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THERMAL ACTIVATION OF CONDUCTING POLYMER POLYPYRROLE/ZEOLITE

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ABSTRACT

In this paper the influence of dopant on the electrical properties of polymer prepared by chemical oxidative polymerization method is investigated using the four point probe technique. Polymers are formed by using Pyrrole and Iron (III) Chloride Hexahydrate ($FeCl_3.6H_2O$) as well as Zeolite as dopant. The current-voltage was measured from 20 to 300 K. The current-voltage characteristic of all samples shows that the 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 of Polypyrrole/Zeolite was found slightly higher than Polypyrrole which to be considered that Zeolite have altered and enhanced the conductivity of the samples. The increase in conductivity may be considered have to improved the thermal stability of the blends. An explanation is proposed based on the character and conduction mechanism of $FeCl_3$/Polypyrrole/Zeolite.

Keywords: Polypyrrole; Iron (III) Chloride Hexahydrate; Zeolite; Conductivity

INTRODUCTION

Recently, polypyrrole (Polypyrrole) 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 Polypyrrole is attributed to the electron hopping along the polymer chains with conjugating bonds [5]. As a result, more positively charged Polypyrrole, more electron available, longer polymer chains and more co-planarity between interchains are favorable for a higher conductivity performance. As shown in the literature [6-7], some efforts had been made in enhancing the conductivity and conductivity stability of Polypyrrole for its practical application. Meanwhile, in order to achieve a new function of Polypyrrole, one of the most efficient means is to confine and encapsulate conducting polymer into an inorganic solid with layered and porous structure since this enables us to combine characteristics of the parent constituent as a consequence of their molecular level interaction.

Zeolite is one of the promising host materials owing their highly ordered pore systems, channels and cages of different shapes and dimensions, and the surface is negatively charge-balanced with exchangeable cations. Besides, it is also expected that this kind of encapsulation protect the polymer from degradation, in 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 Polypyrrole chains into the porous and the improving of their alignment is expected to decelerate aging and to increase their electrical conductivity.

To investigate the influence of Zeolite on the conductivity of Polypyrrole, Polypyrrole/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

The chemical, Pyyrole (FLUKA) was used as a monomer for the synthesis of Polypyrrole. Prior to use, Pyrrole was distilled at a temperature of 131^{o}C at atmospheric pressure stored at 4 ^{o}C avoiding air. Iron (III) Chloride Hexahydrate (HAMBURG) was used as the oxidation material while Zeolite (FLUKA) is introduced into conducting polymer Polypyrrole as dopant. All these chemicals were used without any further purification except for Pyrrole. Distilled water was used in this work.

Pyyrole of 0.4 mole concentrations was mixed with 0.1 to 0.3 $FeCl_3$ 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 was then filtered and washed thoroughly with distilled water to resume the adhered Fe^{3+} and dried under vacuum at 50^{o}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 ton/cm² pressure. From this Polypyrrole and 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 of the current-voltage characteristic of the samples and through the following equation (1).

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

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

RESULT AND DISCUSSION

The Polypyrrole conducting polymer and Polypyrrole/Zeolite polymer were prepared via chemical reaction method. The conductivity at 300 K and activation energy, E_a of Polypyrrole and Polypyrrole/Zeolite blends is shown in Table 1 while the D.C. conductivity versus temperature for Polypyrrole and Polypyrrole/Zeolite blends is shown by the data in Figure 1. The temperature dependence of the D.C. conductivity of polypyrrole is shown in Figure 1 for various doping levels.

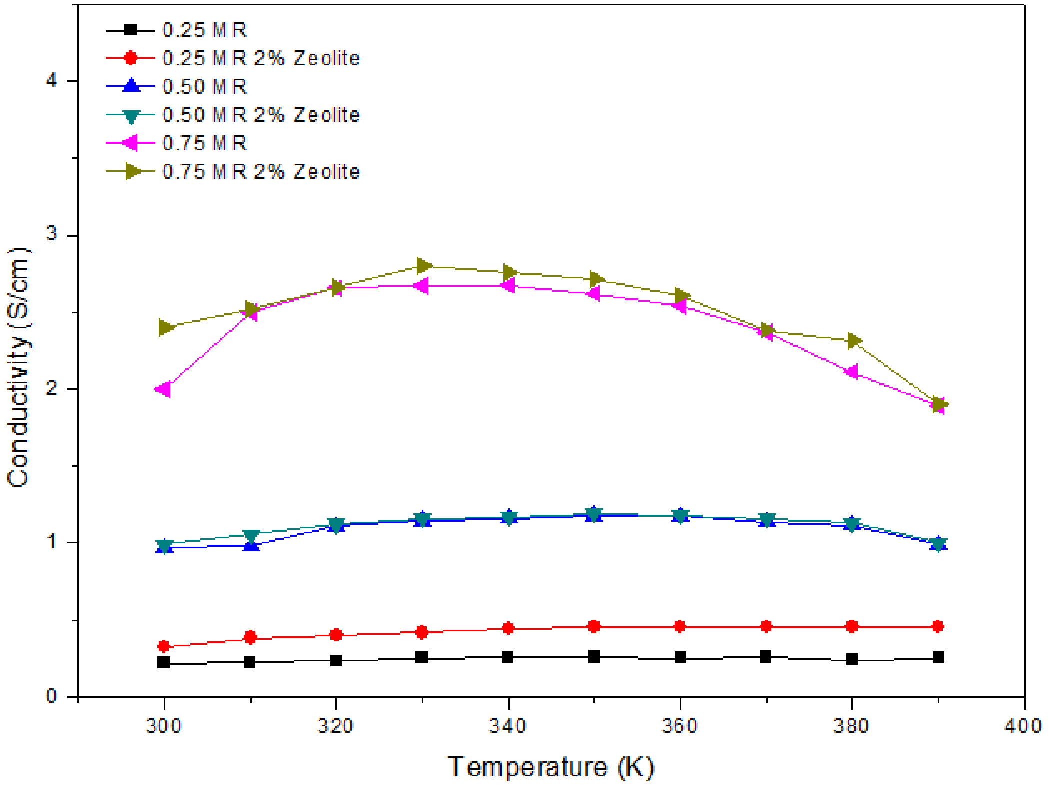

Figure 1: Temperature dependence of the D.C. conductivity of Polypyrrole and Polypyrrole/Zeolite blends for various levels of doping.

