

SYNTHESIS OF POLY PYRROL, IT'S COMPOSITE WITH POLY ACRYLIC ACID AND STUDY OF THEIR ELECTRICAL PROPERTIES

Nadia A. Hussein Al-Assady, Baryham Saad Abdul Samad & Nazar A. Hussein

Department of Chemistry, College of Education, Basrah University, Basrah, Iraq

ABSTRACT

Poly pyrrol, poly acrylic acid, their composite were prepared and identified by FTIR and UV spectroscopy. The thermal stability of the compounds were studied by TG thermal analysis. The study shows that the compounds were stable till about 300 0 C. The x-ray diffraction shows a crystal structures and the d-spacing of the crystallites were calculated. The morphology of the compounds were studied by scanning electron microscope. The dc electrical conductivity of the doped and un-doped compounds were measured and compared.

KEYWORDS: *Poly Pyrrol, Poly Acrylic Acid, Composite, Blend, TG, X-Ray Diffraction, SEM and Dc Electrical Conductivity*

Article History

Received: 20 Jan 2019 | Revised: 01 Feb 2019 | Accepted: 21 Feb 2019

INTRODUCTION

Most of the polymers have low electrical conductivity or insulators so they either used for their mechanical properties, while due to their good electrical insulating properties they usually as electrical insulators (1-4). This picture was changed since 1977 after the discovery of the electrical conduction of some polymers by Alen Heeger, MacDiamid and Shirakawa (5). These kinds of polymers brought a lot of attention, due to their applications in the electrical industris because those materials have many important properties such as cheap prices, ease of manufacture, the possibility of change of their properties with the change of their chemical and crystalline structure, the wide possible area in addition to the possibility of making integrated circuits with micro dimensions. All that make the applications of polymers easier than the application of inorganic semiconducting techniques (5). The applications of the polymers in the electrical applications opened a new field called the molecular electronics (6-9). The basic properties of the bonds). The electrical π -conducting polymers is the presence of conjugated double bonds (conductivity increases with doping of the polymers (by the addition of negative and negative charge carriers). The doping is usually done by the addition of weight percent of the solid dopants or volume percentage of solutions or expose to the material to a vapor of the dopant. The doping is usually done by chemical or electrochemical processes (10-13). There are many applications industrial mechanical and medical and optical fields in addition to the applications in the rechargeable batteries and vital sensitivity (14, 15). They are used as diodes and transistors and light emitter diodes (16-23) and other applications (24-26). In this work, Poly pyrrole, poly acrylic acid, their composite and blends were synthesized and studied their thermal stability, morphology, crystallinity and electrical properties without doping with iodine and without doping.

Synthesis of Poly Pyrrole (PPY)

In a 250 ml conical flask, a solution of 1.48 ml of the monomer, pyrrole, in 50 ml ethanol was added and stirred for 15 minutes. In a 250 ml beaker, another solution was prepared by dissolving 1.623 gm of anhydrous Ferric chloride (FeCl_3) in a mixture of 75 ml ethanol and 25 ml of distilled water. The second solution two was added, by using a separating funnel, to the first solution with continuous stirring by using. The stirring was continued for 24 hours.

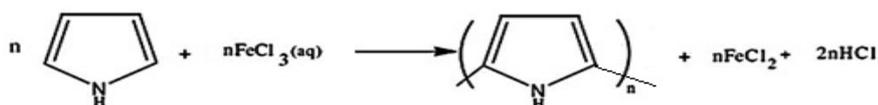


Figure 1: Synthesis of PPY

A black precipitate was formed (27). The black precipitate was filtered and washed with distilled water then with acetone to remove the unreacted pyrrole and ferric chloride. The black precipitate, PPY, was dried at 65 °C. Figure 1 shows the synthesis reaction.

