

Synthesis, Characterization and Electrical Conductivity of Polyaniline Graft Cinnamic Acid and Application as Sensors

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Abstract:

DC conductivity of PANI-g-CA doped films including various Eosin B ratios (0.01, 0.03, 0.05, 0.07, 0.09, 0.12 and 0.15)% Wt in this study, are studied. Through casting techniques, the composite materials have been prepared. Thermogravimetric analysis (TGA), Fourier Transform Infrared Spectroscopy (FT-IR) and Xray diffraction (XRD) analysis have characterized the preparation of PANI-g-CA composites that found the formation of the composite and the Cinnamic acid presence in poly aniline. Studies of DC conductivity demonstrate all composites in thermally activated behavior. Conductance has been found to reduce with increasing temperature showing the semi-conductive behavior for all doping ratios. With doping ratios in coloring and increasing temperature, the activation energy reduced. Maximum conductance in poly aniline has been measured in 0.15% of dye. In sensor technology, Dye sensitization of performing polymeric materials had acquired practical application and wide theoretical interest. The current study provides the effect of polymer presence of dye (conductivity, structure and properties), dye sensitized photo sensors and application in sensors. At the end, advantages and perspectives were included of sensitizing polymers or modifying dye in sensors.

Keywords: Electrical conductivity, Poly aniline, Cinnamic acid, sensors, Activation energy.

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I. INTRODUCTION

The organic–inorganic composite polymeric materials have attracted researchers because of their potential uses in developing new materials and devices [1]. One of the interesting subjects in conducting polymers is the connection of these polymers with base polymers in different properties and creating new properties. These polymers can be connected as block or graft and cause changes in their solubility. Dopant plays an important role in conjugated polymers because these polymers become conductive when charge carriers, generated by dopants are present in their structure [2].

Poly aniline is the one of the most promising conducting polymers due to a good combination of properties, stability, price and ease of synthesis by

different routes [3–4]. It exists in a variety of reversible protonated and oxidized forms, differing for electrical, electrochemical and/or optical properties like many ECPs [5–7]. PANI is difficult to process because it is soluble only in a limited number of organic solvents. Therefore, study of the properties of these conducting polymers with respect to different growing as well as ambient conditions is of high importance. An optical and electrical properties of poly aniline are useful for various device applications such as transistors [8], optical waveguides [9], in optoelectronic devices [10], photovoltaic and photoconductive devices and optical modulator devices [11]. Poly aniline have also been exploited in sensor applications [12].

II. Experimental

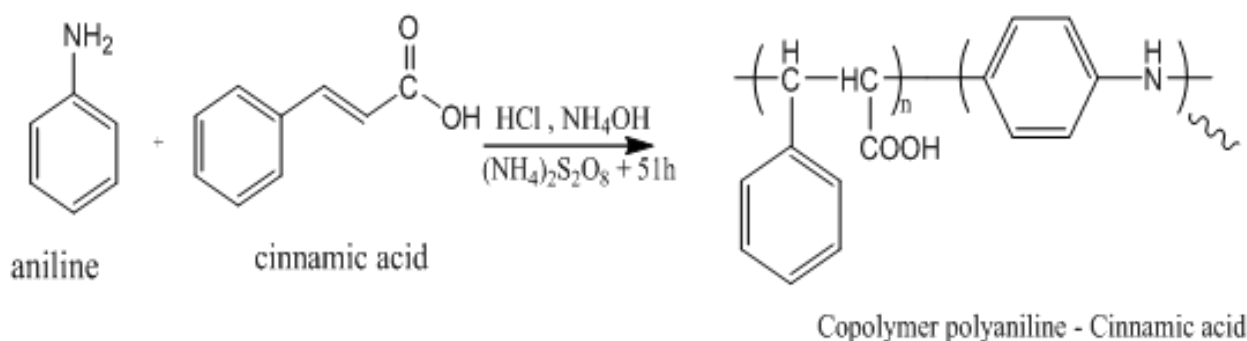
2.1. Materials

The materials tested in this study were aniline, ammonium per sulfate hydrochloric acid, cinnamic acid, methanol, acetone, ammonia and eosin B.

