

Electrical conductivity of polyaniline doped PVC–PMMA polymer blends

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MS received 27 June 2006; revised 7 August 2006

Abstract. The electrical conductivity of polyaniline doped polyvinylchloride (PVC) and poly(methyl methacrylate) (PMMA) thin films has been measured by studying the I – V characteristics at various temperatures in the range 323–363 K. The results are presented in the form of I – V characteristics and analysis has been made by interpretation of Poole–Frenkel, Fowler–Nordheim, Schottky $\ln(J)$ vs T plots, Richardson and Arrhenius plots. The analysis of these results suggests that Schottky and Richardson mechanisms are primarily responsible for the observed conduction.

Keywords. Polyaniline doped PVC–PMMA polymer blends; conductivity.

1. Introduction

Polymer composites have steadily gained growing importance during the past decade. A good amount of work has been reported on the conduction mechanism in polymeric materials. The electrical conduction in polymer film has much importance due to the discovery of the memory phenomenon (Kryezewski 1975) and has wide applications now-a-days in thin film devices (Mead 1961). In recent years, because of the need for electrostatic charges dissipation, electromagnetic shielding etc, new polymers with electrical conductivity have been formulated. This led to new discoveries in the area of conducting polymers, which has now become one of the hot topics of research (Radhakrishnan 2001).

Electrical properties constitute one of the most convenient and sensitive methods for studying the polymer structure (Ferraro and Walkar 1965; Kimura and Kajiwara 1998). The interest in organic and polymeric semiconductors has arisen, particularly because of their electrophotographic and solar cell applications. Many synthetic polymers (Danno *et al* 1983; Kumar *et al* 1985) like polyacetylene, polypyrrole, poly-carbazol etc have been studied.

The electrical conduction in iodine doped polystyrene (PS) and poly(methyl methacrylate) (PMMA) has already been reported (Chakraborty *et al* 1991; Sangawar 1995). Keller *et al* (1991) reported the thermally stimulated discharge current (TSDC) study of polyblends of PS and PMMA. Belsare and Deogaonkar (1998) measured the elec-

trical conductivity of iodine doped polyblend films of polystyrene (PS) and poly(methyl methacrylate) (PMMA).

Electrical conduction of succinic acid doped glycine pellet has been discussed by Burghate *et al* (2004). Karimi *et al* (1987) carried out study of electrical conduction in polyethyleneterephthalate (PET) film. The electrical properties of regenerated cellulose (cello phone) film were studied by Bhat and Makwana (1990). Khare (1994) studied the current–voltage characteristics of malachite green doped cellulose acetate films, for the measurement of electrical conductivity, as function of temperature, field, thickness and dopant concentration, using a conventional sandwich type cell.

Deshmukh *et al* (2005) reported electrical conduction in semiconducting PVC–PMMA thin film. Microhardness and X-ray diffraction studies on polymer blends of polyethylene methacrylate (PEMA) and polyethyleneoxide (PEO) have been reported by Awasthi and Bajpai (2001).

In the case of organic solids, where the conductivity due to electron exiting from valence band to conduction band (Keton 1968; Khare and Shriwastava 1991) is negligible, a complex conduction behaviour (Parak and Garg 1991; Khare 1994) has been explained usually in terms of electron emission from cathode i.e. Schottky–Richardson mechanism (Schottky 1914), or the electron liberation from traps in the bulk of the material i.e. Poole–Frenkel mechanism (Frenkel 1938). However, the possibility of tunneling (Fowler and Nordheim 1928) and space charge limited conduction (Rose 1955) have also been investigated in the literature.

