

The Electrical Properties of Poly(o- toluidine) Doped with DBSA Blend with Polyethylene Oxide PEO as Nano Conducting Polyblend

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Abstract

Poly (o-toluidine) (POT) doped with Dodecyl benzene Sulfonic Acid DBSA synthesis by chemical polymerization method using ammonium persulphate as oxidizing gent. Nano Conducting polyblends POT-DBSA/POE films were prepared by mixed different ratio (0 – 10%, 15%, 25%, 35%, 45% and 50%) of polyethylene oxide polyethylene oxide (PEO) with conducting polymer (POT-DBSA) and prepared by spin coating method . Morphology and diameters of the nanofibers were studied by Atomic Force Microscope (AFM). The diameter of nanfiber was about 85.49 nm (at 15 wt% PEO concentration) and increased with increasing concentration to 105 nm (at 50 wt% PEO concentration). . The electrical properties of conducting polyblends POT-DBSA/POE were measured by two probes method. I-V characteristic of these films at different weigh ratio of POE were investigated .They showed ohmic behavior at all applied voltages . The electrical conductivity increases as POE increase from 7.2×10^{-7} S/cm at 0% to 4.48×10^{-5} S/cm at 50% .The activation energy at temperature were found at rang (293-353)K are also investigated .

Keywords: key words, conducting polyblend, poly (O-toluden)(POT), polyethylene oxide polyethylene oxide (POE), ,electrical properties.

1. Introduction

Poly (O-Toluidine) (POT) and polyaniline (PANI) are considered as the most important conducting polymers (Krichelore 1992) .Conducting polymers have an immense advantage of being simple to synthesis, with their chemical structure tailored to alter their physical properties, such as their band gap. They exhibit an extensive range of electrical conductivity from metallic to insulator value (10^{-9} - 10^5) S/cm. Further to their ease of synthesis and lower cost, they are known to have low poisoning effects(Cao, Y. *et al* 1992, Talib R.A. 2009 .It has attracted great attention in the field of active materials for applications such as organic light emitting diodes (OLEDs) (Burn *et al* 2007) field-effect transistors(OFETs) (Nam *et al* 2011) and solar cells (Kareema *et al* 2012).

(POT) polymer is a PANI derivatives which contains the – CH₃ group in the ortho position of the aniline monomer . Among the ring substituted PANi derivatives(Elmansouri,A., *et al* 2007). POT has been probably the most widely studied one. Indeed ,(Kareema *et al* 2013) have studied the chemical polymerization of (O- toluidine) and its application in solar cell. The electro polymerization 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 (Kareema. & Wejood 2012).

Many research about polymer blend (mixed two or three polymers) were done to improvement the physical properties of polymers (Zainab, *et al* 2008 ; PAN *et al* 2010 ; Nam *et al* 2011).One of these polymers is POE which is used to obtained nanofiber conducting polymers (Tariq J.et al 2013). These fibers have a high surface area to volume ratio, which is useful for many applications (Deitzel *et al* 2001).

In the present work synthesis of conducting polyblend of POT-DBSA/POE. was prepared by chemical polymerization then blended with different weight ratios of POE. The morphology of Prepared material was characterized by AFM . Thin films of these blend prepared by spin coating method on interdigitated Finger electrode.

2. Experimental Procedures

2.1 preparation of poly POT-DBSA:

Poly (O-toluidine) doped with DBSA was synthesized by the oxidative polymerization of (o-toluidine) in acidic media .using a method similar to the research ,(Kareema et al 2013).1 mg of POT-DBSA was dissolved in 10 ml of chloroform (CHCl₃) with stirring for 8-9 hours. The result deep green solution was filtered. PEO (Mw 200.000 provided by (Alpha chemical) was added to POT-DBSA solution and put under stirring for 3 hours. Different weight ratios of POE (10 , 15 , 25, 35, 45 and 50) % were used . Different ratios solution of POT-DBSA/POT were prepared and these solutions were used to prepared thin films samples .

