



COMPOSITION OF CONDUCTING POLYMER POLYTHIOPHENE (PTh) - POLYVINYL ACETATE (PVAC)

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ABSTRACT

The composition of polyvinyl acetate (PVAc) -polythiophene (PTh) were prepared by chemical oxidative polymerization with $ZnCl_2$ as oxidant, in methanol as solvent at room temperature. In this study DC conductivity as a function of temperature was measured. An attempt has been made to investigate the effect of temperature and concentration of $ZnCl_2$ oxidant on the conductivity of Polythiophene and Polyvinyl acetate composite films. The X-ray diffraction technique is used for the determination of amorphous nature. The temperature dependence of conductivity showed Arrhenius behavior. The Nyquist plot suggests Debye type relaxation mechanism.

Key words: Conducting polymer, Polythiophene, Dc electrical conductivity.

INTRODUCTION

Conducting polymers, also sometimes called conjugated conducting polymers or organic polymeric conductors, are materials consisting of polymeric molecules, which have high electrical conductivity. Conjugated polymers have received a great deal of attention in the last decade due to their potential for applications in optoelectronic devices such as photovoltaic cells¹, organic light-emitting diodes (LEDs)² and photo transistors³. A wide range of conjugated polymer systems and their derivatives have been developed, such as poly (1, 4-phenylenevinylene) (PPV)^{4,5}, poly(p-phenylene) (PPP)⁷, polyfluorene (PF)⁶ and polythiophenes (PT)⁸. Among these polymers polythiophenes are being regarded as one of the most promising materials because of their good thermal and chemical stability, as well as for their electronic and optical properties⁹⁻¹². Moreover, it has been observed that by the introduction of a functional group as a side chain substituent the main characteristic can be modified. Indeed, by attaching different functional groups as a side chain substituent and controlling their regioregularity, light emission ranging from blue to near-infrared has been demonstrated^{9,10}.

EXPERIMENTAL

Synthesis of polythiophene

Polythiophene was synthesized at room temperature (303 K) by mixing thiophene with solution of ZnCl_2 and polyvinyl acetate (PVAc) in methanol solvent. A solution of PVAc was first prepared in methanol. The composition of the solution was PVAc: Methanol = 10 : 90 (wt. %). The wt. % of thiophene changed from 5, 10, 15, 18, 20, 22, 25, 30, 35, 40 wt. % of PTh. For each wt. % the molar concentration of ZnCl_2 was kept constant at 1.0 mole. Thus such solutions were prepared for different wt. % of PTh. When monomer thiophene was added to the solution of PVAc – Methanol – ZnCl_2 , a homogenous solution was obtained. This solution was poured on the chemically cleaned and optically plane glass plate at room temperature for the preparation of composite films. The thiophene polymerization progresses and because of the evaporation of the solvent, the transparent thin films were formed, then this films were washed with water to remove the excess ZnCl_2 . The thickness of the films was measured with the electronic Digimatic Micrometers (Japan)

RESULTS AND DISCUSSION

DC electrical conductivity

The dc electrical conductivity of the samples of various wt. % of polythiophene, ZnCl_2 and PVAc is measured in the temperature range 303 to 368 K by measuring the resistance of the samples. It is observed that the value of resistance depends on composition as well as on temperature.

The electrical conductivity with different wt. % of thiophene at various temperatures is as shown in Fig. 2.

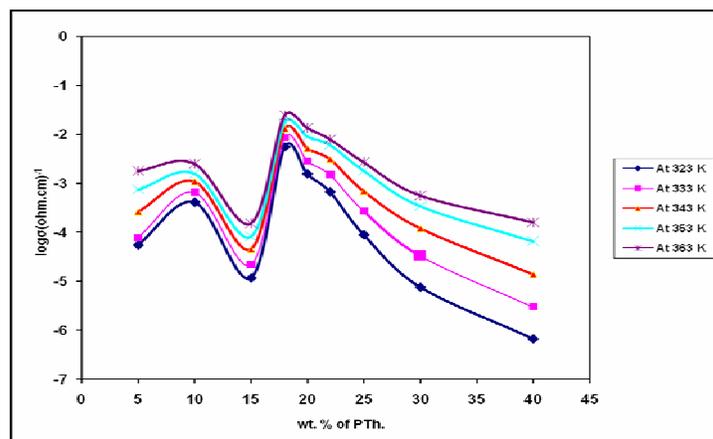


Fig. 1: Variation of conductivity with different wt. % of thiophene at various temperatures

From this fig. 3 it is observed that conductivity increases with increase in temperature. As the temperature increases, mobility of ions increases, which results the rise in conductivity. Uppermost curve belong to 18% wt. of thiophene for which conductivity is maximum. All the curves are linear; hence nature of graph follows Arrhenius law.

Impedance spectroscopy

Frequency dependance of a real part of impedance Z' ($Z \sin \theta$) at different temperature for optimised PTh-PVAc composite sample 1.0 M of ZnCl_2 are shown in Fig. 4.

