

## **THERMAL ACTIVATION OF CONDUCTING POLYPYRROLE/ZEOLITE**

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### **ABSTRACT**

In this paper the influence of dopant on the electrical properties of polymer prepared by chemical reaction method is investigated using the standard four point probe technique. Polymers are formed by using pyrrole and Iron (III) Chloride 6-hydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) as well as zeolite as dopants. The current-voltage was measured from 300 to 400 K. The current-voltage characteristic of all samples shows that measured voltage increased linearly with current. It was found that conductivity increases with temperature and concentration of the dopant. As expected, the d.c. conductivity ( $\sigma$ ) of polypyrrole  $\text{FeCl}_3/\text{PPy}/\text{Zeolite}$  was found slightly higher than  $\text{FeCl}_3/\text{PPy}$  which to be considered that zeolites have altered and enhanced the conductivity of the samples. The increases of conductivity may consider have improved the thermal stability of the blends. An explanation is proposed based on the character and conduction mechanism of  $\text{FeCl}_3/\text{PPy}/\text{Zeolite}$ .

### **INTRODUCTION**

Recently, polypyrrole (PPy) has attracted considerable attention due to its varied potential applications in batteries [1], supercapacitors [2], sensors [3], microwave shielding and corrosion protection [4]. As we know, the electrical conductivity of PPy is attributed to the electron hopping along the polymer chains with conjugating bonds [5]. As a result, more positively charged PPy, more electron available, longer polymer chains and more co-planarity between interchains are favorable for a higher conductivity performance. As shown in literature [6-7], some efforts had been made on enhancing the conductivity and conductivity stability of PPy for its practical application. Meanwhile, in order to achieve a new function of PPy, one of the most efficient means is to confine and encapsulate conducting polymer into an inorganic solids with layered and porous structure since this enables us to combine characteristic of the parent constituent as a consequence of their molecular level interaction.

Zeolites are one of the most promising host materials owing to their highly ordered pore systems, channels and cages of different shapes and dimensions and the surface is negatively charge-balanced with exchangeable cations. In other hand, it is also expected that this kind of encapsulation protect the polymer from degradation, and which oxygen and moisture from the atmospheric air play a leading part. Aging, i.e. the

irreversible decrease of the electrical conductivity of the conducting polymer with time also have been the subject of studies as it has been the main restriction of their use in technological applications. The isolation of the functional PPy chains into the porous and the improving of their alignment are expected to decelerate aging and to increase their electrical conductivity.

To investigate the influence of zeolite on the conductivity of PPy, PPy/zeolite samples with different concentration were prepared and their d.c. conductivity was measured using a standard four point probe technique 300 to 400 K in the range of 5mA to 100mA.

## **EXPERIMENTAL**

### *Materials*

The chemical, pyrrole and zeolite were obtained from FLUKA while iron (III) chloride ( $\text{FeCl}_3$ ) was obtained from HmBG Chemicals. All these chemicals were used without any further purification except for pyrrole. Distilled water was used in this work.

### *Monomer*

Pyrrole (supplied by Fluka) was used as the monomer for the synthesis of PPy. Prior to use, pyrrole was distilled at a temperature of  $131^\circ\text{C}$  at atmospheric pressure stored at  $4^\circ\text{C}$  avoiding air.

### *Methods*

Pyrrole of 0.4 mole concentrations was mixed with 0.1 to 0.3  $\text{FeCl}_3$  together with zeolite dissolved in water and stirred for 6 hours at room temperature. Zeolite was added to the polypyrrole solutions in the proper quantity to obtain 2% w/w content of zeolite. The resulting powder were then filtered and washed thoroughly with distilled water to remove the adhered  $\text{Fe}^{3+}$  and dried under vacuum at  $50^\circ\text{C}$  for 36 hours. These steps were repeated for various mole ratio of oxidant/pyrrole. The sample was then grounded into fine powder and press into pellet at  $7 \text{ ton/cm}^2$  pressure. From this polypyrrole/zeolite disk shaped specimens 13 mm in diameter and about 0.8 mm thick were made in a Carver Hydraulic Presses.

The electrical conductivity was measured by four point probe technique from 300 to 390 K. Calculation of the conductivity was done by obtaining the value of the resistance from the I-V characteristic of the samples and through the following equation (1).

$$P_o = R \times 2\pi S \quad (1)$$

where  $P_o$  is resistivity, R is resistance and S is distance between probes (2.0mm) while the conductivity is inversely proportional to the resistivity.