2.2 Preparation of POT-DBSA / POE thin Films

The thin films of POT-DBSA / POE was synthesized by using spin coating method on interdigitated finger electrode. Figure (1) shows interdigitated finger electrode, that used to measure the surface conductivity of the sample s from the following relationship (Skjolding, L. *et al* 2008).

$$\sigma_s = [I/V] [L/Wt\ell] \quad (1)$$

where, t is thickness of polymer, W is the distance fingers (10mm), ℓ is number of fingers is to be (10), and L is the space between electrodes (100 μ m).

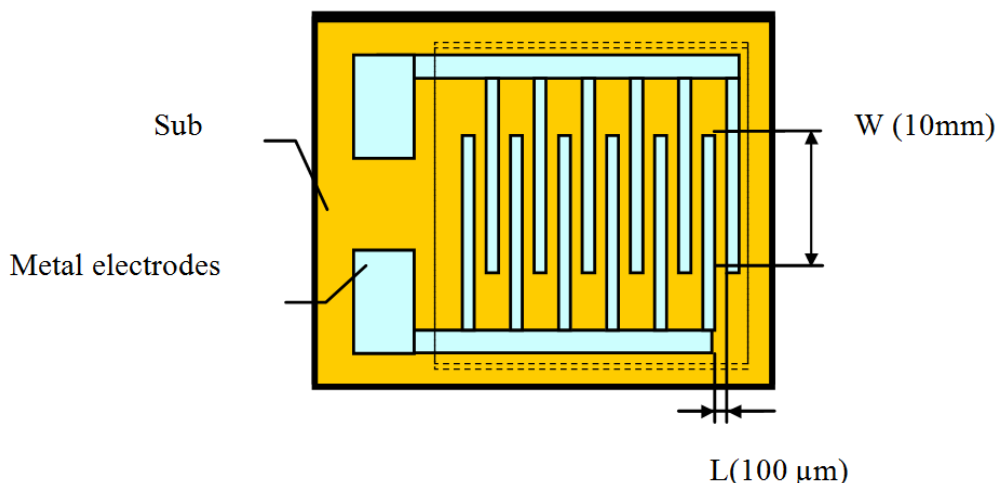


Figure 1. A schematic diagram of interdigitated finger electrode

3. Results and Discussion

3.1 The Morphology of materials

The morphology, of the POT –DBSA and POT-DBSA / PEO blend were examined using AFM. AFM images of pure POT-DBSA and the other sets of POT –DBSA / PEO blends with weight ratios concentrations of PEO 0wt%, 15 wt%, 25 wt%, 35 wt%, 45 wt % and 50% are shown in Figures2. The histograms diameters distributions of the above samples are displayed in Figures3. 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 diameters of POE-DBSA/PEO nanofibers between 85.46 nm at 15% wt%to 105nm at 45% POE.

3.2 Electrical conductivity

Current-voltage characteristic of POT.DBSA/PEO blends for 25% PEO concentration at room temperature is shown in Fig.4. The curve shows ohm behavior. The electric conductivity is calculated by equation (1), for all concentrations, and tabulated at Table (1). The electrical conductivity increase with increasing the PEO concentration found ranging from 7.2×10^{-7} S/cm at 0wt% PEO to 4.48×10^{-5} S/cm at 50wt% PEO concentrations. As increasing weight ratio of POE, in blends the conductivity increase may be the POT-DBSA/PEO blend became Nano fiber material so that Nano fiber structure would increase the conductivity and this agreement with (Norris et al 2000) the high conductivity at high PEO concentration can be attribution to reduce the energy gap with increase the PEO concentration, and from the other hand when the fiber diameter decreases this lead to increase in conductivity of Nano fibers as found by(Sarac, A. S. et al 2012).