Synthesis of Poly Acrylic Acid (PAA)

In a 250 ml conical flask, 5 gm of acrylic acid was dissolved in 10 ml of distilled water. This solution was neutralized, by adding gradually with shaking, a basic solution prepared by dissolving 5 gm of sodium hydroxide in 25 ml of distilled water (28). During the addition the temperature was kept within 50 °C by checking with thermometer. To the neutralized solution 0.025 gm of methen bisacrylic amid, then 2 ml of hydrogen peroxide, then 0.4 gm of ascorbic acid (10%). The mixture was stirred for 2 hours with magnetic stirrer. The solid precipitate was dried under vacuum at 55 °C.

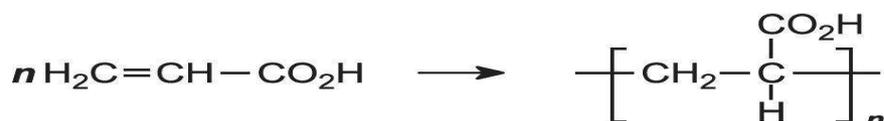


Figure 2: Synthesis of Poly Acrylic Acid

Preparation a Composite of PPY with PAA

To a 250 ml conical flask 1 ml of PPY was added to a mixture of 4.8 gm of anhydrous ferric chloride soluble in 50 ml ethyl acetate. A solution of 0.6 gm of poly acrylic acid soluble in 50 ml of distilled water then added to the above mixture (29, 30). The overall mixture then stirred for five hours. A black precipitate was formed, filtered and washed with distilled water, left to dry at room temperature.

Doping of the Polymers

Iodine doping of the studied compounds (PPY, PAA, composite and blend) where 0.1 gm of the polymer or the composite or the blend was mixed well with 0.01 gm of iodine and less amount of dimethyl formaldehyde (DMF) (31) For conductivity measurement, the mixture was casted on the glass substrate and the solvent was dried.

Identification of the Compounds

a- IR Spectroscopy

Figures 3-5 show the IR spectra for the PPY and PAA and a composite of PPY with poly acrylic acid respectively (27-30). Figure 3 shows bands at 3419 cm⁻¹ which is attributed to the stretching vibration for the NH group. The band at 1550 cm⁻¹ might be attributed to the C-N stretching (32, 33). Figure 3 shows bands at 1714 CM⁻¹ and at 3317 cm⁻¹ which are attributed to the C=O and OH stretching respectively. Figure 5 appears as it is shows features of the constituent's spectrums.