As can be seen in the figure, the conductivity increased for all compositions. The increased of the conductivity is attributed to an increase in charge-carrier concentration. Normally polymers are electrical insulator, but in conducting polymer the 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 polymer chains are compensated by negatively charged counter ions, for example zeolite, which maintain the overall electroneutrality. In doped Polypyrrole, a positive charged and an unpaired electron associated with a quoinoid 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 an increase of conductivity.

Table 1: The D.C. conductivity at 300 K and activation energy, E_a of a series of conducting Polypyrrole and Polypyrrole/Zeolite blends

Sample	MR Polypyrrole	Zeolite	D.C. conductivity (S/cm)	Activation energy, E_a (eV)
1	0.25	0	0.22	0.037
2	0.25	2%	0.32	0.042
3	0.50	0	0.97	0.045
4	0.50	2%	0.99	0.038
5	0.75	0	2.00	0.058
6	0.75	2%	2.40	0.044

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

Polypyrrole samples of 0.25 and 0.5 MR 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 Polypyrrole blends. As can be seen in Table 1, the activation energy of samples 0.25 MR of Polypyrrole increased from 0.037 to 0.042 as the Zeolite were introduced into the blend. In contrast to 0.25 MR samples, the samples 0.5 MR and 0.75 MR show the decrease of activation energy of 0.045 and 0.058 to 0.038 and 0.044 respectively, with the introduction 2% of Zeolite into the blends.

From the data, it can be seen that there is a major effect due to the incorporation of Zeolite into the Polypyrrole. 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 are increased as the mole ratio and dopants for both Polypyrrole and Polypyrrole/Zeolite blends were increased.

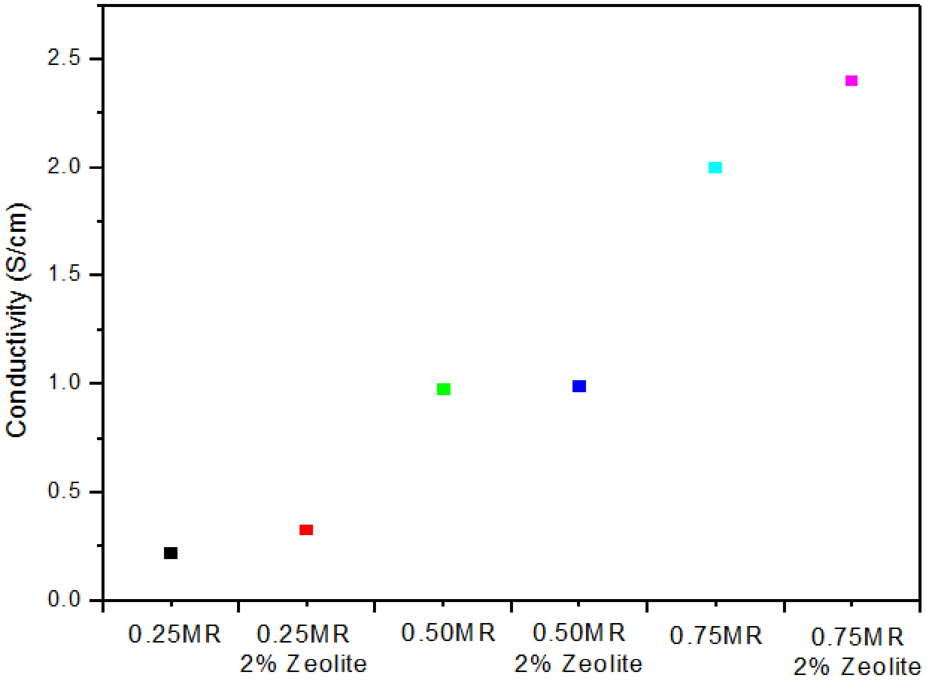

Figure 2: The pattern of D.C. conductivity in the Polypyrrole and Polypyrrole/Zeolite blends with different Fe/Polypyrrole molar ratio at 300K.

It is suggested that the polymer (Polypyrrole) 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 the next. With broader pore size, charge carriers are lesser trapped in the channel walls and resulting in chain-to-chain hopping easier and hence which have increased the conductivity of the samples. A further explanation of this may be Zeolite in Polypyrrole have improved the alignment of the Polypyrrole chains in the conductive grains increasing their conductivity and is assumed to assist decelerate aging. As Zeolite was introduced into the system, the separations between the conductive grains were decreased with the increace of Zeolite content [7]. Due to this mechanism, the conductivity increaseds and improves the thermal stability of the system.

CONCLUSION

The electrical conductivity of the Polypyrrole and Polypyrrole/Zeolite blends samples are influenced by a 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 introduction of Zeolite into Polypyrrole has enhanced the conductivity of the polymer.

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