2.2. Preparation of PANI-g-CA

Aniline (4.93 ml, 0.054 mol) was added to 20 ml of 1M HCl taken in a 250 ml beaker. Ammonium per sulfate (12.3 g, 0.054 mol) dissolved in 30 ml of 1M HCl at and added in the above aniline solution with vigorous stirring and then, cinnamic acid (8 g, 0.054

mol) dissolved in 50 ml of 1M HCl was added to solution. The reaction temperature was maintained at -5°C . After the polymerization reaction, the mixture was filtered and washed with methanol followed distilled water several time, finally the residue was washed with acetone and dried at 60°C . The precipitate dissolve in 45 ml of ammonia solution (25%) and leave it at room temperature with stirring for 3 hours and then filtered the solution and washed with methanol, acetone and distilled water respectively, dried at 60°C .



Scheme (1): preparation of PANI-g-CA.

2.3. Doping of PANI-g-CA

Doping PANI-g-CA with dye eosin is carried out by adding the weighed dye to the appropriate weight of polymer (1g) then the mixture was dissolved in dimethyl methyl sulfoxide after the prepared directly to give a polymer / dye system containing (0.01, 0.03, 0.05, 0.07, 0.09, 0.12 and 0.15) g wt% of doping reagent eosin B [13]. The mixture was stirred well for 15 minutes to guarantee that the homogenous distribution of dye in the polymer matrix, and then coated on a glass substrate fluorine doped tin oxide (FTO) by casting method at room temperature. The thickness of the films were measured using Micrometer

(3032 cm^{-1}). The carbonyl beam appeared at (1735 cm^{-1}) while the C = C beam appeared at (1589 cm^{-1}) [14]. As shown in Figure (1).

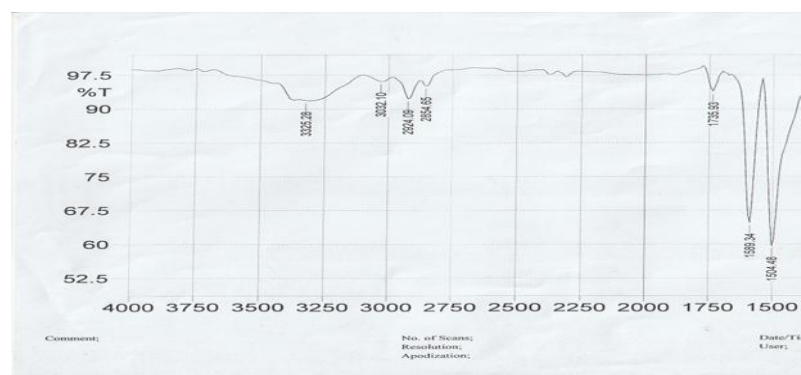


Fig.1:FTIR of pure PANI-g- CA.

III. RESULTS AND DISCUSSION:

3.1. FTIR Study

The infrared spectrum, The spectrum showed a beam at (3325 cm^{-1}) indicating the OH carboxylic group, and a beam at (3350 cm^{-1}) indicating the NH group.

3.2. XRD Studies

The X-ray diffraction pattern of pure PANI-g-CA is shown in Figure (2) In this spectrum, one main signal appeared at (2θ) 19.26 which indicates the semi crystalline nature of PANI-g-CA [15]. When doping copolymer with different ratios of dye, this

peaks shifted to a lower angle and decrease in d-spacing for all doping ratios, and three signals appeared at (2θ) 20.58°, 20.81° and 21.69° attributed physical interaction between the copolymer and dye, as shown in Figure (3) and (4). The crystallite size of the synthesized PANI-g-CA and doping ratios were calculated using Scherer's formula [16] given by

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

Where D is the average crystallite size, λ is the X-ray wavelength (1.5416 Å) and β is full width at half maximum in radian. The grain size for pure PANI-g-CA and doping ratios are tabulated in table 1.

