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Synthesis and characterization of poly (o-toluidine) POT blend with polyethylene oxide PEO as conducting polymer alloys

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ABSTRACT

Conducting polymer alloys films poly (o-toluidine) (POT) blend with polyethylene oxide (PEO) have been prepared in chemical method. These films of POT/PEO blend prepared by mixed different ratio (0 – 10%, 30%, 50%, 70% , 90%) of POT with PEO. Thin films of these blends polymer were prepared by casting and spin coating . The optical properties where study for each ratio of blend. The optical analysis indicated that the transition was direct transition with energy gap degrees as POT increase from (3 eV to 1.4 eV). The electrical conductivity was measured by two probe method. The electrical conductivity increase from (1.85×10^{-8} to 1.06×10^{-5}) as POT increases. All result were discussed and measured by I-V characterized.

Keywords: conducting polymer, poly (o-toluidine), polyethylene oxide, optical and electrical study.

INTRODUCTION

Conducting polymers have been extensively studied in the last 10 years and used for technological applications in electrochromics, batteries, biosensors, gas separation membranes, enzyme immobilization matrices and metal projection against corrosion[1]. Conducting polymers are synthesized by either chemical or electrochemical methods.

Polyaniline (PANI) is an important member of the family of intrinsically conducting polymers (ICPs). Because of its excellent environmental stability and unique electrochemical property, PANI has been widely studied and applied in, for example, secondary batteries, biosensors, anti-static packaging materials, and for corrosion protection.

Polyaniline (PANI) has received much attention as a popular kind of conducting polymer with various exceptional [2].

Since the discovery of high electrical conductivity from blending poly(ethylene oxide) PEO with potassium salts by Fenton et al [3]. Polymer electrolytes have attracted a lot of interest, especially because of their potential use in thin film batteries[3]. Polymer electrolytes consist of polar polymer and ionizable salts. PEO is the most popular polymer used, due to its high solvating power with metal ions, good processability, and outstanding mechanical properties [4-8]. Although the ionic conductivity of PEO polymer electrolyses at 100^{o} C is about to 10^{-4}-10^{-3} S/cm at room temperature it is usually less than 10^{-6} S/cm.

Poly (O- toluidine) (POT) is a PANI derivative which contains the – CH_3 group in the ortho position of the aniline monomer . Among the ring – substituted PANI derivatives as shown in fig. 1 [9], POT has been probably the most widely studied one. Indeed , Ram and Borole [10,11] as well as other authors [12] have studied the electro polymerization of (O- toluidine) 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.

In present work POT/PEO films where prepared by using casting method with different volume ratio(0 – 10%, 30%, 50%, 70% , 90%) of POT with PEO. the optical properties where study for each mixture. The electrical properties of POT/PEO films also investigated.

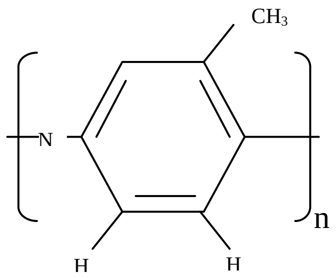


Fig.1 : structure of POT

MATERIALS AND METHODS

- Materials

Polyethylene oxide (PEO) molecular weight (Mw) 200.000 , ammonium persulfate $(NH_4)_2S_2O_8$, hydrochloric acid (HCL) , (o-toluidine) were purchased from Aldrich. These chemicals were used without further purification.

- Sample preparation

Poly (o-toluidine) was synthesized by the oxidative polymerization of (o-toluidine) in acidic media. Using amethod similar to that reported by MacDiarmid et al [13,14] 5 ml of (o-toluidine) was dissolved in 300 ml of 1M HCL and kept at 0^oC, 11.4 gm of $(NH_4)_2S_2O_8$ was dissolved in 200 ml of 1M HCL also at 0^oC and added drop wise under constant stirring to the (o-toluidine/ HCL) solution over a period at 20 mins. The resulting dark green solution was maintained under constant stirring for 24 hrs. and washed with water before being added to ammonium solution. After an additional 24 hrs. the solution was filtered and a deep blue emeraldine base from of (POT) was obtained (POT)EB .