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The doping of iodine in PS (Chakraborty *et al* 1991), in PMMA (Sangawar 1995) and polyblends of PS and PMMA (Belsare and Deogaonkar 1998), have been reported to possess considerable influence on the conductivity although no attempt, so far, seems to have been made to study the effect of polyaniline conducting polymer doped blends. PVC as proton donor and PMMA as proton acceptor are selected for the present study. The choice of these polymers thus takes into account the donor–acceptor capabilities. In the present study, d.c.-conduction of donor–acceptor mixed polymers doped with polyaniline, was measured to identify the mechanism of electrical conduction. It is shown how the I – V data of the sample can be used to arrive at a possible conclusion. Results have been discussed in the light of different mechanisms, such as Poole–Frenkel, Fowler–Nordheim, $\ln(J)$ vs T plots, Schottky plots, Richardson plots and Arrhenius plots. In case of Schottky–Richardson mechanism, the current shows strong temperature dependence but not in case of Poole–Frenkel mechanism. The study of temperature dependence of current density is, therefore, of great importance. The X-ray diffractogram (XRD) shows that the crystallinity is almost negligible showing the sample is amorphous.

2. Experimental

2.1 Preparation of sample

Polyvinylchloride (PVC) of standard grade supplied by Polychem Industries, Mumbai and poly(methyl methacrylate) (PMMA) supplied by Dental Product of India Ltd., Mumbai, were used for the study. The conducting polymer (polyaniline) was prepared by chemical oxidation using ferric chloride by conventional procedure. For the preparation of polyaniline doped thin film, the two polymers, PVC (1.5 g) and PMMA (0.5 g), were taken in the ratio 3 : 1 by weight, 1.5 g of PVC in 15 ml of tetrahydrofuran (THF) and 0.5 g of PMMA in 5 ml of THF dissolved separately and subsequently mixed together. Polyaniline was taken in 2 wt% and was dissolved in 5 ml of THF to produce polyaniline solution. After allowing them to dissolve completely, the three solutions were mixed together. The solution was heated at 60°C for 2 h to allow polymers to dissolve completely to yield a clear solution. A glass plate (15 × 15 cm) thoroughly cleaned with hot water and then with acetone was used as a substrate.

To achieve perfect levelling and uniformity in the thickness of the film, a pool of mercury was used in a plastic tray in which the glass plate was freely suspended. The solution was poured on the glass plate and allowed to spread uniformly in all directions on the substrate. The whole assembly was placed in a dust free chamber maintained at a constant temperature (40°C). In this way, the film was prepared by isothermal evaporation technique (Bahri and Sood 1983; Mehendri *et al* 1996). The film was subjected to 12 h

heating at a constant temperature of 50°C and for another 12 h at room temperature to remove traces of solvent. Finally, the film was removed from the glass plate. It was cut into small pieces of suitable size, which were washed with ethyl alcohol to remove the surface impurities. The X-ray powder diffractogram of the sample, recorded from a Phillips (Holland) automated diffractometer (RSIC, Nagpur) is shown in figure 1. The absence of peak in the X-ray spectra confirmed the amorphous nature of the polymer sample.

2.2 Thickness measurements

For measuring the thickness, micrometer screw gauge (Mahendri *et al* 1996) with least count, 0.001 cm (10 μm), was used. But for greater accuracy and resolution, a compound microscope in conjunction with an acculometer which gives least count, 1.3 μm and 3.3 μm, at the magnification of 1 : 10 and 1 : 100, respectively, was used. A small section of the sample was taken and mounted vertically to get a clear view of the thickness. The film used for the present study is of thickness, 60 μm.

2.3 Electrode coating

The electrode coating on the film of measured thickness was done by using quick drying and highly conducting silver paste (Sangawar 1995; Mehendri *et al* 1996) supplied by Eltecks Corporation, Bangalore. A mask of a circular aperture of 2.5 cm diameter was used while coating, to ensure uniformity in size of coated silver electrode.