Table(1): Grain size for doping PANI-g-CA film with different doping ratio

Doping ratio %	Grain size (nm)
0.00	4.307
0.01	17.218
0.03	19.572
0.05	22.348
0.07	24.231
0.09	27.006
0.12	28.820
0.15	49.843

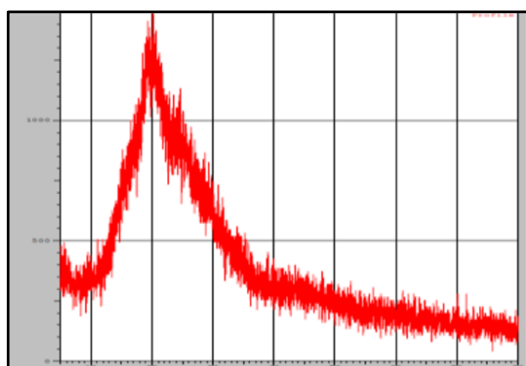


Fig.2: XRD of pure PANI-g-CA

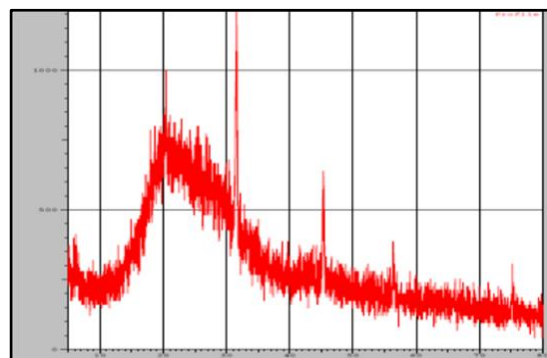


Fig.3: XRD for weight ratio 0.12% of doping PANI-g-CA.

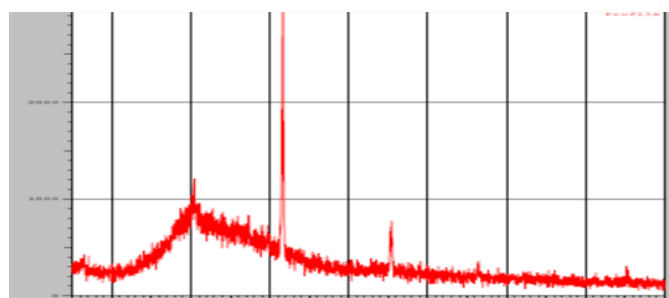


Fig.4: XRD for weight ratio 0.15% of doping PVA-g-AA.

3.3. TGA-DTA Analysis

Figure (5) represents the weighted and differential pyrolysis curve of the PANI-g-CA co-polymer. We observe from the figure several stages of dissociation. The first stage, at a dissociation temperature of 101.46°C, with a weight loss of 2.474%, is due to the loss of water molecules from the polymer. In the second stage, it disintegrates at 237.23°C, with a weight loss of 6.659%. As for the third stage, as is evident from the figure, it decomposes at 626.67°C, with a weight loss of 17.857%. It loses a weight of 19.234% by disassembling it at a temperature of 900 °C. Also, we note that the joint polymer loses half its weight at a temperature of 973.5°C and has a charcoal content at a temperature of 714°C of 53.95% carbon solid.

