International Journal of Sciences: Basic and Applied Research (IJSBAR)

ISSN 2307-4531
(Print & Online)

http://gssrr.org/index.php?journal=JournalOfBasicAndApplied

---

# Electrical Properties of Blend Polymers of Polyvinyl Alcohol/Poly (O-Toluidine)

R. K. Fakher Alfahed[a*], K. I. Ajeel[b]

[a,b] *University of Basra/College of Education for pure Science/ Physics Department*

[a]*Email: rrr80kkk@yahoo.com*

**Abstract**

The chemical polymerization method was used to prepare a poly (o-toluidine) which was characterized by different techniques including (FTIR, XRD, SEM) while, blend polymer of poly (o-toluidine)/polyvinyl alcohol (PVA) was made by mixing different volume ratios of PVA and POT (1:1, 1:2, 2:1)respectively. Thin films of the blend polymers were prepared by spin coating method on interdigitated fingers electrodes. I-V characteristics of the prepared samples were measured by two probes method and ohmic behaviours were shown. The surface conductivity of the thin films for blend polymers was recorded at different ranging temperature degrees (308-378K). The semiconducting nature of the prepared samples was observed by winning increase in the conductivity with increasing temperature degrees. The activation energies were calculated according to Arrhenius model.

***Keywords:*** Polyvinyl alcohol; Poly (o-Toluidine); Electrical conductivity.

## 1. Introduction

Conducting polymers were considered as most interesting polymers due to their important characteristics and excellent properties like, the optical and electrical properties, inexpensiveness and environmental stability as well as easy of synthesis and preparation as thin films on a large area [1, 2].

---

* Corresponding author.

E-mail address: RRR80KKK@yahoo.com.

One of the conducting polymers is poly (o-toluidine) which is mostly used in different application fields such as schottky diodes, LED, FET, sensors and inhibitor for carbon steel [3-7]. In other hand, the Polyvinyl alcohol is polymer possessing very good physical properties such as a water soluble polymer with a low electrical conductivity, excellent film forming capacity, good transparency and compatibility with additives [8-10] in addition to other properties like, a cheap, non-toxic and biocompatible polymer [11, 12]. Based on these properties , the PVA received attention of researchers to use it as most important material in biomedical , chemical , physical applications in addition to mix it with other materials or polymers as crosslink materials to enhance and obtain better properties for blended materials [10, 11, 13-18]. Several previous studies focused to investigate the processing conditions, thermal, and mechanical properties of blend films [19-21], besides many successful attempts were performed to enhance the electrical and optical properties of the PVA/Polymer by doping blend polymers with inorganic dopants [16, 18].

In this study, the poly (o-toluidine) was prepared by chemical polymerization that was characterized by FTIR and XRD techniques. The blend polymer of PVA/POT was made, and electrical properties of the prepared polymers were investigated.

## 2. Experimental

### *2.1 Preparation of Poly (o-Toluidine)*

The chemical polymerization was used as method for synthesis of the poly (o-toluidine) (POT) by dissolving 0.27M of o-Toluidine monomer(provided by Fisher scientific) in 0.25M HCL by using constant stirrer at (0-5) ℃ for 30 min., while 10 gm of ammonium per sulphate{ $(NH_4)_2\ S_2O_8$}(provided by sigma-Aldrich) was dissolved in distilled water which was added to the dissolved monomer as drop by drop for ~20 min. to keep a ratio of the monomer to oxidizing agent as (1:2).After completing dropping ammonium per sulphate, the mixture continued in stirrer for 24hr´s more to obtain a greenish-black precipitate of the polymer which was filtered and washed three times by distilled water , methanol and acetone respectively to remove unreacted material and oligomers and then dried in vacuum oven at 60℃ for 24h´s [22].