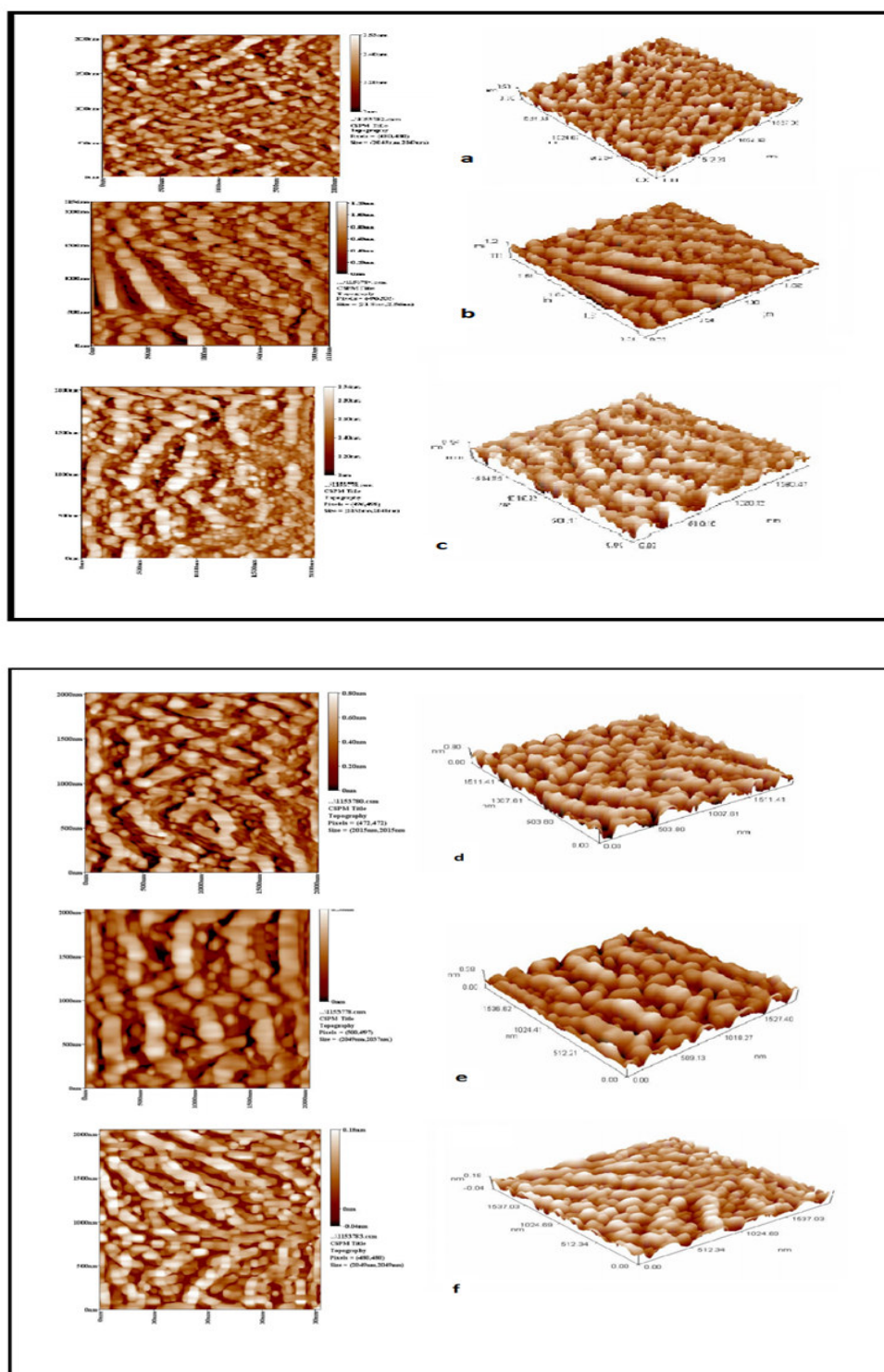


Figure 2. AFM of POT-DBSA/POE blend

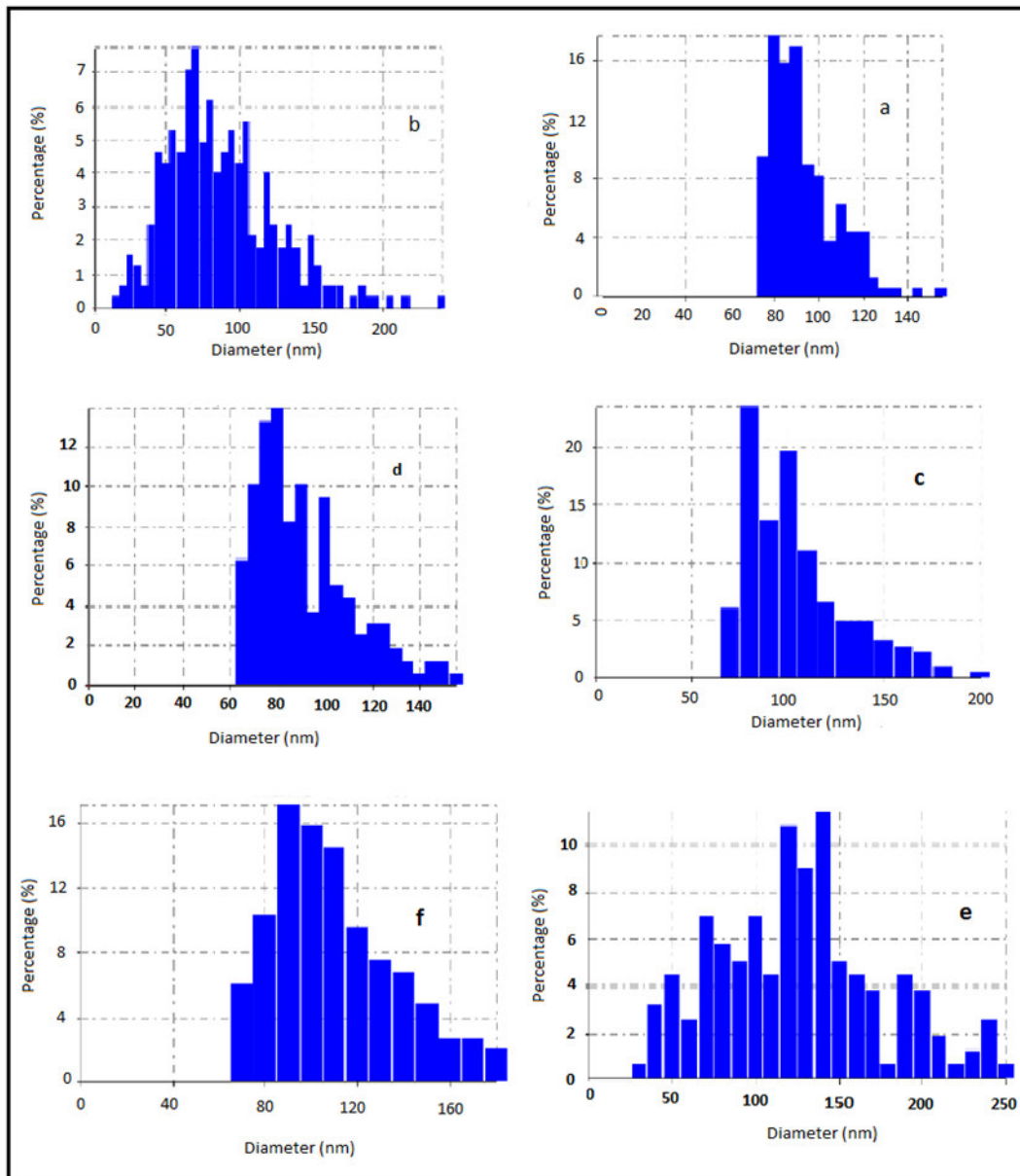


Figure 3. Size distribution of diameters in POT-DBSA/PEO Blend at (a) 0%PEO(POT-DBSA) (b)15%PEO (c)25%PEO (d)35%PEO (e) 45%PEO (f) 50%PEO