The emeraldine base (100 mg) to dope it and dissolving it in (10 ml) of (1M) HCL. For half an hour and the same time (PEO) 100 mg dissolving matrix (PEO) with (POT) thin films of conducting polymer alloys POT/PEO prepared by mixed different volume ratio of POT with PEO as show in table 1 [15].

Table 1: The volume ratio of POTin PEO as POT/POEblends

POT (cm^3)	PEO (cm^3)	Volume ratio of POT in POE %
0	100	0 %
10	90	10 %
30	70	30 %
50	50	50 %
70	30	70 %
90	10	90 %

POT film characterize by FT-IR . The optical properties of POT/PEO films measured by UV spectrophotometer with range (200- 900 nm) and electrical properties measured by two probe method at room temperature.

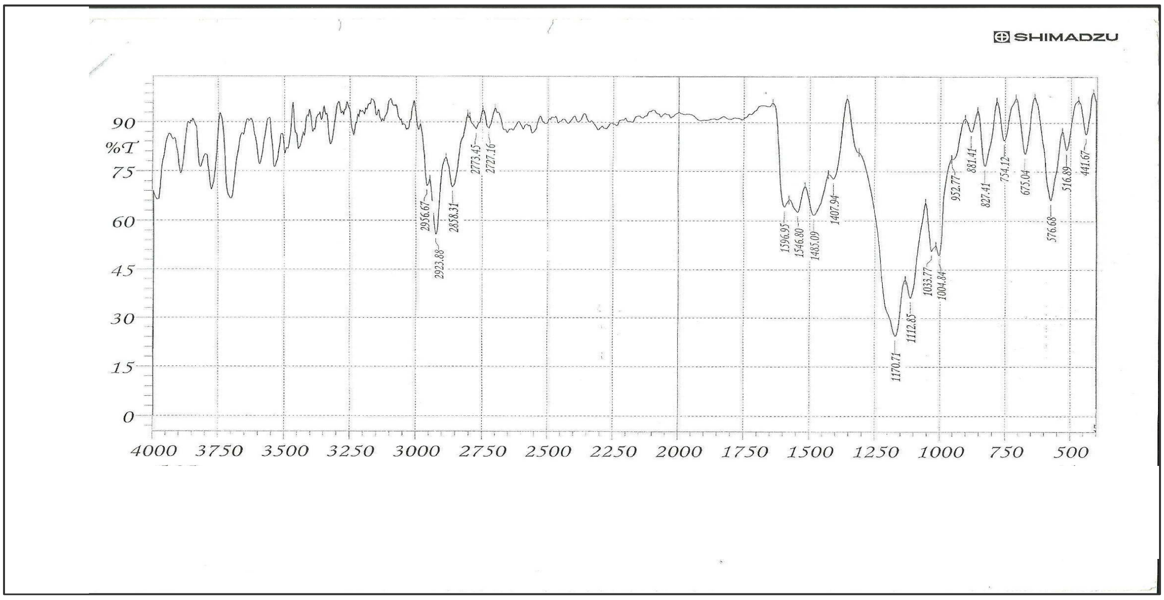
Table 2: FT-IR for doping POT

Wave number (cm^{-1})	Raman assignments
441	C-N stretching in SQ and Q rings
516.89	C-C stretching in SQ and Q rings
576.68	C-C stretching in B ring
827	C-C stretching in B ring
1112.85	C-C methyl-substituted SQ and Q rings
1170.71	C-H in SQ ring
1485.09	C-N stretching of benzenoid ring
1596.95	C-N stretching of Quinoid ring
2923.88	C-H stretching due to substituted methyl group

RESULTS AND DISCUSSION

The FT-IR spectra of poly(o-toluidine) doped with HCL are presented in Fig.2. The peak positions related to the corresponding chemical bonds are listed in the table 2 [16,17].

Fig . 2 : FT-IR spectrum of POT



The absorption coefficient (α) have been estimated after correction for the reflection losses. The absorption coefficient is giving by [18]

$$\alpha = \left[\frac{2.303}{d}\right] A' \qquad (1)$$

Where d is the thickness of the sample and A' is the absorption after correction, which can be estimated as:

$$A' = A - A^o \qquad (2)$$

A is the absorbance and A^o is the correction after reflection.
to obtained information about the direct band gap.