### *2.2 Preparation of POT and PVA blend polymer*

The blend polymer of polyvinyl alcohol (PVA) ( $[CH_2CH(OH)]_n$ )( Purchased from sigma-Aldrich) and poly (o-toluidine) were prepared by separately dissolving 10mg of both POT and PVA in tow tubes by use of 1 ml of formic acid as solvent for each one under condition of magnetic stirrer for 3hr´s until completing dissolving, then different volume ratios (1:1, 1:2, 2:1 V/V) of both POT and PVA were mixed together by using magnetic stirrer for 5hr ´s to obtain completing mixture. The final mixture was filtered and deposited on the interdigitated finger electrode substrate through use of spin coating method, then carried out on a hot plate to be heated up to 90℃ for 15 min. to remove the solvent. Three thicknesses of the prepared thin films were measured by Ellipsomertry spectroscopic to be presented as (45.5, 44.5, 50.35nm) for PVA:POT of volume ratio (1:1), (1:2) and (2:1) respectively.

### *2.3 The Electrical circuit measurement system*

The electrical properties of blend polymers are measured by two probe method and the circuit consists of Keithley electrometer (Model 65174) was used, to measure a current as a function of applied voltage and capable to supplying a voltage in range (1-20V) in step of 1V and also the digital hot plate was used to raise the temperature degree of the samples while the system was interfaced to a computer.

### *2.4 Fourier Transform Infrared (FT-IR) studies*

The FTIR spectra were used to characterize the poly (o-toluidine) with a wave number range of 500-4000$cm^{-1}$. This technique provided information about structure and chemical bonding of material.

### *2.5 X-Ray diffraction*

X-ray diffraction was considered as important technique to give information about nature and structure of the materials which is used to illustrate the crystallinity case for poly (o-toluidine).

## 3. Results and discussions

### *3.1 FTIR Spectra*

The structure of POT was characterized by FTIR as shown in figure (1), where the absorption band at 1112.82 $cm^{-1}$ corresponding to C-C methyl-substituted SQ and Q rings. The band around 1170.71$cm^{-1}$ indicated to C-H in SQ ring while other two bands (1280, 1324$cm^{-1}$ ) due to benzenoid and quinoid ring asymmetric stretching vibrations. The bands at about 1485.09, 1596.95$cm^{-1}$ were assigned to the C-N stretching of benzenoid and Quinoid ring respectively. The characteristic of band at 2923.88$cm^{-1}$ was referred to C-H stretching as result as substituted methyl group [23, 24].

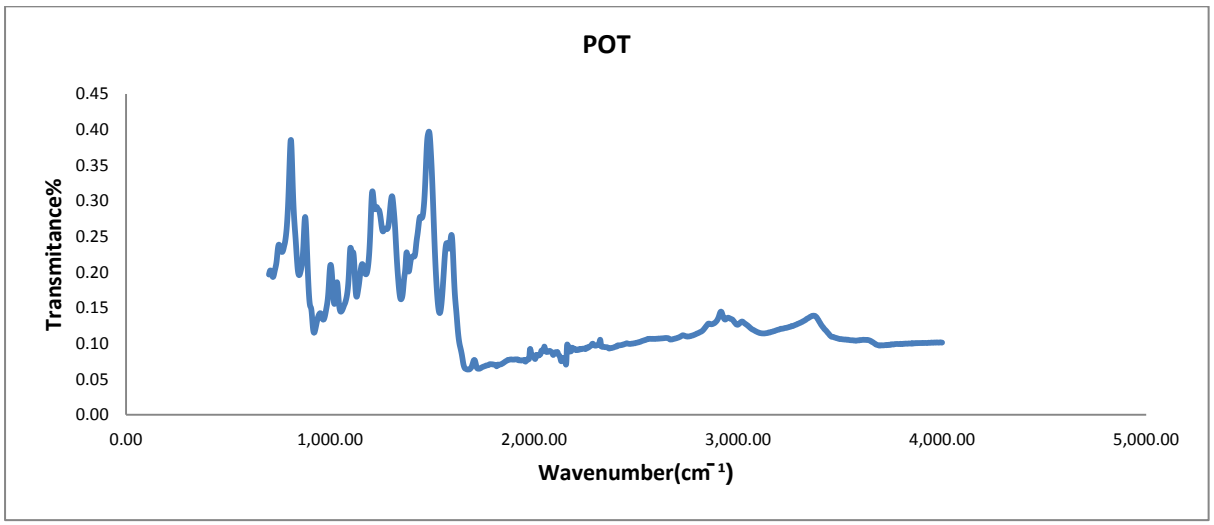



**Figure 1:** FT-IR absorption spectra of POT.

### 3.2 XRD characterization

The XRD pattern of the POT as illustrated in figure (2).exhibited an amorphous structure with small peaks at 16.87° and 25.5° which were interplanar distance of o-toluidine-o-toluidine [25].This result was agreed with previous study which showed that the conducting polymers have semicrystallne or amorphous structure [26].

