Effect of Cobalt's Chloride on the Electrical Properties of Poly (O-Toluidine)

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Abstract: The effect of cobalt's chloride on the prepared polymer by chemical polymerization is clear in surface morphology of thin film, surface conductivity in addition to activation energy of the POT. The roughness of surface morphology is increased with increasing the volume ratio of dopant which also noted that, the conductivity is increased from1.70E-04 S/cm for pure POT to be 1.459E-3 S/cm at dopant ratio of 30% cobalt's chloride.

Key words: Poly (O-Toluidine), cobalt's chloride, surface conductivity.

1. Introduction

The electrical properties of polymers are considered as important studies due to their applications in different fields in today life. The poly (O-Toluidine) is one of promised polymer because of used it in various aria of applications such as light emitted diode, filed effect transistor, schottky diode, solar cell and sensors [1-5]. The Polymeric materials have many physical properties which make them mostly used in microelectronic devices, in addition to inexpensiveness, environmental stability, easy of fabrication as thin films on a large area substrate, rods and disk according to the required applications [6, 7]. In scientific research area it is possible to control the electrical conductivity of polymers over the range from insulating to metallic as needed in the field of technological applications. Electrical conductivity of the polymer materials can be investigated either by the synthesis of a polymer of definite chemical structure (such as polymer with a system of conjugated bounds and their doping) or by the introduction of an electrically conductive filler (i.e. metal powders, carbon black, graphite)[8]. According to above futures the POT is doped by different volume ratios of cobalt's chloride as attempt to get better electrical properties.

2. Procedure and Experimental Work

2.1. Preparation of Poly (o-Toluidine) (POT)

The POT is prepared according to our previous work by using the chemical polymerization method. 0.27M of O-Toluidine monomers (C_7H_9N provided by fisher scientific) are dissolved in 0.25M HCL (provided by sigma Aldrich) under the conditions of constant stirrer and temperature degree in range (0-5°C) for 30 min. 10gm of ammonium per sulphate [$(NH_4)_2\,S_2O_8$ provided by sigma Aldrich] are dissolved by 0.25M HCL and added to dissolve monomers as drop by drop for 20min. The final mixture is stilled under constant stirrer for 24h more, to complete the reaction and then the greenish-black precipitate is filtered and wished by distilled water, methanol, and acetone to remove unreacted materials and dried in vacuum oven at 60℃ for 24h [9].

2.2. Preparation of Doped POT

10 mg of the obtained polymer (POT) are dissolved in 1ml of formic acid ($HCOOH$ provided by sigma Aldrich) while the cobalt's chloride ($CoCl_2.H_2O$ provided by sigma Aldrich) is dissolved in formic acid also to be in concentration of 0.042M. The doping process is done as different volume ratios of the dissolved cobalt's chloride (5%, 10%, 20%, 30%, and 40% V/V) are mixed with dissolved POT by using magnetic stirrer for 5h.

2.3. Preparation of Samples and Measurement System

The samples are prepared by spin coating method. The glass substrate is used for the SEM analysis and thickness measurement and also the interdigitated finger substrate (see figure 1) is used for the study of electrical properties. The thin film thicknesses which are prepared for this study are (45.86, 55.7, 55.75, 55.94, 56.69, and 58.2 nm) for pure POT and doped POT by ratios (5%, 10%, 20%, 30%, and 40%) of cobalt's chloride respectively.