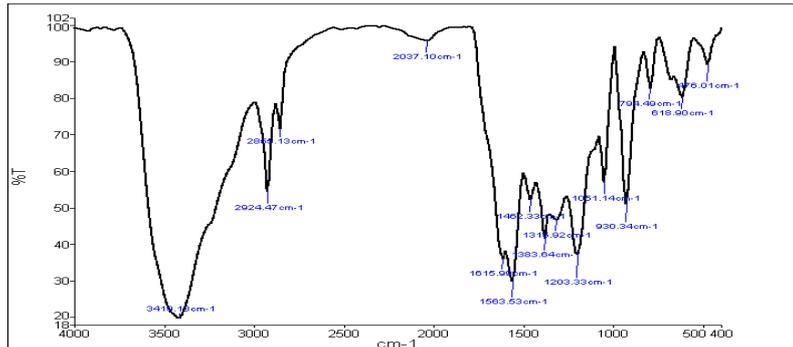


Figure 3: The IR of PPY

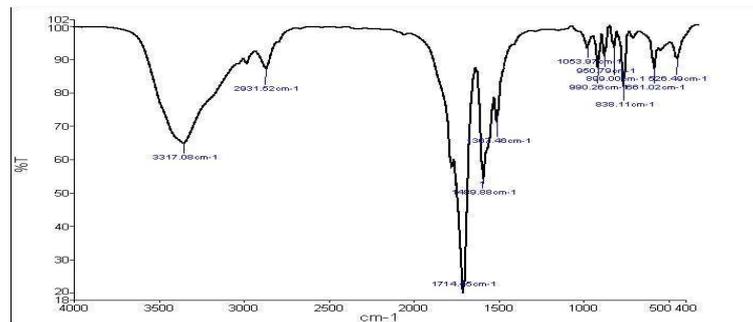


Figure 4: The IR Spectrum of PAA

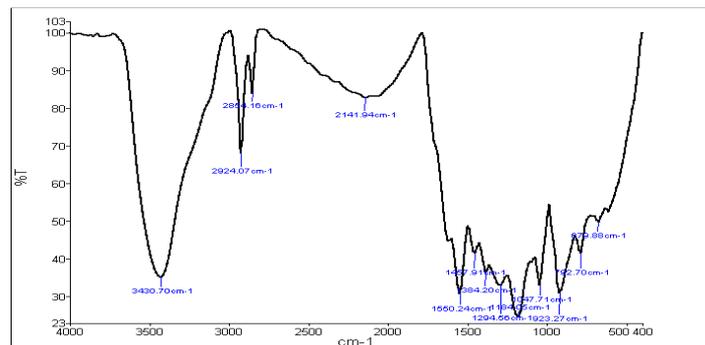


Figure 5: The IR Spectrum of the Composite PPY and PAA

Uv Spectroscopy

Figures 6 shows the uv spectrum for PPY. The figure shows main band with λ max at 502 nm in addition to a band with λ max at 343 nm. Figure 7 shows the Uv spectrum for a composite of PPY and poly acrylic acid (30, 33). These bands are attributed to the π→π* and n→π* transitions.

