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The Morphology and Electrical Characterization for external doping (POT)

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Abstract: In this work, Poly (o-toluidine) have been Built up by oxidizing polymerization (otoluidine) in an acid medium. The polymer was distinguished by emissions by EDX, SEM, and the electron. external doping has been used. N-methyl-2-pyrrolidone (NMP) is a solvent used in a thin-film mixture. Two-probe methods have been used in the measurement of electrical conductivity. The effect of different temperatures on conductivity has been studied. We find low conductivity about 0.0202*10⁻⁴ S/cm.

Keywords: Poly (o-toluidine), Electrical and Optical characterization, external doping.

INTRODUCTION

Poly (o-toluidine) is a member of PANI, Owing to its higher processability and solubility compared to PANI, POT was selected as the conductive polymer Including PANI derivatives, poly(o-toluidine) (POT), polymer derived from o-toluidine (OT), (a substituted aniline with a CH₃ group at the ortho-position aromatic ring), structural properties and redox and electrochromic activity have been reported to be closely related to PANI., Poly (otoluidine) Was researched as large as possible. In the case of polyaniline-based copolymers, pioneering work on aniline-polymerization with (o-toluidinetoluidine) and aminoacet Ophenone has conductivity properties of a broad range. [1-4].

The highest one commonly studied was possibly POT. Besides, the chemical polymerization of (O-toluidine) [5]. The principle of doping is the special, essential, unifying theme that separates polymerization from all other polymers. A chemical dopant is a material in the conducting polymer subject, A very limited quantity of which is radically changed by mechanical, electrical, magnetic. The structural properties of the polymer and the strong growth in conductivity are observed [6].

POT is regularly taken into consideration ideally suited over poly (aniline) because of its ease in processability, due to higher dissolution houses of POT in solvents in evaluation to polyaniline. Improve and optimize systems for applications intercept method of conduction, Experiments of the conductivity of undertaking polymers could be very important. Although there has been studied on the mobility of the natural surface place in touch with the insulator by way of the hall effect and the discipline effects on the normal field-effect transistors, the temperature dependence of the conductivity of undertaking polymers has no longer been researched in-depth [7–8].

N-methyl-2-pyrrolidone (NMP) is a famous solvent for immaculate Poly (o-toluidine) or organic acid -doped PANI yet it's the doped POT films made from NMP solutions are often small Electric conductivity 10^{-1} - 10^{-4} S/Cm. Dedoping reaction is discovered when the doped POT solution is highly diluted with NMP. This result is attributable to a strong effect interaction between the NMP and the doping acid. The rivalry between the NMP and the POT is responsible for the weak configuration of the doped POT in the NMP solution and the weak conductivity. NMP is a very slow solvent to evaporate. This has a boiling limit of around 202 ° C. A thin NMP film takes more than 15,000 s for 90% evaporation at room temperature. [9]

The principle of external doping will be explained by the use of polyaniline and its derivatives. The effect of external doping on the electrical conductivity was also determined based on their spectroscopic data showing a dramatic increase in conductivity the analysis also indicates that there is external doping enhanced conjugation for π [10].

The primary dopant for a conductive polymer is a material that changes the polymer's electrical, optical, magnetic, and structural houses significantly and is followed by a broad conductivity boom [11]. An external dopant is an essentially "inert" material that causes additional changes in the above-mentioned polymer residences, consisting of a significant rise in conductivity when applied to a primary-doped polymer. The use of polyaniline and its derivatives can be explained with the concept of secondary doping [12].

We explored the effect of external doping in this paper on the conducting polymer POT as well as the solvent NMP how to decreases the conductivity, activation energy at a different temperature, finally studied the optical properties, energy gap.

EXPERIMENTAL METHODS

2.1 Components: O-toluidine monomer was provided by Fisher scientific company. Fluka Company provided hydrochloric acid (HCl). Dodecylbenzene sulfonic acid (DBSA) and ammonium persulfate $(NH_4)_2S_2O_8$ was provided by Aldrich company solvent were used dissolving POT N-Methyl-2-pyrrolidone (NMP).



Figure (1): Structures of (a) NMP (b) POT

PREPARATION EMERALDINE SALT OF POT

Chemical polymerization polymerized o-toluidine (POT-HCl). The Ammonium persulfate (APS) used as an oxidizing agent. O-Toluidine monomer was dissolved in 10 ml (1M/HCL), then APS was an addition to it under constant mechanical stirring at (0-5) $^{\circ}$ C. The reaction was put under a magnetic stirrer for 24 h. Finally, the producer of the polymer was placed in the oven 24 hours at 50 C° to dry.

