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Temperature Dependent Conductivity of Polypyrrole and Montmorillonite Composites

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Abstract

Polypyrrole (PPy) and Montmorillonite (MMT) composites of different weight percentage using $FeCl_3$ as oxidant have been synthesized using in-situ polymerization. The electrical conduction is studied as function of temperature. The electric conductivity increases with an increase in the temperature in each of the composites. Mott's 1-D, 2-D and 3-D variable range hopping (VRH) models have been plotted. The $\ln(\sigma)$ versus $T^{-1/4}$ curve has been discussed, wherein the linear relationship provides an evidence for three dimensional variable range hopping electron transport mechanism in all the composites.

Keywords: Polypyrrole, Montmorillonite, DC conductivity, Variable range hopping.

1 Introduction

Polypyrrole is an intrinsic conducting polymer which can be made to have conductivities up to 1000 S/cm[1]. The PPy conducting polymer is processable when doped with either inorganic or organic acid with various methods such as chemical and electrochemical methods[2]. Clays are the most abundant inexpensive and natural materials with high mechanical strength and high chemical resistance. They possess a layered structure, which can be exfoliated to yield an appreciable surface area which can be used

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for the adsorption of molecules[3].

Clay minerals especially Montmorillonite (MMT) has recently been adapted to the field of nanocomposites because of their small particle size and intercalation properties[4]. Clay/polymer nanocomposites offer tremendous improvement in a wide range of physical properties.

The electrical transport in polymeric materials has become an area of increasing interest in research because these materials possess a great potential for solid state devices[5]. The electrical conductivity of PPy is attributed to the electrons hopping along and across the polymer chains with conjugating bonds[6].

The electronic properties of any material are established by its electronic structure. The most reasonable explanation of electronic structure of materials is achieved by the band theory. According to quantum mechanism the electrons of an atom can only have specific or quantized energy levels. However, in the lattice of a crystal, where the atoms are closely spaced, the energy levels form bands. The highest occupied electronic levels constitute the valence band and the lowest unoccupied levels constitute the conduction band. Depending on how the bands are filled, the electrical properties of conventional materials are determined[7].

The band theory is insufficient to explain the electrical conduction in electrically conducting organic materials such as polyphenylene, polyacetylene or polypyrrole where the charge-carrying species (electrons or holes) are spinless. Although the mechanism is not fully understood, conduction by polarons and bipolarons is now thought to be the dominant mechanism of charge transport in organic materials. This concept is also used for explanation of the drastic deepening of color changes produced by doping.

A polaron which is a term used in solid-state physics is defined as a radical cation that is partially delocalized over several monomer units (e.g. in a polymer segment) where a bipolaron is a diradical dication. Doping level determines formation of polaron and bipolarons. Low doping levels gives rise to polarons, whereas higher doping levels produce bipolarons. Both polarons and bipolarons are mobile and can move along the polymer chain[8].

From past many years the research on conducting polymer nanocomposites is going on. The study of PPy/MMT composites is a recent addition to it. In last one decade few authors have reported characterization and conductivity studies of the composites but that is for a smaller wt% ratio of MMT[9]. In this paper the authors have tried to study the DC conductivity of PPy/MMT composites as a function of temperature for much higher wt% ratio of MMT in the composites and have also tried to find the reasons of the trend being depicted by the composites.

2 Experimental

As reported in our previous paper the

PPy and PPy/MMT composites were synthesized using in-situ polymerization using $FeCl_3$ as oxidant. The polymerisation was performed at 0°C temperature. The greenish-black precipitate resulting from the reaction was washed with distilled water and methanol and then dried under vacuum for 6-8 hrs This process was repeated several times to remove all the adhering substances[10,11]. The monomer pyrrole supplied by Sisco Research Laboratories Pvt. Ltd. Mumbai, India and Montmorrilonite clay supplied by Sigma Aldrich, USA (CAS No. 1302-78-9) was used as the clay material.

A Hand Press instrument for pellets preparation was used. The obtained (composites) powder was made pellets by using stainless steel mold applying 10 ton/cm^2 pressures under vacuum for 10 minutes. The DC electric measurements of the obtained composites were performed within the temperature range of 273 K to 400 K using standard four probe method. The experiments were carried out in Indian standard temperature measurement unit degree Celsius °C and have been converted into the international standard temperature measurement unit of Kelvin (K).