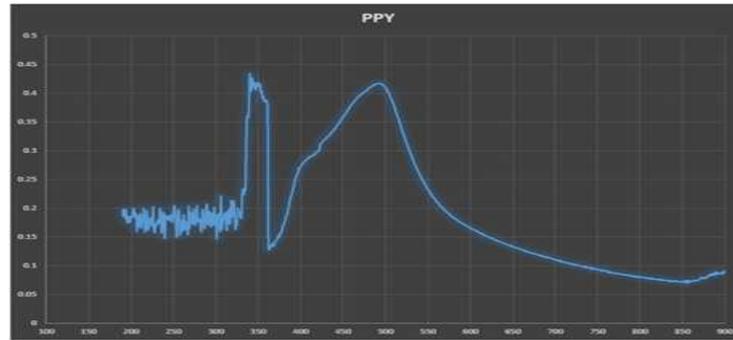


Figure 6: The UV Spectrum of PPY

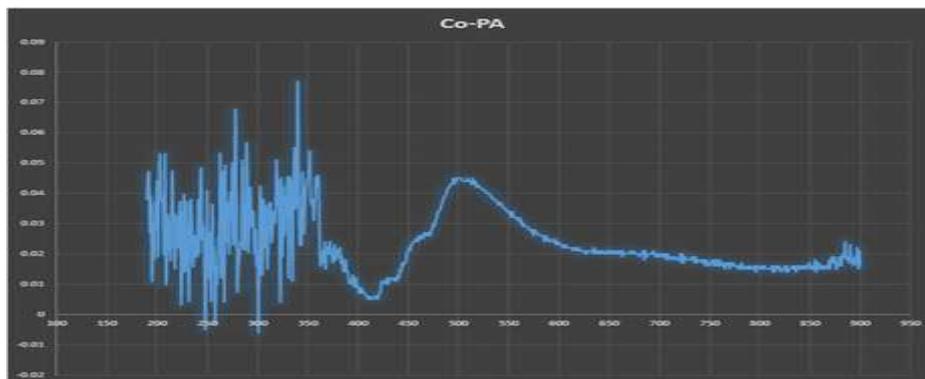


Figure 7: the UV Spectrum of PAA

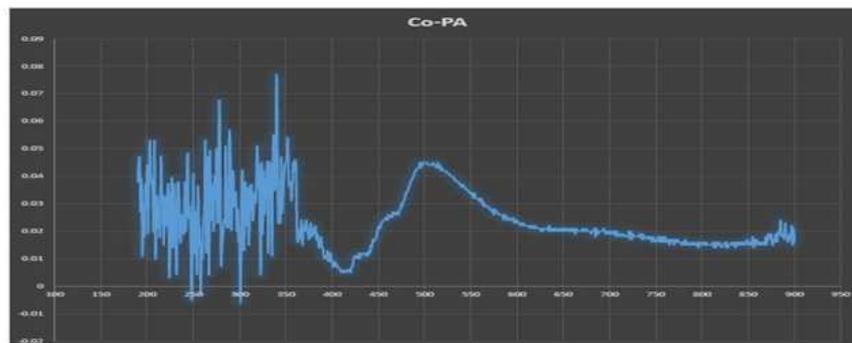


Figure 8: the UV Spectrum of (PPY/PA)

Thermal Analysis

Figures (9-11) show the TGA thermogram for PPY, PAA acrylic acid and a composite. Table 1 shows a thermal functions (T_i , $T_{50\%}$ and T_f) of the studied compounds. The Tg diagrams and table1 shows the stability of the polymers and their composite. From the table the T_i is the highest for the Composite while the T_f is for the PPY which might be because the composite increases the temperature of decomposition⁽³⁰⁾

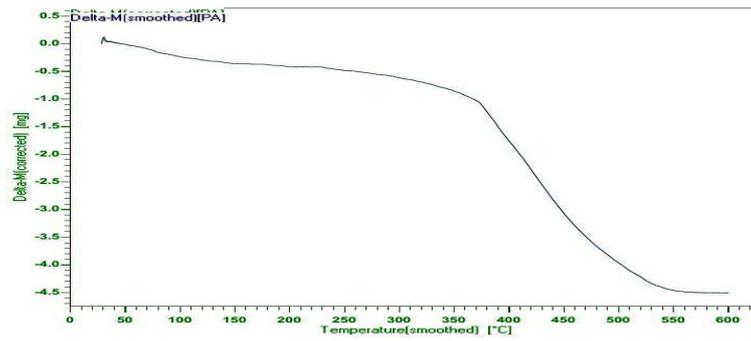


Figure 9: The TG Thermogram of the PAA

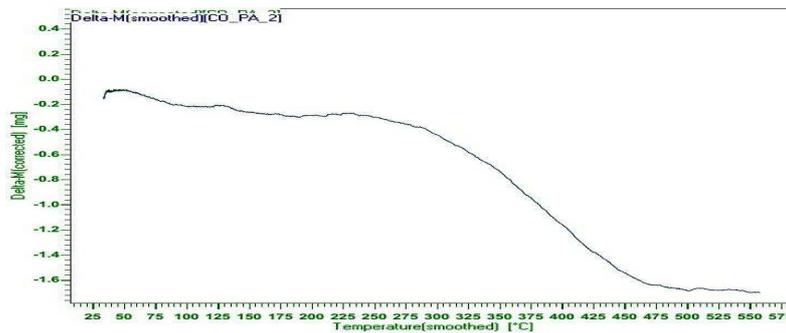


Figure 10: The TG Thermogram of the Composite of PPY with PAA

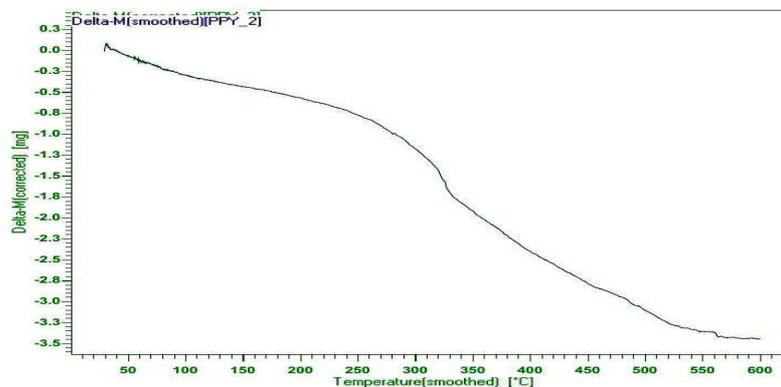


Figure 11: The TG Thermogram of the Composite of PPY

Table 1: the Thermal Function of the Polymers and Their Composite

Compounds	T _I °C	T _{50%} °C	T _f °C
PPY	240	340	560
PAA	350	440	540
Composite	380	370	460