EXTERNAL DOPANT OF POT

POT (ES) emeraldine salt transforms to emeraldine base by adding ammonia and remains about 6h, then dried in a vacuum oven at 50 C°. Weight 0.1 g from POT (EB) and added 2ml NMP with the stirring for 2 h after that adding 0.13g Dodecylbenzene sulfonic acid (DBSA) and remains on the mechanical stirrer. [12]. The spin coating technique was used to produce the thin films of (POT-DBSA) on glass substrates for SEM measurement. The electrical measurement used an interdigitated finger electrode. After POT salt (ES) is transformed into a POT base (EB) and during dissolving in NMP, the color transforms from green to blue, became the POT base has very low conductivity compared to POT salt.

RESULTS AND DISCUSSION

FT-IR SPECTRUM OF POT

POT film Characterisation was carried out using the FTIR analytical method as shown in figure (2). Table (1) tabled the functional group of (POT) functions [13].



Figure (2) Diagram FT-IR of POT (EB)

Table (1): Spectrum the peaks (FTIR) for POT

Functional spectrum	Vibrations(cm ⁻¹)
Hydrogen-bonded(N-H)	3375.43,3338.78,3209.55,3140.11
stretching vibration of the methyl(-ch ₃)	1950,1800
Quinoid	1593.20
Benzenoid	1400.32,1379.10
Symmetric deformation of methyl group	1328.95,1217.08
C-N	1328.95,1303.88,1217.08
С-Н	1155.36,1114.86,1006.84
С-Н	993.19,881.47,813.96,623.01,526.57

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MORPHOLOGY OF SEM (POT/NMP)

SEM images of the blend polymers POT-DBSA was illustrated in fig (3). This figure gave information about surface morphology for thin films and the diameter, the main diameter about $1.636 \mu m$.



Figure (3) SEM for (POT/NMP)

EDX OF (POT/NMP)

Figure (4) and Table (2) display the POT-DBSA chemical composition calculated via an EDX analysis. The peaks considered within the curve and found to have 11% Si, 14%, O, and 66.06% C. Si may come from a substrate.



Fig (4) EDX pattern of (a) POT+NMP

The POT-chemical composition was operated using an EDX analysis. The peaks considered within fig.4 refer to elements C, O, S, and Si. The thin film's elementary constitution was estimated to have weight The thin film's elemental charter was found to have weight percentage at 11 percent Si, 14 percent O, and 66.06 percent C. Si may come from a substrate.

El	AN	Series [wt.%]	unn. C [wt.%]	norm. C [at.%]	Atom. C	Error (1 [wt.%]	Sigma)	
С	6	K-series	36.76	50.16	66.06		8.85	
Si	14	K-series	15.56	21.23	11.96		0.76	
0	8	K-series	10.98	14.98	14.80		3.44	
S	16	K-series	3.86	5.27	2.60		0.25	
Ca	20	K-series	2.82	3.84	1.52		0.21	
Na	11	K-series	2.49	3.39	2.33		0.26	
Mg	12	K-series	0.83	1.13	0.73		0.12	
Total: 73.29 100.00 100.00								

(b) Elemental composition table.

THE ELECTRICAL CHARACTERIZATION

The polymer (POT/EB) became dissolved in NMP and deposited on the interdigitated finger electrode. The conductivity can be calculated from this equation:

t: Is polymer thickness.
W: the finger distance (10 mm).
t: is the finger count (10), and L is the electrode space (100μm) [13-14].

$$\sigma_{\rm s} = \frac{I}{Vt} \frac{100*10^{-6}}{10*10*10^{-3}} \qquad \dots (2)$$

$$\sigma_{\rm s} = \frac{I}{Vt} 10^{-3} \, {\rm s/cm}$$
 (3)



Figure (5) diagram of interdigitated finger electrode [16]

Depends on the measurement process of the electrical conductivity in polymers on the study (I-V) characteristic. Fig (6) Shows I-V characteristic for (POT/EB) with solvent (NMP) the current increase linearly with increase the



applied voltage on the substrate films for voltage at (5 volt - 10 volts) this reflects the ohmic behaviour for this film. Based on current and voltage values, it was calculated the electrical conductivity from equation (1)

Fig (6) I-V characteristic (POT+DBSA/NMP)

Fig (7) shows the relation between the electrical conductivity and temperature (POT-DBSA). It can be noticed ohmic behavior at temperatures $30C^{\circ}$ and $40C^{\circ}$, for all voltage applied, and with rising temperature, the current increases. At temperature above $40C^{\circ}$, the ohmic behaver show only at applied voltage least than 2V.