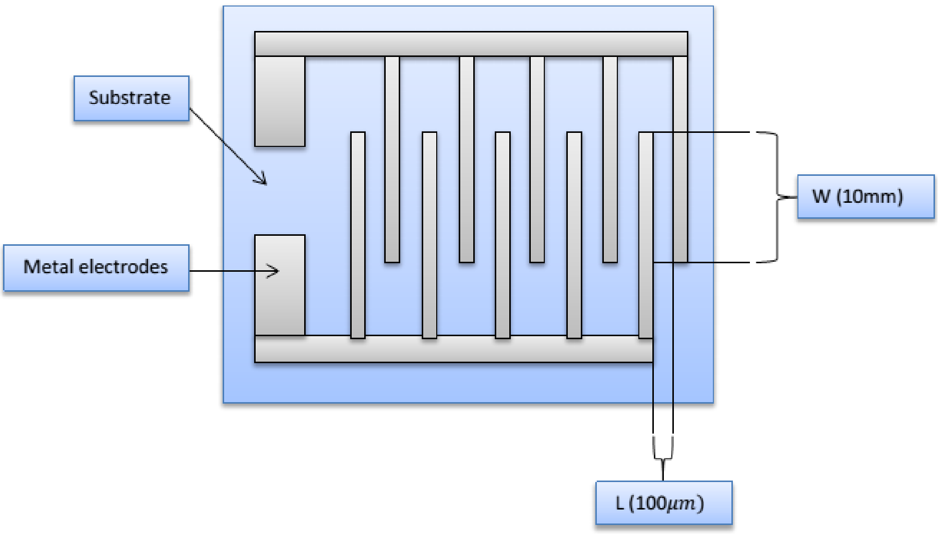


Fig. 1. A schematic diagram of interdigitated finger electrode.

The two probe method is used to study electrical properties of prepared polymer and the circuit used in this method including on the Keithley electrometer instrument (Model 65174) and Digital hot plate (IKA RET basic) for measure a current as a function of applied voltage in the range of (1-40 V) in steps of (2 V) and to provide heating in the range of (308-378 K) in steps of (10 K) respectively.

3. Results and Discussion

3.1. FT-IR Spectroscopy Analysis

The Fig. 2 shows the FT-IR absorption spectra of prepared POT in which the absorption band at 1112.82 cm^{-1} attributes to C-C methyl-substitutes SQ and Q rings. The absorption band at 1170.71 cm^{-1} due to C-H in SQ ring and the bands around (1280, and 1324cm^{-1}) indicated to benzenoid and quinoid ring asymmetric stretching vibrations. The bands at 1485.09 and 1596.95cm^{-1} are assigned to C-N stretching of benzenoid and quinoid rings respectively while athe band at 2923.88cm^{-1} is referred to C-H stretching as substitute's methyl group [10-11].

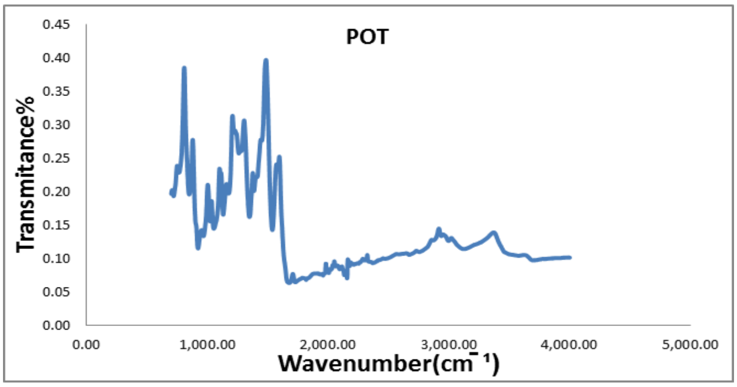


Fig. 2. FT-IR absorption spectra of POT.

3.2. XRD Analysis

The Fig. 3 shows X-ray diffraction pattern of the POT and exhibits an amorphous structure with two small peaks at 16.78° and 25.5° which are iterplanar distance of o-Toluidine-o-Toluidine. The result of structure of POT is agreed with previous study which shows that the conducting polymers have semicrystalline or amorphous structure [12-13].

