



EFFECT OF ZINC OXIDE NANOPARTICLE DOPED PVC FILMS ON ACTIVATION ENERGY AND ENERGY GAP

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Abstract:

Zinc oxide nanoparticles having a size of 7.7nm were doped in PVC solution at different concentrations and made films of thickness 0.035 cm each. The conductivity is measured for different applied fields and temperatures for ZnO nanoparticle doped and undoped films. The activation energy is calculated from $\ln\sigma$ versus $1/T \times 10^{-3}$ K plot and found to increase with the increase of doping. The energy gap is calculated from the slope of $\ln R$ versus $1/T \times 10^{-3}$ K plot and found to decrease with the increase of doping rate and applied voltage, which shows the semiconducting nature.

Keywords: ZnO, PVC films, Arrhenius equation, Semiconductor, Activation energy and Energy gap.

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Introduction:

Polymers are known to have good insulating properties and are among the most used materials in the modern world. Conducting polymers are polymer materials with metallic and semiconductor characteristics, a combination of properties not exhibited by any other known material. Over the past decade, there has been significant progress in studying the properties of conducting polymer nanocomposites as it has a wide range of applications in the various fields of electronics, optics, energy devices, medicine, actuators, and composites as a viable alternative to metallic or inorganic semiconductor counterparts. The advantage of conducting polymer nanocomposites is their processability mainly by dispersion. Conducting polymer nanocomposites 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 synthesis and advanced dispersion techniques¹. The most recent research in conducting polymers is to develop high conducting with stability and acceptable processing attributes.

There has recently been a huge demand for developing flexible or wearable electronics, displays and other devices, in which conducting polymer nanocomposites can ultimately be used as true flexible organic conductors or semiconductors. The most notable property of conducting polymer nanocomposites is their inherent electrical conductivity, which is closely connected to the charge transfer rate and electrochemical redox efficiency. Most conducting polymer nanocomposites act as semiconductors in terms of conductivity although several studies on metallic conducting polymers have been reported. Unlike their counterparts, a weak intermolecular overlap of electronic bands and low mobility of charge carriers.

Polyvinyl chloride (PVC) is one of the most versatile plastics; it is the second-largest manufactured resin by volume worldwide. After a comparatively short half-century, PolyVinyl Chloride (PVC) has invaded almost all applications of traditional materials, such as clay, cast iron, steel and asbestos cement, and has become the premier pipe material. PVC is popular due to its advantages of immunity to corrosion and biological resistance. It has excellent electrical insulation properties, impact strength and

resistance to weather conditions, which is not considered as a conducting polymer².

The modification of polyvinyl chloride lies basically in the dichlorination process, including both substitution and elimination; because of the peculiarities of the material relevant to its applications, the chemical fictionalization of polyvinyl chloride seems permanent to improve and modify the polymer³.

ZnO is a semiconductor of groups II-VI and a promising material for various applications. It is actively used due to its very attractive properties and nontoxic nature. Among metal oxides, nanostructured zinc oxide (ZnO) exhibits exceptional electronic, optical, and electrochemical properties. 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 nanodevices⁴. In addition to this, the wide bandgap (3.37 eV) and massive exciton binding energy (60 meV) permit the material to operate at much higher voltage, frequency, and temperature than conventional semiconductors⁵. Moreover, ZnO-based composites have shown potential applications in the field of industrial electronic devices like transducers, electrochemical sensors, solar cells, supercapacitors, and lithium-ion batteries⁶. ZnO is one of the most demanded materials in the electronic industry due to its very attractive properties like wide availability, nontoxicity, and cost-effectiveness. Nanocomposites of ZnO have been explored by various researchers⁷.

In the present study, an attempt is made the variation of activation energy and energy gap of pure PVC film and ZnO nanoparticle doped PVC film at different applied voltage, temperature and doping rate.

2. Experimental details:**(i) Sample preparation:**

PVC granule form supplied by the Reliance industry Surat, Gujarat and cyclohexanone supplied by S D Fine Chem Ltd, Mumbai for the present study form a solution (4 gram of PVC and 20 cc of cyclohexanone). The solution was 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 to ensure uniform thickness. The whole system was allowed to evaporate at room temperature in dust dust-free chamber for 6 days and after complete

evaporation, the film was detached from the glass plate. Thus a pure (PVC + cyclohexanone) PVC (Sample A) film is formed.

