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Effect on conductivity of ZnO nanoparticle doped PVC films

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We have prepared pristine and ZnO nanoparticle doped PVC films with varying doping concentration and thin films thicknesses. The conductivity is measured by applying different applied fields and temperatures for pristine and ZnO doped PVC thin films. The Lnσ verses 1/T x 10^{-3} K plot exhibited nonlinearity nature and it is found that the conductivity increases more sharply for doped sample than the undoped sample at intermediate temperature. The activation energy is calculated by employing arrhenious equation and found that it increases with increase in doping concentration of ZnO in PVC film.

Key words: ZnO nanoparticles, Arrhenious equations, PVC films and Activation energy.

1. Introduction:

Conducting polymers are organic polymers that conduct electricity[1]; such compound may have metallic conductivity or can be a semiconductor. The advantages of conducting polymers are their easy processability and wide range of availability of raw materials. Conducting polymers are generally not plastic like insulating polymer. They can offer high electrical conductivity but do not show mechanical properties as other commercially used polymers do. The electrical properties can be fine-tuned using the wide verities of organic synthesis methods[2] and advanced dispersion techniques[3.] The most recent research in conducting polymers is to develop high conductivity materials with excellent stability and acceptable processing methods. So for most well studied conducting polymers are (i) nitrogen containing polymers, i.e. poly(pyrrole)s (PPY), polyanilines (PANI). (ii) Sulfur containing polymers, i.e. Poly(thiophene)s (PT), Poly(3,4 –ethylenedioxythiophene) (PEDOT), Poly(P-phenylenesulfide)(PPS) and (iii) other polymers i.e. Poly(acetylene)s (PAC), Poly(p-phenylene vinylene)(PPV), Polyethylene terephthalate (PET) etc.

Polymer viz, polyvinyle chloride (PVC) having an excellent electrical insulation property, impact strength and resistant to weather conditions, which is not consider as a conducting polymer and less amount of work has been reported about its electrical conduction, however, production of thermally stimulated discharge conductivity by doping charcoal has been studied[4]

The ZnO material is a wide band gap 3.3 eV (at room temperature) n-type semiconductor. Advantages associated with a large band gap include higher breakdown voltage ability to sustain large electric field, lower electronic noise, and high temperature and higher power operation. The band gap of ZnO can further be tuned to 3-4 eV by alloying with magnesium oxide or cadmium oxide [5]

Nanostructured ZnO material is considered highly important for electronic, optic , photonic, gas sensors and molecular electronics applications. The nano-structured exhibit novel electrical, mechanical, chemical and optical properties which are believed to be due to the surface confinement effects. These one dimensional objects are of great importance in understanding some basic physics related phenomena in the low dimension system to form the basis of next generation higher performance nano-devices [6].

As ZnO has high electron mobility and wide band gap so, ZnO nanoparticle is doped in PVC film, electrical property of the nano-composite film will change from the pure PVC film. In the present study, an attempt is made the variation of electrical conductivity and activation energy of pure PVC, (having excellent electrical insulation property as mentioned above) and ZnO nanoparticle doped PVC films at different applied voltage, temperature and doping concentrations.

2. **Experimental details**

(i) *Sample preparation:*

PVC granule were obtained from the Reliance industry Surat, Gujarat and cyclohexanon was supplied by S D Fine Chem. Ltd, Mumbai for the present study. The solution kept at room temperature for one week. For complete dissolution the solution is poured on the glass plate to make a thin film. The glass plate is placed over a pool of mercury for perfect leveling so as to ensure uniform thickness. The whole system was allowed to evaporate at room temperature in dust free chamber for 6 days and after complete evaporation the film was detached from the glass plate. Thus a pure (PVC + cyclohexanon) PVC film is formed.

After a solution is formed as above, ZnO [7] nanoparticles supplied by Material Science Laboratory, B N College, Patna, were doped with different quantities i.e. 0.00325 gm/cc, 0.00653gm/cc and 0.01303 gm /cc. Now, the mixture (PVC + ZnO) is stirred by Magnetic stirrer (Eltect-MS 205) for 8 hrs¸ then the mixtures is poured on the glass plate and proceed as above. Thus, the ZnO nanoparticle doped PVC film was formed. The sample preparation is same as that reported earlier[8]. The thickness of the sample was measured by screw gauge having least count of 0.01 mm and found to be 0.035 cm, 0.0175 cm, 0.03 cm and 0.019 cm.