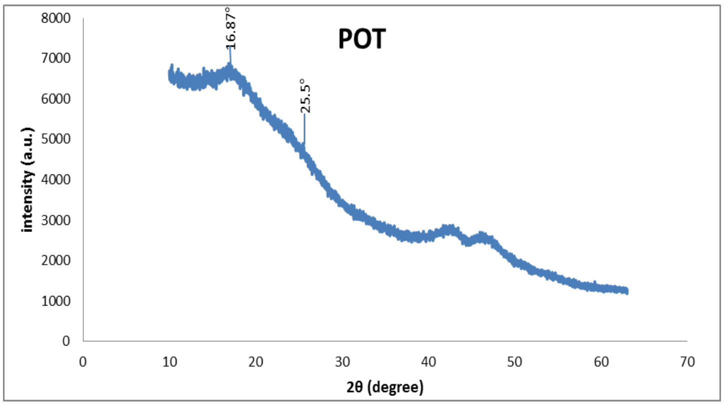
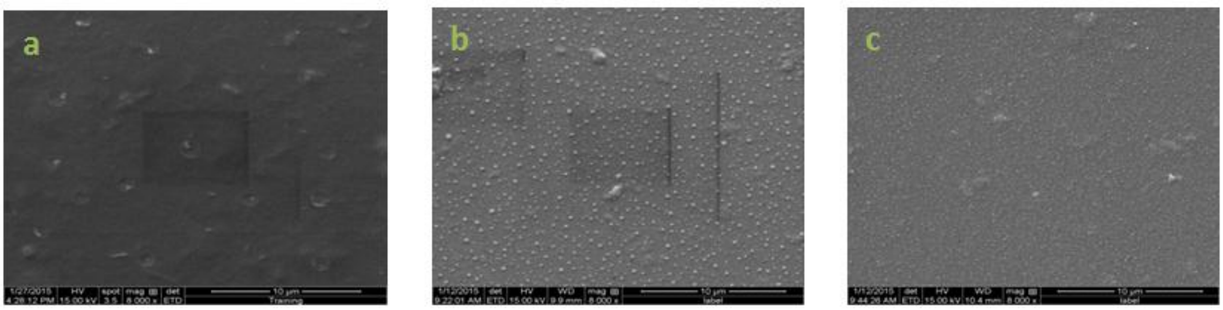


Fig. 3. XRD scattering pattern of poly (o-toluidine) POT.

3.3. SEM Analysis

The morphology of the POT and doped POT are illustrated in Fig. 4 a, b, c, d, e, f. It is shown that the roughness's of the surfaces of these samples increase with increasing the dopants which are POT/salt composite films dispersed in POT matrix and displayed surfaces without pin holes, high roughness and more compact because of the present of HCL and this result is agreed with previous study [14]. At the volume ratio of dopant (20%), the surface has less roughness because of the dopant and polymer reaching to complete mixed [15].



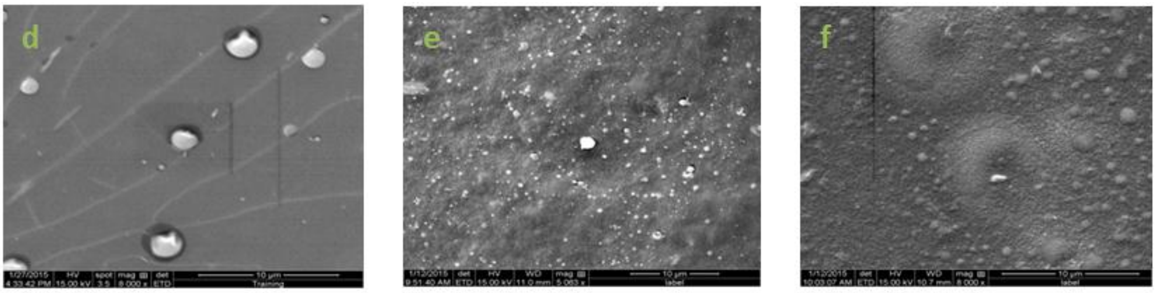


Fig. 4. SEM image of POT and doped POT (a) pure POT, (b) 5% cobalt's chloride, (c) 10% cobalt's chloride, (d) 20% cobalt's chloride, (e) 30% cobalt's chloride, (f) 40% cobalt's chloride.