X-Ray Diffraction (XRD)

Figures (12-14) shows the X-ray diffraction patterns of PPY, PAA and PPY-PAA composites. The XRD results shows that PPY is more amorphous while PAA compound has more crystalline reigns. Table 2 shows the twice value of the diffraction angle and the crystallites of the polymers calculated according to Bragg's law ^(27- 29). The poly acrylic acid shows more crystalline sites as it is shown in figure 12.

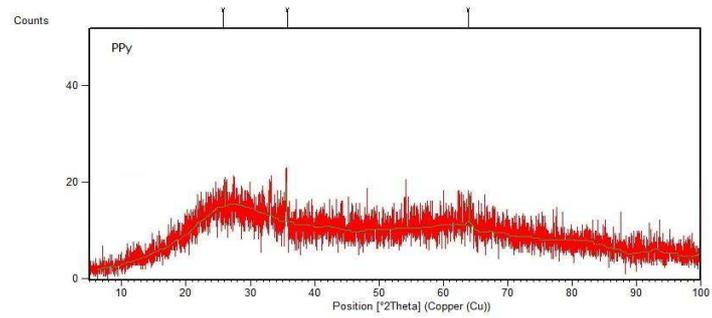


Figure 12: The X-Ray Diffraction of PPY

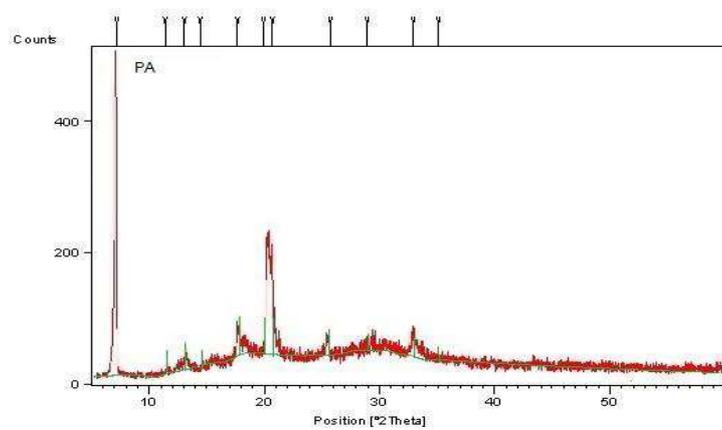


Figure 13: The X-Ray Diffraction of PAA

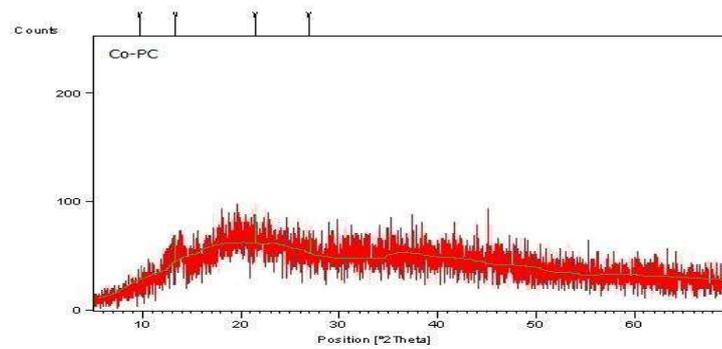


Figure 14: The X-Ray Diffraction of the Composite

Table 2: The X- Ray Diffraction Data Taken from the x-Diffraction Figures

The Compounds	[.Th2 ⁰]	Spacing Å-d
PPY	26.03	3.66
	35.31	2.95
	64.85	1.76
PAA	12.65 11.39	9.02
	14.24	8.13
	15.37	7.21
	21.25	6.39
	33.05	4.85
		3.14
Composite	18.57	5.46
	3.35.13	2.97

Scanning Electron Microscopy (SEM)