2.4 Measurements

The thermostatically controlled oven supplied by the Tempo Industrial Corporation, Mumbai, was used for heating purpose. A mercury thermometer with an accuracy of ± 1°C was used for recording temperatures. The regulated power supply supplied by Nupur, India, was used as the voltage

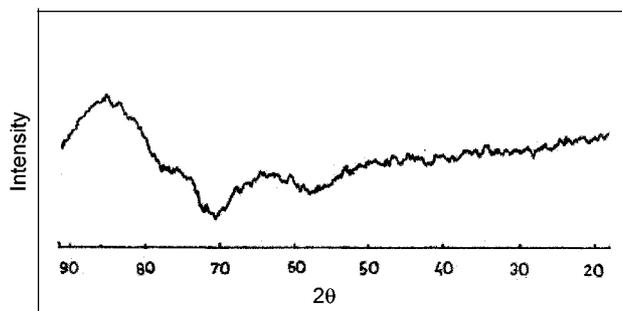


Figure 1. X-ray diffractogram of sample, polyaniline doped PVC–PMMA polymer blends.

source, while current was recorded by using highly sensitive Pico-Ammeter (Model DPA 111) with an accuracy of $\pm 0.2\%$ supplied by Scientific Equipments, Roorkee.

The sample film with silver electrodes was sandwiched between two brass electrodes (diameter, 2.4 cm) of the sample holder specially fabricated in our laboratory. This formed the metal-insulator-metal (M-I-M) system, which was placed in the furnace. The current (I)-voltage (V) measurements were done at various temperatures from 323–363 K.

3. Results and discussion

$\ln(I)$ vs $\ln(V)$ plots of polyaniline doped PVC-PMMA thin films at various temperatures 323 K, 333 K, 343 K, 353 K and 363 K are shown in figure 2. The current increases non-linearly with applied voltage and does not follow a power law, $I = kV^m$, where k and m are constants. The possibility of ohmic conduction as well as space charge limited conduction is ruled out from the observed behaviour of I - V characteristics. This is also evident from the fact that Ohm's law follows from the free electron model of a metal. The free electron in a metal undergoes frequent collisions, which are not billiard-ball collisions with other electrons, but represent the scattering of electron waves by irregularities in the crystal structure, both defects such as impurity atoms and also atoms temporarily out of place as they vibrate (The atom of a perfect crystal lattice do not scatter free electron wave except under certain specific circumstances). In the present case the constituents of blends are itself insulators and blends almost amorphous, giving wide scope for irregularities in the structure and so ruling out ohmic conduction.

Regarding space charge limited conduction, it follows that electrical conduction may occur through the movement of either electrons or ions. The polymeric subgroup falls at low conductivity end. In most polymeric materials it is very difficult to observe any electronic conductivity at all and

what conductivity there is, usually depends upon movement of adventitious ions. Naturally with so feeble a charge carrier density, space charge limited conduction seems a remote possibility.

We now discuss analytically the probable mechanism of conduction.

3.1 Poole-Frenkel mechanism

The current-voltage relationship for Poole-Frenkel mechanism is expressed as

$$J = B \exp \left[\frac{-\phi}{kT} + \beta_{\text{PF}} E^{1/2} \right],$$

where

$$\beta_{\text{PF}} = \frac{e}{kT} \left[\frac{e}{\pi \epsilon \epsilon_0 d} \right]^{1/2} = \text{constant}, \quad (1)$$

where B is a constant and all other symbols have their usual meanings. The Poole-Frenkel mechanism predicts a field dependent conductivity as

$$\sigma = \sigma_0 \exp \left[\frac{\beta_{\text{PF}} E^{1/2}}{2kT} \right], \quad (2)$$

$$\text{or } \ln \sigma = \ln \sigma_0 + (\beta_{\text{PF}} E^{1/2} / 2kT), \quad (3)$$

so that the Poole-Frenkel mechanism is characterized by the linearity of $\ln \sigma$ vs $E^{1/2}$ plots i.e. Poole-Frenkel plots predicted by (3) are linear with a +ve slope.

In the present case of polyaniline doped polyvinyl chloride (PVC) and poly(methyl methacrylate) (PMMA) thin films, it can be inferred from the Poole-Frenkel plots in figure 3 that this mechanism does not contribute significantly to the conduction as $\ln \sigma$ does not show appreciable dependence on $E^{1/2}$ axis, indicating absence of PF mechanism.

