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Electronic transition of nano blend conducting Polymers(PEDOT: PSS)

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Electronic Transition of Nano Blend Conducting Polymers(PEDOT: PSS)

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Abstract. Thin films of nano blend conducting polymers, poly (3,4-ethylene dioxythiophene)-poly (styrene sulfonate) (PEDOT: PSS) were prepared . Field-emission scanning electro microscopy FESEM and atomic force microscopy AFM were used to analyse nano blend morphology.Fourier-Transform Infrared FTIR was utilised to examine the existence of functional groups of materials. UV-visible spectrometer was also used to determine the absorbance spectrum. The data was analyses to find energy gap of (PEDOT: PSS) is approximately 3.70 eV. The electrical conductivity was measured by two -probe methods (Lab View 2018) , using Indium-Tin oxide glass (ITO glass) as a substrate. The electrical conductivity calculated about 4.44 S/cm.The effect of temperature on electrical conductivity also measured .as a result the activation energy were calculated at approximately 0.48 eV.
KeyWords: Optical properties, Electrical conductivity, Nano blend Conducting polymer, PEDOT: PSS

INTRODUCTION

Poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives are amongst the most successful conducting polymers. Organic semiconductor poly (3,4-ethylene dioxythiophene) (PEDOT) doped with poly (4-styrene sulfonate) (PSS) has been identified for various applications in organic optoelectronics [1]. Organic electronics has promising prospects and introduces new possibilities in electronic devices [2]. Moreover, organic electronics have recently been used in various device applications, some of which have become commercially available. The use of polymer electrodes, such as organic light-emitting diodes [3] and organic thermoelectric devices [4], is one of the most important aspects of this area. Additionally, the application of PEDOT: PSS in organic field-effect transistors [5] illustrates its versatility in the field of organic electronics. PEDOT: PSS is a polymer electrolyte comprising conducting conjugated PEDOT with positive charges and insulating PSS with negative charges. Oxidised PEDOT is highly conductive but insoluble in water, whereas the insulating PSS facilitates PEDOT dispersion in water and allows for a stabilised PEDOT configuration via coulombic attractions [6]. Thiophene-based polymers have good chemical stability and conductivity amongst conducting polymers but are not solution-processable. PSS doped PEDOT polymer is solution-processable and has high chemical stability, high transparency (>90%) in the visible region and easily grown in thin-film forms [7,8]. PEDOT: PSS is created through oxidative polymerisation of EDOT monomers in water in the presence of PSS. A separate oxidising agent is needed to polymerise EDOT and doped PEDOT because PSS lacks an oxidising effect [9]. PEDOT: PSS dispersion polymerisation enables solution processability by balancing PEDOT nanoparticles with a polyanion PSS, that is, PEDOT: PSS.

PEDOT: PSS was the first anti-electrostatic agent with conductive coatings produced and commercialised by Bayer AG. The aqueous dispersions of PEDOT: PSS with deep-blue opaque colours have been commercialised under the trade names of Baytron by Bayer AG and Clevios by Heraeus [10-12]. Amongst intrinsically conductive polymers, PEDOT: PSS is one of the most successful conductive polymers of the last two decades because of its high electrical conductivity (up to 1000 S cm^{-1}), transparency and thermal stability [13]. This research examines the electrical and optical properties of pristine PEDOT: PSS with deionised (DI) water. Results showed that the electrical conductivity is 4.44 s/cm, and the energy band gap is 3.70 eV.

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EXPERIMENTAL PARTS

Materials: PEDOT: PSS aqueous solution (A1 4083, Batch: 2015POO23, Quantity: 100 ml, Read MSDS before use, WWW.Ossila.com, (ITO)) P/Ono.: JSYC14-061, Coating: 20 ohm/sq ITO glass, pattern: KTY C19, Size: 24 × 24 × 1.1 mm.

Thin Film Preparation of PEDOT: PSS

PEDOT-PSS material was dissolved in DI water, then mixed by ultra-sonicated for 2 h untel get a homogeus solusion of PEDOT-PSS.The thin-film of the PEDOT: PSS was prepared and examined by FTIR, XRD, AFM and FE-SEM.The material was deposition on the glass substrate by spin-coated method for (3000 rpm for 20s) .these thin films were used for measurements FE-SEM ,AFM, and optical properties.