3.4. Electrical Properties of POT and Doped POT

The current-voltage (I-V) characterizations of preparation samples, as shown in Fig. 5, are displayed ohmic behaviour in addition to semiconductor material which is clear from the increments in the surface conductivity (which is calculated according to equation 2) with the increasing in temperatures due to the increase of efficiency of charge transfer [7, 16-17]. The increasing in volume ratio of dopants leads to an increase the conductivity which is increased with the temperatures also, as tabulated in the Table 1

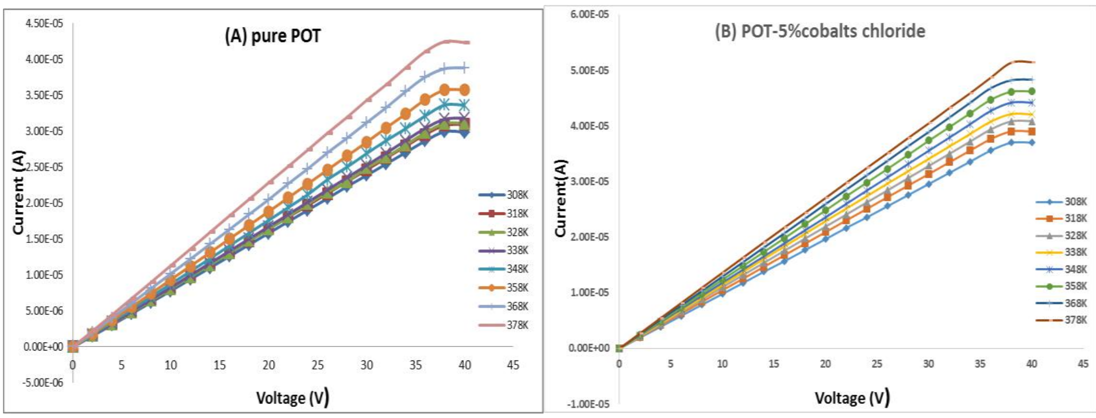
$$\sigma s = [I/V] \ [L/Wtl] \tag{1}$$

where, L is the space between electrodes (100 μm), 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 [18].
So that;

$$\sigma s = \frac{I}{Vt}\left(\frac{100\times10^{-6}}{10\times10\times10^{-3}}\right) = \frac{I}{Vt}(10^{-3}\,\frac{S}{M}) \tag{2}$$

Table 1. The Electrical Conductivity of Pure and Doped POT at Different Temperature Degrees.

T (K)	σ_s(S/cm) pure	σ_s(S/cm) 5%doped	σ_s(S/cm) 10%doped	σ_s(S/cm) 20%doped	σ_s(S/cm) 30%doped	σ_s(S/cm) 40%doped
308	1.70E-04	1.780E-4	2.011E-4	2.459E-4	1.459E-3	2.577E-4
318	1.794E-4	1.876E-4	2.163E-4	2.655E-4	1.629E-3	2.878E-4
328	1.83E-04	1.965E-4	2.252E-4	2.8867E-4	1.761E-3	3.075E-4
338	1.86E-04	2.037E-4	2.332E-4	3.1361E-4	1.825E-3	3.265E-4
348	1.97E-04	2.127E-4	2.404E-4	3.4212E-4	1.931E-3	3.453E-4
358	2.09E-04	2.244E-4	2.503E-4	3.8133E-4	1.975E-3	3.539E-4
368	2.31E-04	2.343E-4	2.574E-4	4.232E-4	1.958E-3	3.685E-4
378	2.39E-04	2.414E-4	2.654E-4	4.6686E-4	2.046E-3	3.643E-4