Figures (15-17) shows the scanning electron microscopic images of the prepared compounds, PPY, PAA and PPY-PAA composite. The SEM image of PPY polymer is appeared that the prepared sample is formed as circular particles aggregated together. However, the particles of PPY have diameter less than that for PAA and also it is appeared more aggregated. The SEM images (Fig. 13C) shows that the composite sample has various surface morphology. PPY-PAA is formed as a bulk and some of sample appeared as a slides overlapping each other. The composite figure shows a morphology with large bodies with scale of 5µm⁽²⁷⁻²⁹⁾. Patel et al. noted that the PPY that prepared through chemical bath is structured as spherical granular⁽³⁴⁾.

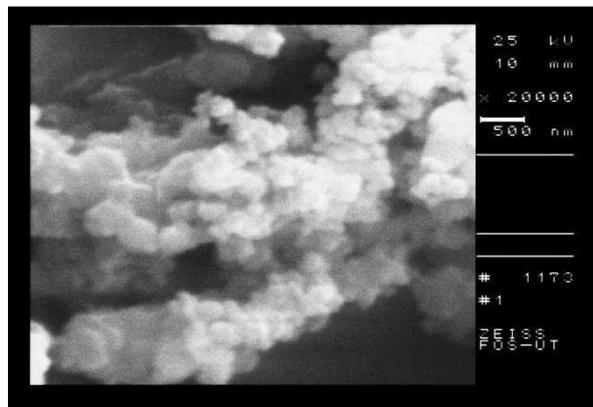


Figure 15: SEM for PPY

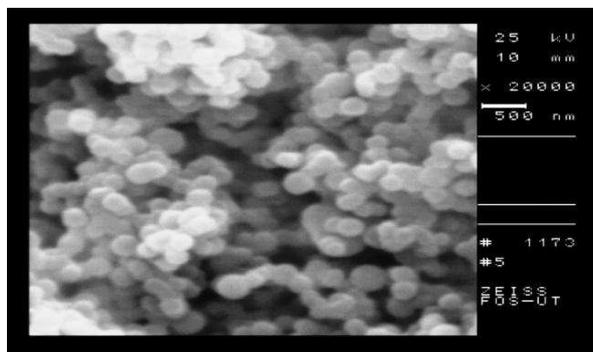


Figure 16: SEM for PAA

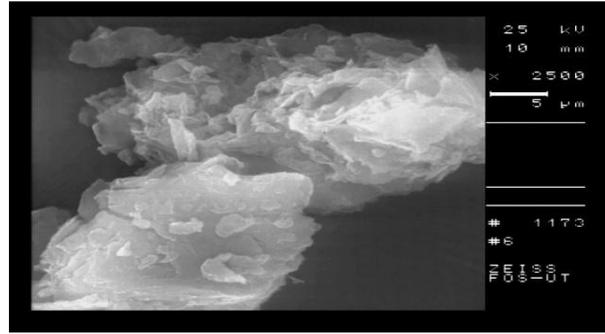


Figure 17: The SEM for the Composite

The Electrical Properties

The DC electrical properties of the prepared compounds (Iodine doped and un doped) were carried out using a circle containing voltmeter and ammeter. The samples were casted as thin films on glass cells made up of fluorine tin oxide (FTO) as sandwich cells (Figure 18). The FTO is conductive from one side which is connected to the circuit electrodes. The sample thickness (L) was 0.5 mm (measured by micro Vernier). The area of the electrode (A) is 1 cm². The cell constant (L/A) is 0.05 cm². The cells were placed in variable temperature cryostat (27, 35). The DC conductivity was measured in a temperature range 300- 400 K (see Fig)

