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## Synthesis of Poly Pyrrole, it's Composite With Poly Methyl Methacrylate and Study of Their Electrical Properties.

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### Abstract

Poly pyrrole, poly methyl methacrylate, their composite were prepared and identified by FTIR and UV spectroscopy. The thermal stability of the compounds were studied by TG/DSC thermal analysis. The study shows that the compounds were stable till 225-2500C. The x-ray diffraction shows a kind of crystal structures and the d-spacing of the crystallites were calculated. The dc electrical conductivity of the doped and un-doped polymers were measured and compared.

**Key Words:** Poly pyrrole, poly methyl methacrylate, composite, TG, x-ray diffraction, and dc electrical conductivity.

### 1.Introduction

Most of the polymers have low electrical conductivity or they are insulators so they either used for their mechanical properties, while due to their good electrical insulating properties they usually used 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 industries because those materials have many important properties such as their cheap prices, ease of manufacture, the possibility of changing 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[4,5]. The applications of the polymers in the electrical applications opened a new

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field called the molecular electronics. The basic properties of the conducting polymers is the presence of conjugated double bonds ( $\pi$ -bonds). The electrical conductivity increases with doping of the polymers by the addition of negative or positive charge carriers[6-9].

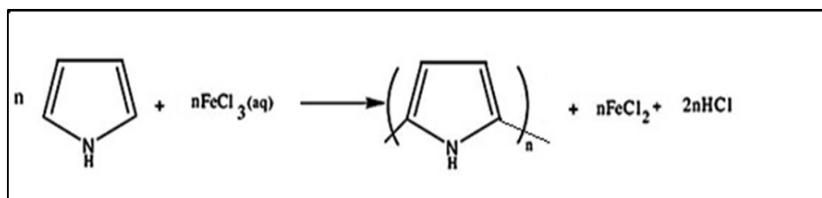
Doping is usually done by the addition of weight percent of the solid dopants or volume percentage of solutions or exposure of the material to a vapor of the dopant. The doping is usually done by chemical or electrochemical processes [ 10-13]. There are many other applications in industrial, mechanical, 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 methyl methacrylate, their composite were synthesized and their thermal stability, morphology, crystallinity and electrical properties without and with iodine doping were investigated.

## 2. Method

### 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 ( $\text{FeCl}_3$ ) in a mixture of 75 ml ethanol and 25 ml of distilled water. Fig.1. The second solution two was added gradually by using a separating funnel, to the first solution with continuous stirring. The stirring was continued for 24 hours.



**Fig. 1- Synthesis of PPY.**

A black precipitate was formed[3,27]. The black precipitate was filtered and washed with distilled water and then with acetone to remove the unreacted pyrrole and ferric chloride. The black precipitate, PPY, was dried at 65  $^{\circ}\text{C}$ . Figure1 shows the synthesis reaction.

### Synthesis of poly methyl methacrylate(PMM):

( $\text{C}_5\text{H}_8\text{O}_2$ )<sub>n</sub> was purchased from Aldrich chemical company with purity of 98%.

This polymer can be synthesized by free radical or ionic addition polymerization[28]. Fig2.

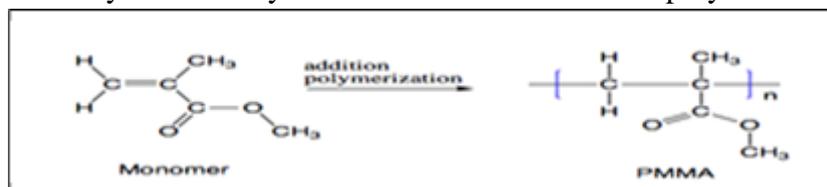


Fig. 2- Synthesis of PMM

### Preparation of PPY/PMM composite:

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 methyl methacrylate dissolved in 50 ml of chloroform 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, PMM, composite) was carried out by mixing of 0.1 gm of the polymers or the composite with 0.01 gm of iodine and less amount of dimethyl formaldehyde (DMF)[31].The mixture was casted on a glass substrate and the solvent was dried.