Fig.(3) show the absorption coefficient (α) of POT/PEO as function of photon energy, hν, for different of volume ratio of POT (0 %, 10%, , 30%, , 50%, 70%, 90% POT) in POT/PEO . the absorption data were analyzed for evidence of inter band transition ,direct and indirect band gap. For high absorption coefficient $\alpha > 10^4$ cm^{-1} the inter band transition refer to direct transition.

αhυ=A(hυ-Eg)n (3)

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu} \qquad (4)$$

Where Eg is the band gap corresponding to particular transition occurring in film, A is a constant, υ is transition frequency and the exponent n characterizes the nature of band transition [19].

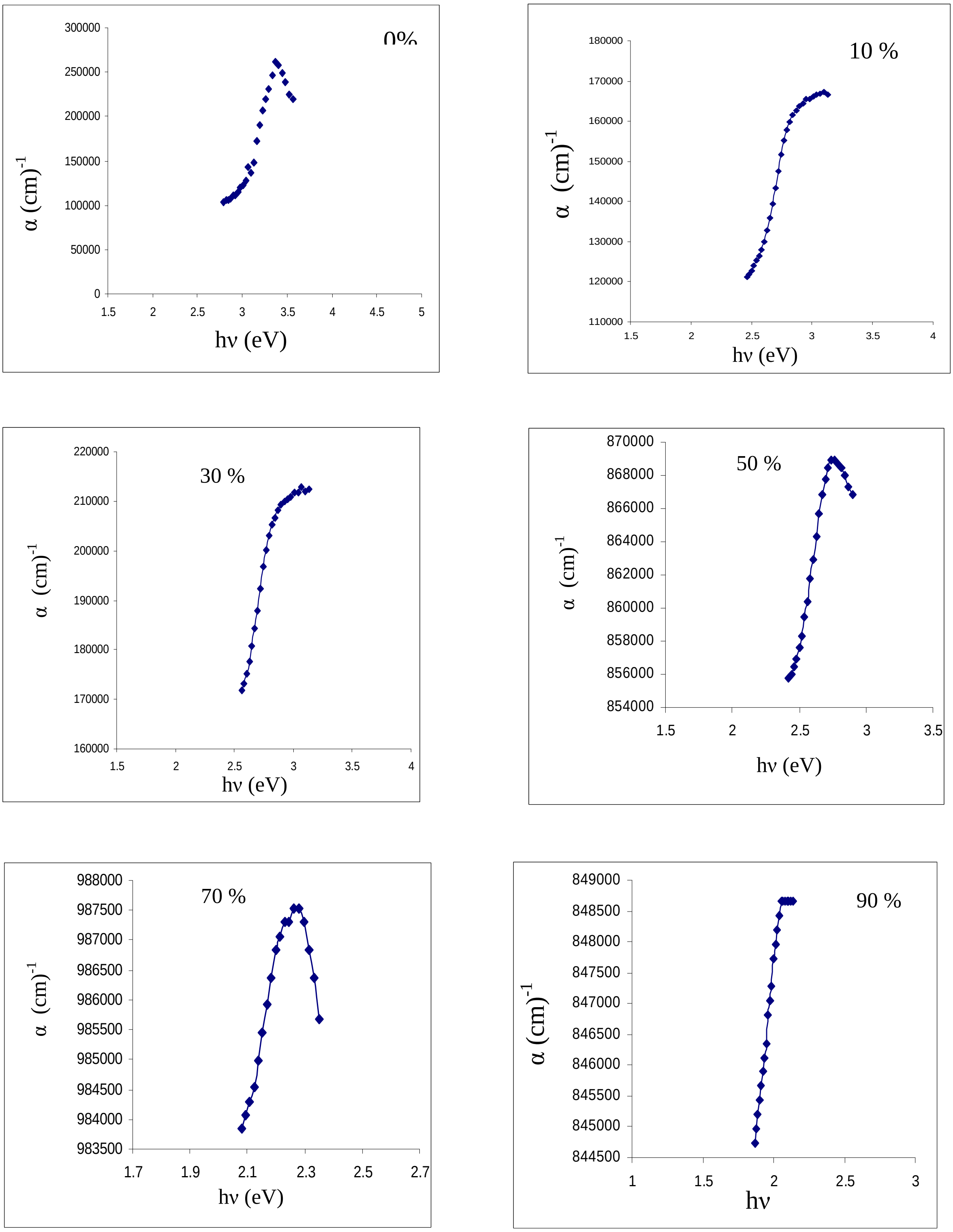


FIG.3 the absorption coefficient α as a function of photon energy for different ratio of POT in POT/PEO alloys film

Fig.(4) show the photon energy dependence on $(\alpha h\nu)^2$ for all ratio of POT/PEO films. The plot of $(\alpha h\nu)^2$ agent hν yields a straight line, which show good fit with eq.(4), extrapolation of the straight line to $(\alpha h\nu)^2=0$ gives the direct energy gap, which are tabulated at Table 3.

The result that plotted in fig.5 , show mixture of POT with PEO reduce the energy gap from (3 eV to 1.4 eV). These dicated that the increasing of POT ratio the create polaron states between valance band and conduction band for all details about a mechanism of conductivity in conducting polymers [20].

Table3: Energy gap POT/PEO for all volume ratio of POT in PEO

Energy gap (eV)	volume ratio of POT in PEO
0%	3
10%	2.5
30%	2.4
50%	1.6
70%	1.5
90%	1.4

Table4: Electrical Conductivity of POT/PEO for all volume ratio of POT in PEO

Conductivity (S/cm)	Ratio %
0	1.85×10^{-8}
10	0.39×10^{-7}
30	$1.8\ 5 \times 10^{-7}$
50	2.91×10^{-7}
70	0.79×10^{-6}
90	1.06×10^{-5}