(ii) *Measurement of conductivity:*

The sample is cut circularly slightly greater than the surface area of the electrode having area 5.067 x 10^{-4}sq-cm to avoid edge effect. The sample is placed between the two electrodes under light constant pressure in the sample holder. The sample holder is placed inside the temperature controlled bath, Ultra-thermostat (U-10, *Germany*)

The different potential is applied across the sample by the power supply (EHT-11) supplied by Scientific Equipment Roorkee. The value of potential across the sample is varied from 0 to 1400 volt by an interval of 100 volt at constant temperature. The potential drop across 1 MΩ resistor is recorded by digital multimeter. The same operation is repeated for different values of temperature from room temperature 300 K to 373 K by an interval of 10 K. In order to make uniform heating the sample is kept at constant temperature for 30 minute for each consecutive reading. The conductivity measurement is same as that reported earlier[9].

3. **Result and Discussion**

In the present study fig (1 – 4) shows the plot of Lnσ (mho/m) and $\frac{1}{T}$ x 10^{-3} of the pristine and ZnO nanoparticle doped PVC film. The slight increase in the conductivity up to 353 K and sharply increase in the conductivity up to 373 K are observed for all applied voltage (100 V to 1400 V) which shows the nonlinear field dependence in pristine and ZnO nanoparticle doped PVC film. The electrical conductivity of polymer is largely affected by the presence of free ions which are not associated chemically with the macromolecules. The chemical constituents produce its effect indirectly on the ions mobility. In both prisinte and nanoparticle doped PVC films shows the semiconducting nature. So the variation of electrical conductivity with temperature can be represented by the Arrhenious equation,

$$\sigma = \sigma_o exp \mid - E_a / KT \mid$$

Where σ_o = pre exponential factor,

E_a = the activation energy of conduction and

K = the Boltzmann constant.

Table (1 – 3) shows the variation of activation energy which is calculated from Lnσ vs $\frac{1}{T}$ x 10^{-3} plot within low intermediate and high temperature regions. Low activation energy corresponds to electronic current and high value of ionic current[10]. When the temperature increases beyond the glass transition temperature the ionic mobility increases owing to the considerable mobility of the chain unit.

In polymer there is independent movement of chain sections which contain monomeric segments. In addition to the segments, polymers consists of side chains or individual atomic groups. The relaxation time of main chain segments are greater than that of the side chains. The polymer has side chain (polar group) which is independent to each other and different relaxation time and capable of orientation in an electric field, then many dipole group loss maxima due to the presence different polar group.

It is known that a pure PVC is largely an amorphous polymer which is characterized by three relaxation, i.e. (i) relaxation occurring at low temperature (ii) relaxation around glass rubber transition temperature (T_g) and (iii) relaxation occurring at a temperature well above T_g. The absence of peak in the curves might be due to low applied field.

In PVC various types of molecular relaxations are possible. The only possible motions due to low temperature are local motion of molecular groups, i.e. rotation of side groups or internal motion within the side groups. Hence, at low temperature there may be slight decrease and then rise in the conductivity which is due to mobility of main chain segments increases with the increase in temperature[4].When ZnO nanoparticle is doped at the rate 0.00325 gm/cc, 0.00653 gm/cc