## 3. Results and Discussion

### Identification of the compounds

#### IR spectroscopy:

Fig. 3-5 show the IR spectra for the PPY and PMM and a composite respectively [27-30]. Figure 3 shows bands at  $3419\text{ cm}^{-1}$  which is attributed to the stretching vibration for the N-H stretching group. The band at  $1550\text{ cm}^{-1}$  might be attributed to the C-N stretching[32, 33]. Figure 4 shows bands at  $2996\text{ cm}^{-1}$ ,  $1732\text{ cm}^{-1}$  and  $1390\text{ cm}^{-1}$  which are attributed to C-H stretching, aliphatic, and C=O stretching and C-N stretching respectively. The band at  $3438\text{ cm}^{-1}$  could be attributed to O-H stretching which could be attributed to the trace of water. Figure 5 shows bands at  $3436\text{ cm}^{-1}$ ,  $2924\text{--}2864\text{ cm}^{-1}$ ,  $1771\text{ cm}^{-1}$  and  $1630\text{ cm}^{-1}$  which is attributed to N-H stretching, C-H stretching aliphatic, C=O stretching and C-N stretching respectively.

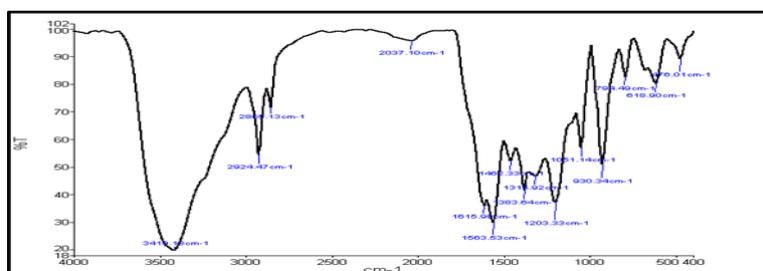
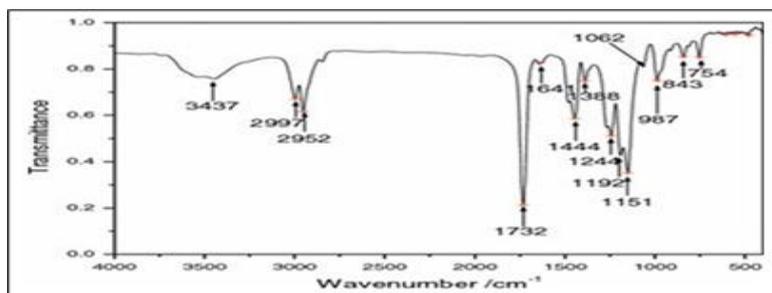
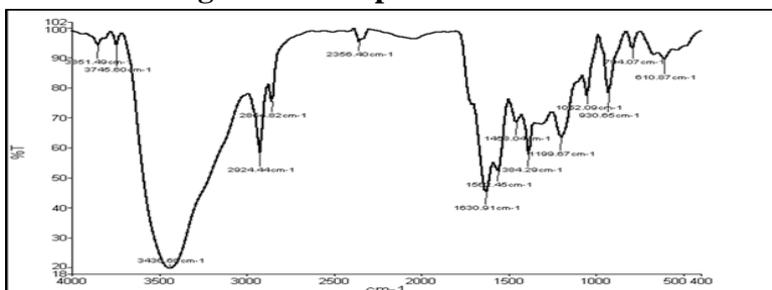


Fig. 3-The IR of PPY.



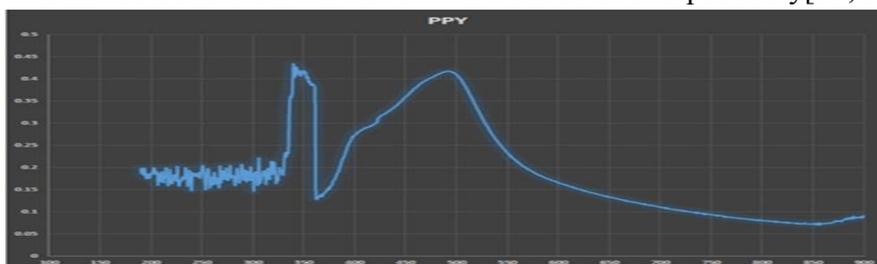
**Fig. 4-The IR spectrum of PMM.**



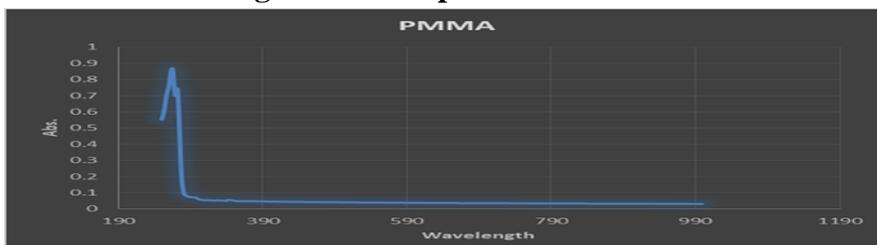
**Fig. 5-The IR spectrum of the composite of PPY and PMM.**