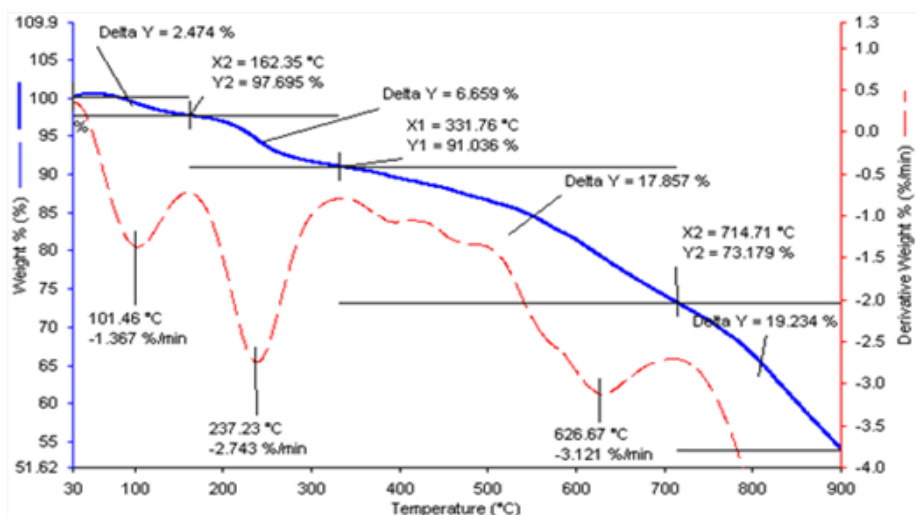


Fig.5: TGA and DTA for PANI-g-CA.

3.4. DC Conductivity Studies

Figures (6)-(13) show the relationship between current-voltage characteristics of PVA-g-AA and dye (0.01% to 0.15%wt) films at the temperature range (303-393) K. The current increases with increasing temperature and the applied voltage is identical to the characteristics of semiconductor materials. When temperature increases, more localized electrons have the energy to bridge the gap and the system becomes more ordered, then decreasing amount of localized states present allowing for more mobile of charge carriers [17]. On other hand, the molecular structure of the polymer greatly influences the charge carrier mobility according to the (I-V) characteristics.

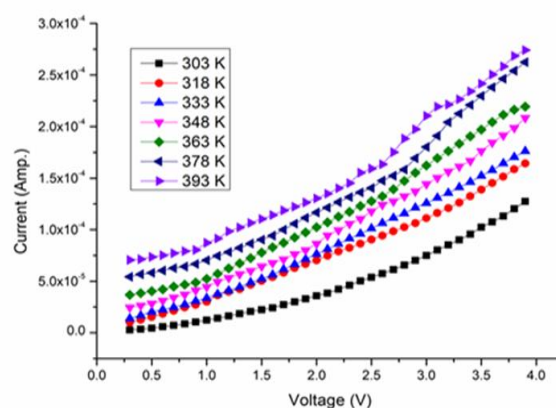


Fig.7: (I-V) Characteristics at different temperatures for weight ratio 0.01% of doping PANI-g-CA.

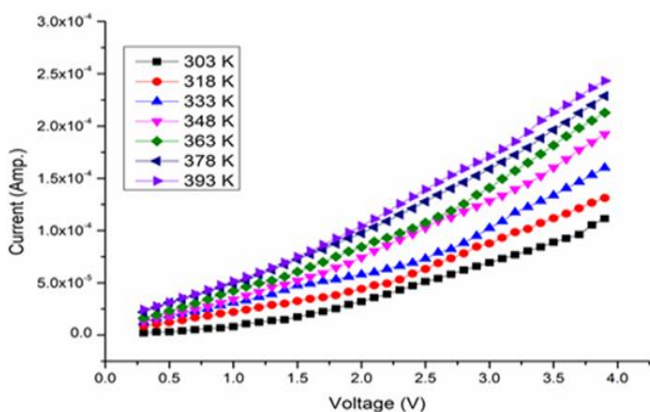


Fig.6: (I-V) Characteristics at different temperatures for PANI-g-CA.

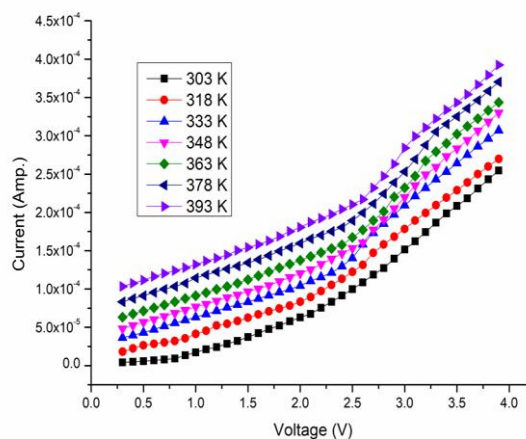


Fig.8: (I-V) Characteristics at different temperatures for weight ratio 0.03% of doping PANI-g-CA.