## **RESULTS AND DISCUSSIONS**

The PPy conducting polymer and PPy/zeolite polymer were prepared through chemical reaction method. The conductivity at 300 K and activation energy,  $E_a$  of PPy and PPy/Zeolite blends is shown in Table 1 while the d.c. conductivity versus temperature

for PPy and PPy/Zeolite blends is shown by the data in Fig 1. The temperature dependence of the d.c. conductivity of polypyrrole is shown in figure 1 for various doping levels.

As can be seen in the figure, the conductivity increased and then decreased after hit an individual maximum temperature. The increased of the conductivity is attributed to an increase in charge-carrier concentration. Normally polymers are electrical insulator, but in conducting polymer backbone structure is conjugated and the existence of ionic dopant results in a delocalization of double bond electrons. Doping the acceptor or donor impurities can increase the conductivity of conducting polymers [8]. The positively charged in a polymer chain are compensated by negatively charged counterions, for example zeolite, which maintain the overall electroneutrality. In doped PPy, a positive charged and an unpaired electron associated with a quinoid structure is formed as a result of removal of an electron from a polymer chain [9]. It may be possible that zeolites form stronger bonds with electrons, which results in a increased of conductivity.

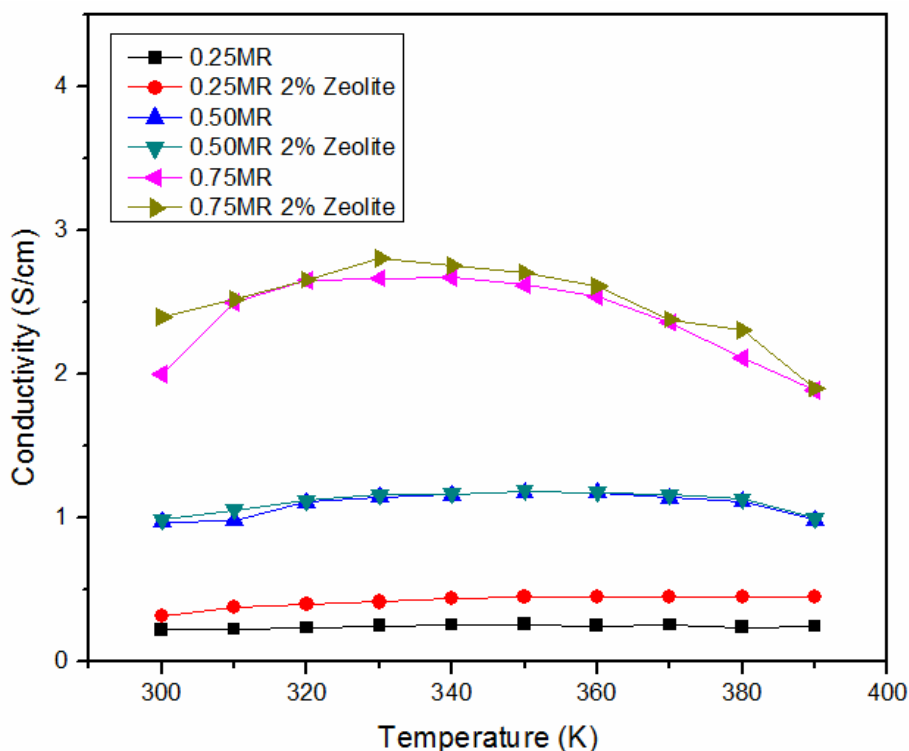


Figure 1: D.C. conducting versus temperature for PPy and PPy/Zeolite blends

Figure 2 (data listed in Table 1) shows the conductivity of PPy and PPy/zeolite polymer with different concentrations. The highest conductivity was recorded in the sample of PPy samples of 0.75MR is 2.00S/cm and PPy/zeolite of 0.75MR shows the highest conductivity 2.40 S/cm among all the PPy and PPy/zeolite samples. PPy samples of