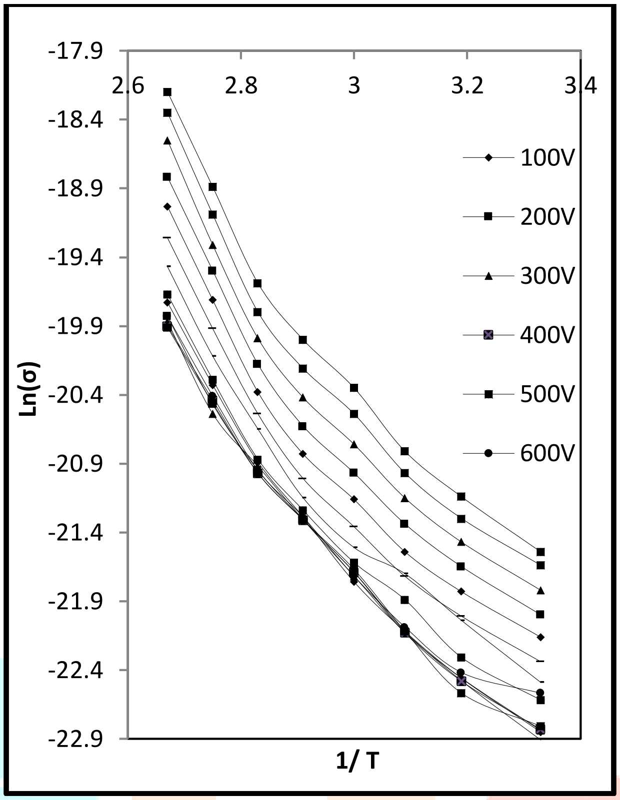

Fig.1. Plot between (1/Tx 10^{-3}) verses Lnσ for pure PVC

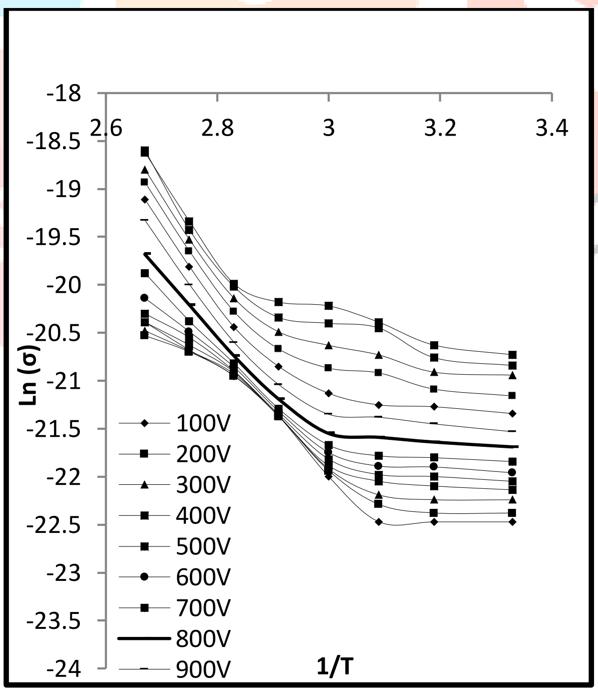

Fig.2 Plot between (1/T x 10^{-3}) verses Ln(σ) for PVC with ZnO nanoparticle doped at 0.00653 gm/cc

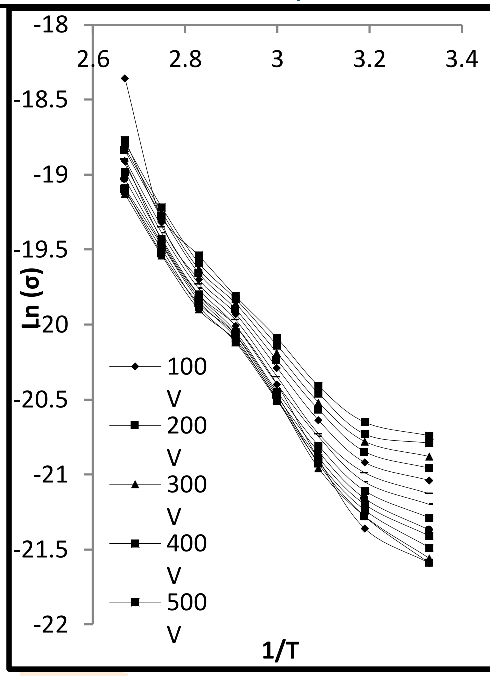

Fig.3. Plot between (1/T x 10^{-3}) verses Ln(σ) for PVC with ZnO nanoparticle doped at 0.0130 gm/cc