After the solution is formed ZnO having size 7.7 nm⁽⁸⁾ is doped with different quantities i.e. 0.00325 gm/cc, (Sample B), 0.00653 gm/cc (Sample C) and 0.01303 gm/cc. (Sample D). Now, the mixture (PVC + ZnO) is stirred by a Magnetic stirrer (Eltect-MS 205) for 8 hrs, then the mixture is poured on the glass plate and proceeds as above. Thus, the ZnO nanoparticle-doped PVC film was formed. The sample preparation is the same as that reported earlier⁹. The thickness of the sample was measured by a screw gauge having the 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 and ultra-thermostat (U-10, Germany)

The different potential is applied across the sample by the power supply (EHT-11). The value of potential across the sample is varied from 0 to 1400 volt by an interval of 100 volt at a constant temperature. The potential drop across 1 MΩ resistor is recorded by a 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. To make uniform heating the sample is kept at constant temperature for 30 minute for each consecutive reading. The conductivity measurement is the same as that reported earlier¹⁰.

Result and Discussion:

The transfer of electrons from one molecule to another is the main stumbling block for good conduction on the microscopic scale in a system of long polymeric molecules one could assert with some justification that the intermolecular conduction problem is much less important because relatively few intermolecular transfers are required. In applying the model to polymers, we are concentrating our attention on the intermolecular motion of charge carriers¹¹.

A key property of a conductive polymer is the presence of conjugated double bonds along the backbone of the polymer. In conjugation, the bonds between the carbon atoms are alternately single and double. Since the electrons in a

conjugated system are only loosely bound, electron flow may be possible. Every bond contains a localized σ bond which forms a strong chemical bond. In addition, every double bond also contains a less strongly localized π bond which is weaker. These enable the electrons to be delocalized over the whole system and so be shared by many atoms. This means that the delocalized electrons may move around the whole system. However, conjugation is not enough to make the polymer material conductive. In addition, the polymer material needs to be doped for electron flow to occur¹².

Once doping has occurred, the electrons in the π bonds can jump around the polymer chain. As the electrons are moving along the molecule, an electric current occurs. For better conductivity the molecules must be well ordered and closely packed to limit the distance jumped by the electrons. The conductivity of conducting polymers can be tuned by chemical manipulation of the polymer backbone, by the nature of the dopant, by the degree of doping, and by blending with other polymers¹³.

As ZnO exhibits high quantum efficiency due to greater order of electron mobility $200\text{--}300 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ and has a wide band gap $3.37 \text{ eV}^{(14)}$. So, the electrical properties of the ZnO nanoparticle-doped PVC film will change from the pure PVC film.

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

Pure ZnO has fixed and specific electric properties like bandgap, electron mobility, thermal conductivity, and exciton binding energy. The band gap of ZnO can be tuned to a high or low value by adding some dopant. The electrical and dielectric properties of ZnO depend upon the concentration of the dopant. So, these properties can be tailored by adding some other materials in it and creating the composite¹⁵.

The curves Fig (1 – 4) between $\text{Ln}\sigma (\Omega^{-1}\text{m}^{-1})$ and $1/T \times 10^{-3} \text{ K}^{-1}$ of the pure and ZnO nanoparticle-doped PVC film. A slight increase in the conductivity up to 353 K and a sharp 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 pure 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. Both pure and nanoparticle-doped PVC films show a 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.

Table (1 – 4) shows the variation of activation energy which is calculated from $\text{Ln}\sigma$ ($\Omega^{-1}\text{m}^{-1}$) vs $1/T \times 10^{-3} \text{ K}^{-1}$ plot within low intermediate and

high-temperature regions. Low activation energy corresponds to electronic current and a high value of ionic current¹⁶. 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 an independent movement of chain sections containing monomeric segments. In addition to the segments, polymers consist of side chains or individual atomic groups. The relaxation time of the main chain segments is greater than that of the side chains. The polymer which has a side chain (polar group) is independent of each other and different relaxation times and is capable of orientation in an electric field, then many dipole groups lose maxima due to the presence of different polar group¹⁷.