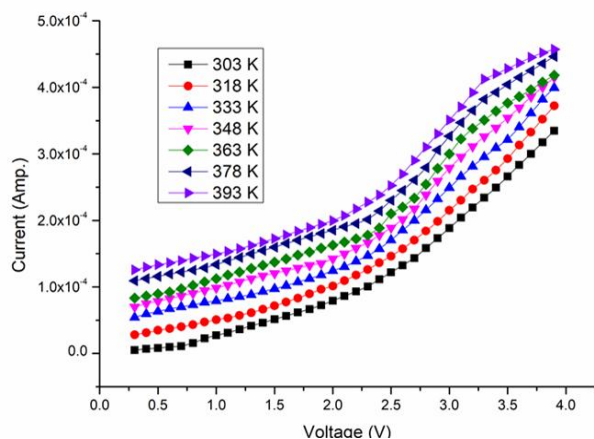


Fig.9: (I-V) Characteristics at different temperatures for weight ratio 0.05% of doping PANI-g-CA.

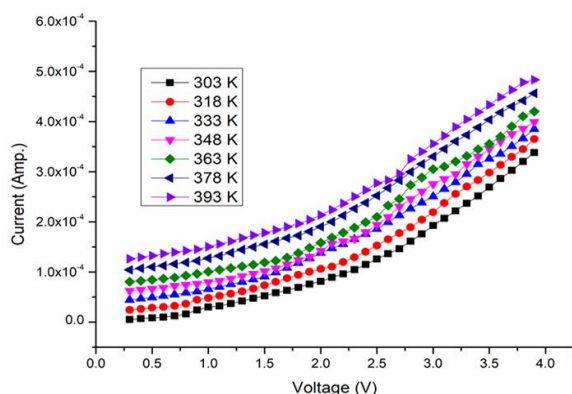


Fig.10: (I-V) Characteristics at different temperatures for weight ratio 0.07% of doping PANI-g-CA.

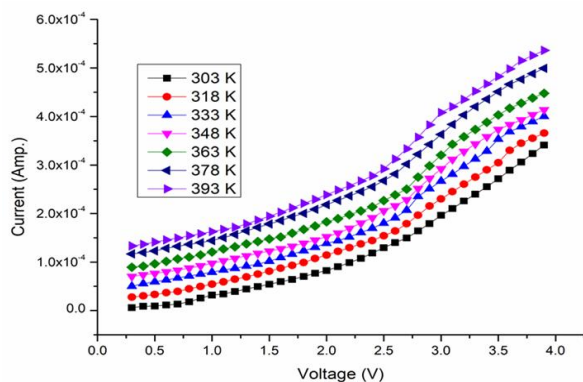


Fig.11: (I-V) Characteristics at different temperatures for weight ratio 0.09% of doping PANI-g-CA.

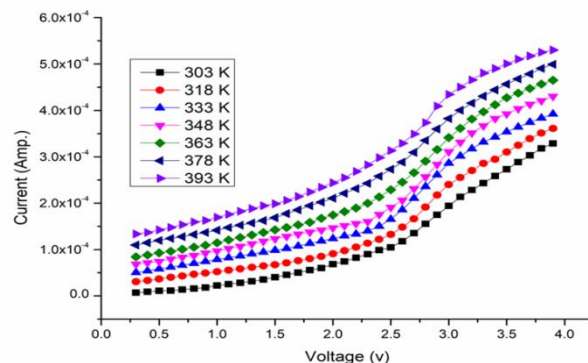


Fig.12: (I-V) Characteristics at different temperatures for weight ratio 0.12% of doping PANI-g-CA.

