



Electrical properties of ZnO nanoparticle doped in PVC films

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Abstract

ZnO Nanoparticle doped on PVC with different concentration with different were prepared by solution cast method. The electrical conductivity was measured for different range of temperature and applied fields. The conductivity verses inversion of temperature for virgin and doped has been plotted and from the plot the conductivity decreases for the doped sample. The activation energy of doped sample is less than the doped sample which shows the semiconducting property is increasing with doping concentration.

Key words: PVC, thermostat, Activation energy.

Introduction:

The study of electrical conductivity of insulating and semiconducting materials sandwiched metal electrodes is becoming popular now a days¹. The advantages of conducting polymers are their process ability mainly by dispersion. Conducting polymers are generally not plastic but like insulating polymer, these are organic materials. 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 method of organic synthesis² and by advance dispersion techniques³. The most recent research in conducting polymers is to develop high conducting with stability and acceptable processing attributes. 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-phenylenevinylene) (PPV), Polyethylene terephthalate (PET) etc.

Polymer viz, polyvinyl 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 electrical conduction in it, but production of thermally stimulated discharge conductivity by doping charcoal has been studied⁴

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 its alloying magnesium oxide or cadmium oxide⁵

Nanostructured ZnO materials are current importance in electronic, optic and photonic applications and for the basis of nanotechnology applications in sensors and molecular electronics. The nanostructured exhibit novel electrical, mechanical, chemical and optical properties which are believed to be due to the surface confinement effects or nanostructures in one dimension. 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 devices⁶.

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. 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), film and ZnO nanoparticle doped PVC film at different applied voltage, temperature and doping concentrations.

Experimental:

(i) *Sample preparation:*

PVC granule form supplied by the Reliance industry Surat, Gujarat and cyclohexanon supplied by S D Fine Chem Ltd, Mumbai for the present study form a solution (4 gram of PVC and 20 cc of cyclohexanon). 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.

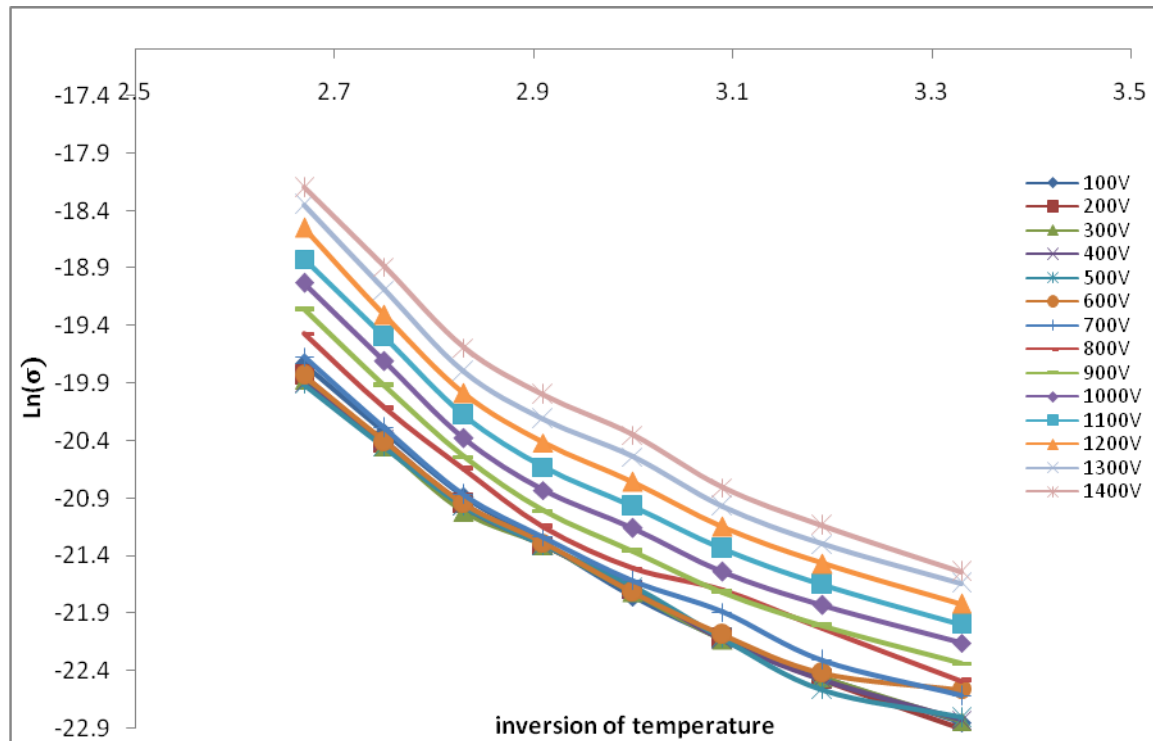
After a solution is form as above, ZnO⁷ nanoparticles supplied by Material Science Laboratory, B N College, Patna, is doped with different quantities i.e. 0.00325 gm/cc, 0.00653gm/cc and 0.01303gm/cc. Now, the mixture (PVC + ZnO) is stirred by Magnetic stirrer (Eltect-MS 205) for 8 hrs, then the mixtures 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 earlier⁸. 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:*