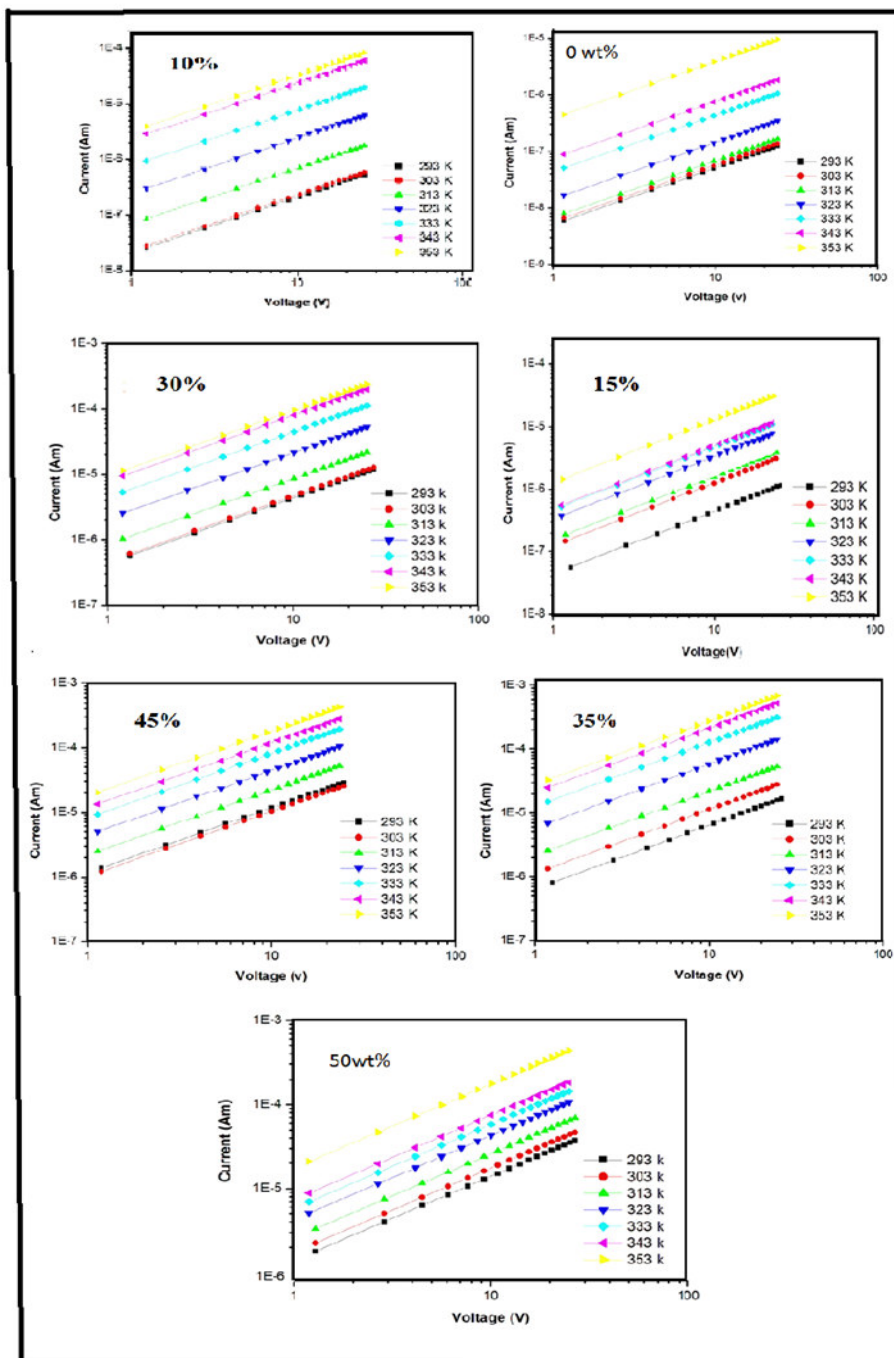


Figure 4. Current –Voltage characteristic of POT-DBSA/POE for all concentration

Table 1. The the electrical conductivity of POT-DBSA/POT he electrical conductivity of POT-DBSA/POT