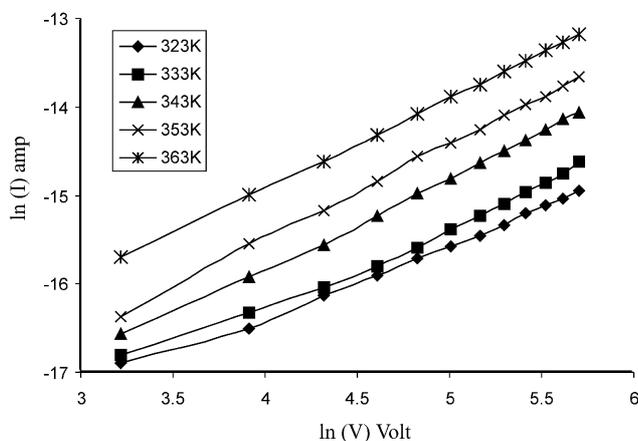


Figure 2. Current-voltage characteristics.

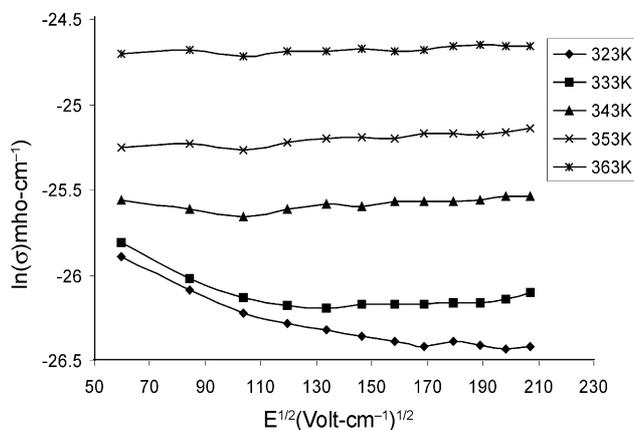


Figure 3. Poole-Frenkel plots.

3.2 Fowler–Nordheim mechanism

The Fowler–Nordheim relation (Fowler 1928) for current density is

$$J = AV^2 \exp\left[\frac{-\phi}{V}\right], \quad (4)$$

so that,

$$\ln\left[\frac{J}{V^2}\right] = \ln A - \left[\frac{\phi}{V}\right],$$

and the $\ln J/V^2$ vs $1000/V$ plots is expected to be a linear straight line relation with a $-ve$ slope.

In the present case, the $\ln(J/V^2)$ vs $1000/V$ plots for the sample are presented in figure 4, which are nearly straight lines with a $+ve$ slope for higher as well as lower values of V indicating the absence of tunneling current as suggested by $F-N$ relation.

3.3 Schottky plots

The Schottky–Richardson current voltage relationship is expressed as

$$J = AT^2 \exp\left[\frac{-\phi_s}{kT} + \beta_{SR} E^{1/2}\right], \quad (5)$$

β_{SR} being the field lowering constant given by,

$$\beta_{SR} = \frac{e}{kT} \left[\frac{e}{4\pi\epsilon_0 d} \right]^{1/2}, \quad (6)$$

and hence $\ln J = \ln AT^2 - \phi_s/kT + \beta_{SR} E^{1/2}$ and that $\ln J$ vs $E^{1/2}$ plots should be a straight line with a $+ve$ slope. The results plotted with axes marked in this way are referred to as Schottky plots and linear $+ve$ slope on Schottky plots generally characterize Schottky–Richardson mechanism. Schottky plots for the case (figure 5) are straight lines