### Uv spectroscopy:

Figs. 6-7 shows the Uv-visible spectrum for PPY. The figure shows main band with  $\lambda_{max}$  at 475 nm which is attributed to  $\pi \rightarrow \pi^*$  in addition to a band with  $\lambda_{max}$  at 343 nm which is attributed to  $n \rightarrow \pi^*$ . Figure 7 shows the Uv –visible spectrum for PMM. It shows band at 206 nm which is attributed  $\pi \rightarrow \pi^*$  transition. no more bands are appear at the higher wave lengths suitable for use as uv filters due to their high absorption in the region 400 nm[34]. Figure 8 shows the uv-visible spectrum for the composite(PPY/PMM). It shows bands at 360 nm and 506 nm which is attributed to the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions respectively[30, 33].



**Fig. 6- The uv spectrum of PPY.**



**Fig. 7- The Uv spectrum of PMM.**

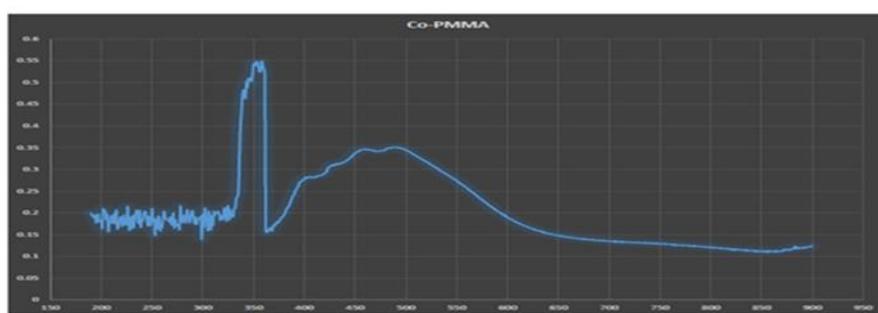


Fig. 8- The UV spectrum of (PPY/PMM)

### Thermal analysis:

Figs. 9-11 show the TGA / DSC thermogram for PPY, PMM and their composite. Table 1 shows a thermal functions ( $T_i$ ,  $T_{50\%}$  and  $T_f$ ) of the studied polymers. Figures 9 and 11 shows that the PPM and the composite might release water molecules which might be caused by humidity. The diagrams and table1 show the stability and the weight change of the polymers and their composite with heating till 7000C . From the table the  $T_i$  is the highest for the PMM while the  $T_f$  is for the composite which might be because the composite structure increases the temperature of decomposition[(30)].

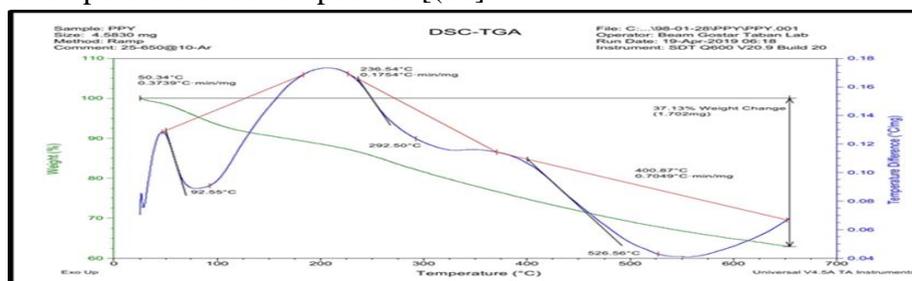


Fig. 9- The TG/DSC thermogram of the PPY.

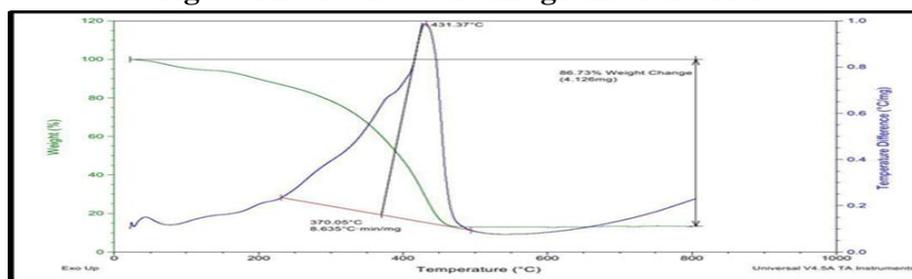


Fig. 10- The TG/DTA thermogram of the composite of PMM.