For electrical properties ,casting method was used for deposition PEDPT-PSS on (ITO) glass .The samplels put in oven at 60 Co for 5h.then used for mesurment eletricl conductivity explain by Manal et al [14].

RESULTS AND DISCUSSION

Fourier-Transform InfraredFTIR

Figure 1 show the spectrum of PEDOT: PSS ,it is displays bands associated with the O–H group at 3556.74 cm^{-1}. The vibrations at 1641.42 are attributed to the C=C [14]. The band at 1120 is assigned to the SO_3H group of PSS. The O–H stretching modes of the hydroxyl groups demonstrate the band at 1641.42 cm^{-1}, as shown in Table 1. The peaks at 1516.05 and 1367.53 cm^{-1} are ascribed to c=c and c-c stretching in the thiophene ring of PEDOT-PSS, respectively [15,16]. Bands approximately 840–1000 cm^{-1} are due to c-s bond stretching of the quinoidal structure of the thiophene ring [17,18]. The absorption peaks between 1000 and 1200 cm^{-1} may be ascribed to the ethylenedioxy group [19].

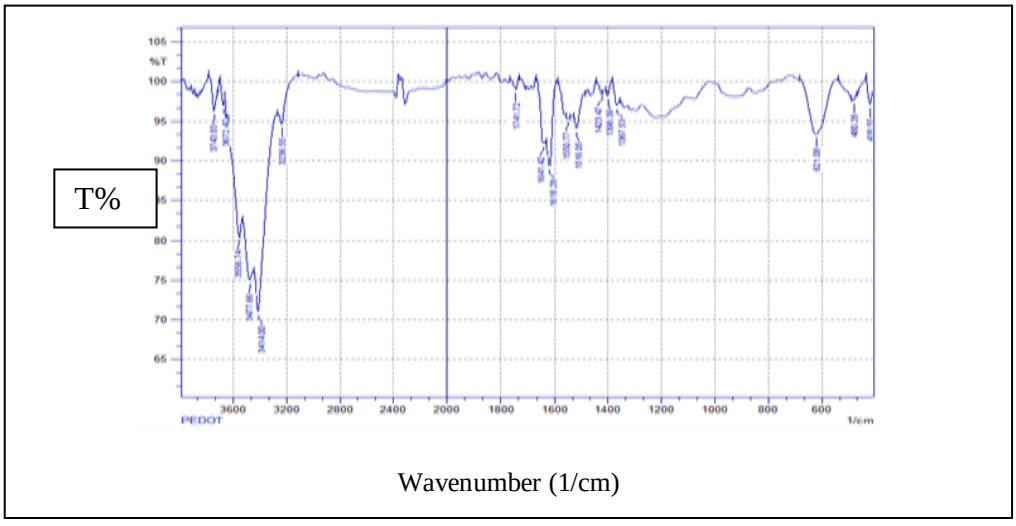


FIGURE 1. Functional group of PEDOT: PSS.

Table 1. Vibration types of pure PEDOT: PSS**.**

Bond	PEDOT: PSS	Ref
C=C	Vibrations at 1641.42 cm^{-1}	[14]
C=C	1516.05 cm^{-1}	[15,16]
C-C	1367.53 cm^{-1}, stretching in the thiophene ring	[15,16]
O–H stretching	3556.74 cm^{-1}	[14]
SO_3 group of PSS	1120 cm^{-1}	[15,16]
C-S stretching	840–1000 cm^{-1}	[17,18]
ethylenedioxy group	1000–1200 cm^{-1}	[19]

Filed Emission Scanning Eletron Microscopy(FESEM)

The morphology of PEDOT: PSS was examined using FE-SEM to investigate changes in the microstructures as shown in figure 2. The pictures of FESEM show the appearance of nanofiber structures at 200 and 500 nm. The diameter of the fiber is approximately 40 nm, and its length is 300 nm. The nanofiber is closely spaced together [20,21].