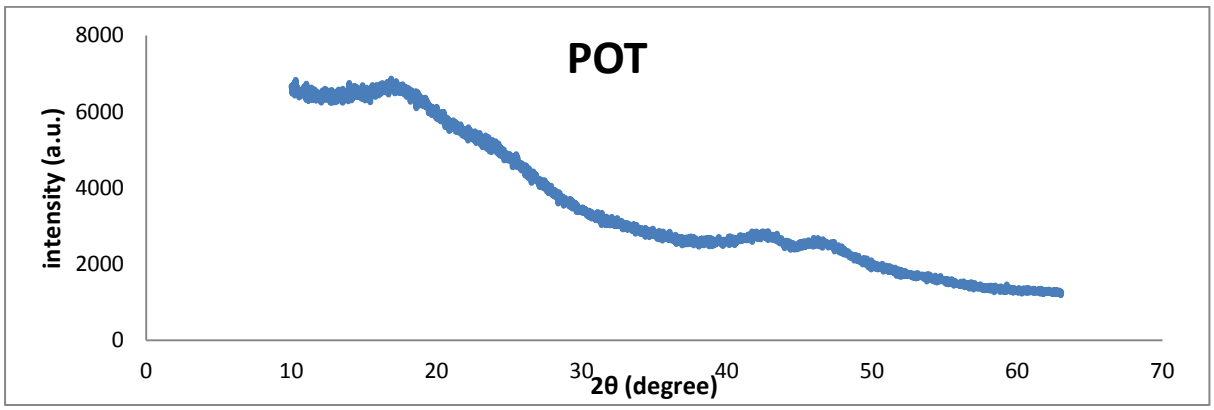
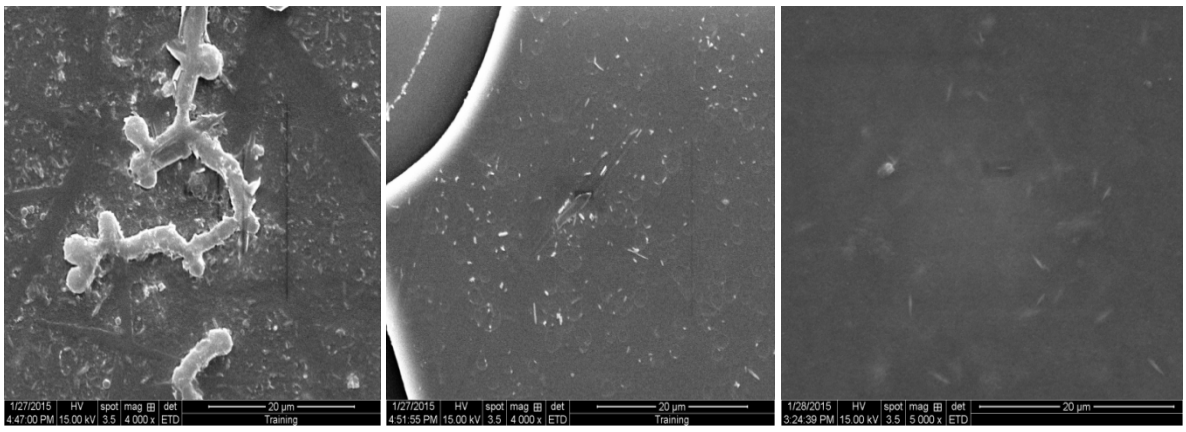



**Figure 2:** XRD scattering pattern of POT.

### 3.3 Morphology

SEM images of the blend polymers (PVA:POT) that were as illustrated in figure (3) gave an information about surface morphology for thin films of the different volume ratios which did not reveal any pinholes or porosity . The thin film surface for ratio of PVA2:POT1 can be seen and explained that POT incorporated in PVA matrix. Sample of the PVA1:POT1 formed a smooth surface and low roughness compared with other samples. The ratio of (PVA1:POT2) sample exhibited better thin film surface with very low deformity which indicated that the PVA was completing forming inside POT as nanofibers.