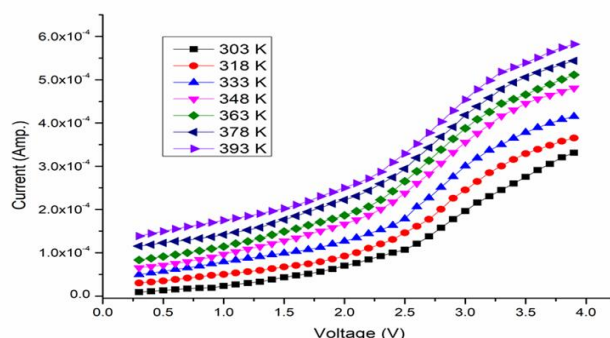


Fig.13: (I-V) Characteristics at different temperatures for weight ratio 0.15% of doping PANI-g-CA.

Figure (14) shows the effect of doping ratio with Eosin B enhanced electrical conductivity in this order: (pure < 0.01 < 0.03 < 0.05 < 0.07 < 0.09 < 0.12 < 0.15) % wt. This is due to electrostatic interaction in emulsion and powder between laser dye and lignin resin, and the small amount of dye which make it diffuse within the matrix of polymer.

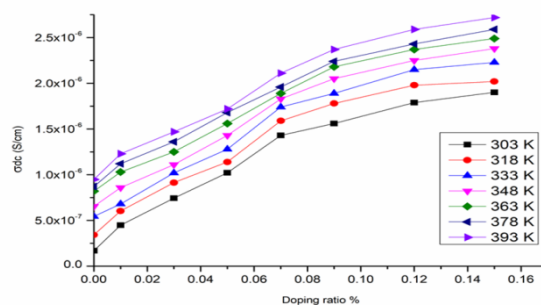


Fig.14: The relationship between σ_{dc} and weight ratio of doping PANI-g-CA at different temperatures.

Figure (15) shows a typical $\ln \sigma$ vs. T plot for PANI-g-CA with doping ratios. The conductivity increased with increase in temperature and the rate of increase was different in different temperature from (30-120) °C that was because of the increasing charge carrier in conduction band, this indicating semiconductor-like behavior. The sharp increase of dc conductivity between 363 K to 393 K can be related to segmental motion as a result of increasing temperature. However, the electrical conductivity increases linearly beyond 363 K as exactly detected for another system [18-19].

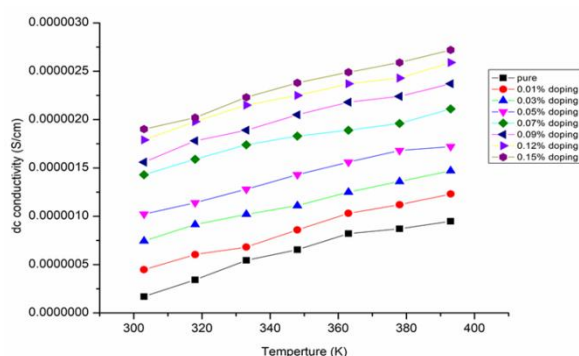


Fig.15: DC conductivity for doping PANI-g-CA with different temperatures.

Figure (16) shows the relation between $\ln \sigma$ and $1/KT$ (eV), the activation energy has been determined from the slopes of these curve by using the relation [18].

$$\ln \sigma_{dc} = \ln \sigma_0 - E_a/kT \quad (2)$$

Where σ is the conductivity at temperature T , E_a is the activation energy, and k is the Boltzmann constant.

It was found that the values of activation energy decrease with the increase of the ratios of doping for all ratios. At 303K and 393K, the dc electrical conductivity of pure PANI-g-CA was found to be $4.691 \times 10^{-6} \text{ Scm}^{-1}$ and $9.495 \times 10^{-6} \text{ Scm}^{-1}$ respectively. As content of dye increases from 0.01% to 0.15% in PANI-g-CA matrix, the conductivity of PANI-g-CA composite increases from $0.648 \times 10^{-6} \text{ Scm}^{-1}$ to $1.126 \times 10^{-6} \text{ Scm}^{-1}$ at 308K, similarly at 393K it increases from $1.679 \times 10^{-6} \text{ Scm}^{-1}$ to $2.491 \times 10^{-6} \text{ Scm}^{-1}$. The increase in conductivity with increase of temperature is the characteristic behavior of semiconductors [20].