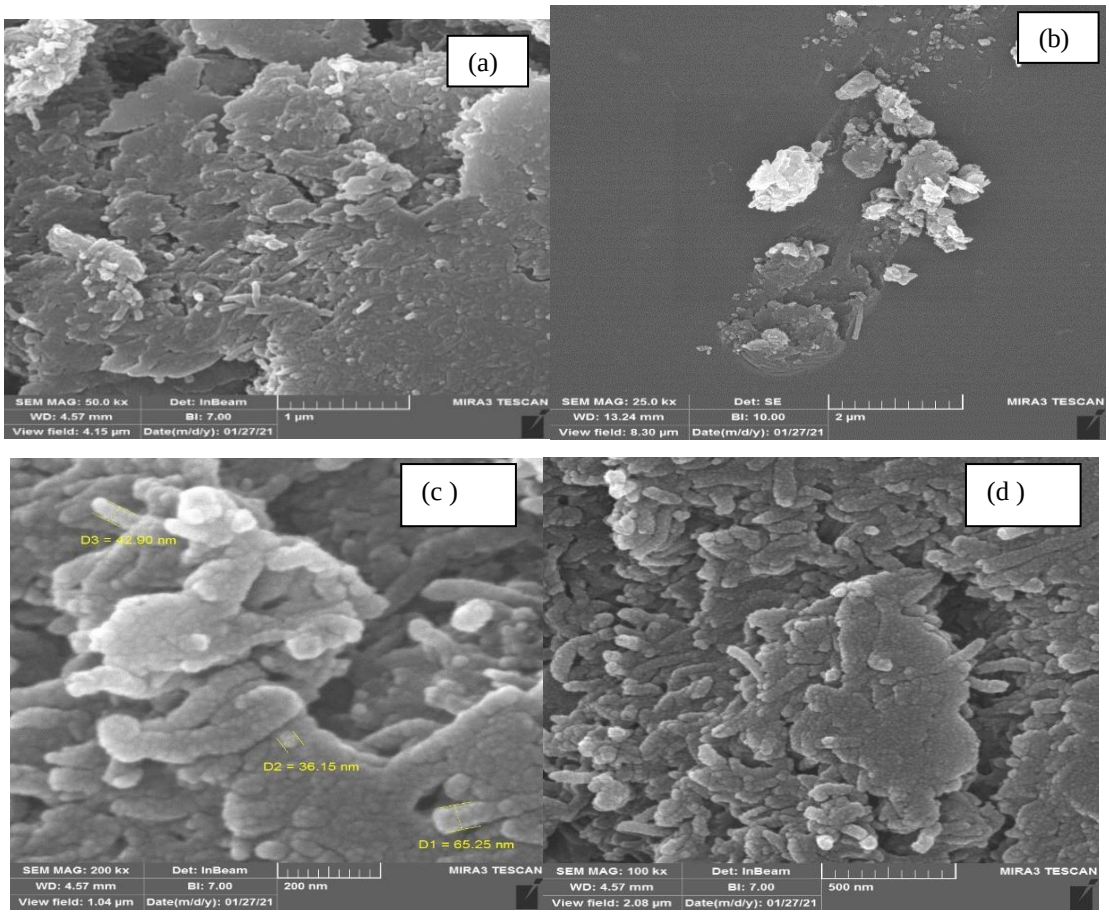


FIGURE 2.FE-SEM micrographs of PEDOT: PSS**.**

Atomic Force Microscope (AFM)

The spin-coated method for PEDOT: PSS onto a glass substrate was used in accordance with AFM measurements. Considering thin-film roughness, thin-film morphologies were also investigated in the current study. AFM is well-known as one of the most useful tools for analysing surfaces. Figure3 shows the average diameter between 10 and 15 nm.

Figure 4 refers to the 2D and 3D representations of the 4 × 4 μm zone and size distribution of PEDOT: PSS in DI water, respectively. Table 2 shows smooth surfaces, with an average surface roughness of 2.35121 nm (ten-point height, Sz 17.6043 nm). The differences in AFM contrast are often related to changes in surface topography. However, some researchers believe that the AFM contrast in PEDOT: PSS can be attributed to variations between PEDOT-rich (bright) and PSS-rich (dark) zones (dark areas) [22,23].

Table 2. Average roughness and root mean square.

