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

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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].
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) °C for 30 min., while 10 gm of ammonium per sulphate \((\text{NH}_4)_2\text{S}_2\text{O}_8\) (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°C for 24h’s [22].

2.2 Preparation of POT and PVA blend polymer

The blend polymer of polyvinyl alcohol (PVA) \(([\text{CH}_2\text{CH(OH)}]_n)\) (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°C 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.](image-url)
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 semicrystalline or amorphous structure [26].

![XRD scattering pattern of POT.](image)

**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.

![SEM image of the blend polymers.](image)

**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.](image)

The electrical conductivity was calculated according to following relationship.

\[ \sigma = \frac{I}{V} \times \frac{L}{Wt} \]  \[\text{equation (1)}\]

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

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

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\sigma_s$ (S/cm)</th>
<th>$\sigma_s$ (S/cm)</th>
<th>$\sigma_s$ (S/cm)</th>
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<tbody>
<tr>
<td></td>
<td>Ratio of (1:1)</td>
<td>Ratio of (1:2)</td>
<td>Ratio of (2:1)</td>
</tr>
<tr>
<td>308</td>
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<tr>
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<td>5.75968E-06</td>
</tr>
</tbody>
</table>

**Figure 5:** Plot of Ln $\sigma$ 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 \( \ln\sigma \) 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 ohmic behaviours in addition to semi-crystalline nature.

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References