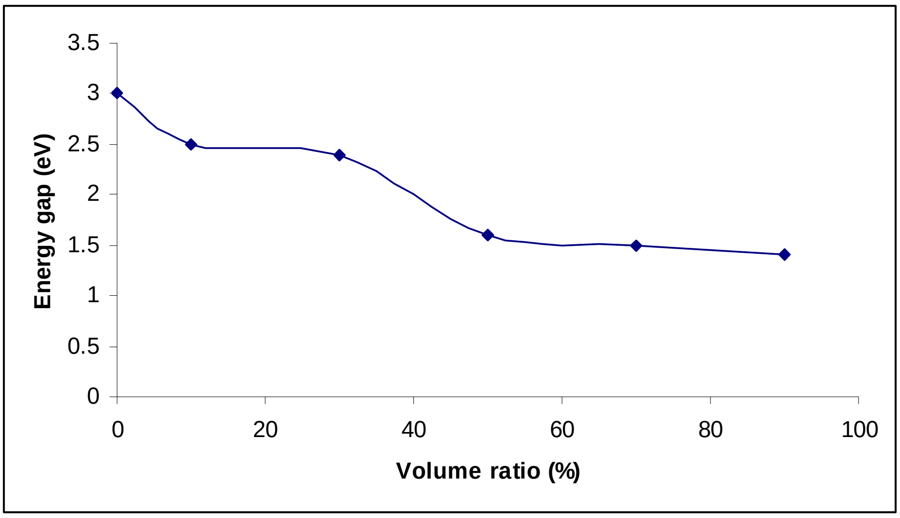


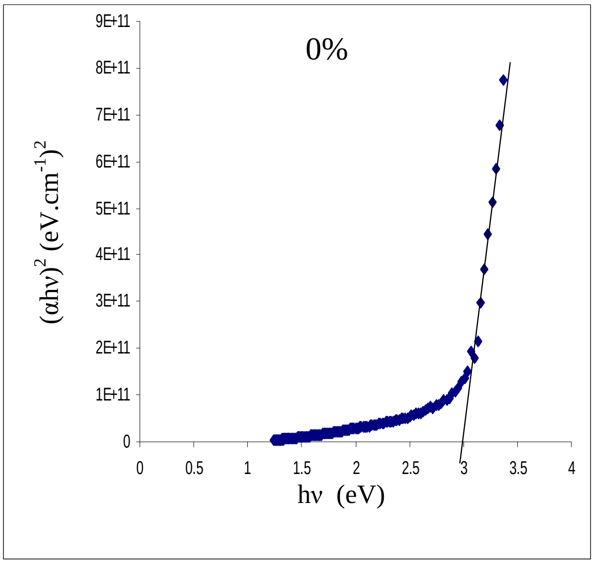
Fig. 5 : Eergy gap and Volume ratio

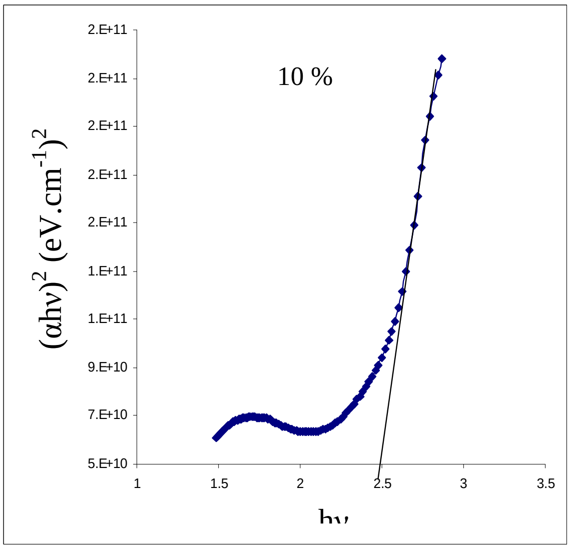
Electrical conductivity has been measured for polymers thin film by two probe method using eq.5 [21]:

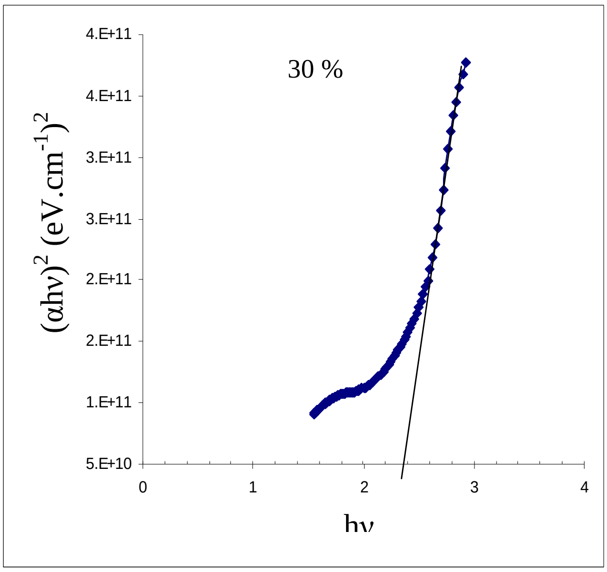
$$\sigma = \frac{d}{A_0}\frac{I}{V} \qquad (4)$$

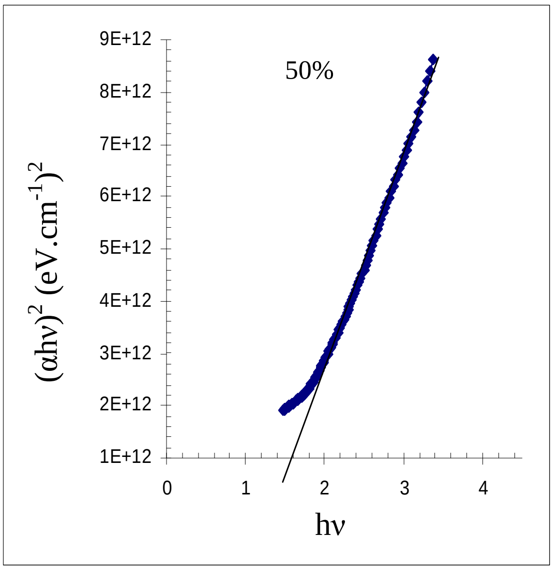
d is thickness of film, A_0 area of section, I current pass into film, and V the voltage is applied on film.