The electrical characterization for polymeric materials depends on the structural polymer and crystal size and the electrical characterization for conducting polymers greatly affected the preparation method used [17].



Fig (7) I-V characteristic with different Temperature

Can be described the conductivity by used the Arrhenius equation [17]:

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_0 \exp - \boldsymbol{E}\boldsymbol{a} / \boldsymbol{K} \boldsymbol{T} \qquad \dots \quad (4)$$

 E_a : the activation energy.

K_B: The Boltzman constant.

T(K): Absolute temperature.

The activation energy whose value 0.28 (eV) can be calculated by drawing the relationship between log conductivity and Absolute temperature. Ln σ and 1000/T (K⁻¹) as shown below in Fig (8).



Fig (8) ln σ with temperature T(K⁻¹)

OPTICAL PROPERTIES

For secondary doped POT, the UV-VIS absorption spectrum shown in Fig. (9), the absorption edge scale from 450 nm to 320 nm.



Fig (9) the relationship between Absorbance and wavelength

The equation used to determine the absorption coefficient (α) from the absorbance(A) and thin film thickness (d) is [18]:-

$$\alpha = \frac{2.303}{d} A \qquad \dots \dots (5)$$

The relation between the POT(EB)+NMP absorption coefficient and photon energy displayed in Fig. (10)

Defining the type of transition is significant of (α) value. The value (α) shown in equation (5) was higher than (10⁴ cm⁻¹) that refers to the direct transition. The relationship between α and the photon energy hv is provided by the optical absorption theory. as [18]:

$$\alpha = \frac{A(h\nu - E_g)^m}{h\nu} \qquad \dots \quad (6)$$

A is a constant and m is (1/2, 3/2) prohibited for permissible direct transitions, and (2, 3) prohibited for indirect and indirect transitions. Eg is the distance in an optical band.

Under equation (5) and fig. 10 The optical band difference, which indicated in the form of transition.



Fig (10) POT+NMP absorption spectra related to POT+NMP Photon energy absorption coefficients



Fig (11) The relation (α hv)2 for POT+NMP with Photon Energy

It is shown in Fig (11) from the plotting of $(\alpha hv)^2$ vs. photon energy, was found to be equal to 2.18 eV.

Within a small molecule with an isolated double bond, the absorption of a photon with energy greater than the energy gap (E_g) between the two orbitals will facilitate a pi-electron from the lower energy state to the higher energy state. Due to the decreased energy gap resulting from orbital interactions, a lower energy photon can allow a pi-electron from HOMO to LUMO; hence, the energy gap Eg will be even smaller in conjugated polymers [19].

Making a low energy gap (2.18 ev) and higher conductivity. That can explain the polymer POT condition that polaron creates at the energy gap [20]

CONCLUSION

- 1. External doping of POT with DBSA was successfully synthesized using a process of chemical oxidation polymerization.
- 2. The morphology refers to the diameters of the particle was about 1.636 µm.
- 3. The electrical conductivity at room temperature about ($0.0202 * 10^{-4}$ S/cm). With increasing temperature, the conductivity increases; this means that the POT-DBSA/ has a negative thermal coefficient and activation energy 0.28eV.

REFERENCE

[1] Wei Y, Focke W.W, Wnek GE, Ray A, and MacDiarmid AG. Synthesis and electrochemistry of alkyl ringsubstituted polyanilines. Journal of Physical Chemistry. 1989; 93(1):495- 499. http://dx.doi.org/10.1021/j100338a095.

[2] Wei Y, Hariharan R, and Patel SA. Chemical and electrochemical copolymerization of aniline with alkyl ring-substituted anilines. Macromolecules. 1990; 23(3):758-764. http://dx.doi.org/10.1021/ ma00205a011.

[3] Salma Bilal, Shehna Farooq, Anwar-ul-Haq Ali Shahb, Rudolf Holze, Synthetic Metals, ElSEVIER, 197 (2014) 144–153

[4] Ravi Kumar G, Vivekanandan J, Mahudeswaran A and Vijayanand PS. Synthesis and characterization of novel poly(aniline-co-m-aminoacetophenone) copolymer nanocomposites using dodecylbenzene sulfonic acid as a soft template. Iranian Polymer Journal. 2013; 22(12):923-929. http://dx.doi.org/10.1007/ s13726-013-0191-x.