3 Results and Discussion

In our previous paper the DC conductivity for the pellets of various weight% was studied and the DC conductivity initially was found to increase in the range of 0 to 1% of MMT thereby it decreases up to 10% MMT and then rising from 10 to 15% MMT beyond which the conductivity decreases up to 25% at room temperature[12].

The nature of rise in conductivity with wt% presented in our work is broadly consistent with that of comparable composites of Polypyrrole with MMT reported by Kassim Anuar *et al*[9]. However, there authors used very low loadings of MMT in PPy (from 0.2 to 1 wt%) whereas in the this work, the samples had a wide range of MMT loading (from 1% to 20 wt%).

Electrical Conductivity: Electron transport (conduction) mechanism in a material can be categorized into the following two modes. In the metallic conduction, the electrical conductivity σ will linearly increase with a decrease in temperature. In the second semiconductor type, conductivity increases generally with an increase of temperature[13].

A similar trend as reported in our previous study of wt% Vs conductivity[12] has been noticed in the further study carried on temperature Vs DC conductivity for various pellets of different wt%. As shown in Fig. 1 the electric conductivity increases with an increase in the temperature in each of the composites. This can simply be associated to the contribution of the charge carrier mobility. In this case, the polarons or bipolarons might move with higher diffusion velocity when the temperature increased and thus increased the conductivity[14]. The most optimum being the increase in conductivity of 15wt% of MMT sample, from 11.1 mS/cm to 14.8 mS/cm. The conductivity of all the nanocomposites is significantly higher than that of pure polypyrrole.

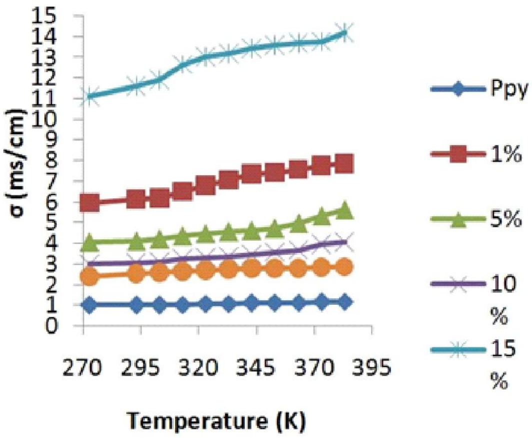

Fig 1. Plot of conductivity (σ) as a function of temperature ranging from 273K to 388 K.

Electron Transport Mechanism: Conducting polymers are amorphous with short conjugation lengths. Therefore, it has been suggested that electrical conduction takes place by charge hopping between polymeric chains. The model used to describe the conduction process is the conduction model originally developed for amorphous silicon by Mott and Davis. When applied to conducting polymers, it assumes that electron transport originates from localized or fixed states within the polymer chain. The charge transfer between the chains takes place by hopping, referred to asphonon-assisted hopping, between two localized states[14].

The models for thermally activated and Mott's variable range hopping (VRH) is given by Equations (1) and (2) respectively:

$$\sigma = \sigma_0 \exp(-E_a/K_B T) \quad 1$$

$$\sigma = \sigma_0 \exp\{-(T_0/T)^{1/(1+d)}\} \quad 2$$

where, σ is conductivity of sample at temperature T(K), σ_0 is pre-exponential factor (S/cm), E_a is the activation energy, K_B is the Boltzmann constant (8.616×10^{-5} eV K^{-1}), T is the temperature, d=1,2,3 is the dimensionality of the conduction process and T_o is associated with the degree of localization of the electronic wave function.

The plots of ln σ versus $(T)^{1/(1+d)}$ in Figure 2 (b), (c) and (d) show that d=1, 2 and 3. All give straight linear curve.

For three dimensional VRH mechanisms, d = 3 and by taking the natural logs of both sides of Eq. (2), the following relationship is obtained:

$$\ln \sigma = \ln \sigma_0 - (T_0^{1/4})(T^{-1/4}) \quad 3$$

As seen in Figure 2(c), a linear relation between ln σ(T) and $T^{-1/4}$ from the experimental results is obtained which justifies the validity of Eq. 3 for the nanocomposites. It also indicates a three dimensional (3-d) variable range hopping (VRH) electron transport mechanism in the nanocomposites[15].

