. Photovoltaic device performance

The open circuit voltage ( $V_{oc}$ ), short circuit current density ( $J_{sc}$ ), fill factor (FF) and power conversion efficiency (PCE) of the devices under study were calculated using J-V measurements. Fig. (6) shows the J-V curves for solar cell devices with structure (ITO/PEDOT:PSS/POT-DBSA-PEO:ICBA/Al). It is well known that  $V_{oc}$  for the organic solar cell is determined by the difference between the lowest unoccu-

pled molecular orbital LUMO of the acceptor molecules and the highest occupied molecular orbital HOMO of the donor molecules [25]. Therefore, the lower  $V_{oc}$  can be associated with the loss in charge carriers in the electrodes. In addition, the interface between the POT-DBSA-PEO and the ICBA molecules could play an important role in modifying the  $V_{oc}$  [26]. In the bulk heterojunction layer, the holes move through the conjugated polymer matrix, while



the electrons transfer by hopping between the ICBA molecules [27, 28]. Light absorbed by the active layer results in excitation generation, which are then separated into electron-hole pairs. The POT-DBSA-PEO:ICBA heterojunction controls the separation and transfer of the charge carriers to the electrodes and prevent the recombination between them, and leading to improved photocurrent. The parameters of the solar cell devices are shown in Table (3). We note from the result in the table the short circuit current density  $J_{sc}$  increases from (3-5.25) mA/cm<sup>2</sup> and the series resistor

$R_s$  decreases, while the shunt resistor  $R_{sh}$  increases as the PEO ratio in the mixture is one of the important reasons that increase the open circuit voltage and thus increase the efficiency of the solar cell from (0.46) to (1.58) when the PEO ratio increases in the active layer mixture. This increase in the device efficiency is due to an increase in the number of secondary levels between the valence and conduction bands, which contribute to the increase in the movement of electrons and holes in the direction of the anode and cathode electrodes, thus increase in the short circuit current.

**Table (3): Parameters for the Solar cell devices**

sample	Wt% PEO	$V_{oc}$ (Volt)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF	PEC%	$R_s$ ( $\Omega$ )	$R_{sh}$ ( $\Omega$ )
A1	0%	0.38	3	0.4	0.46	583	3571
A2	10%	0.34	4.7	0.47	0.75	428	2857
A3	80%	0.7	5.25	0.43	1.58	381	4762

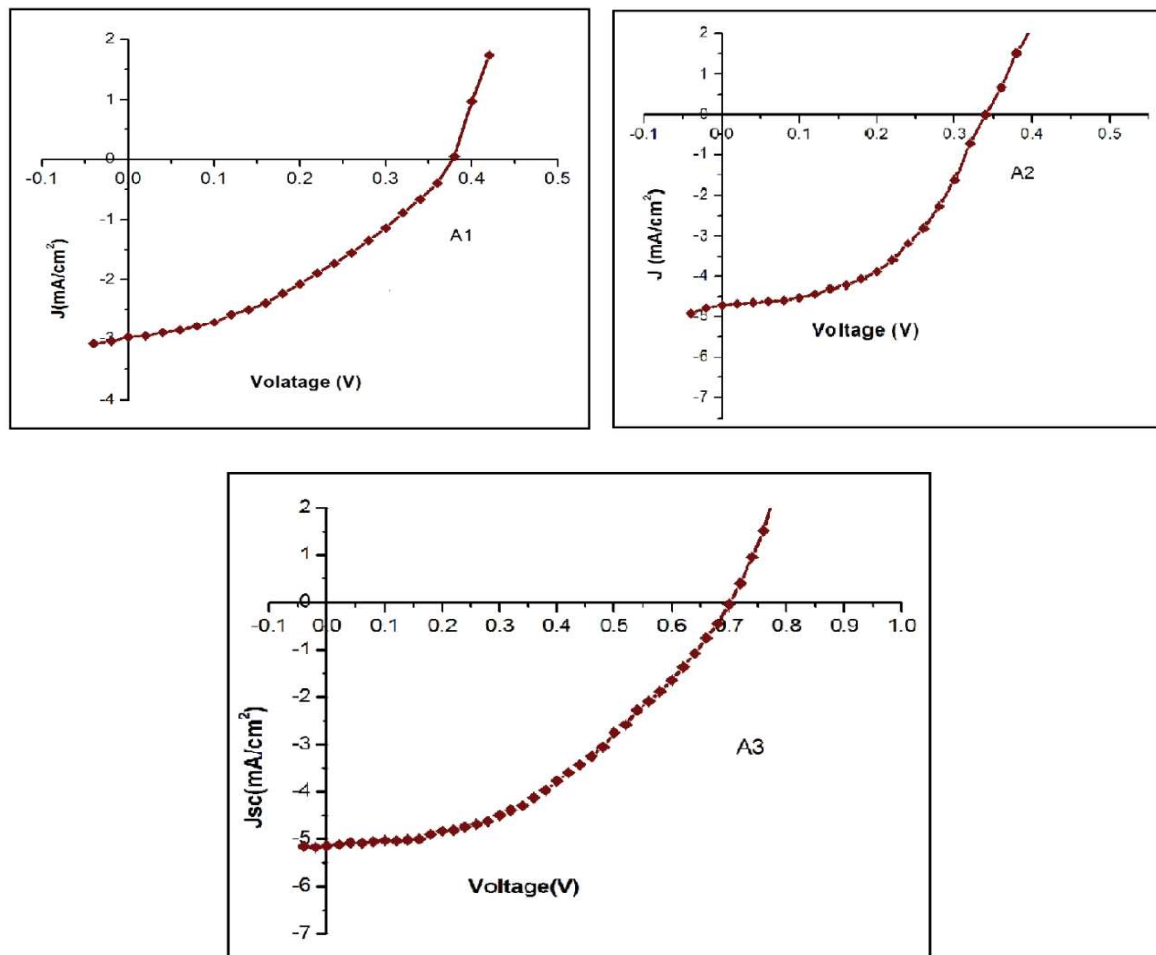


Fig. (6): The J-V curves for the solar cell devices.

#### 4. Conclusion

Conducting poly blend of POT-DBSA/PEO were prepared from different weight ratios of PEO with POT-DBSA. The chemical structure of prepared samples was characterized by the FTIR spectra. We can see from that, the effect of blending PEO in the two different ratios with the POT-DBSA on the FT-IR spectrum lead to change in the wave number values increases or decreases indicates a successful a common mixture. The morphology surface studied by AFM indicated combination of DBSA doped POT structure makes the polymer-surfactant system

useful in fabricating multifunctional materials for future technological applications such as solar cell and we can conclude that increasing the PEO ratio in the mixture reduces the surface roughness and the granules are grouped together to form nanofibers. As for the electronic application of nano poly blend (POT-DBSA/PEO) in solar cell type (ITO/PEDOT:PSS/POT-DBSA-PEO:ICBA/Al) were fabricated. The parameters and the efficiency of solar cell at different ratio of PEO in POT-DBSA/PEO were calculated. The result indicated that the efficiency increased as PEO in the blend.





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