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SYNTHESIS AND CHARACTERIZATION OF POLYPYRROLE-POLYETHYLENE OXIDE-ZNO COMPOSITE FILMS

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Abstract: Polypyrrole (PPy) - Polyethylene oxide (PEO) - Zinc oxide (ZnO) composite thin films were synthesized by chemical oxidative polymerization method with the solution of ferric chloride ($FeCl_3$) oxidant in methanol. The surface morphology of (PPy-PEO-ZnO) polymer composite films was studied by scanning electron microscopy (SEM). Their dc conductivity as a function of temperature (308 to 338 K) was measured. Initially the conductivity increases, reaches to 7.82 x 10^{-8} S/cm for 7 wt % of ZnO then decreases with ZnO concentration. The temperature dependence of conductivity shows cross over from Vogel-Tamman-Fulcher (VTF) to Arrhenius behaviour. The cross over from VTF to Arrhenius takes place at different temperatures for the films synthesized with different concentration of ZnO.

Keywords: PPy-PEO-ZnO composites, SEM, Conductivity.

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INTRODUCTION

Conducting polymers are important materials emerging with lot of applications in various fields. Research in the field of such polymers aims mainly at some suitable modifications of existing polymers so that their applicability can be improved. Some of these modifications involve preparing hybrid materials in which organic materials and inorganic oxides or salts of different metals, viz. SnO_2 [1], CeO_2 [2], V_2O_5 [3], TiO_2 [4], fly ash composites [5], Fe_3O_4 [6], ZrO_2 [7] etc. combine in some special fashion with the conducting polymers to give rise to the composites. In almost all the cases some specific nature of association between the two components have been observed. Polypyrrole is an important conducting polymer with high electrical conductivity and appreciable environmental stability [8]. Many research workers have studied synthesis and charge transport in composites and blends. Most of them explained the charge transport behavior as a charge carrier hopping (Mott's VRH) between localized states. On the other hand, in the case of ionically conducting solid polymer electrolytes, the temperature dependent behavior of conductivity is more completely explained by the VTF (Vogel-Tamman-Fulcher) equation [9-11].

The present paper focuses on the synthesis of PPy-PEO-ZnO films by oxidative (chemical) polymerization and effect of the doping concentration on electrical conductivity of composite films to know the conduction mechanism and structural behavior.

and structural behavior.

2. EXPERIMENTAL

Anhydrous Ferric chloride ($FeCl_3$) (AR-grade), Zinc nitrate from S. D. Fine Chem (India) , Ethanol from Changshu Yangyuan Chemical (China) pyrrole from Sisco (India) (AR-grade) and PEO from Across Organic (USA) are obtained All these chemicals were used as purchased.

2.1 Synthesis of ZnO nanoparticles

ZnO nanoparticles were prepared by precipitation method using zinc nitrate and sodium hydroxide as precursors and soluble starch as stabilizing agent. 0.3 g starch is dissolved in 100 ml of distilled water. 10 ml of 0.1 M zinc nitrate is added to starch solution. After complete dissolution of zinc nitrate, 10 ml of 0.2 M sodium hydroxide solution was added. The reaction is allowed to proceed for 2 h after complete addition of sodium hydroxide. After the completion of the reaction, the solution is centrifuged. In order to remove the byproducts and excessive

starch bound to the nanoparticles, the precipitate was washed with ethanol repeatedly. The powder of ZnO nanoparticles was obtained after drying at 100^0C. Fig. 1 shows the TEM picture of pure ZnO. The grain size of ZnO is found to be from 20 to 60 nm.

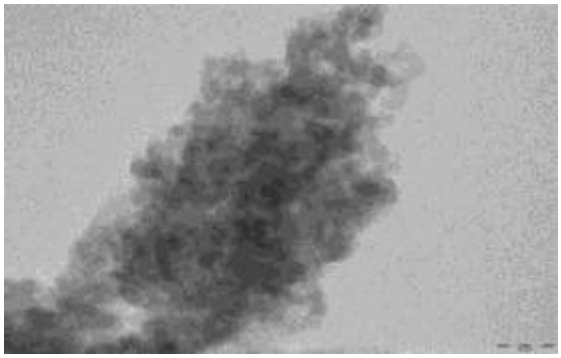

Fig. 1: TEM picture of pure ZnO

2.2 Sample Preparation

The PPy-PEO-ZnO composites were prepared by chemical oxidative polymerization by using $FeCl_3$ as oxidant in methanol solvent. Firstly, PEO dissolved in methanol. This solution was kept in test tube for 12 h. A suitable amount of oxidizing agent (0.2M) was added to the solution. PEO- $FeCl_3$ solution was homogenized by constant magnetic bar stirring. After this ZnO nanopowder was added to this solution. Then monomer pyrrole was added dropwise to the homogeneous solution of PEO, $FeCl_3$ and ZnO. This mixture was constantly stirred for 3-4 h, a dark black homogeneous solution was obtained which was then poured on chemically cleaned polypropylene plane dish to prepare the films of composite. After evaporation of solvent the thin films were formed.