(A) (B) (C)

**Figure 3:** SEM image of the blend polymers: (A) PVA2:POT1, (B) PVA1:POT1, (C) PVA1:POT2.

### 3.4 Electrical properties

The electrical properties of the prepared samples were measured by two probe method. The keithley electrometer (model 65174) was used to measure a current as a function of the applied voltage. The I-V characteristics of the thin films of blend polymers were recorded at different temperatures which led to be linear and showed ohmic behaviour at all applied voltages [2, 23, 27] as illustrated in figure (4).

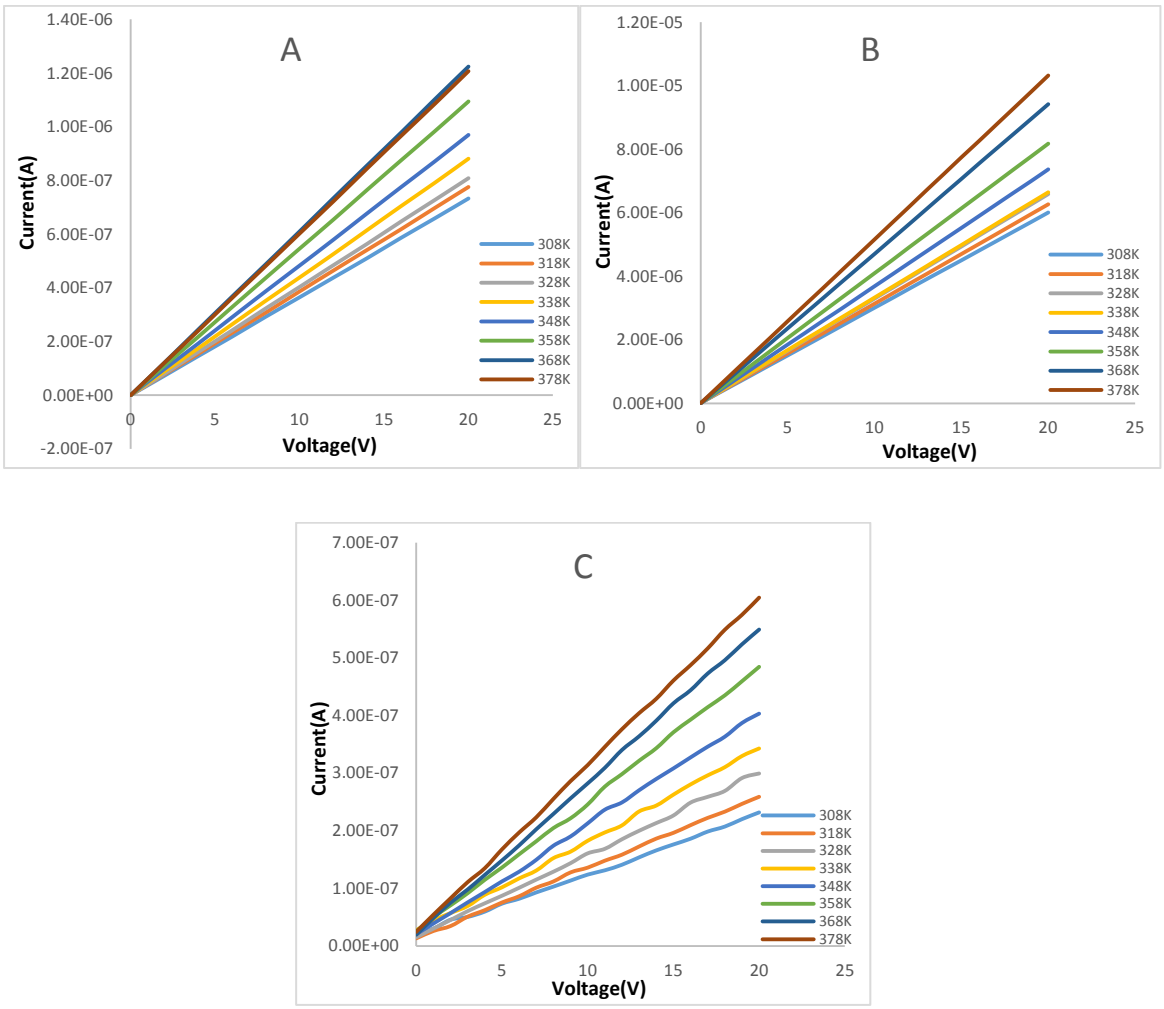



**Figure 4:** I-V curves of blend polymers: (A) PVA1:POT1, (B) PVA1:POT2, (c) PVA2:POT1.

The electrical conductivity was calculated according to following relationship.

$\sigma s$ = [I/V] [L/Wtl] …….. (1)

where L is the space between electrodes ( 100 $\mu$m ) , W is the distance fingers ( 10 mm) , l is the number of the fingers is to be ( 10 ) and t is the thickness of the film[23,28].

The increase in electric conductivity of the different ratios of blend polymers attributed to effect of poly (o-