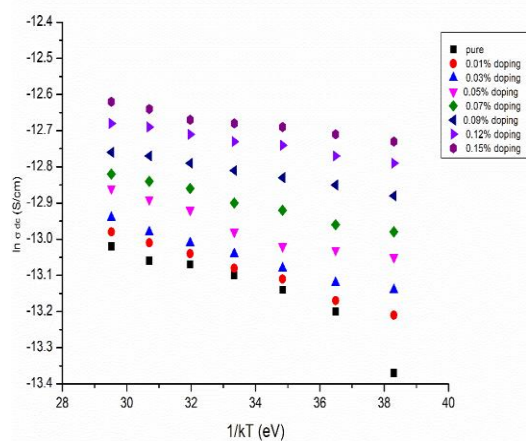


Fig.16: The activation energy of the pure PANI-CO-CA polymer.

Table (2) reports the results of the E_a and R^2 activation energies and their standard deviations.

Table 2: Activation energies, R^2 and SE values for doping PANI-CO-CA film with different doping ratio

Doping ratio %	E_a (ev)	R^2	SE
0.00	0.180	0.954	0.015
0.01	0.114	0.973	0.013
0.03	0.074	0.986	0.012
0.05	0.062	0.987	0.010
0.07	0.049	0.990	0.008
0.09	0.046	0.994	0.005
0.12	0.040	0.995	0.004
0.15	0.043	0.998	0.004

3.5. Optical Sensors

Figure (17) and (18) Indicate the light and dark weight relationship between current-voltage characteristics of weight ratio 0.12% and 0.15% of doping PANI-g-CA at room temperature. The photocurrent increased in the light at voltage (1.2-1.8) V than dark case is identical to the increase in conductivity, and the resistance difference (ΔR) are 3.56 k Ω and 8.00 k Ω for the doping ratios 0.12% and 0.15% respectively. The optoelectronic effects are attributable to the association of π - π and the existence of bifunctional groups. Most dyes and CPs are blamed for their insolubility because of their strong conjugation and planar structure [21].

However, these large dye conjugation systems may exert electronic interference with the CP's π -system, resulting in a series of changes in the properties and morphology of dye-doped conductive polymers (DPCs). It has been shown that DCPs' electrical and photo electrochemistry is immune to chemical agents; this offers the possibility of sensor growth. The results of dye dopants on PANI-g-CA conductivity and optical properties demonstrated that the color and conductivity shifts could be used to establish optical and electrochemical sensors [22].

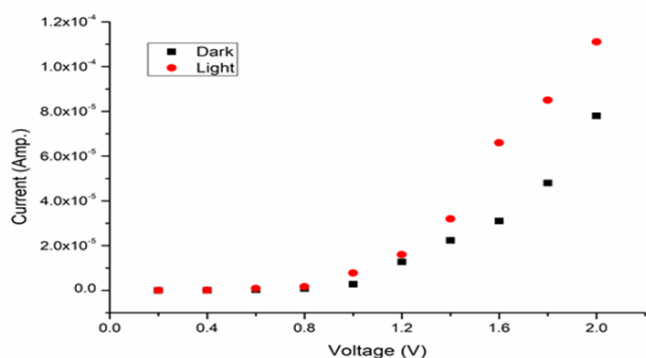


Fig.17: Current -voltage characteristics under light and dark for 0.12% of doping PANI-g-CA.

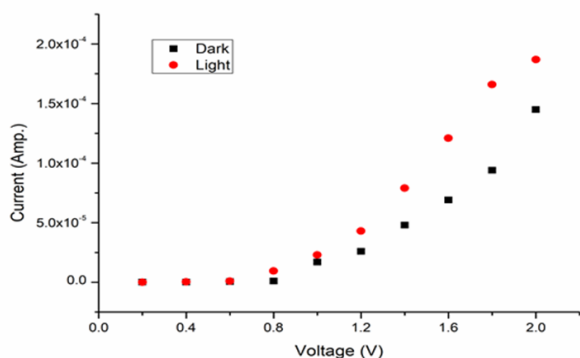


Fig.18: Current -voltage characteristics under light and dark for 0.15% of doping PANI-g-CA.