T(K)	%0 PEO $\sigma(\text{S.cm}^{-1})$	10% PEO $\sigma(\text{S.cm}^{-1})$	15.6% PEO $\sigma(\text{S.cm}^{-1})$	25% PEO $\sigma(\text{S.cm}^{-1})$	35% PEO $\sigma(\text{S.cm}^{-1})$	45% PEO $\sigma(\text{S.cm}^{-1})$	50% PEO $\sigma(\text{S.cm}^{-1})$
293	7.2×10^{-7}	3.5×10^{-6}	4.72×10^{-6}	6×10^{-6}	7.4×10^{-6}	1.2×10^{-5}	4.48×10^{-5}
303	7.9×10^{-7}	6.4×10^{-6}	9.8×10^{-6}	1.5×10^{-5}	2.9×10^{-5}	7×10^{-5}	1×10^{-4}
313	1.09×10^{-6}	1.2×10^{-5}	1.25×10^{-5}	5.7×10^{-5}	1.96×10^{-4}	2.8×10^{-4}	3.2×10^{-4}
323	2.3×10^{-6}	4×10^{-5}	7.3×10^{-5}	1.53×10^{-4}	2.9×10^{-4}	4.8×10^{-4}	6.8×10^{-4}
333	7×10^{-6}	8.2×10^{-5}	1.3×10^{-4}	3.3×10^{-4}	4.5×10^{-4}	7.3×10^{-4}	9.5×10^{-4}
343	1.22×10^{-5}	3.9×10^{-4}	4.5×10^{-4}	5×10^{-4}	5.56×10^{-4}	1.5×10^{-3}	2.8×10^{-3}
353	6.28×10^{-5}	5.5×10^{-4}	7.8×10^{-4}	1.2×10^{-3}	3.3×10^{-3}	4.9×10^{-3}	7.6×10^{-3}

3.3 Temperature dependence of electrical conductivity

Current-voltage characteristic of POT-DBSA /PEO samples with different PEO concentration at different temperature range (293-353 K) is shown in Fig.5 . The figure shows ohmic behavior at all applied voltage at all range of temperature. Also note an increase in the current value with the increase in temperature due to the increase in the concentration and mobility of charge carriers with the increase of temperature as high temperature works on the exponential increase in the number of charge carriers and mobility. This leads to increasing in electrical conductivity with temperature. This is similar to what was obtained by the researchers(PAN et al 2010) W, when studying the electrical properties of co- polymers. Figure 6 shows the $\ln \sigma$ as a function of $10^3/T$ for the POT-DBSA/PEO blends at different PEO concentration. From this figure see the D.C conductivity increases with increasing temperature, this means that the POT-DBSA/PEO have negative thermal coefficient for all PEO concentration. It can be also be seen that POT-DBSA/PEO of weight ratio (0,10,15)% of POE have divided in two regions one at range(293-322)K and other at range (353-322)K. In the first region the temperature is enough to move the carrier from valence band to bipolar on band .The conductivity follows the free carrier translation in an extended state over the chain length in addition to the interchain transition. The activation energy, E_{a1} , is calculated by the relation(Kireev 1978).

$$\sigma = \sigma_0 e^{-E_a / KT} \quad (2)$$

where E_a , K , T are the activation energy, Boltzmann constant and temperature. As temperature is lowered, second region(322-293)K, the number of holes in valence band decrease and shift away to localized bipolaron state. In this region can be explained according to happening through a tail states between adjacent sites. (Kareema 1997)At high weigh (25,35.45and 50)% one activation energy observed at range (293-353)K . The conductivity follows the free carrier translation in an extended state over the chain length in addition to the interchange transition. The values of E_{a1} and E_{a2} were tabulated at Table 2, and from this table see decreasing the activation energy with increases PEO.

Table 2. The the electrical the activation energy of POT-DBSA/POT for all concentration

Concentration of PEO%	$E_{a1}(\text{eV})(353-322)$	$E_{a2}(\text{eV})(322-293)$
0	1.05	0.69
10	0.98	0.53
15	0.95	0.42
	$E_{a1}(\text{eV})(353-293)$	
25	0.92	
35	0.9	
45	0.86	
50	0.75	