toluidine) in the matrix of PVA as tabulated in the table (1), but when comparing the conductivity of ratios of blend polymers with pure POT, it's clear that, the conductivity decreased with increasing ratio of PVA in the blend polymer because of lowering degree of conjugation of $\pi$ orbitals in addition to hindering charge transfer between chains decreased [29].

**Table 1:** Electrical conductivity as function of temperatures for a PVA : POT blend polymers

| T (K) | $\sigma_s$ (S/cm) Ratio of (1:1) | $\sigma_s$ (S/cm) Ratio of (1:2) | $\sigma_s$ (S/cm) Ratio of (2:1) |
|---|---|---|---|
| **308** | 8.18681E-06 | 6.72285E-05 | 2.06223E-06 |
| **318** | 8.61538E-06 | 7.02758E-05 | 2.42469E-06 |
| **328** | 8.97802E-06 | 7.397E-05 | 2.84508E-06 |
| **338** | 9.8022E-06 | 7.43446E-05 | 3.21086E-06 |
| **348** | 1.07363E-05 | 8.25843E-05 | 3.87289E-06 |
| **358** | 1.21319E-05 | 9.1573E-05 | 4.60113E-06 |
| **368** | 1.35165E-05 | 1.05805E-04 | 5.37901E-06 |
| **378** | 1.33846E-05 | 1.1573E-04 | 5.75968E-06 |