Table 1: Pure PVC (sample A)

	100 V	400 V	700 V	1000V	1300V
Region 1	0.239	0.2153	0.1907	0.2030	0.2092
Region 2	0.3468	0.3671	0.3376	0.3441	0.3590
Region 3	0.6244	0.5760	0.6460	0.7265	0.7806

Table 2: PVC + ZnO doped at 0.0130 gm/cc (sample B)

	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: PVC + ZnO doped at 0.00653 gm/cc (sample C)

	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 4: PVC + ZnO doped at 0.003265 gm/cc (sample D)

	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

Value of activation energy in eV for different samples at different applied voltage

In PVC various types of molecular relaxations are possible. The only possible motions due to low temperature are the local motion of molecular groups, i.e., rotation of side groups or internal motion within the side groups. Hence at low temperatures, there may be a slight decrease and then a rise in the conductivity which is due to the mobility of main chain segments increasing with the increase in temperature¹⁸. For different samples, i.e., A, B, C and D there is a change in conductivity, which is due to the injection of charge carrier (i.e. electrons) from ZnO directly to PVC.

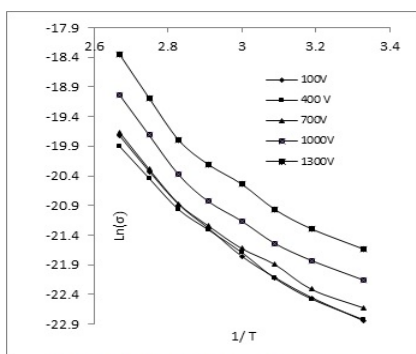


Fig.1. Plot between $(1/T \times 10^{-3})$ versus $\text{Ln}(\sigma)$ for pure PVC

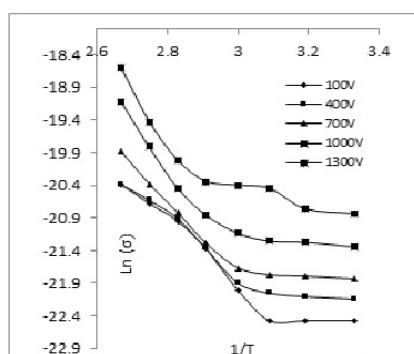


Fig.2. Plot between $(1/T \times 10^{-3})$ versus $\text{Ln}(\sigma)$ for PVC with ZnO nanoparticle doped at 0.00653 gm/cc

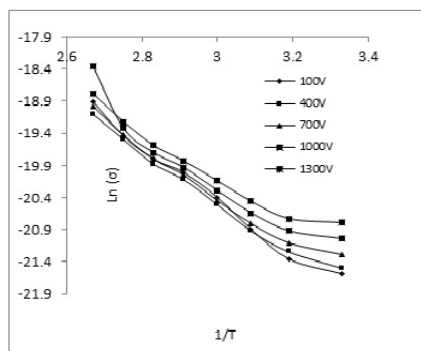


Fig.3. Plot between $(1/T \times 10^{-3})$ versus $\text{Ln}(\sigma)$ for PVC with ZnO nanoparticle doped at 0.0130 gm/cc

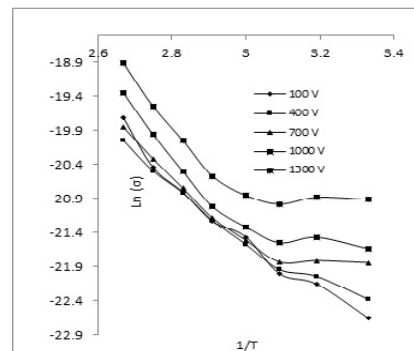


Fig.4. Plot between $(1/T \times 10^{-3})$ versus $\text{Ln}(\sigma)$ for PVC with ZnO nanoparticle doped at 0.003265 gm/cc