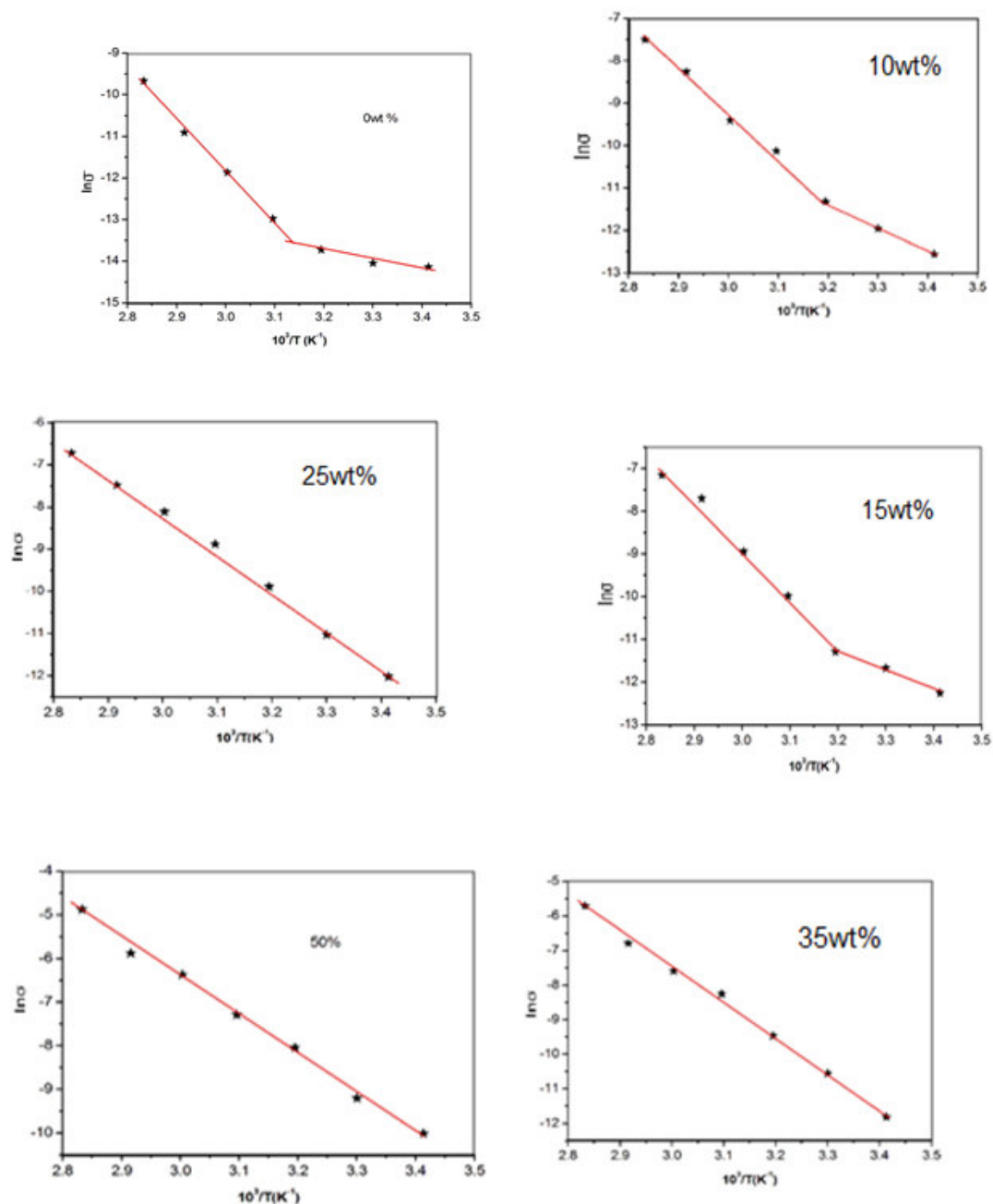


Figure 6. The electrical conductivity POT-DBSA/PEO as a function of reciprocal absolute temperature ($1/T$). for all concentration

5. Conclusion

- 1- Conducting blend of POT-DBSA /POE were prepared from different weight ratio of POE with POT.
- 2- the morphology indicated nanostructure and diameters of the nanofiber was about 85.49 nm (at 15 wt% PEO concentration) and increased with increasing concentration to 105 nm (at 50 wt% PEO concentration).
- 2) I-V characteristics of all ratio show ohmic behaviors with electrical conductivity increase as POE increases from 7.2×10^{-7} at 0% to 4.48×10^{-5} at 50% .
- 3) The activation energy decreases with increase POE weigh ratio from 1.05 eV at 0% to 0.75 eV at 50%.

