



Temperature and Field Dependence of Thermally Stimulated Discharge Current in Polymer Nanocomposite Electret

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Abstract

Thermally stimulated discharge current has been measured for both pure and ZnO nanoparticle doped PVC films. The value of thermocurrent has been calculated by employing Arrhenius equation and found that the conductivity of doped sample is increase more sharply with temperature than that of pure sample for intermediate range of temperature, and shows the semiconducting nature but beyond the transition temperature the conductivity of doped sample decrease with rise of temperature which shows the metallic nature.

Keywords: Arrhenius plot, conductivity, polymer, nanocomposite, TSDC

Introduction

Thermally Stimulated Depolarized Conductivity (TSDC) technique in polymer electrets is a basic tool to identify and evaluate the dipole orientation process, trapping and recombination levels. Polymer have emerged as a very important class of material because of their unique electrical, optical, thermal properties, high strength, light weight, good flexibility, resistance to chemicals, also for fabrication into complex shapes in different colors and potential in the application of wide spectrum of technological fields. With the advancement of science and technology polymer materials are used in spacecraft, electronic and telecommunication, medical science, even replacing of human organ. So, it is the main task to the researcher is to investigate the electrical, mechanical, thermal and chemical properties of polymer. Among the properties, the combined effect of electric and thermal energy on electrical conducting polymer is important one.

The study of electrical conduction in polymer is of considerable significance from two major points of view—firstly, for its own sake, because charge transfer characteristics are of fundamental interest and secondly for the information studies can provide the nature of electrical contacts, which may have a great influence on the measured electrical properties. The charge storage property of polymer can be considerably modified with the help of suitable dopants Khare et al (1998)[1]. The broadest method that can be applied to enhance the conductivity of polymeric material in the formation of molecular aggregates or charge transfer complexes. The electrical conduction behaviour of a number of polymer charge transfer complexes and molecular aggregates have been investigated by several workers, yet the mechanism of conduction and the role of the impurity of these systems is not known to any degree of certainty.



The simultaneous existence of transport and polarization phenomena, characteristic of the polymeric materials, usually makes the interpretation of experimental data difficult. But on the other hand, those phenomena may be used as a source of valuable information on high resistivity materials. Especially useful for the investigation of these materials apart from the dc measurement methods are connected with the electric relaxation currents. Applying these methods to the polar dielectrics, to which the polymer belongs, one can differentiate the relaxation of dipole groups and space charge. At the same time the space charge relaxation is directly related to the conduction process.

In conducting polymers, the effect of temperature and biasing voltage influence conductivity and in many semiconductor, transition temperature, pressure effects the conductivity such phase transition are found to be interesting phenomena. Electrical conduction in polymers has been investigated by several workers but a little has been reported about the nature of conduction both for polarized & unpolarized condition.

Several workers have investigated the d.c. conductivity of polymers with different mechanism of conduction. The effect of thermal aging on conductivity has been explained with the help of cluster model Perepechko I I (1975)[2] for the polymer, which display typically two temperature transition in the glassy region. This model is useful to understand the crystalline or amorphous state of the polymer. By cluster we mean here, that region with molecules or their parts being more closely packed or with more ordered arrangement of these as compared with the looser and disordered bulk of the substance. On basis of cluster model it may be supposed that the low temperature transition in glassy region is associated with the unfreezing of segmental motion in the disordered region. The high temperature transition is apparently associated with the unfreezing of the segmental motion inside the more ordered regions. A change in temperature coefficient of conductivity between different regions of conduction may be a tool to recognise the temperature transitions in the glassy region as displayed by many polymers. Karimi et al (1987) [3].

A number of groups have reported on the electrical conductivity and dielectric properties of composites of variety of conductivity and dielectric properties of conducting polymers, Gangopadhyay et al (2001)[4]. It has been shown that the conductivity of these heterogeneous systems depends on number of factor, such as concentration and interfacial interaction between filler molecules and host matrix.

Since the discovery of carbon nanotubes by Sumio Iijima in (1991) [5], increasing attention has been paid to the newly emerging material due to its remarkable mechanical and electrical properties. In connection to nanomaterials polymer nanocomposite represents a redical alternative to conventional field polymer. So, the study of the electrical properties of the conducting polymer nanocomposite is an emerging area in present day electronics.

The present paper we report the thermally stimulated depolarized conductivity of ZnO nanoparticle doped in polyvinyl chloride films.



Polyvinylchloride

Polyvinylchloride (PVC) is a thermoplastic polymer and it is third most widely produced plastic, after polyethylene and polypropylene. PVC is widely used in construction because it is cheap, durable and easily worked. It can be made and more flexible by the addition of plasticizers, the most widely used being phthalates. In this form, it is used in clothing and upholstery, electrical cable insulation, inflatable products and many applications in which it replaces rubber.

Zinc oxide

Zinc oxide in powder form is widely used as an additive into numerous materials and products including plastics, ceramics, glass, cement, rubber (e.g., car tires), lubricants[6], paints, ointments, adhesives, sealants, pigments, foods (source of Zn nutrient), batteries, ferrites, fire retardants, first aid tapes, etc. ZnO is present in the Earth's crust as the mineral zincite, however, most ZnO used commercially is synthetic.