Table 1: Values of σ_0 and T_0 for Pure PPy and Different MMT wt% loadings

Sample	σ_0(S/cm)	To (K)
Pure PPy	9.18×10^{-3}	6.56×10^{3}
1% MMT	0.1466	2.85×10^{4}
5% MMT	0.2421	7.68×10^{4}
10% MMT	0.151	6.55×10^{4}
15% MMT	1.336	16×10^{4}
20% MMT	0.023	7.6×10^{3}

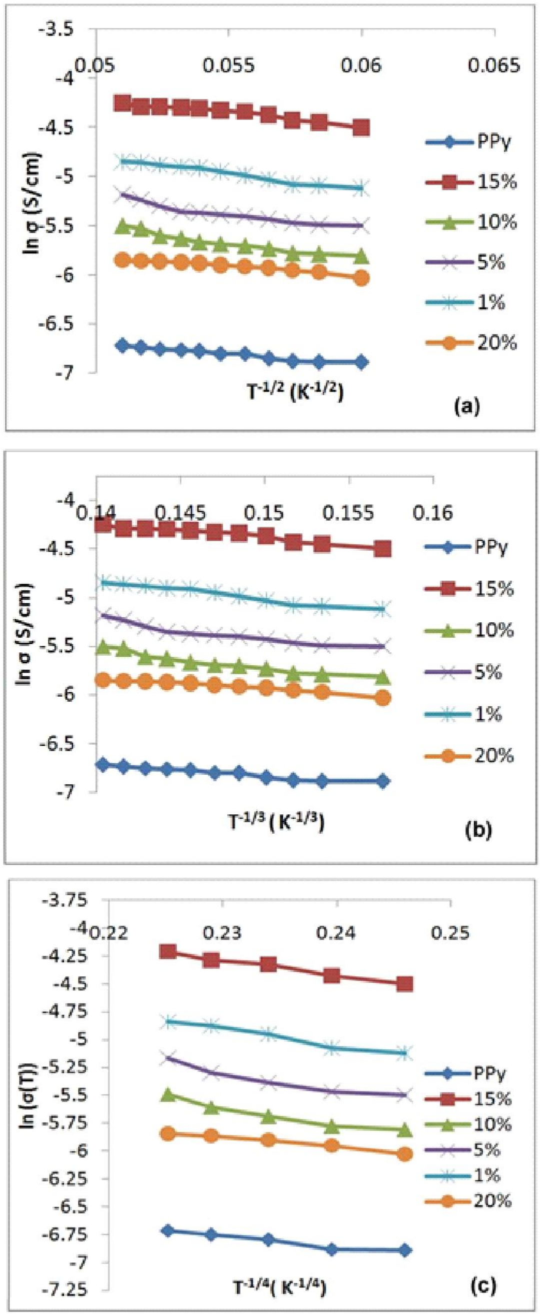

Figure 2. Plots of ln (σ(T)) as a function of **a.** $T^{-1/2}(K^{-1/2})$ **b.** $T^{-1/3}(K^{-1/3})$ **c.** $T^{-1/4}(K^{-1/4})$ for different wt%.

The fitting of the experimental temperature dependence data reveals that the Mott's 3-D variable range hopping mechanism is the most suitable mechanism for PPy conducting polymer behavior.

Pre exponential factor σ_0 and temperature T_0 were calculated from the slopes and *y* - intercepts of the plots in Figure 2 and are reported in Table 1. The value of T_0 contains geometrical parameters, distance between grains and columbic interaction energy[16]. A small T_0 implies a weak localization of the charge carriers[17].

4 Conclusions

In continuation to the study of conductivity based on wt% of MMT in PPy, the study of dependence of conductivity on temperature was carried out. The dopant concentrations and their temperature dependent electrical transport properties were studied by the standard four probe technique. The electric conductivity in the temperature range 273 K to 388 K increases with increase in temperature in each of the composites. The maximum conductivity is found to be 14.8 mS/cm of 15 wt% MMT at 388 K whereas for the same sample the conductivity at 273 K is found to be 11.1 mS/cm. This reveals a fair rise in the conductivity with increase in temperature. Mott's 1-D, 2-D and 3-D variable range hopping (VRH) models are plotted and a 3-d variable range hopping conduction mechanism is justified by the temperature dependent conductivity investigation.

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