Sample name	Root Mean Square nm	Average roughness (nm)	Average (nm)
PEDOT: PSS	3.42554	2.35121	13.031

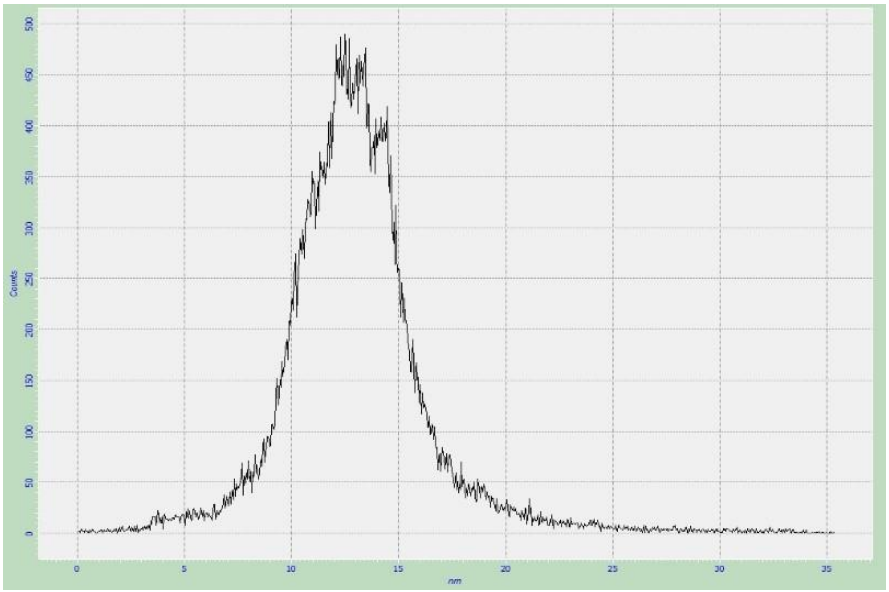
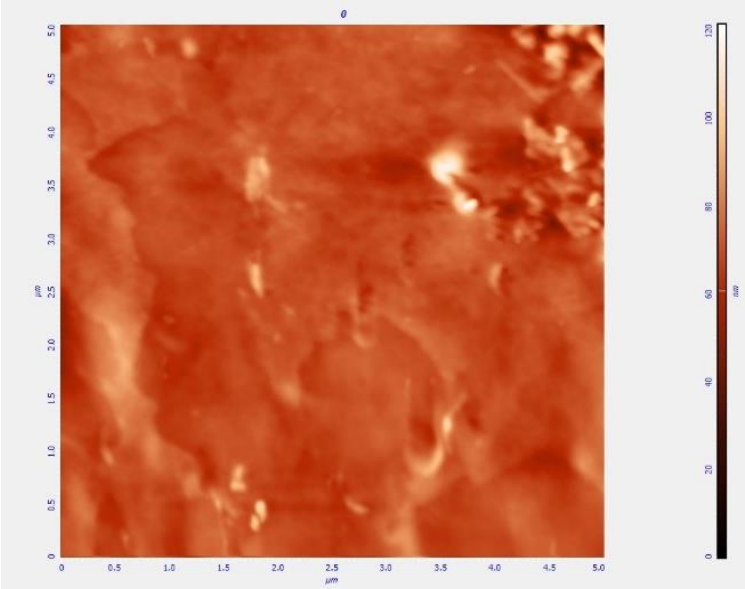
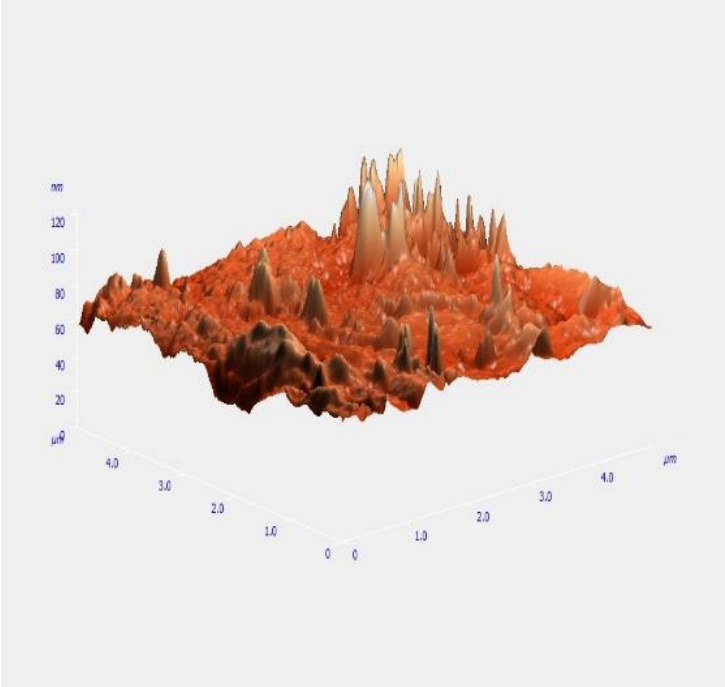


FIGURE3. Size distributions of pure PEDOT: PSS.