In materials science, of the II-VI semiconductor group (since zinc and oxygen belong to the 2nd and 6th groups of the periodic table, respectively). The native doping of the semiconductor (due to oxygen vacancies) is n-type. This semiconductor has several favorable properties: good transparency, high electron mobility, wide band gap, strong room-temperature luminescence, etc. Those properties are already used in emerging applications for transparent electrodes in liquid crystal displays and in energy-saving or heat-protecting windows, and electronic applications of ZnO as thin-film transistors and light-emitting diodes are forthcoming. Current limitations to p-doping do not limit electronic and optoelectronic applications of ZnO, which usually require junctions of n-type and p-type material. Known p-type dopants include group-I elements Li, Na, K; group-V elements N, P and As; as well as copper and silver. However, many of these form deep acceptors and do not produce significant p-type conduction at room temperature.

ZnO has a relatively large direct band gap of $\sim 3.3\text{eV}$ at room temperature. Advantages associated with a large band gap include higher break down voltages, ability to sustain large electric field, lower electronic noise, and high-temperature and high power operation. The band gap of ZnO can be tuned to $\sim 3\text{-}4\text{ eV}$ by its alloying with magnesium oxide or cadmium oxide[7]. Most ZnO has n-type character, even in absence of intentional doping[8]. Controllable n-type doping is easily achieved by substituting Zn with group-iii element such as Al, Ga, In or by substituting oxygen with group-vii elements chlorine or iodine[9] .

Reliable p-type doping of ZnO remains difficult. This problem originates from low solubility of p-type dopants and their compensation by abundant n-type impurities. This problem is observed with GaN and ZnSe. Measurement of p-type in “intrinsically” n-type material is complicated by inhomogeneity of sample.



Current limitations to doping does not limit electronic and optoelectronic applications of ZnO, which usually require junctions of n-type and p-type material. Known p-type dopants include group-I elements Li, Na, K; group-V elements N, P and As; as well as Cu and Ag. However, many of these form deep acceptors and do not produce significant p-type conduction in room temperature [10].

Electron mobility of ZnO strongly varies with temperature and has a maximum of $\sim 2000 \text{ cm}^2 / (\text{V}\cdot\text{s})$ at 80K. Data on hole mobility are scarce with values in the range $5\text{-}30 \text{ cm}^2 / (\text{V}\cdot\text{s})$ [11].

Experimental

Sample preparation

The PVC granule form which is supplied by the Reliance industry Surat, Gujarat, cyclohexanon supplied by S D Fine Chem Ltd, Mumbai and ZnO nanoparticles, supplied by Material Science Laboratory, B N College, Patna are used for the present study

2.1.1. Formation of pure film

The PVC granule form and cyclohexanon (4 gram of PVC and 20 cc of cyclohexanon) form solution. The solution kept at room temperature for one week. For complete desolation, 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.

2.1.2. Formation of ZnO nanoparticle doped film

After a solution is formed, ZnO nanoparticles 0.01303 gm/cc is doped using top loading balance. Now, the mixture (PVC + ZnO) is stirred by Magnetic stirrer (Eltect-MS 205) for about 8 hrs, then the mixture 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 earlier³. The thickness of the sample was measured by travelling microscope and found to be 0.03 cm.

Conductivity measurement

The sample is cut circularly slightly greater than the surface area of the electrode having area $5.067 \times 10^{-4} \text{ sq-cm}$ 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) and heated up to 800C (the transition temperature). The electric field strength of desired strength is applied across the sample and maintain at constant temperature (800C) for 1 hr. The electric field strength are different for each observation but the polarising temperature are the same. The sample holder containing sample is removed from the thermostat and cool down to room temperature in presence of applied field. After it attains room temperature the sample is short circuited for



20 minute and thus formed electret. Now the sample holder containing sample is placed inside the thermostat and current is measured by Solid State Electrometer (610- model) by maintaining different temperature. This operation is repeated for different temperature.

The same operation is repeated for ZnO nanoparticle doped sample.

Result and discussion

The $\ln \sigma$ and I/T curves are plotted for different applied voltage and temperature, the value of activation energy (E_a) for different regions are calculated from the relation:

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

where σ_0 is pre-exponential factor and k is Boltzmann's constant. The present study on the polarizing field and temperature dependence of the electrical conduction in pure and doped films of PVC has been carried out to understand the role of dopants when doped at the rate of 0.01303 gm/cc. Fig. (1) shows the thermally stimulated dipolarized conductivity (TSDC) thermogram ($\log \sigma$ vs $103/TK-1$ plot) for pure and Fig. (2) shows ZnO nanoparticle doped PVC film at various polarizing fields (0.66kV/cm, 1kV/cm, 1.33kV/cm, 1.66kV/cm and 2kV/cm for both pure and doped sample). In pure PVC film the continuous increase in conductivity is observed for all polarizing field at for all range of temperature. A non linear field dependence is evident, which is due to the mobility of main chain segment increase with rise of temperature. The constituent of pure PVC is largely an amorphous polymer; it is characterized by three transitions: β relaxation occurring at low temperature, α relaxation at glass rubber transition temperature and α_1 relaxation occurring at a temperature well above glass rubber transition temperature. The absence of peak is due to low applied field. In polymeric materials, various types of molecular relaxations are possible. Only the possible at low temperature are local motion of molecular groups, e.g. the rotation of side groups or internal motion within the side groups so the thermoelectret show the semiconducting nature in all range of temperature[12].