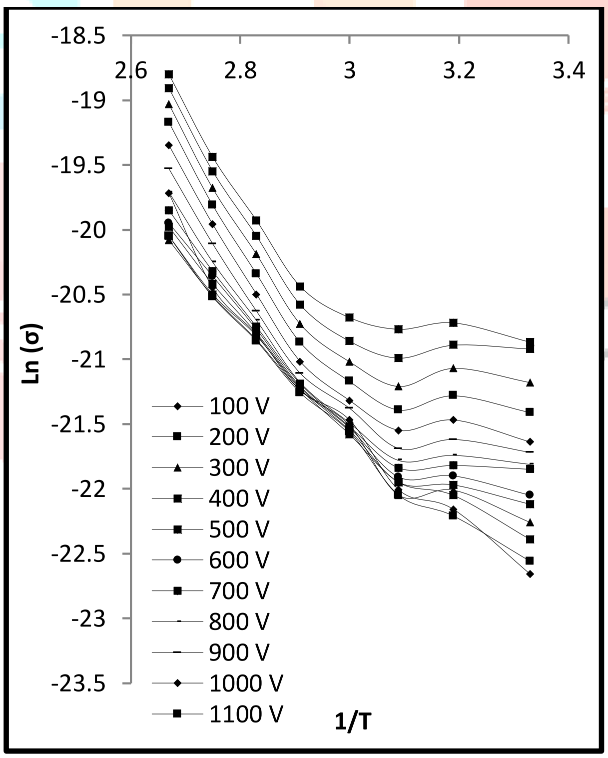

Fig.4 Plot between (1/Tx 10^{-3}) verses Ln(σ) for PVC with ZnO nanoparticle doped at 0.003265gm/cc

and 0.01303 gm/cc in PVC, there is a change in conductivity. Initially increase in conductivity at low temperature is due to injection of charge carrier (i.e. electrons) from ZnO directly to PVC.

Table 1. Activation energy in eV for PVC film doped with 0.0130 gm/cc of ZnO

	100 V	400 V	700 V	1000V	1300V
Region 1	0.1415	0.1538	0.1107	0.0738	0.0369
Region 2	0.3850	0.3375	0.3233	0.3013	0.2783
Region 3	0.4791	0.5306	0.4416	0.4630	0.4307

Table 2. Activation energy in eV for PVC film doped with 0.00653 gm/cc of ZnO

	100 V	400 V	700 V	1000V	1300V
Region 1	0.1415	0.1538	0.1107	0.0738	0.0369
Region 2	0.3850	0.3375	0.3233	0.3013	0.2783
Region 3	0.4791	0.5306	0.4416	0.4630	0.4307

Table 3. Activation energy in eV for PVC film doped with 0.003265 gm/cc of ZnO

	100 V	400 V	700 V	1000 V	1300 V
Region 1	0.4371	0.1046	0.0180	0.1046	0.0184
Region 2	0.3789	0.3670	0.3553	0.3395	0.3043
Region 3	0.5969	0.4145	0.4845	0.6191	0.6137

The nature of change in conductivity at low temperature is different for different rate of doping concentration i.e. 0.00325 gm/cc, 0.00653 gm/cc and 0.01303 gm/cc of ZnO. The current increases with increase in temperature (313 K, 333 K and 373 K). So if the rate of doping is increased there will be sharply increased in conductivity up to certain value.

In both doped and undoped samples the increase in conductivity at higher temperature may be due to softening and mobility of main chain segments as well as the rotation of side groups and creation of more and more dipoles are orientations resulting in higher equivalent surface charge density.

ZnO has high electron mobility. As temperature increases, mobility of electrons are increase and the mean free path of electrons are decrease. So in ZnO nanoparticle doped PVC film has lower conductivity than the undoped PVC film at higher temperature. This is due to the disturbance of ionic mobility in PVC by electron mobility.

Conclusion

The present experimental investigation reveals that the conductivity of ZnO nanoparticle doped PVC film increases more sharply than the undoped PVC film within intermediate range of temperature. The electronic current is operative because of its low activation energy low (<1 eV). So it is concluded that such polymer nanocomposites could be used as good semiconducting materials for many electronic devices.

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