2D



3D

FIGURE4. AFM image of PEDOT: PSS at 2D and 3D.

X-RAY Diffraction (XRD) of Pure PEDOT:PSS

The XRD for a thin film of polymer PEDOT: PSS shows the absence of any sharp peaks in the pure PEDOT: PSS. Figure 5reveals the XRD patterns of PEDOT: PSS, which indicates the substantial amorphous nature of the PEDOT: PSS film. Similar results were also obtained by different research groups [24,25].The curve noisy because the polymer PEDOT:PSS is amorphous.

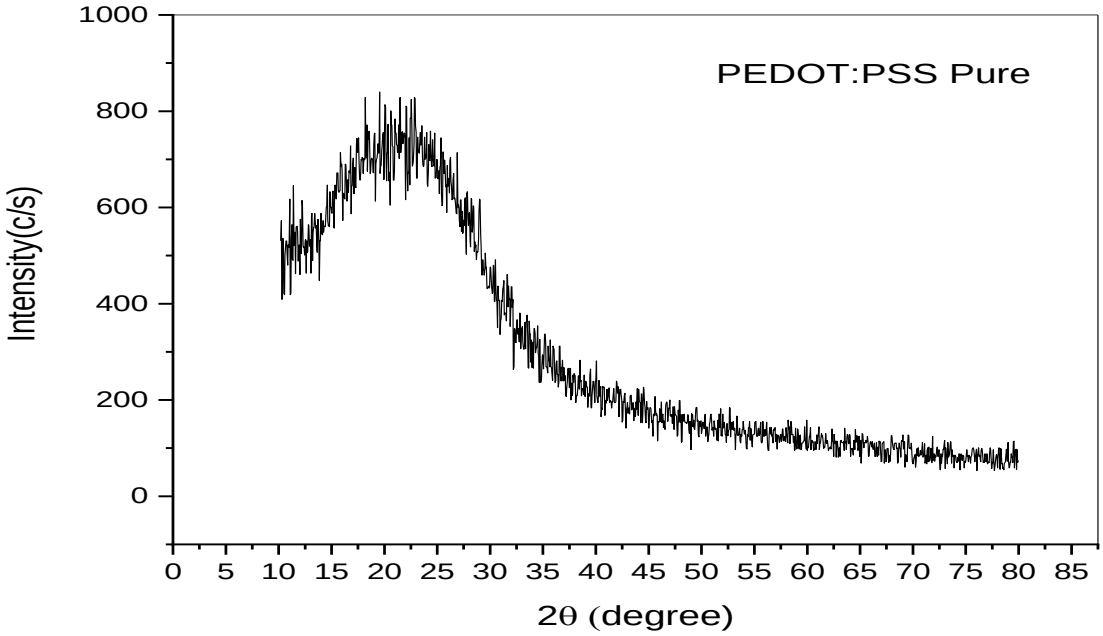


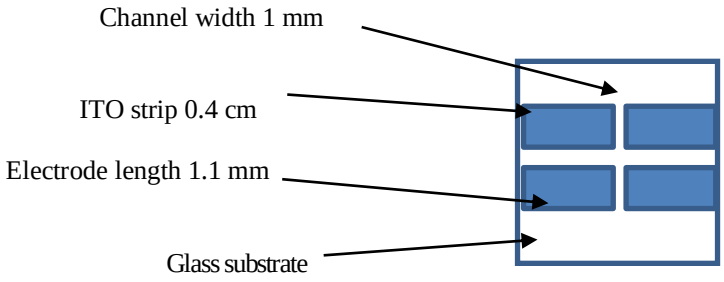
FIGURE5. XRD patterns of PEDOT: PSS.

Electrical Characterisation

The DC conductivity of the collected thin films was investigated using two-point measurements on two locations on the sample (LabVIEW 2018). The PEDOT: PSS solution was deposited on a substrate ITO-glassin figure 6-a, and Figure 6-b shows the system devices used. The conductivity values are calculated from the current via the following equation [27,28]:

$$\sigma = \frac{I}{V}\frac{S}{L\,l}\,, \qquad (2)$$

where V represents the applied voltage between the electrodes, I is current, S is the width amidst the electrodes, L is the thickness of the sample and l is the length of the electrodes.