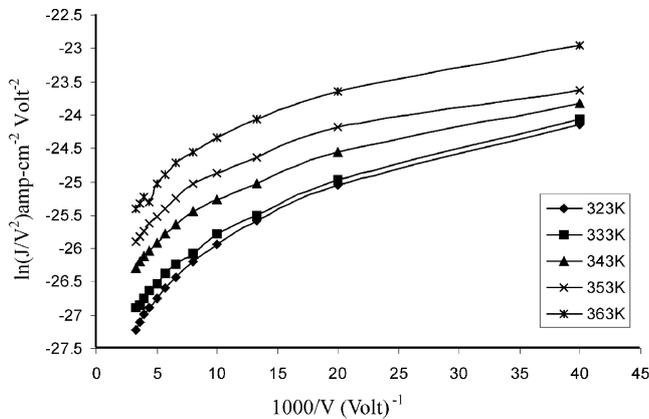


Figure 4. Fowler–Nordheim plots.

with positive slope indicating the applicability of the mechanism. Further, in the case of Schottky–Richardson mechanism the current shows strong temperature dependence but not in case of the Poole–Frenkel mechanism. The study of temperature dependence of current density is, therefore, of great importance.

3.4 Current density vs temperature plots

The temperature dependence of current density is presented in the form of $\ln(J)$ vs temperature plots (figure 6) which shows that $\ln(J)$ increases linearly with temperature. The strong temperature dependence is in agreement with the Schottky–Richardson mechanism. Further, the straight line with constant slope is observed for all the fields indicating the absence of any thermodynamic transition in the temperature range studied.

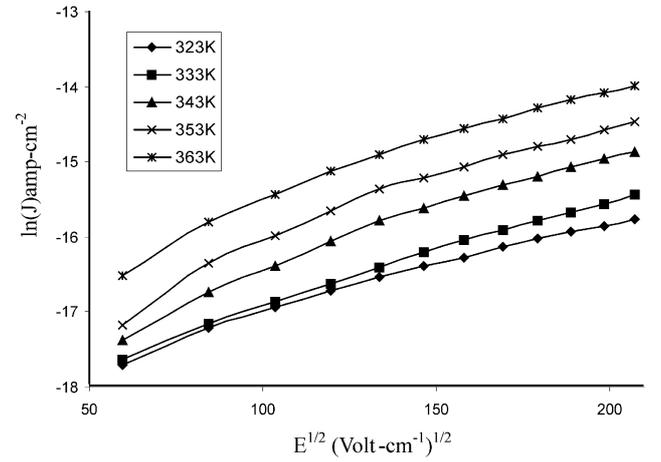


Figure 5. Schottky plots.

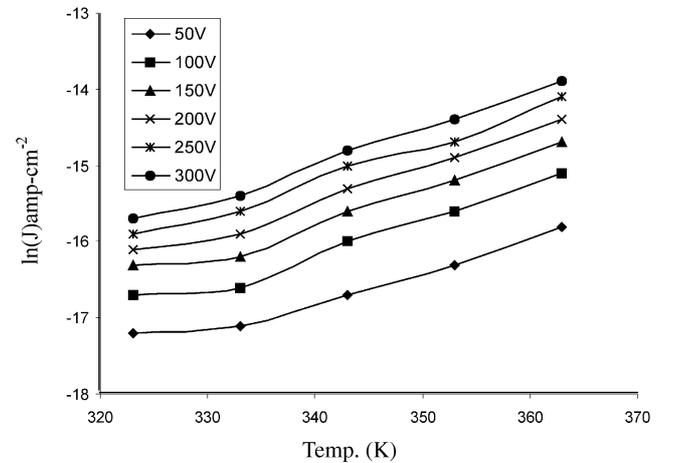


Figure 6. Current density vs temperature plots.

3.5 Richardson mechanism

The Richardson current–voltage relation is expressed as

$$J = AT^2 \exp\left[\frac{-\phi_s}{kT} + \beta_{SR} E^{1/2}\right],$$

$$\frac{J}{T^2} = A \exp\left[\frac{-\phi_s}{kT} + \beta_{SR} E^{1/2}\right],$$

$$\ln \frac{J}{T^2} = \ln A + \left[\frac{-\phi_s}{kT} + \beta_{SR} E^{1/2}\right],$$

$$\ln \frac{J}{T^2} = \ln A + \beta_{SR} E^{1/2} - \frac{\phi_s}{kT}.$$

The graph between $\ln(J/T^2)$ vs $(1/kT)$ from this relation should be a straight line with a –ve slope. These plots are referred to as Richardson plots and Schottky–Richardson mechanism requires linearity of these plots. In the present case such straight line graphs have been obtained with a –ve slope. The linearity of the plots support Schottky–Richardson mechanism (figure 7).