This depends upon whether the sample receives the charge of same sign or opposite to that of electrode i.e. homocharges or heterocharges to which the surface of sample was in contact during polarization.

It was observed in our case that electrical conductivity of pure film is increase with rise of temperature which shows the semiconducting nature but for ZnO nanoparticles doped film electrical conductivity increase for intermediate range of temperature and decrease for higher temperature which shows the metallic nature. Since heterocharge and homocharge are assumed to have opposite sign. The heterocharge develops due to reorientation of dipoles due to polarizing field there may be no more dipole to be oriented. It is observed that there constitute homocurrent which dominate over the heterocurrent after

polarizing the sample. The homocharge arise and depends upon electrode-dielectric work function and also due to injected charge carriers from electrodes[13].

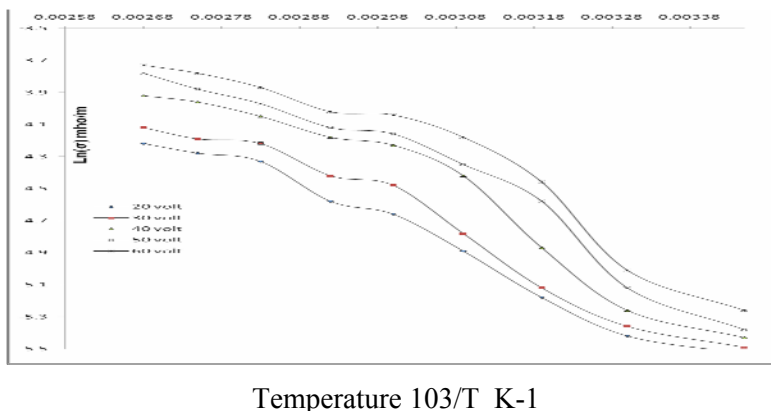


Fig.1. Plot between inversion of temperature versus $\text{Ln}(\sigma)$ for pure PVC

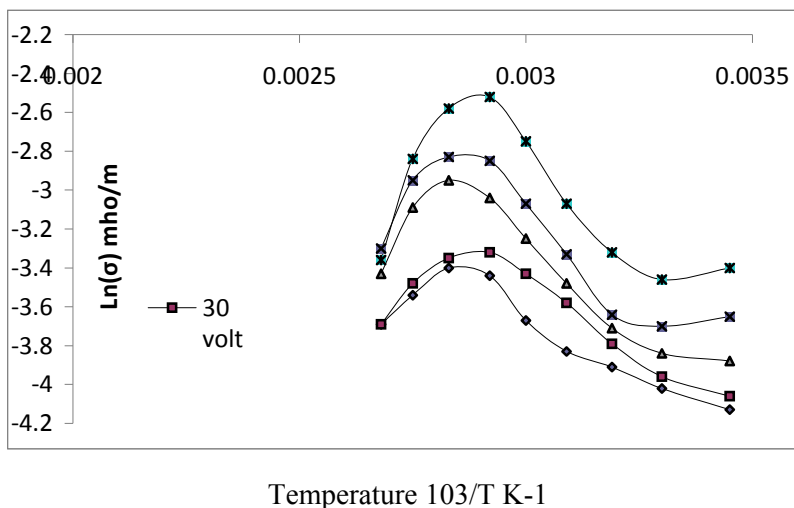


Fig.2. Plot between inversion of temperature versus $\text{Ln}(\sigma)$ for PVC with ZnO nanoparticle doped at 0.003265 gm/cc

It is observed that difference between becomes minimized but in some samples was found to be greater than i.e. homocharges produce less effect than heterocharges hence the homocharge deposition does not take place due to spark discharges in the air gap. Hence the conductivity is enhanced in polymer electrets. This result further supports that space charge injection takes place from electrodes i.e. homocharge injection through connecting electrodes.

Conclusion

The present experimental investigation reveals that at low temperature the width band gap is decrease due to thermal energy in ZnO nanoparticle doped PVC film in compare with the pure PVC film, so the



conductivity of ZnO nanoparticle doped PVC film increases more sharply with temperature than the undoped PVC film within intermediate range of temperature. But the valence band and the conduction band at high temperature (beyond the glass transition temperature) the width band gap are overlapped which results the conductivity of ZnO nanoparticle doped PVC film decrease and shows the metallic nature. So, it is concluded that such polymer nanocomposites could be used as good semiconducting materials for many electronic devices at low temperature.

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