(a)

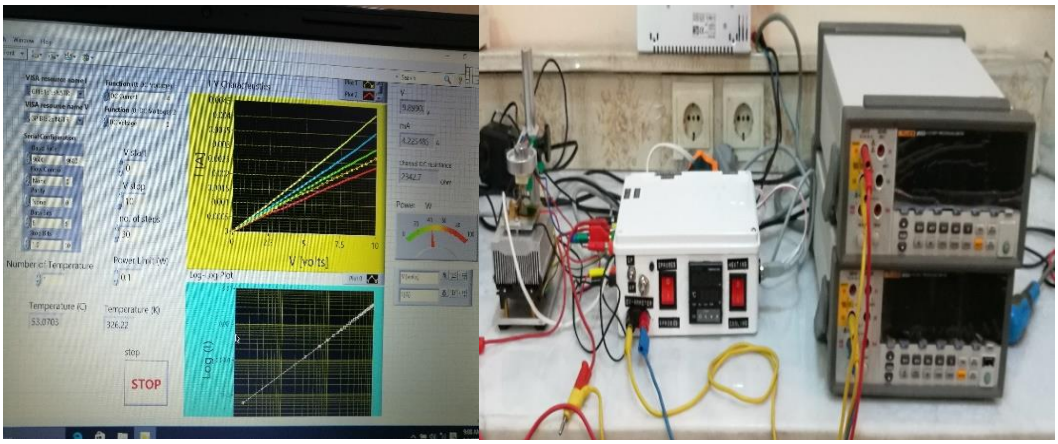


FIGURE 6.(a) ITO Substrate, (b) Device System of I-V Curves.

Figsure 7a and b show the I-V curves of the characteristic under the laboratory temperature of 27 °C (300 K). The same behaviour is observed at other temperatures, and the conductivity increases with the temperature. The temperatures range from 303 K to 353 K at the ohmic behaviour from 6 V to 10 V, and the electrical conductivity increases with rising temperature.

Almost linear behaviours of the ohmic or rectification characteristics of metal and semiconductors as they come into contact are respectively determined by the work function and electron affinity of the metal and semiconductor. Charge carriers freely pass into or out of the semiconductor because of the nominal resistance around the contact interface, whilst the metal–semiconductor interface is ohmic. A metal must have a work function that is equal to or higher than the semiconductor to achieve ohmic interaction with p-type semiconductors, such as PEDOT: PSS.

The resistance decreases with increasing temperature, and the conductivity increases with rising temperature [29]. The sheet resistance, which is equal to 3238.1 Ω, can be calculated from theslope (I/V).

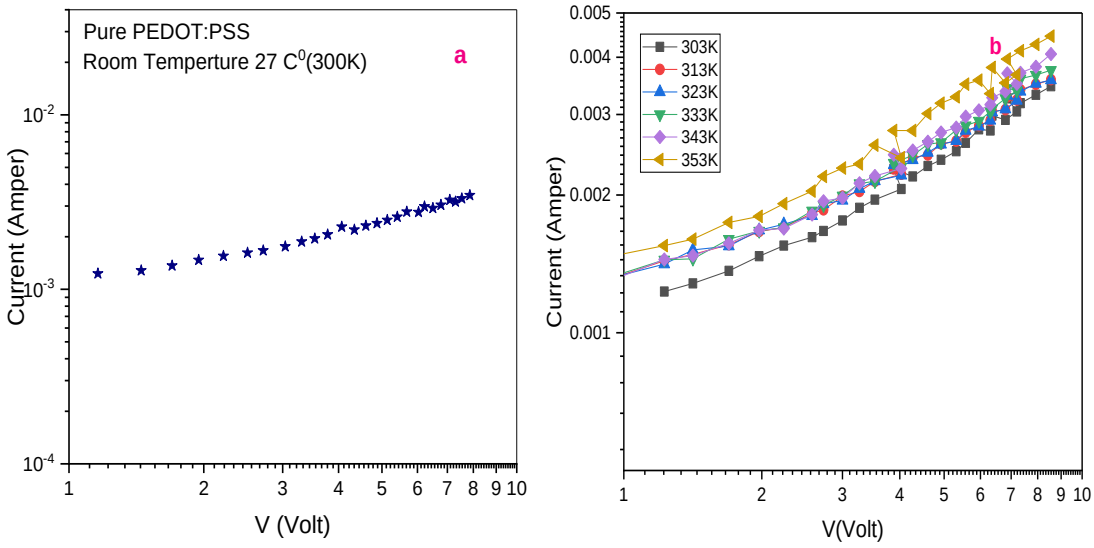


FIGURE7.(a) I-V Characteristic of PEDOT: PSS at room temperature,(b) I-V Characteristics in different temperatures