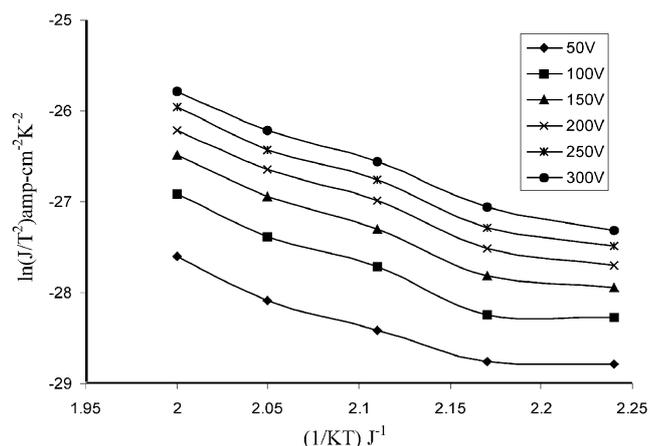


Figure 7. Richardson plots.

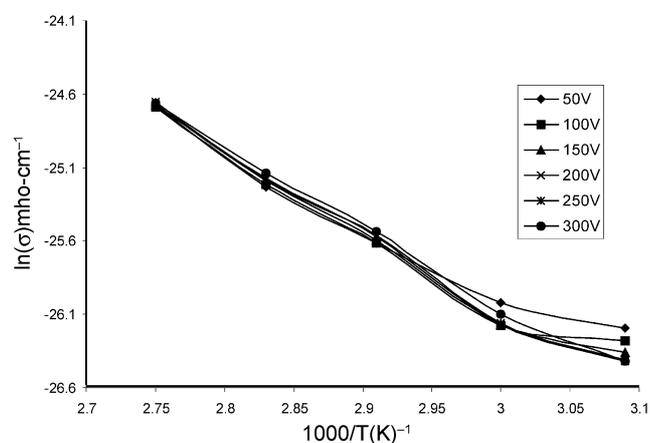


Figure 8. Arrhenius plots.

In case of PF mechanism, the current is due to the thermal excitation of trapped electrons via field assisted lowering of trap depth. While in Schottky model it is due to the thermal activation of electrons over metal–insulator interface barrier with added effect of applied field reducing barrier height. Also in former electrons are liberated from traps while in the latter electron emission takes place from cathode. Further no strong temperature dependence current is observed in the former while the latter shows a strong temperature dependence.

FN mechanism characterizes tunneling currents. In the light of the comparative characteristic features of different mechanisms of conduction and the observed behaviour of the sample, it can be safely concluded that it is the Schottky–Richardson mechanism that is operating in the present case.

3.6 Arrhenius plots

The temperature dependence of conductivity of polyaniline doped PVC–PMMA thin film is presented in the form of Arrhenius plots (figure 8) i.e. $\ln(\sigma)$ vs $1000/T$ plots at all values of applied voltage, showing a straight line with a –ve slope. From the slope of the straight line, the activation energy is calculated and found to be in the neighbourhood of 0.51 eV. This is in good agreement with the reported order of magnitudes.

4. Conclusions

After studying electrical conduction through doped sample film under various existing mechanisms, it is observed that in the present case, the behaviour cannot be described by P–F and F–N mechanisms but can be closely described by Schottky and Richardson mechanisms. This is also evident from Arrhenius plots, which give activation energy of 0.51 eV, which lies in the semiconducting range. This is the case with the present sample, polyaniline doped PVC–PMMA.

Acknowledgement

The authors are thankful to Prof. V G Bhamburkar, Principal, Shri Shivaji Science College, Amravati, for providing necessary laboratory facilities during the course of this work.

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