2.3 SEM characterization

Surface morphological study of composite films was done by using Field Emission Gun - Scanning Electron Microscope (JSM-7600 F) operating with an accelerating voltage of 0.1 to 30 KV at SAIF, IIT Bombay, Powai, Mumbai.

2.4 DC conductivity measurement

The dc electrical conductivity of the samples was measured by two-probe method, in which resistance of the sample was measured. A dc regulated power supply and a pico ammeter with resolution of 1 pA is used for measurement. The composite film was sandwitched between two

conducting electrodes and then placed in a muffle furnace. Temperature of the furnace was increased from room temperature 303 to 338 K.

3. RESULTS AND DISCUSSION

3.1 SEM analysis

The surface morphology of the composite films of 6, 7 and 8 wt % of ZnO was analyzed by SEM and the pictures are shown in Figs. 2(a), 2(b) and 2(c) respectively. SEM images show regular crystalline structure arranged in disordered manner having circular shape grannuals and the nanocrystalline particles deposited on it. Alongwith this many microcracks throughout the pictures are seen. With higher magnification, a nanometer size needle shaped fibres are observed. Within these fibres nanovoids and nanogaps are created.

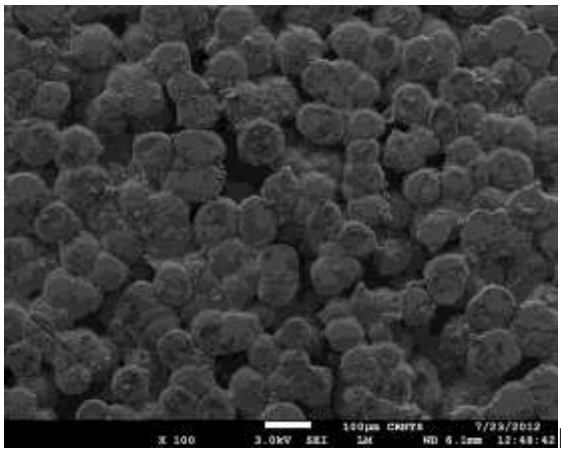

Fig. 2(a)

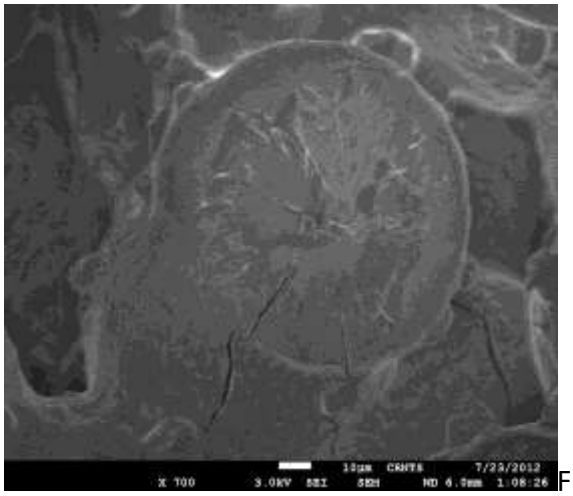

Fig. 2(b)

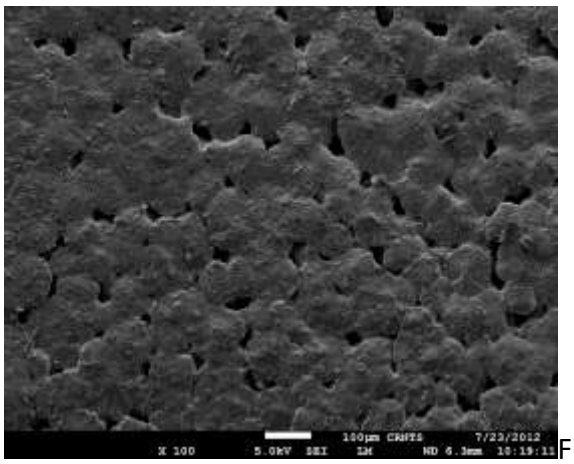

Fig. 2(c)

3.2 DC conductivity

The variation of log $б_{dc}$ with wt % of ZnO for PPy-PEO-ZnO composite films at temperature 318 K is shown in Fig. 3. Initially the conductivity increases, reaches to 7.82 x 10^{-8} S/cm for 7 wt % of ZnO then decreases with ZnO concentration.

The temperature dependence of conductivity for different wt % of ZnO is shown in fig. 4.