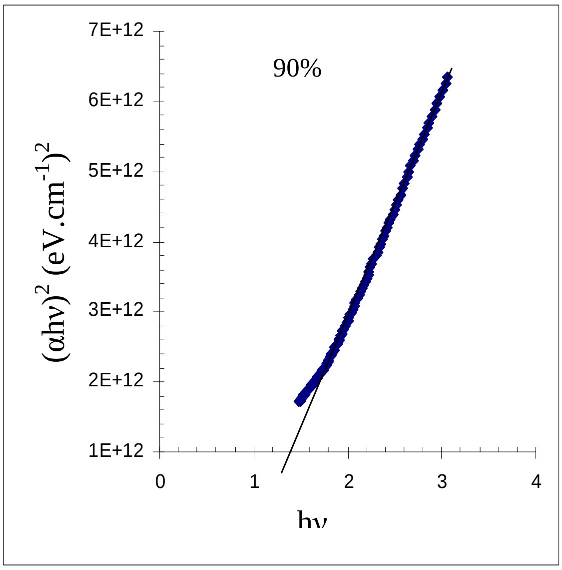
Fig.6 show the (I-V) characterization of different ratio of POT in POT/PEO films. The figures show that the current increases as POT increase in POT/PEO blend. Fig.7 show the conductivity as a function volume ratio of POT in POT/PEO films. And tabulated at table 4 . produce low energy gap and high electrical conductivity. That can be explain the condition polymer POT create by polaron at energy gap the result Argument with other [22].


0%
$(\alpha h\nu)^2$ (eV.cm^{-1})^2
9E+11
8E+11
7E+11
6E+11
5E+11
4E+11
3E+11
2E+11
1E+11
0
0
0.5
1
1.5
2
2.5
3
3.5
4
hν (eV)


10 %
$(\alpha h\nu)^2$ (eV.cm^{-1})^2
2.E+11
2.E+11
2.E+11
2.E+11
2.E+11
1.E+11
1.E+11
9.E+10
7.E+10
5.E+10
1
1.5
2
2.5
3
3.5
hν


30 %
$(\alpha h\nu)^2$ (eV.cm^{-1})^2
4.E+11
4.E+11
3.E+11
3.E+11
2.E+11
2.E+11
1.E+11
5.E+10
0
1
2
3
4
hν


50%
$(\alpha h\nu)^2$ (eV.cm^{-1})^2
9E+12
8E+12
7E+12
6E+12
5E+12
4E+12
3E+12
2E+12
1E+12
0
1
2
3
4
hν


90%
$(\alpha h\nu)^2$ (eV.cm^{-1})^2
7E+12
6E+12
5E+12
4E+12
3E+12
2E+12
1E+12
0
1
2
3
4
hν

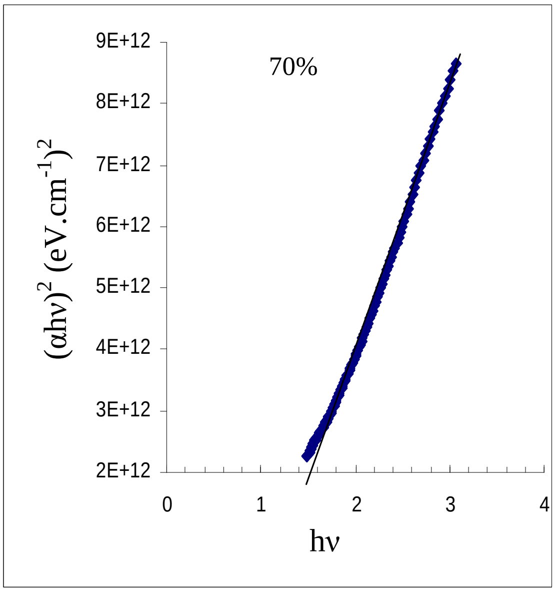

70%
$(\alpha h\nu)^2$ (eV.cm^{-1})^2
9E+12
8E+12
7E+12
6E+12
5E+12
4E+12
3E+12
2E+12
0
1
2
3
4
hν