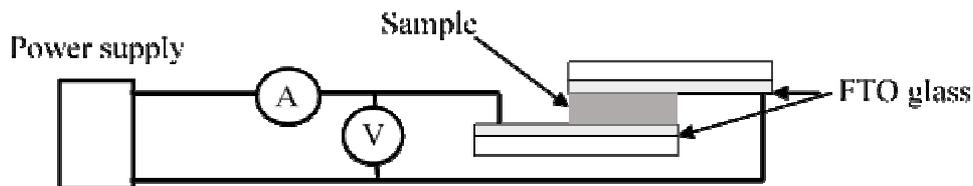


Figure 18: The Electrical Circuits Used for the Dc Electrical Conductivity

Using Arrhenius equation $\ln \sigma = \ln \sigma_0 - \frac{\Delta E}{kT}$ where σ_0 is the pre-exponential factor and σ is the dc conductivity. The relations between $\ln \sigma$ and the reciprocal temperature were drawn and the activation energy for each relation were calculated from the slope of the graphs. Figure 19 shows the dc electrical conductivity vs. the reciprocal temperature for undoped PPY, PAA and the composite. In general, the compounds show semiconducting properties due to the increase of conductivity with temperature. The picture shows the following sequence:

Composite > PAA > PPY

It seems that composite and blend act as alloys and shows better conductivity in compared the polymers themselves.

Figure 20 shows the dc electrical conductivity vs. the reciprocal temperature for doped PPY, PAA, and their composite. They show, also, semiconducting properties because the increase of conductivity with temperature. The picture shows the following sequence:

Composite > PAA > PPY

Iodine increase the conductivity for all compounds which may be due to the oxidation of the compounds (n-doped)

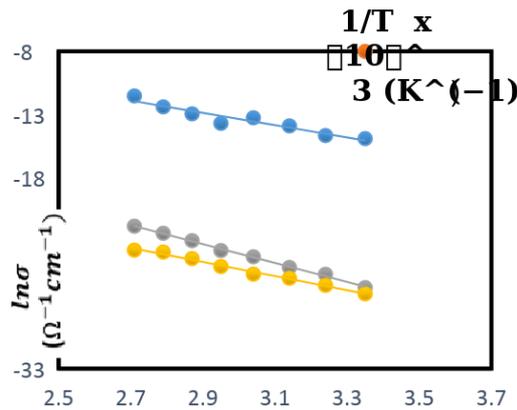


Figure 19: The Dc Electrical Conductivity for Undoped Compounds The Composite, 2. PAA, 4. PPY

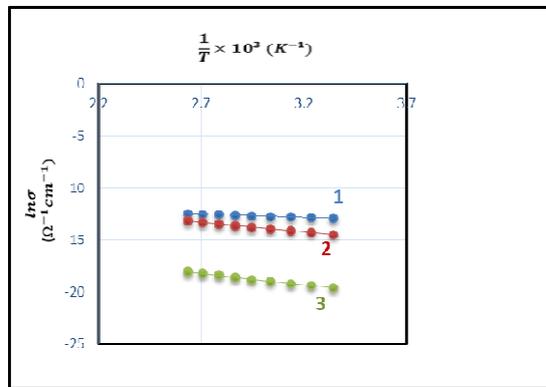


Figure 20: The Dc Electrical Conductivity for the Doped Compounds The Composite, 2. PAA, 3. PPY

CONCLUSIONS

From the experimental results we can conclude that the composite is more electrical ngconductive than the PPy and PAA before and after dopin

ACKNOWLEDGMENT

Our sincere thanks to Dr. Mazin M. Awni for his valuable assistance in the electrical properties measurements in addition to his other assistances and advices. The compounds shows thermal stability with amorphous and crystalline regions

REFERENCES

1. R. W. Dyson, "Specialty Polymers", Champan and Hall, N.Y., 3 (1986).
2. A. R. Blyth, "Electrical Properties of Polymers ", Cambridge University Press, London (1977).
3. S. D. Sentukia, ANTEC 43, 414 (1985).
4. J. Mot and G. Pfisten, "Electronic Properties of Polymers ", John Wiley and Sons INC.(1982).