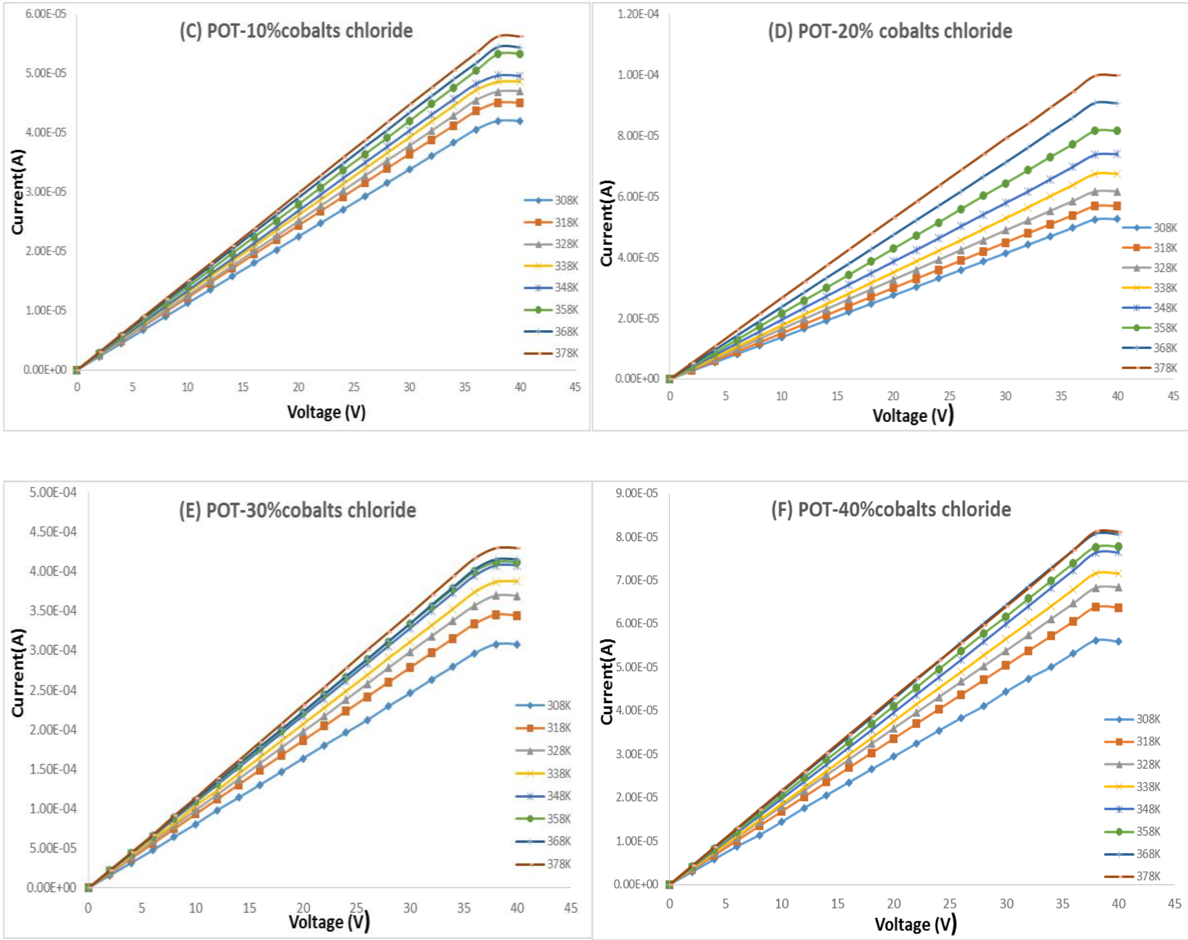


Fig. 5. I-V characterization of POT and doped POT (a) pure POT, (b) 5% cobalt's chloride, (c) 10% cobalt's chloride, (d) 20% cobalt's chloride, (e) 30% cobalt's chloride, (f) 40% cobalt's chloride.