FIG.4: between $(\alpha h\nu)^2$ and hν for all weight ratio

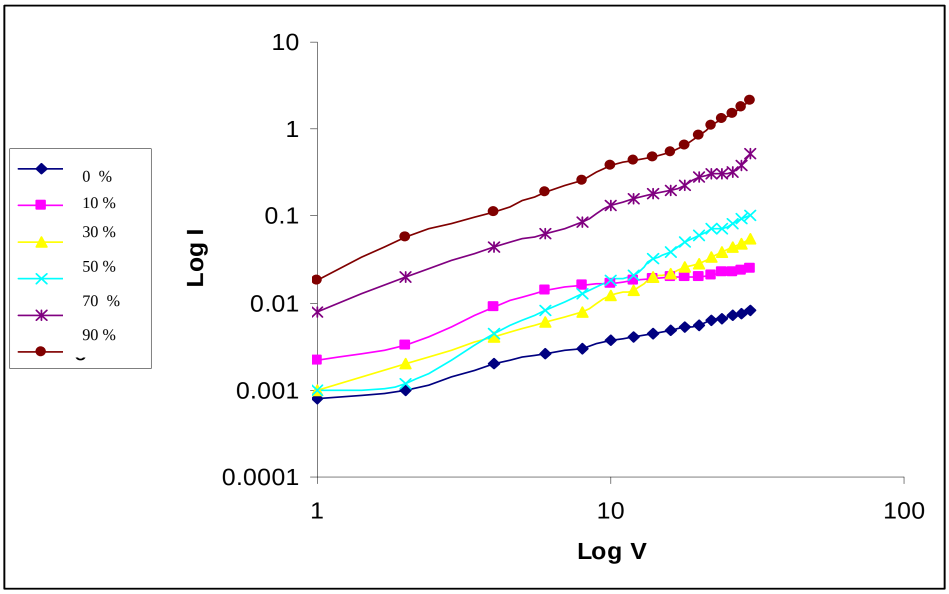


Fig.6 : I-V Characterization

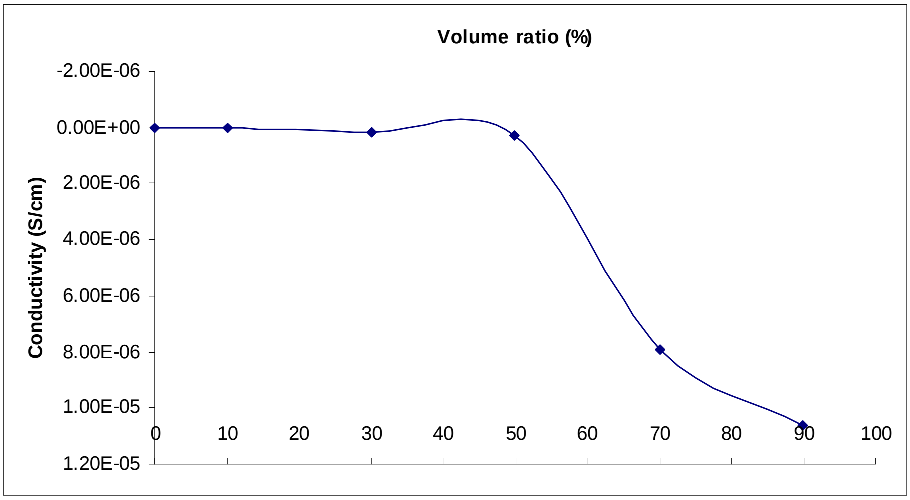


Fig. 7 : Volume ratio and Conductivity

The result indicated that the conductivity increase as POT increases in POT/PEO films. The table indicated that the conductivity increase about three order, So that we can increase the conductivity of PEO from 1.85×10^{-8} to 1.06×10^{-5} S/cm at 90% POT/PEO . the optical and electrical properties refer the same result that the increase of POT ratio in POT/PEO films.

CONCLUSION

1)At mixing between POT and PEO the variety from 1.85×10^{-8} (S/cm) to 1.06×10^{-5} (S/cm) .
2)The E_g variety from 3 eV to 1.4 eV .
3)PEO gave high stability and stick to POT.
4)We can use this compose as nanofiber as ref.[23].

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