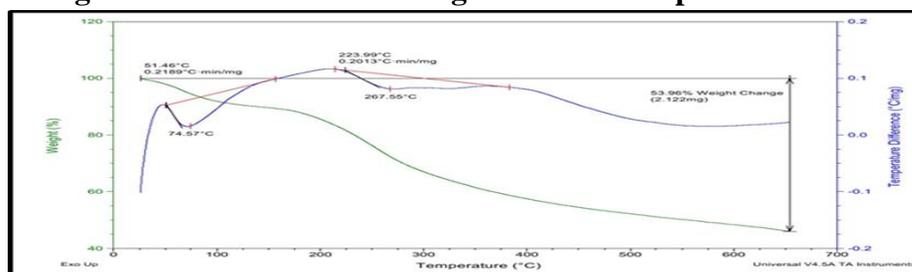


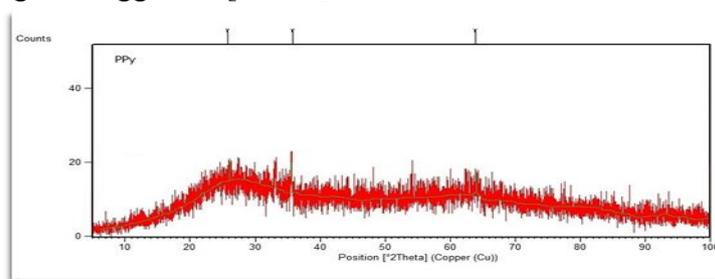
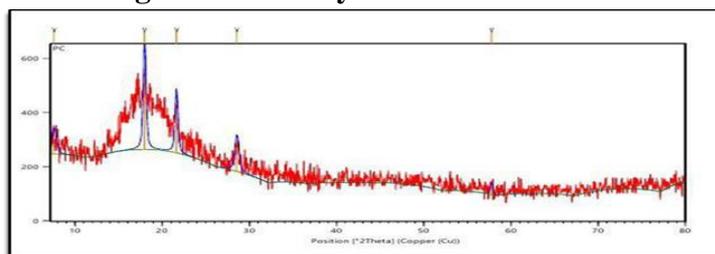
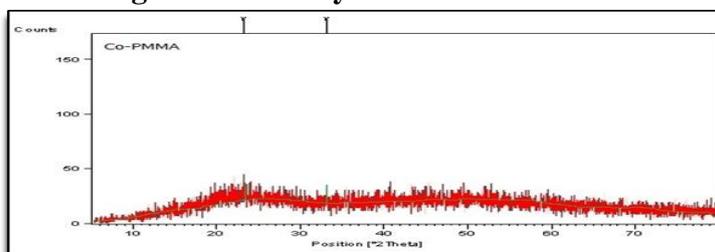
Fig. 11- The TG/DSC thermogram of the composite of PPY/PMM.

**Table 1- The thermal functions of the polymers and their composite.**

Compounds	T <sub>i</sub>	T <sub>50%</sub>	T <sub>f</sub>
PPY	240	340	520
PMM	250	350	475
Composite	225	267	600

**X-ray diffraction (XRD):**

Figs. 12-14 shows the X-ray diffraction patterns of PPY, PMM and the composites. The XRD results shows that PPY and the composite are more amorphous while PMM compound has some crystalline region due to the presence of sharp peaks. Table 2 shows d-spacing calculated according to Bragg's law[27- 29].

**Fig. 12- The x-ray diffraction of PMM****Fig. 13- The x-ray diffraction of PMM.****Fig. 14- The x-ray diffraction of the composite.****Table 2- The main x- ray diffraction data taken from the x-diffraction figures.**

Polymer	2 <sup>0</sup> Th	d-spacing Å
PPY	26.03	3.66
	35.31	2.95
	46.85	1.76

PMM	14.32	6.18
	15.43	5.74
Composite	23.13	4.46
	33.04	3.14

### The electrical properties:

The DC electrical properties of the studied polymers (Iodine doped and un doped) were carried out using a circuit containing voltmeter and ammeter. The samples were casted as thin films on glass cells made up of fluorine tin oxide (FTO) as sandwich cells (Fig. 15). 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  $1 \text{ cm}^2$ . The cell constant ( $L/A$ ) is  $0.05 \text{ cm}^2$ . The cells were placed in variable temperature cryostat [27, 35,36]. The DC conductivity was measured in a temperature range 300- 400 K (see Figs-16-20).