References

- Abdiryim, T., Gang, Z., & Jamal, R. ,(2005) "Synthesis and characterization of POT Doped with Organic sulfonic acid by solid-state polymerization", Journal of Appl. Polymer science, Vol.96, 1630-1634.
- A. Elmansouri, A. Outzourhit, and A. Oueriagli, (2007), Active and Passive Electronic Components,

- Burn, P., Shih-Chun Lo. and Samuel, I. W. (2007) "The development of light-emitting dendrimers for displays", *Advanced Materials*, 19, 1675-1688.
- Cao, Y., Smith, P., Heeger A.J., (1992) "Counter-ion induced processibility of conducting polyaniline and of conducting polyblends of polyaniline in bulk polymers", *Synth. Met.*, 48, 91-97
- Deitzel J.M., (2001) "The Effect of Processing Variables on the Morphology of Electrospun Nanofibers and Textiles", *Polymer*, 42(1), 261-272.
- Hussein, F., Kareema M.Z., Ajeel, K.I., (2011) "Syntheses and study some electronical properties of poly(o-Toluidine) doped with para toluene acid." *J. Basrah Science A*, 27(1), 157-164.
- Nam, S., Jang, J., Kim, K., Yun, W. M., Chung, D. S., Hwang, J., Kwon, O. K., Chang, T. and Park, C. E., (2011), "Solvent-free solution processed passivation layer for improved long-term stability of organic field-effect transistors", *Journal of Materials Chemistry*, 21, 775-780.
- Norris, I. D., Shaker, M., Ko, F. K. & MacDiarmid A. G., (2000), "Electrostatic fabrication of ultrafine conducting fibers: polyaniline polyethylene oxide blends", *Synthetic Metals*, 114, 109-114.
- PAN, W., ZHANG, Q., & YAN, C., (2010) "Characterization of PAN/PANI-DBSA blend nanofibers produced by electrospinning method" *OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS*, 4, 2118 – 2122
- Kareema M.Z. (1997), The electrical and optical properties of conducting polymers PT, PT/PTFE, PT/PVC and their application in rechargeable batteries "PhD thesis, Basrah university, Basrah Iraq.
- Kareema. M. Ziad & Wejood T.S., (2012) "Study of the electrical characteristics of polyaniline prepared electrochemical polymerization", *Energy procedia*, 19, 71-79.
- Kareema, M. Z., Hussein, F., and Ajeel K.I., (2012) "Study of the electrical characteristics of poly(o-toluidine) and application in solar cell", *Energy Procedia* 18, 157 – 164.
- Kareema. M. Z., Hussein, F., & Ajeel, K.I., (2013) "Study of the electrical characteristics of poly(o-toluidine) doped with para-toluene sulphonic acid/n-type silicon heterojunction solar cells", 2nd international conference on solar energy materials (solar Asia 2013) 22-24 Aug, Universiti Malaya, 50603, Kuala Lumpur, Malaysia 250.
- Kireev, P. S., (1978) "Semiconductor Physics", Translated from Russian by M. Somkhvalov, MIR publishers, Moscow.
- Krichelore, H.R., (1992) "Hand Book of Polymer Synthesis Part B", Mersel Dekkei N. Y.
- Sarac, A. S., (2012), "Nanofibers of conjugated polymer composites", *J. Nanomed Nanotechol*, 3, (9) 77-78.
- Skjolding, L., Spegel, C., Ribayrol, A., Emneus, J. & Monteius, L., (2008) "Characterization of nano-interdigitated electrodes", *Journal of physics*, 100, 052045.
- Talib R.A., (2009) :preparation of conducting polymr (PAni) by chemical method, Study some of physical properties and its application as ammonia gas sensor", MSc Thesis, mustansrey University, Baghdad, Iraq.
- Tariq J. Alwan, Kareema M. Z., & Kadhum K. Kadhum, (2013) "Alignment Nanofibers Conducting Polymer (PAni, CSA/PEO) Preparation by Electrospinning Technique, *International Review of Physics (I.RE.PHY.)*, 7, 185-193
- Zainab, R.A.li, Zeadan A.M, & Kareema M.Z., (2008) "The optical properties of Polyaniline blend with polymethal methacrylate PAni/PMMA as conducting polymer alloys" *J. Basrah Science A*, Vol.20 22-34.



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