IV. Conclusion

Poly aniline-Graft-cinnamic acid doped with various weight percentages of Eosin B dye. The FTIR result showed that PANI-g-CA was established. Reports in X-ray diffraction show changes from amorphous to crystalline. Analysis of TG-DTA indicates the polymer is thermally stable. Conductivity variation

in temperature, π , was measured and found to be a type of semiconductor. Maximum conductivity was observed in 0.15.% of dye in PANIA-g-CA. Activation energy, E_a , for conduction was determined, when increase in ratio of dye content, E_a decreased and σ increased. The dyes presence in the performing polymers alters the polymer's electrical and optical properties. It is generally possible to synthesize the dye doped polymers quicker than pure polymers.

References

- [1] Zein S.H.S., Boccaccini A.R., Zainal W.N.H.W., World Appl. Sci. J. 6 (6),737–747 (2009).
- [2] L.M.H. Groenewoud, A.E. Weinbeck, G.H.M. Engbers, J. Feijen, Synth. Met., 126 , 143(2002).
- [3] Schmid A. L., Torresi. S. I. C., Bassetto A. N., Carlos I. A., Journal of the Brazil Chemical Society, 11, 317–323 (2000).
- [4] Ansari R., Keivani M. B., Journal of Chemistry, 3, 202–217 (2006).
- [5] da Silva P. J. E., Temperini M. L. A., Torresi S. I. C., Journal of Brazil Chemical Society, 16, 322–327 (2005).
- [6] Plesu N., Hiescu S., Ilia G., Popa A., Muntean C., Turkey Journal of Chemistry, 30, 155–163 (2006).
- [7] Draman S. F. S., Daik R., Ahmad M., Malaysian Journal of Chemistry, 8, 37–44 (2006).
- [8] Daik R. and Maniam S., Malaysian Journal of Chemistry, 9, 16 (2007).
- [9] Jahia M., Journal of Nonlinear Optical Physics &Maerialst,19, 269,280(2010).
- [10] Fichou D., Journal of Material Chemistry, 10, 571,588(2000).
- [11] Bloisi F., Cassinese A., Papa R., Vicari L., and Califano V., Thin Solid Films, 516, 1594,1598, (2008).
- [12] X. Ma, G. Li, H. Xu, M. Wang, and H. Chen, Thin Solid Films,515, 2700, 2704(2006).
- [13] Amir E., Antoni P., Campos L. M., Damiron D., Gupta N., Electronic Supplementary Material (ESI), The Royal Society of Chemistry Journal, (2012).
- [14] Ishchenko,A.A., Pure Appl. Chem., 80,1525–1538 (2008).

- [15] Gandhi S., Ramakrishnan T., Sivabalan A., Dhanalakshmi V., J. Mater. Sci., 45,1688 (2010).
- [16] Gupta V. and Mansingh A., Journal of Applied Physics, 80,1063-1073 (1996).
- [17] Lentz C., Samuel B., Foley H. and Haque M., Publishing Corpoation, Journal of Nanomaterials,1,8 (2011).
- [18] Harun M., Saion E., Kassim A., Hussain M., Mustafa I. and Omer M., Malaysian Polymer Journal (MPJ), 3,24-31 (2008).
- [19] Samah H. K.,Journal of Thi-Qar University ,13(1),25-42(2018)
- [20] Samah H. K., Athraa H. M, Global Journal of Pure and Applied Chemistry Research, 5,1-8 (2017).
- [21] Mahanta D., Madra G., Radhakrishnan S. and Patil S., J. of Physc. Chemisty, 113,2293 (2009).
- [22] Akansson E. H., Lin T., Wang H. and Kaynak A.,Synth. Meta. , 156,1194 (2006).