The electrical conductivity and temperature can be described by using the Arrhenius equation[30]:

$$\sigma = \sigma_0 \, exp - \frac{Ea}{KT} \, , \qquad (3)$$

where Ea is the activation energy, K; and the Boltzmann constant is 8.617×10^{-5} eV K^{-1}.

The activation energy can be estimated from Eq. 3, which is also equal to 0.48 eV as shown in figure 8.
The electrical conductivity can be used to measure the necessary activation energy (Ea) for the charge carrier hopping [31]. E_a is 0.48 eV at different temperatures from 303 K (30 °C) to 353 K (80 °C) based on Eq. 3.

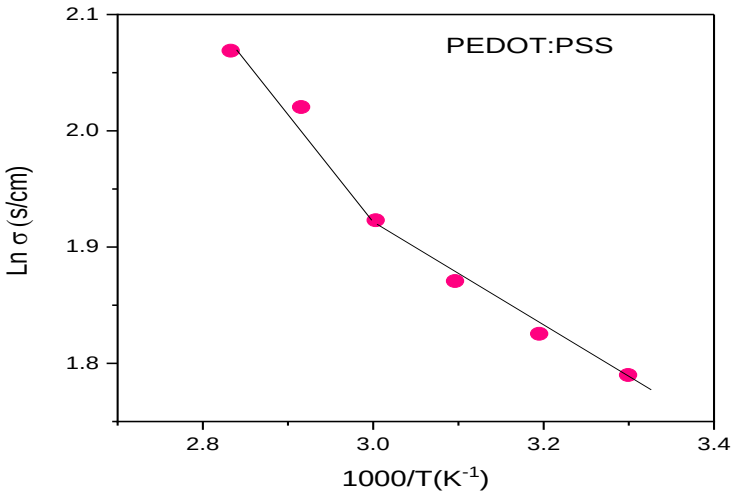


FIGURE8. Relation between Ln σ and T(K^{-1})**.**

Optical Properties

UV-visible spectroscopy was used to analyse the optical properties of thin films of pristine and modified PEDOT: PSS. The absorption spectra of films are presented in figure 8.
Equation (4) was used to determine the absorption coefficient (α) from the absorbance (A) and thin-film thickness (d):

$$\alpha = \frac{2.303}{d} A, \qquad (4)$$

Figure 9a shows the relation between the absorbance and the wavelength from 200 nm to 1000 nm, whilst Fig. 9b shows the absorption coefficient as a function of the photon energy of PEDOT: PSS. The absorption coefficient data were analysed for the observed band electronic transition in the fundamental absorption region. The optical absorption region $\alpha > 10^4$ cm^{-1} was analysed to obtain information on direct transition considering the theory of Bardeen et al. (1956).
The energy band gap was calculated using the Tauc relation as follows:

$$\alpha . h . \nu = A\left(h . \nu - E_g\right)^n , \qquad (5)$$

where α is the absorption coefficient, υ is the frequency, h is Planck's constant, A is a constant, E_g is the energy band gap and n = 1/2 and 2 for the allowed direct and indirect transitions, respectively, and (2, 3) for the prohibited direct and indirect transitions, respectively.
The transformation from n to π* in the PEDOT backbone causes the characteristic peak at 380 nm [32,33]. Transitions $\alpha > 10^4$ cm^{-1} refer to direct transitions. $(\alpha h \upsilon)^{1/2}$ versus hυ is plotted in accordance with Eq. 5 as shown in figure 10. The value of the energy band gap is approximately 3.7 eV based on the obtained curve.