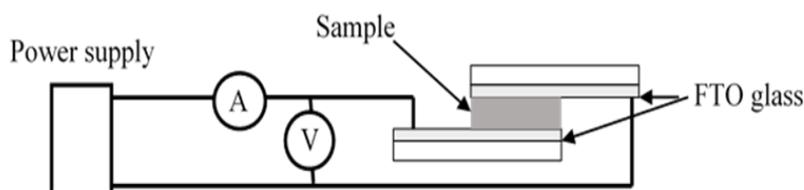


Fig. 15- The electrical circuits used for the Dc electrical conductivity.

Using Arrhenius equation  $\ln \sigma = \ln \sigma_0 - \Delta E / KT$

Where  $\sigma$  and  $\sigma_0$  are the dc conductivity and pre-exponential factor.

The relations between  $\ln \sigma$  and the reciprocal temperature were drawn up and the activation energy for each relation were calculated from the slope of the graphs.

Fig. 16 shows the dc electrical conductivity vs. the reciprocal temperature for undoped PPY, PMM and the composite. In general, the compounds show semiconducting increase of conductivity with temperature. The conductivity sequence is due to behaviors

$$\text{Composite} > \text{PMM} > \text{PPY}$$

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

Fig. 17 shows the dc electrical conductivity vs. the reciprocal temperature for doped PPY, PMM, and their composite. They show, also, semiconducting behaviors due to increase of conductivity with temperature. The conductivity sequence is:

$$\text{Composite} > \text{PPY} > \text{PMM}$$

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

The activation energy calculated from Arrhenius equation and the exponential factor calculated at 25 °C is shown in table 1. The table shows that the doped polymers have lower

activation energy and the doped composite is of the lowest activation energy. The low activation energy of the un-doped polymers in general refers that conductivity is extrinsic due to the presence of oxygen[37].

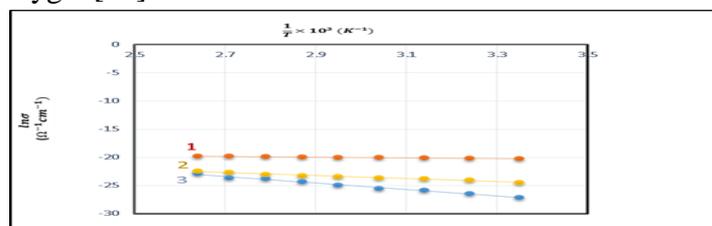


Fig. 16- The dc electrical conductivity for undoped PMM,1-composite, 2-PMM, 3- PPY.

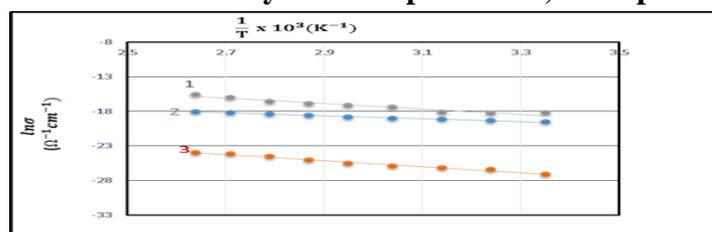


Fig. 17- The dc electrical conductivity for doped PMM 1-Composite.I, 2-PPY.I, 3-PMM.I

Table1- The activation energy and the pre-exponential factor.

Polymer	$\Delta E(\text{eV})$	$\sigma_0$ $\text{ohm}^{-1}\text{cm}^{-1}$
PPY	0.047	$8.5 \times 10^{-21}$
PPY.I	0.032	$1.2 \times 10^{-17}$
PMM	0.067	$9.2 \times 10^{-23}$
PMM.I	0.038	$1.8 \times 10^{-22}$
Composite	0.039	$5.5 \times 10^{-20}$
Composite. I	0.025	$4.9 \times 10^{-15}$

#### 4. Conclusion:

From the experimental results we can conclude that the composite is more electrical conductive than the PPY and PMM, PMM is better crystalline structure and more thermal stability.

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