5. H. Shirakawa, E. J. Louis, A.G.MacDiarmid, CK. Chiang, A.J. Heeger., *J. Chem. Soc. Chem. Commun.*, 80,578(1977).
6. G. Tourillon and F. Garnier, *J. Electro. Chem.*, 135, 173 (1982).
7. J. paloheimo, E. Punkka, P. Kuivalain, H. Stubb and P. Yli," *Acta Polytechnica Scandinavica*, " , 64, 178(1989).
8. K. Kaneto, T. Asano and W. Takashinma" *Jpn. J. Appl. Phys.*" 30, 215,(1991).
9. T. A. Skotheim, "*Hand Book of Conducting Polymer*", Marcel Dekker, N.Y., (1988).
10. D. D. Zhou, XT. Cui, A. Hines, R. J. Greenberg" *Conducting polymers in neural*
11. *Stimulation applications*". Springer, Berlin (2010).
12. N. K. Guimard, N. Gomez, C. E. Schmidt. "Pro. Poly. Sci"32, 876(2007).
13. M. C Cortés, J. C. Moreno"Polymers"41(2003).
14. K. J. Gilmore. "Biomaterials"30,304(2009).
15. K. Tapan. Das and Smita Prusty" *Polymer-Plastics Technology and Engineering*" 51, 1487, 2012.
16. K. E. Geckeler, B. Muller" *Naturwissenschaften*" (1993).
17. J. Kanicki, "Polymer Semiconductor Contacts and Photovoltaic Applications, In: *Handbook of Conducting Polymers*" Marcel Dekker, New York (1986).
18. J. H. Burroughes, C. A. Jones, R. H. Friend" *Nature*",137, 335 (1988).
19. G. Horowitz, F. Garnier" *Solar Energy Matter*"13, 47 (1986).
20. A. Tsumura, H. Koezuka, T. Ando" *Appl. Phys. Lett*". 9 (1986) 1210
21. W. Kobel, H. Kiess, M. Egli" *Synth. Met*" 22, 265 (1988).
22. R. H. Friend "Synth. Matt"51, 357 (1992).
23. P. L. Burn, A. B. Holmes, A. Kraft, D. D. C. Bradley, A. R. Brown, R. H. Friend, R. W. Gymer," *Nature*" 47 (1992) 356.
24. S. Roth, W. Graupner, "Synth. Matt" 55, 3623(1993).
25. K.-H. Kochem, U. Meer, H. Millauer," *Kunststoffe*" 82,575 (1992).
26. N. F. Colameri, L. W. Schacklette, "IEEE Trans. Instrum. Meas"9. 41 (1992).
27. D. H. Kim, S. M. Richardson-Burns, J. L. Hendricks, C. Sequera, D. C. Martin. "Adv Funct Matter" 17, 79(2007).
28. K. Hemant, V. B. Narendra. E. Vasant and N. Ganesh; *Journal of Sensor Technology*, 1,47(2011).
29. J. Loiseau, N. Doerr, J. M. Suau, J. B. Egraz, M. F. Liauro and N. Ladayire; *Macromolecule*, 36(9),2066(2003).
30. V. Vetriselvi and R. J. Santhi; *Res, J, Chem. Sci*, 4(5),1(2014)

31. P. J. Ichikadokawa, M. Akimurakumi and Y. Kaneko, "Composite science and technology", 68(2), 493(2008)
32. G. J. Cruz, M.G. Olayo, O. G. López, O. M. Gómez, J. Morales and R. Olayo, *Polymer*, 19, 4314 (2010).
33. M. Nakayama, J. Yanok. N. KOgura; *Synthetic Metals*, 138(3), 419(2003)
34. B. K. Sharma, *Spectroscopy*, GOEL publishing house, India (2005). 34. D. S. Patil, S. A. Pawar, A. S. Kamble, P. S. Patil," Silver Incorporated Polypyrrole/Polyacrylic) Acid Electrode for Electrochemical Supercapacitor, International conference on recent trends in applied physics and materials science AIP Conf. Proc. 1536, 1182(2013).
35. S. Madakbas, F. Dumbudag, E. M. Eminoglu, F. Sen. and M. V. Kahraman; *Progress in organic coating*, 80, 33(2015).