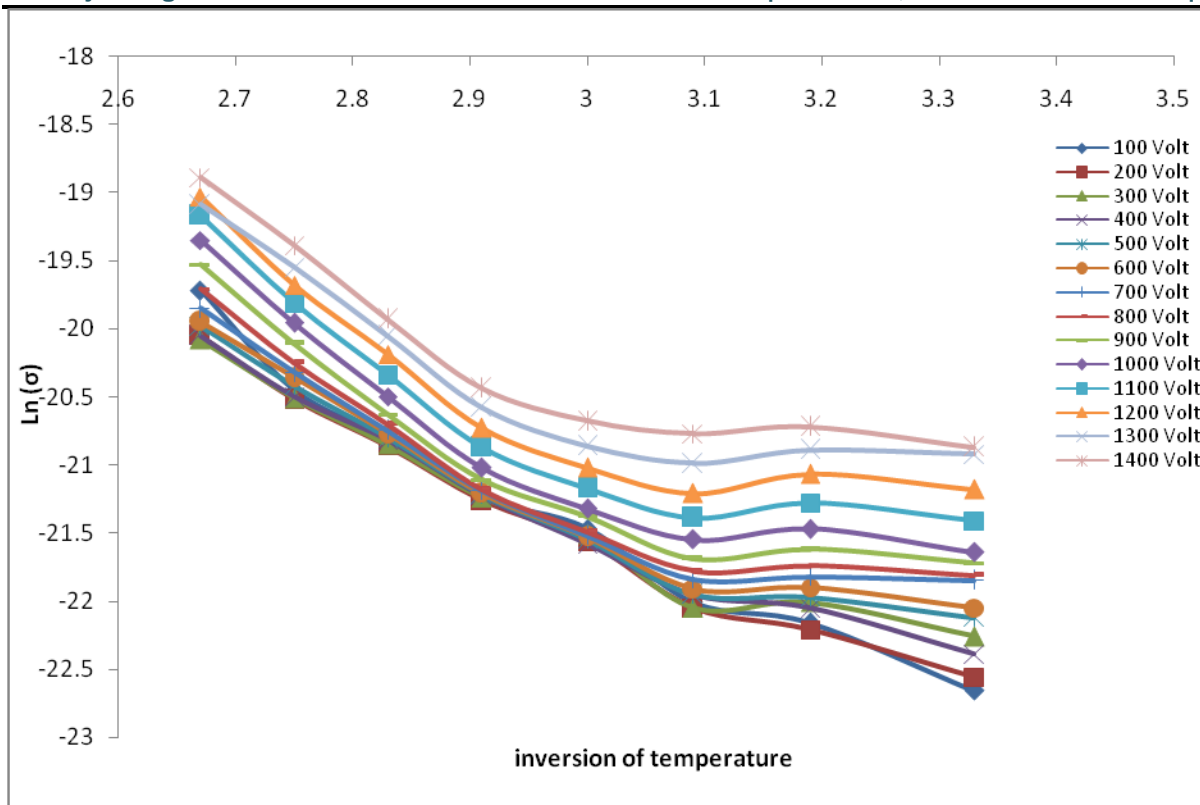
The sample is cut circularly slightly greater than the surface area of the electrode having area 5.067×10^{-4} sq-cm to avoid edge effect. The sample is placed between the two electrodes under light constant pressure in the sample holder. The sample holder is placed inside the temperature controlled 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 earlier⁹.

3. Result and Discussion:



Plot between inversion of temperature versus Ln(σ) for pure PVC film



Plot between inversion of temperature versus $\ln(\sigma)$ for PVC with ZnO nanoparticle doped at 0.003265 gm/cc

In the present study the figures are the curves between $\ln \sigma$ (mho/m) and $\frac{1}{T} \times 10^{-3}$ of the virgin 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 virgin and ZnO nanoparticle doped in 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 virgin and nanoparticle doped PVC films shows the semiconducting nature. So the variation of electrical conductivity with temperature can be represented by the Arrhenius equation,

$$\sigma = \sigma_o \exp \left[- \frac{E_a}{KT} \right]$$

Where σ_o = pre exponential factor,

E_a = the activation energy of conduction and

K = the Boltzmann constant.

	100 V	400 V	700 V	1000 V	1300 V
Region1	0.2399	0.2153	0.1907	0.2030	0.2092
Region 2	0.3468	0.3671	0.3376	0.3479	0.3590
Region 3	0.6244	0.5760	0.6460	0.7265	0.7752

Activation energy for virgin sample

	100 V	400 V	700 V	1000 V	1300 V
Region1	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

PVC + ZnO doped at 0.003265 gm/cc

Value of activation energy in eV for different applied voltage for the doped samples (PVC + ZnO doped at 0.003265 gm/cc).

Tables shows the variation of activation energy which is calculated from $\ln \sigma v s \frac{1}{T} \times 10^{-3}$ plot within low intermediate and high temperature region. Low activation energy corresponds to electronic current and high value of ionic current¹⁰. 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 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 which has side chain (polar group) 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 temperature⁴. When ZnO nanoparticle is doped at the rate of 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.

The nature of change in conductivity at low temperature are different for different rate of doping of 0.01303 gm/cc of ZnO, the current first increase up to 313 K, 333 K and 373 K respectively. So if the rate of doping is increase 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 becomes easier also more and more dipoles are oriented 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. In such sample electronic current is operative as its activation energy low (<1 eV). The activation energy of doped sample is less than the undoped sample which shows the semiconducting property is increasing with doping So it is concluded that such polymer nanocomposites could be used as good semiconducting materials for many electronic devices.

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