There are many factors influencing on the conductivity of polymer like, size of cations which means the smaller size of cations that increase the conductivity in addition to PH of prepared samples [19]. Accordingly, we can interpret those results because of the small size of cobalt cations increases the electron delocalization length as the interchain distance increased. Furthermore, the cobalt cations have maximum positive doping effects [20].When viscosity reaching to certain limited, that influence on the conductivity of the polymer because of the fluidity of the doping polymer will be decreased with increasing the viscosity or because of the interfacial resistance between electrode/electrolyte is increased. Salt networks in polymer become in contact with electrode which reduce the affective surface area for electron transfer between polymer and electrode that explains the decrease in the conductivity with 40% doped [21-22].

The conductivity of polymer with different ratios of dopants suggests that the conductivity of polymer with low dopants ratio results from polaron (radical cations) due to ionized chain of polymer by dopants and these cations contribute in conductivity but not significantly. While in high ratio of dopants like 30% cobalt's chloride, the bipolarons (spinless dications) are produced as a result of combine polarons or ionize and also, the bipolarons are extended over rings of polymer. The doping process results dopants associated with alternation of aromatic configuration even to quinoid configuration (has high energy) and then confines the charge localized along the chain which increases the conductivity [10].

The activation energy of pure POT and doped POT with different volume ratios of cobalt's chloride is calculated according to Arrhenius model [23] in which the conductivity (σ) is given by the following:

$$\sigma = \sigma_0 \ \exp(-E_a/K_B T) \quad (3)$$

$$ln\sigma = (-E_a/K_B T) + ln\sigma_0 \quad (4)$$

This equation has same form of straight line and then the plot of lnσ Vs 1/T (as shown in Fig. 6) can determine the slope which is multiple by K_B to investigate activation energy of polymers which are (0.0478, 0.044, 0.0442, 0.0908, 0.0374, 0.0495 eV) for pure and doped POT with 5%, 10%, 20%, 30%, 40% cobalt's chloride respectively. The activation energy of POT doped by 30% cobalt's chloride is smaller than other which means that, the localized state in this ratio was greater than other ratios which refer to need lower energy for transition [24].

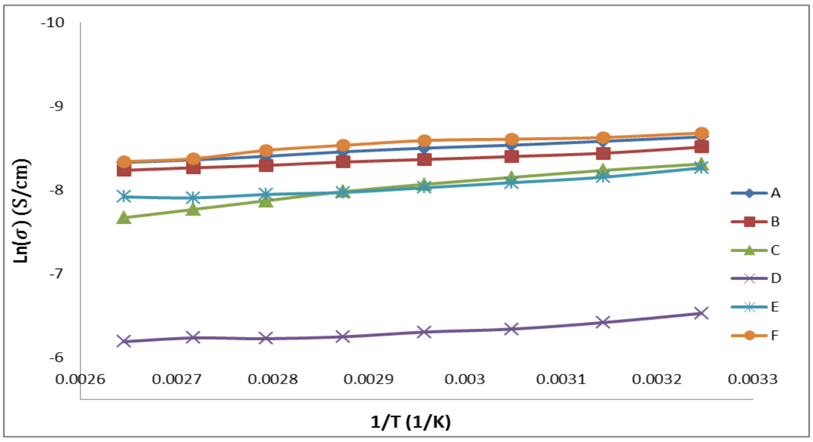


Fig. 6. Plot of Ln σ versus 1/T for POT and doped POT: (A) pure POT, (B) POT-5%cobalts chloride, (C) POT-10%cobalts chloride, (D) POT-20%cobalts chloride, (E) POT-30%cobalts chloride, (F) POT-40%cobalts chloride.

4. Conclusion

- The chemical polymerization method is used to prepare POT and then doped it by different volume ratios of cobalt's chloride as (5%, 10%, 20%, 30%, and 40%).
- The prepared POT is characterized by XRD which shows amorphous structure.
- The FT-IR spectroscopy shows that the prepared material is POT according to previous study.
- The electrical properties of prepared samples are studied and show that, all samples displayed ohmic behavior in addition to semiconductor materials. The electric conductivity at 308 K is increased from1.70E-04 S/cm for pure POT to be 1.459E-3 S/cm at dopant ratio of 30% cobalt's chloride.
- The activation energy of prepared samples is calculated also.

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