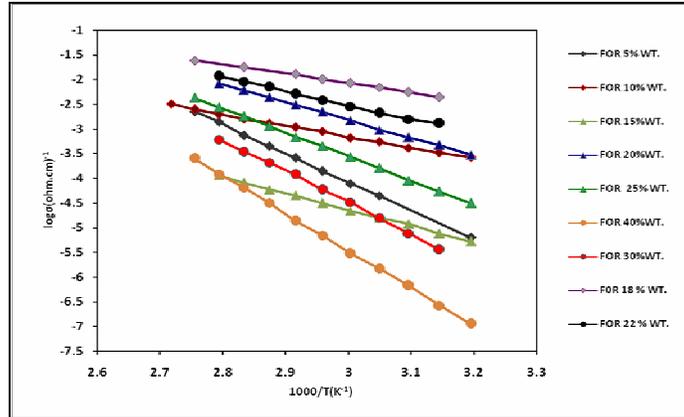


Fig. 3: Plot of variations of dc conductivity with temperature for different wt % of thiophene in PTh-PVAc films

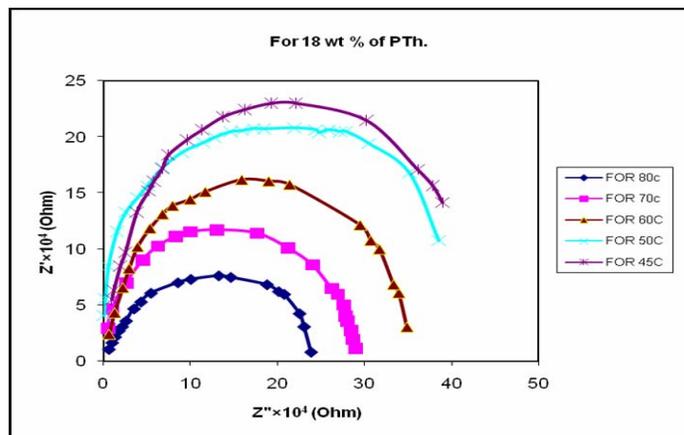


Fig.4: Nyquist plots Z' versus Z'' at various temperature for 18 wt. % of thiophene

It is observed that Z' decreases with increase in both frequency as well as temperature. The Z' value for all temperatures merge above 10 KHz.

The curve shows that the value of Z' increases initially then decreases with the increase in frequency at lower temperature. At lower temperature end, a slight increase in the Z' value is observed with increase in

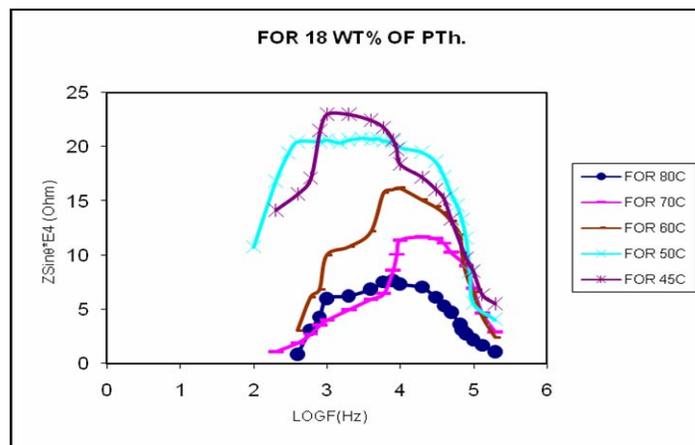


Fig. 5: Nyquist plots Z' versus Z'' at various temperature for PTh-PV composite with $ZnCl_2$ -1.0 M

temperature. However as temperature increases, value decreases drastically and a broad peak merged in frequency. The broadness of peak increases with increase in the temperature. It is observed that these Z' peaks are found to shift towards higher frequency side with increase in the temperature. All the curves merge into single curves after some frequency. The diffuseness of Z' peak indicate the distribution of relaxation frequency and increase in full width at half the Z' maximum value with the increase of the temperature indicates increase of relaxation frequency distribution.

The Impedance data at room temperature do not take the sharp shape of semicircle in the Nyquist plot, which having certain slope, suggesting the some type of insulating behaviour of composite at room temperature.

CONCLUSION

Polythiophene (PTh)-Polyvinyl acetate (PVAc) composite films were synthesized by chemical polymerization using different wt. % of thiophene. The dc conductivity is measured by Ohm's law method. The plot of $\log \sigma$ Vs $1/T$ shows almost linear behavior within the studied temperature range. The resistance of the sample decreases with increase in temperature and follows Arrhenous behavior. In the present case $\log \sigma$ Vs $1/T$ shows single straight line indicates a one type of defect is mobile. Therefore one type of conduction mechanism i.e ionic is present. For higher temperature we get semicircular plots. It provides the information about the nature of dielectric relaxation. As the Nyquist plots are single semicircle with the centre located on the (Z')axis, relaxation process is pure monodispersive Debye process. For polydispersive relaxation, these argand plane plots are close to circular arcs with ends points on the real axis and the center below this axis. The complex impedance in such situations is known to be described by Cole-Cole formalism, which suggests the Debye type relaxation.

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