0.25 and 0.5MR shows a slightly lower conductivity of 0.22 and 0.97 S/cm and was found to increase to 0.32 and 0.99 as the zeolite is introduced into Fe/PPy blends. As can be seen in Table 1, the activation energy of samples 0.25MR of Fe/PPy increased from 0.037 to 0.042 as the zeolite been introduced into the blend. In contrast to 0.25MR samples, the samples 0.5MR and 0.75MR shows the decreased of activation energy of 0.045 and 0.058 to 0.038 and 0.044 with the introduction 2% of zeolites into the blends. From the data it can be seen that there is a major effect due to the incorporation of zeolites into the the PPy. Major effect that can be considered with the increasing value of conductivity is obtaining a higher degree of structural order inside the samples [10]. These results suggest that the regularity of the structure and the degree or order is increased as the results for both PPy and PPy/zeolite blends increased. It is suggested that the polymer (PPy) have been encapsulated in broader pore size of zeolite which may cause the electrons easier to jump or move in the pore of zeolite materials. In order to conduct current efficiently, electrons must be able to move from one polymer chain to next. With broader pore size, charge carriers are lesser trapped in the channel walls and producing in chain-to-chain hopping easier which have increased the conductivity of the samples. A further explanation of this may be zeolite in PPy have improves the alignment of the polypyrrole chains in the conductive grains increasing their conductivity and is assumed helps decelerating aging. As zeolite was introduced in the system, it has changed the separation between the conductive grains and will be decreased as zeolite content is increased [7]. Due to this mechanism, the conductivity had increased and improves the thermal stability of the system.

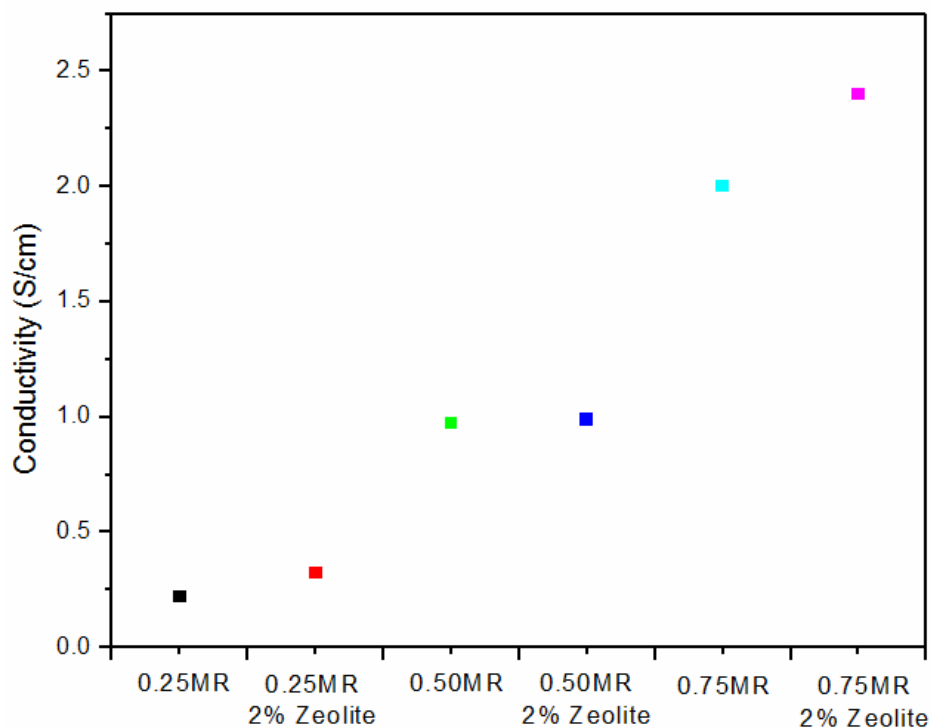


Figure 2: The pattern of conductivity in the PPy and PPy/Zeolite blends with different Fe/PPy molar ratio at 300 K.

Table 1: The conductivity,  $\sigma$  and activation energy,  $E_a$  of a PPy and PPy/Zeolite blends

Fe/Py ratio with zeolite, used to prepare compound	Conductivity of prepared compound (S/cm) at 300 K	Activation energy, $E_a$ (eV)
0.25 MR PPy (without zeolite)	0.22	0.037
0.25 MR PPy with 2% zeolite	0.32	0.042
0.50 MR PPy (without zeolite)	0.97	0.045
0.50 MR PPy with 2% zeolite	0.99	0.038
0.75 MR PPy (without zeolite)	2.00	0.058
0.75 MR PPy with 2% zeolite)	2.40	0.044

## CONCLUSION

The electrical conductivity of the PPy and PPy/zeolite blends samples is influenced by variety of parameters used to prepare the compound including the concentration of pyrrole monomer, Fe/Py ratio, and introduction of zeolite and applied current. The effect of introduction of 2% zeolite into PPy was found to enhance the conductivity of the polymer. The expected role of the zeolite as improving their alignment with its porous structure seems to be prominent for PPy and protect the polymer chains from aging processes, although not yet conclusive, is highly suggestive. This ensures that that the role of zeolite in the system is significant in increasing the conductivity and improves the thermal stability of the system.

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