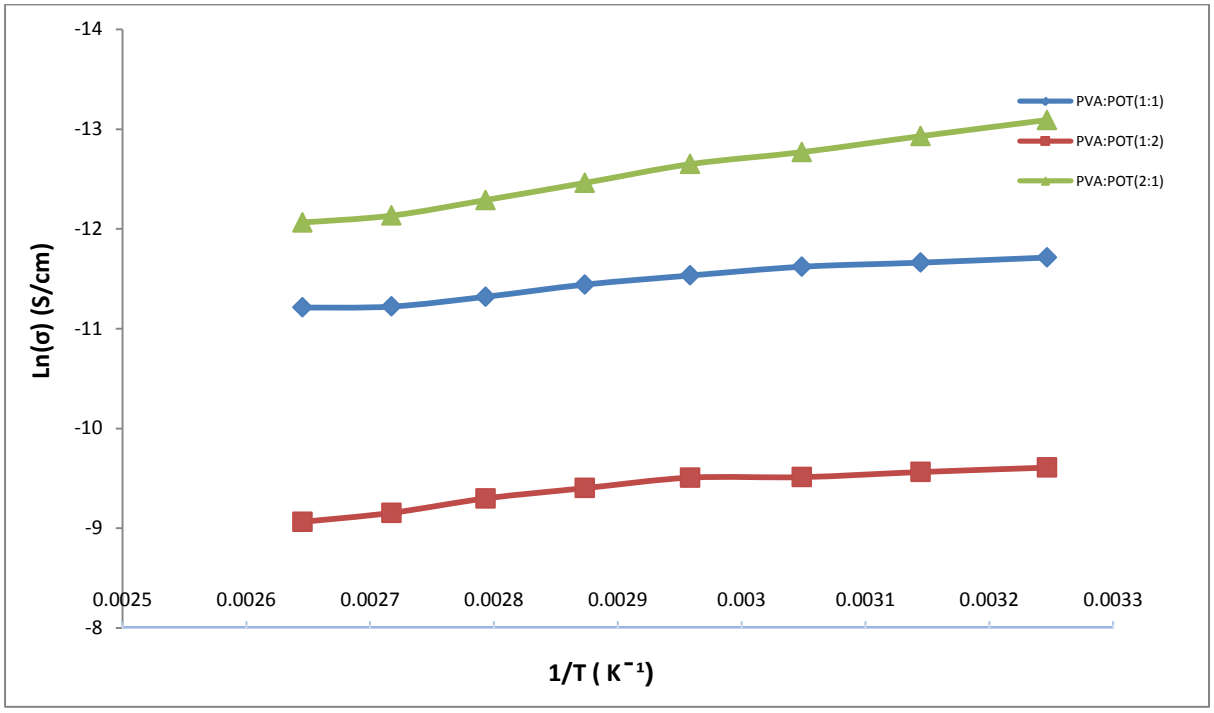



**Figure 5:** Plot of Ln σ versus 1/T for blend polymers.

The temperature dependence for each ratio of blend polymers is a major method to confirm semiconducting property. In this study, the semiconducting property was confirmed by test of the conductivity of prepared samples with temperature degrees (ranging from 308K to 378K) which led to increase the conductivity with temperature due to increase efficiency of the charge transfer [2, 30-32] and also effects of thermal curling on the chain alignment of the polymer leading to increase the conjugation length. Furthermore, the heating led to molecular rearrangement of molecules of the blend polymers to be favourable for electron delocalization [2,33].

The activation energies of the prepared samples were determined according to Arrhenius model [34]. The slopes of plots of Lnσ VS 1/T gave an information about activation energies for different ratios of the blend polymers (1:1, 1:2, 2:1 PVA: POT) to be presented as (0.07868, 0.07654, 0.15098ev) respectively as shown in figure (5).

## 4. Conclusion

The Poly(o-Toluidine) was synthesis by chemical polymerization method and characterized by (FTIR, XRD) techniques then the blend polymers of PVA/POT was made which were deposited on the interdigitate finger for study the electrical properties. All prepared samples showed ohomic behaviours in addition to semi-crystalline nature.

## Acknowledgements

The authors would like to thank Sheffield Hallam University/Material and Engineering Research Institute/UK for supported us and provide all the capabilities to complete the research in their laboratories.

## References

[1] Anand Kumar, Vazid Ali, Sushil Kumar, M. Husain. “STUDIES ON CONDUCTIVITY AND OPTICAL PROPERTIES OF POLY (O-TOLUIDINE)-FERROUS SULFATE COMPOSITES.” International Journal of Polymer Anal. Charact. , vol. 16, pp. 298–306, 2011.

[2] Hasoon Salah Abdulla, Abdullah Ibrahim Abbo. “Optical and Electrical Properties of Thin Films of Polyaniline and Polypyrrole.” Int. J. Electrochem. Sci., vol. 7, pp. 10666 – 10678, (2012).

[3] Yu-Kai Han, Mei-Ying Chang, Ko-Shan Ho, Tar-Hwa Hsieh, Jeng-Liang Tsai, Pei-Chen Huang. “Electrochemically deposited nano polyaniline films as hole transporting layers in organic solar cells.” sol. Energy Mater. Sol. Cells, vol. 128, pp.198-203, (2014).