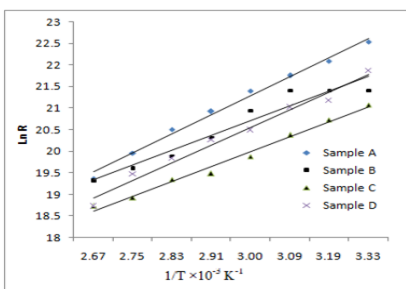


Fig.5. Plot between $(1/T \times 10^{-3})$ versus LnR for different samples at 100 volt

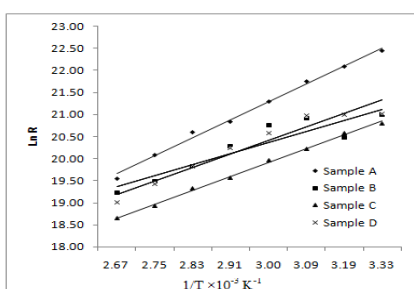


Fig.6. Plot between $(1/T \times 10^{-3})$ versus LnR for different samples at 100 volt

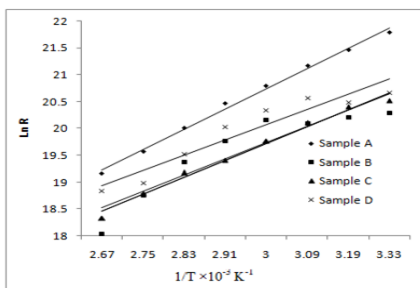


Fig.7. Plot between $(1/T \times 10^{-3})$ versus LnR for different samples at 1000 volt

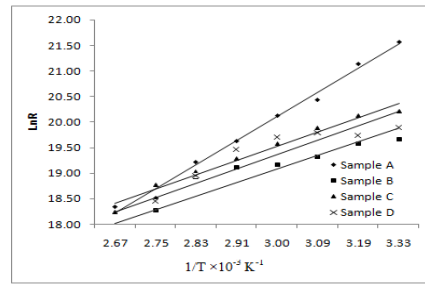


Fig.8. Plot between $(1/T \times 10^{-3})$ versus LnR for different samples at 1400 volt

In both doped and undoped samples the increase in conductivity at higher temperatures may be due to the 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 density¹⁹.

Table 5: Energy Gap (E_g) for ZnO nanoparticle doped PVC films (in eV)

Sample	100 volt	500 volt	1000 volt	1400 volt
A	0.789	0.784	0.740	0.721
B	0.680	0.636	0.608	0.407
C	0.676	0.614	0.560	0.517
D	0.656	0.592	0.547	0.514

The fig (5–8) show the plot of $\ln R \Omega$ versus $1/T \times 10^{-3} \text{ K}^{-1}$ for different samples at different applied voltages. From the slope of the plot, the band gap is calculated. The decrease in band gap with the increase in doping rate is shown in Table -5. PVC is partially syndiotactic material, with sufficient irregularity of structure that crystallinity is quite low²⁰. i.e. almost amorphous in nature. The presence of amorphous regions gives rise to a localized state. Since there are many localized states, the release or excitation carriers in these states dominate the conduction process. The dopants ZnO are presents in sufficient quantity and remarkably affect the position of Fermi level²¹. The molecules of dopants enter either in the amorphous regions of the polymer or at the disordered regions chain folds. If they are present in low concentration they will give rise to additional molecular sites for trapping of charges. Such localized sites formed by dopant molecules can be defined in molecular terms using the difference in ionization potential as an indication of trap depth. If the dopant concentration is increased, the dopant molecules start bridging in separating the two localized states and lowering the potential barrier between them, thereby facilitating the transfer of charge carriers between the two localized states²². The dopant ZnO has high mobility also an n-type semiconductor so if it is doped to pure PVC the energy level lies just below the conduction band, i.e. the width of the band gap is decreased, which results in electrons moving into the conduction band with increased of the applied field.

Conclusion:

The activation energy and band gap are calculated from $1/T \times 10^{-3} \text{ K}^{-1}$ verses $\ln \sigma (\Omega^{-1} \text{ m}^{-1})$ and $1/T \times 10^{-3} \text{ K}^{-1}$ verses $\ln R$ plot respectively. The activation energy varies with the doping of nanoparticles and the energy gap decreases with the increase of doping rate. The present experimental investigation reveals that there is a direct correlation between the doping of ZnO nanoparticles in polymers and their electrical properties.

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