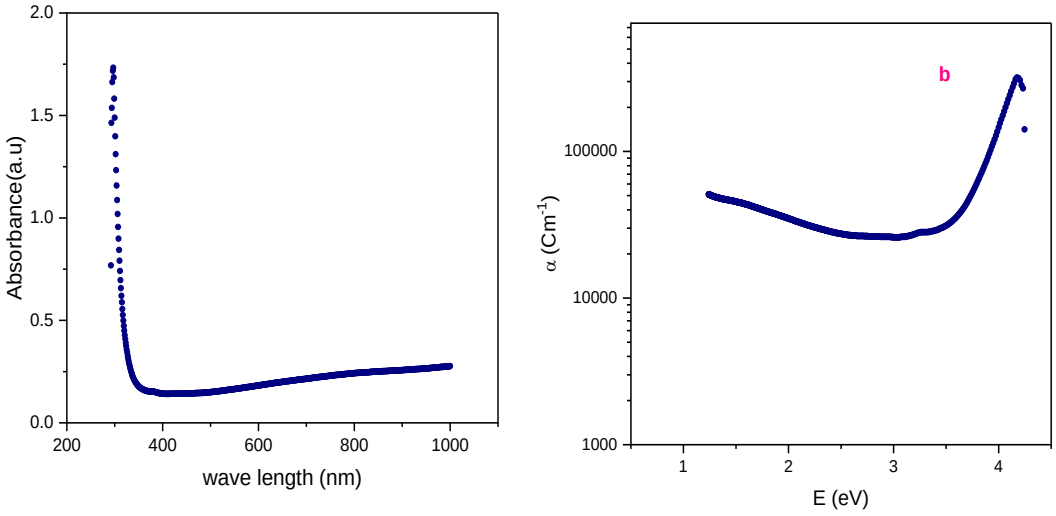


FIGURE 9.(a) Relationship between absorbance and wavelength, (b) PEDOT: PSS absorption spectra related to photon energy absorption coefficients**.**

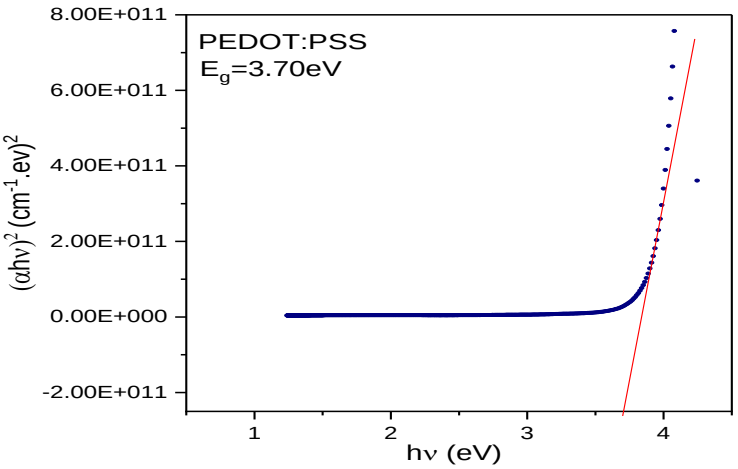


FIGURE 10. Relationship between $(hv)^2$ and photon energy for Pure PEDOT: PSS.

The absorption in the visible spectrum is notably low, as shown in figure 10. The transmission is high because most active layers absorb in the 200–1000 nm region, making it ideal for solar cell applications. Furthermore, the reduction in absorption spectrum near 500 nm corresponds to the distance at which most polymers demonstrate the most absorption. The transformation from n to π* in the PEDOT backbone causes the characteristic peak at 380 nm [32,33].

Polarons and uncoupled bipolaron transitions in the benzenoid or quinoid structure of PEDOT correspond to the wide absorption plateau above 700 nm. The development of freely flowing solitons, polarons and bipolarons increases conductivity during PEDOT: PSS doping [33].

CONCLUSIONS

The thin film of conducting polymer PEDOT: PSS was prepared and examined by FTIR, SEM, XRD and AFM. FE-SEM results indicate the appearance of PEDOT: PSS in the form of nanofibers with diameters of 65.25, 36.15 and 42.90 nm at SEM MAG kx 200 nm. The measured electrical conductivity of the PEDOT: PSS nano blend is 4.44 S/Cm. The sheet resistance is equal to 3238.1 Ω. The activation energy (0.48 eV) depends on two processes, namely

crystallisation and melting, of the polymer. The analytical optical properties indicated that the energy band gap is approximately 3.70 eV under the direct transition.

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