[4] A. Elmansouri, A. Outzourhit, A. Lachkar, N. Hadik, A. Abouelaoualim, M.E. Achourc, A. Oueriagli, E.L. Ameziane. “Influence of the counter ion on the properties of poly (o-toluidine) thin films and their Schottky diodes.” Synthetic Metals, vol. 159, pp. 292–297, (2009).

[5] T.P.Nguyen, C.W.Lee, S.Hassen, H.C.Le. “Hybrid nanocomposites for optical applications.” Solid state Sciences, vol. 11, pp.1810-1814, (2009).

[6] Jeongwoo Lee, Eun Ju Park, Jaewon Choi, Jinho Hong, Sang Eun Shim. “Polyurethane/PEG-modified MWCNT composite film for the chemical vapours sensor application.” Synthetic Metals, vol.160, pp 566–574, (2010).

[7] A. Benchikh, R. Aitout, L. Makhloufi, L. Benhaddad, B. Saidani. “Soluble conducting poly (aniline-co-orthotoluidine) copolymer as corrosion inhibitor for carbon steel in 3% NaCl solution.” Desalination, vol.249, pp.466–474, (2009).

[8] O. Nakhaei, N. Shahtahmassebi, M. Rezaeeroknabadi, M.M. Bagheri Mohagheghi. “Synthesis, characterization and study of optical properties of polyvinyl alcohol/CaF2nanocomposite films.” Sci. Iran. Vol.19 (6), pp.1979–1983 (2012).

[9] S. Rajendran, M. Sivakumar, R. Subadevi, “Investigations on the effect of various plasticizers in PVA–PMMA solid polymer blend electrolytes”, Mater. Lett. Vol. 58, pp. 641–649, 2004.

[10] N. Khalifa, H. Kaouach, R. Chtourou, “Improvement of a Si solar cell efficiency using pure and Fe3+ doped PVA films”, Optical Materials, Vol. 45, pp. 9–12, 2015.

[11] Ana M.M. Sousa, Hiléia K.S. Souza, Joseph Uknalisb, Shih-Chuan Liu, Maria P. Gonc¸alves, LinShu Liu, “Electrospinning of agar/PVA aqueous solutions and its relation with rheological properties”, Carbohydrate Polymers Vol. 115, pp. 348–355, 2015.

[12] Greiner, A., & Wendorff, J. H. (2007). Electrospinning: A fascinating method for the preparation of ultrathin fibres. Angewandte Chemie International Edition, 46(30), 5670–5703.

[13] Dowan Kim, Jeyoung Jung, Su-il Park, Jongchul Seo, “Preparation and characterization of LDPE/PVA blend films filled with glycerin-plasticized polyvinyl alcohol”, J. APPL. POLYM. SCI., DOI: 10.1002/APP.41985, 2015.

[14] Elbadawy A. Kamoun, Xin Chen, Mohamed S. Mohy Eldin, El-Refaie S. Kenawy, “Crosslinked poly(vinyl alcohol) hydrogels for wound dressing applications: A review of remarkably blended polymers”, Arabian Journal of chemistry, Vol. 8, pp.1-14 2015.

[15] Ganesh V. More, Kirtikumar C. Badgujar and Bhalchandra M. Bhanage, “Kinetic resolution of secondary alcohols with Burkholderia cepacialipase immobilized on a biodegradable ternary blend polymer matrix as a highly efficient and heterogeneous recyclable biocatalyst”, RSC Adv., Vol.5, pp.4592, 2015.

[16] Omed Gh. Abdullah , Dlear R. Saber, Luqman O. Hamasalih, “Complexion Formation in PVA/PEO/CuCl2 Solid Polymer Electrolyte”, Universal Journal of Materials Science, Vol. 3(1), pp. 1-5, 2015.

[17] Hassan, C. M., & Peppas, N. A., “Structure and morphology of freeze/thawed PVA hydrogels.

Macromolecules", Vol. 33(7), pp. 2472–2479, 2000.

[18] Bikash Chandra Nath, Biswajit Gogoi, Monalisha Boruah, shyamalima Sharma, Momina Khannama, Gazi Ameen Ahmed, Swapan Kumar Dolui , "High performance polyvinyl alcohol/multi walled carbon nanotube/polyaniline hydrogel (PVA/MWCNT/PAni) based dye sensitized solar cells", Electrochimica Acta, Vol. 146, pp. 106–111, 2014.