The conductivity versus temperature curves of the samples shows increase in conductivity. Initially the rate of increase of conductivity is slow and after a certain temperature the rise is fast. Thus it leads to two activation regions (I and II as shown in fig. 4) giving two different activation energies. Above curves shows the curvature type behavior below a certain temperature T_c, called knee temperature, and above which the curves are nearly linear in nature. The non-linearity in Arrhenius plot indicates the ionic transport facilitates by the segmental motion of polymer chains. Thus Vogel-Tamman-Fulcher (VTF) (equation 1), may more effectively represent the results.

$$\sigma = \frac{A}{T^{1/2}} exp\left(\frac{-B}{k(T-T_0)}\right) \qquad (1)$$

In high temperature region the curves no longer fits the VTF equation. The cross over from VTF to Arrhenius is clearly visible in the high temperature region. The Arrhenius equation (2) fits the region above T_c,

$$\sigma = \sigma_0 exp\left(\frac{-E_a}{kT}\right) \qquad (2)$$

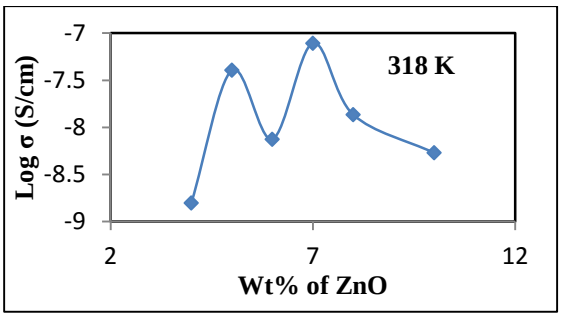

Fig. 3: Variation of conductivity with wt % of ZnO at 318 K.

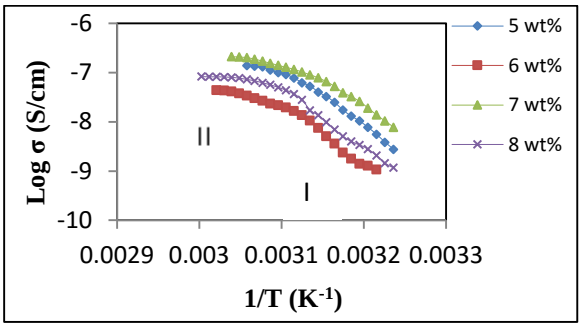

Fig. 4: Temperature dependence of conductivity for different wt % of ZnO

The VTF fits plot for ZnO doped PPy-PEO composite films are shown in fig. 5.

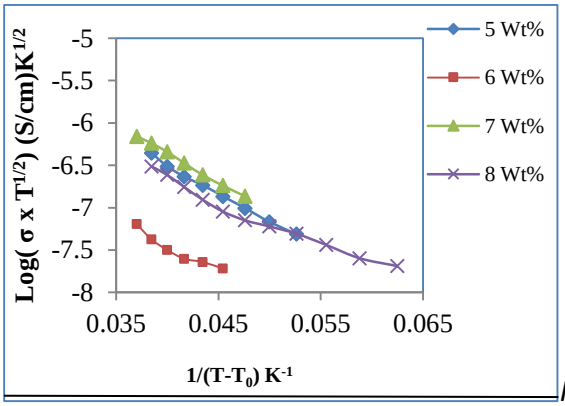

Fig.5: VTF plots for different wt % of ZnO

The VTF fit parameters are summarized in table 1.

In present study, the cross over from VTF to Arrhenius observed may be due to some sort of transition in energetic of local ion motion and reduction in effective ion density on undergoing order-disorder transition at temperature T_c. Thus T_c can be linked to order-disorder temperature. Below T_c the curves fits the VTF equation. When the ionic conduction follows the VTF equation, a linear relation between ln ($\sigma T^{1/2}$) and 1/ ($T-T_0$) is expected. Such relationships are shown in fig. 5 for different wt % of ZnO composite samples. The correspondence between dependence of pseudoactivation energy *'B'* with concentration of ZnO (Table1) is observed. The minimum pseudoactivation energy *'B'* (0.0041 eV) is observed for 8 wt % of ZnO.

4. CONCLUSION

The PPy-PEO-ZnO composites were prepared by chemical polymerization of pyrrole by different concentration of ZnO. The surface morphology of polymer composite films were characterized through scanning electron microscopy (SEM). SEM images show regular crystalline structure arranged in disordered manner having circular shape grannuals and the nanocrystalline particles deposited on it. With higher magnification, a nanometer size needle shaped fibres are observed. The temperature dependent conductivity behaviour of the PPy-PEO-ZnO composite shows a VTF to Arrhenius crossover. The correspondence between dependence of pseudoactivation energy *'B'* with concentration of ZnO is observed. The minimum pseudoactivation energy *'B'* (0.0041 eV) was observed for 8 wt % of ZnO.

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Table1: Arrhenius and VTF equation fitting parameters for different ZnO wt %.

Sr No.	ZnO wt %	Activation Energy Ea (eV) (Region II)	Pre-exponential factor σ_0 (S/cm) (Region II)	Pseudo Activation energy B (eV) (Region I)	Pre-exponential factor σ_0 (S/cm) (Region I)	Knee temperature T_c (K)	Ideal glass transition temperature T_0 K
1	5	0.36	7.51×10^5	0.0057	1.39×10^{-4}	320	290
2	6	0.41	8.17×10^6	0.0051	8.32×10^{-6}	319	289
3	7	0.31	2.23×10^4	0.0059	2.49×10^{-4}	318	288

4	8	0.18	3.07×10^{-1}	0.0041	1.74×10^{-5}	323	293

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