[5] Elmansouri, A. Outzourhit, and A. Oueriagli, Active and Passive Electronic Components, (2007).

[6] M. K. Ram, M. Joshi, R. Mehrotra, S. K. Dhawan, and S. Chandra, vol., (1997) 304.

[7] Ravi Kumar G, Vivekanandan J, Mahudeswaran A, and Vijayanand PS. Synthesis and characterization of novel poly(aniline-co-m-aminoacetophenone) copolymer nanocomposites using dodecylbenzene sulfonic aicd as a soft template. Iranian Polymer Journal. 2013; 22(12):923-929. http://dx.doi.org/10.1007/ s13726-013-0191-x.

[8] Kazumasa Yamadaa,□, Bunju Shinozakia, Takashi Narikiyoa, Yousuke Takigawaa, Norihiro Kurodab, Toru Bandob, Hiroaki Nakamura. Temperature dependence of mobility of conducting polymer polyaniline with secondary dopant, Synthetic Metals 247 (2019) 124–130

[9] Yanhou Geng, Ji Li, Xiabin Jing* and Fosong Wang Polymer Physics Laboratory, Changchun Institute of applied Chemistry, Chinese Academy of Sciences. Changchun ,Synthetic Met& 84 (EISEVIER, P.R.China ,1997) 97-98,

[10] Kedir Mamma, Khalid Siraj* and Nathan Meka, J Polym Eng 2013; 33(9): 785–792Synthesis and effect of secondary dopant on the conductivity of conducting polymer polyaniline. DOI 10.1515/polyeng-2013-0098.

[11]V. Ali, R. Kaur, N. Kamal, S. Singh, S. C. Jain, H. P. S. Kang, M. Zulfequar, M. M. Haq and M. Husain, "Synthe-sis and Characterization of Se Doped Poly (o-toluidine)," Journal of Physics Chemistry of Solids, Vol. 67, 2006, pp. 68-69.

[12] A. G. Macdiarmid, R. I. Mammone, J. R. Krawczyk and S. J. Porter, "Advanced Electronic and Photonic Materials and Devices," Molecular Crystals and Liquid Crystals, Vol. 105, 1984, pp. 89-105. doi:10.1080/00268948408071645

[13] DALAL K. THBAYH,1 KAREEMA M. ZIADAN2, LIQUID CRYSTALS, AND POLYMERS, 2018, ISSN 2071-0194. Ukr. J. Phys. 2018. Vol. 63, No. 3.

[14] K. Ziadan, H. Hussein, K. Ajeel. Study of the electrical characteristics of poly (o-toluidine) and application in the solar cell. Energy Procedia 18, 157 (2012).

[15] M.Z. Kareema, F. Hussein, K.I. Ajeel. Study of the electrical characteristics of poly(o-toluidine) doped with Para toluene sulphonic acid/*n*-type silicon heterojunction solar cells. In: 2nd international conference on solar energy materials (solar Asia 2013) 22–24 Ague, Universiti Malaya, 50603, Kuala Lumpur. Malaysia 250 (2013).

[16] L. Skjolding, C. Spegel, A. Ribayrol, J. Emneus, and L. Monteius, "Characterization of nano-interdigitated electrodes", Journal of Physics, 100, 052045, 2008.

[17] Thesis, College of Science – University of Basra, Dalal Karad Thbay B.Sc.Physics, 2010.

[18] P. K. Sahu, R. Das, and R. Lalwani, "Incorporation of tin in nanocrystalline CdSe thin films: a detailed study of optoelectronic and microstructural properties," Appl. Phys. A Mater. Sci. Process., vol. 124, no. 10, p. 0,2018.

[19] Manisha Bajpai,1 Ritu Srivastava,2 Ravindra Dhar,1 and R. S. Tiwari3, Review on Optical and Electrical Properties of Conducting Polymers, Hindawi Publishing Corporation Indian Journal of Materials Science, Volume 2016, Article ID 5842763, 8 pages http://dx.doi.org/10.1155/2016/5842763.

[20] K. M. Zaidan, R. A. Talib, M. A. Rahma, and F. H. Khaleel, Synthesis and characterization of poly (o-toluidine) POT blend with polyethylene oxide PEO as conducting polymer alloys, Pelagia Research Library Der Chemica Sinica, 2012, 3(4):841-848.