[19] Razif Nordin, Hanafi Ismail, Zukifli Ahmad, Azura Rashid, "Performance improvement of (linear low-density polyethylene)/poly(vinyl alcohol) blends by *in situ* silane crosslinking" J. Vinyl. Addit. Techn. Vol.18(2), pp. 120-128, 2012.

[20] Rahman, W. A. W. A.; Sin, L. T.; Rahmat, A. R.; Samad A.A., "Thermal behaviour and interactions of cassava starch filled with glycerol plasticized polyvinyl alcohol blends.",Carbohydr. Polym., Vol.81(4), pp.805-810, 2010.

[21] Jang, J.; Lee, D. K. "Oxygen barrier properties of biaxially oriented polypropylene/polyvinyl alcohol blend films.", Polymer, Vol. 45(5), pp.1599-1607, 2004.

[22] A. Elmansouri, A. Outzourhit, A. Lachkar, N. Hadik, A. Abouelaoualim, M.E. Achourc, A. Oueriagli, E.L. Ameziane, "Influence of the counter ion on the properties of poly(o-toluidine)thin films and their Schottky diodes", Synthetic Metals, Vol. 159, pp. 292–297, 2009.

[23] Kareema. M. Ziadan , Hussein. F. Hussein, K.I.Ajeel, "Study of the electrical characteristics of poly(o-toluidine) and application in solar cell", Energy Procedia, Vol. 18, pp. 157 – 164, 2012.

[24] Shihai Ding, Xiaofeng Lu, Jiani Zheng, Wanjin Zhang, "Synthesis, characterization and electrical properties of poly(o-toluidine)/multi-walled carbon nanotube composites", Materials Science and Engineering B Vol.135, pp. 10–14, 2006.

[25] S.Oliveira, Luis P.N. Rebelo, Isabel M. Marrucho, "Influence of different inorganic salts on the iconicity and thermophysical properties of 1-Ethyl-3-methylimidazolium acetate ionic liquid", J. Chem. Eng. Data, Vol. 60, pp. 781-789, 2015.

[26] Mohammad, F., ed. 2007. Specialty polymers: Materials and Applications. New Delhi:I.K. International pub.House,pp. 40-75.

[27] KAREEMA.M.ZIADAN, HUSSEIN.F.HUSSEIN, ASEEL.K.HASSAN, K.I.AGEEL, "Study of the electrical characteristics of poly(o-toluidine) doped with para-Toluene sulphonic acid/N-type silicon heterojunction solar cells", solar Asia,2013, CIUM.

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

[29] Xiping Lei, Zhixing Su, Novel conducting polyaniline copolymers of aniline and N-phenylglycine, Material Letters, Vol. 61, pp. 1158-1161, 2007.

[30] M. Leclerc, G. D. Aparno and G. Zotti., "Structure-property relationships in polyaniline derivatives." , Synth Met., Vol.55 (2-3), pp. 1527-1532, 1993.

[31] F. Zuo, M. Angelopoulos, A. G. Macdiarmide and A. J. Epstein, "Transport studies of protonated emeraldine polymer: A granular polymeric metal system.", Phys Rev B., Vol. 36 (6-15), pp. 3475, 1987.

[32] M. A. Chougule, S. G. Pawar, P. R. Godse, R. N. Mulik, S. Sen and V. B. Patil, "Synthesis and Characterization of Polypyrrole (PPy) Thin Films", Soft. Nanosci. Letter., Vol. 1 (1), pp. 6-10, 2011.

[33] A.Kobayashi, H.Ishikawa, K.Hmano, M.Satoh, E.Hasegawa, "Electrical conductivity of annealed polyaniline ", J.Appl.Phys., Vol. 74 (1), pp. 296, 1993.

[34] R.CHEN, G.A.HABER," Calculation of Glow Curves Activation Energies by Numerical Initial Rise Method", CHEMICAL PHYSICS LETTERS, Vol. 2, pp.7 ,1968.