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Schottky -Richardson Mechanism in Oxalic acid Doped (PVC-PMMA) Blends

Dakre A. B[1], Lamdhade G.T [2]

[1]Department of Physics, P.R. Pote (Patil) College of Engineering & Management, Amravati (M.S.) India -444604

[2]Department of Physics, Vidya Bharati Mahavidyalaya, Camp, Amravati (M.S.) India -444602

Abstract: ***We have measured the electrical conductivity of Oxalic acid doped Polyvinyl Chloride (PVC)- Polymethyl Methacryalate (PMMA) blends at temperatures (313K - 373K). The current voltage characteristic of blends does not obey the power law and there is absence of ohmic conduction. The electrical conduction mechanism discussed by various models such as Poole–Frenkel, Fowler–Nordheim, Schottky ln(J) Vs T plots, Richardson and Arrhenius Plots. Out of this, Schottky - Richardson mechanism is conscientious for the observed conduction mechanism in the Polyblends.***

Keywords: PVC, PMMA, Polyblends, Oxalic Acid

1. Introduction

The blending of two polymers is found to be new polymeric material which new materials may be promising candidate than indivisible polymer [1]. There are many investigations on polymer blending [2]. The conductivity study gives the origin of the charge carrying species, their number, and the way in which they move through the bulk of the material. These parameters are interlinked with the chemical composition of the microstructure and the morphology of the particular material.

The electrical conductivity of organic solid shows complex conduction behavior, while the conductivity due to electrons excited from valence band to conduction band is negligible [3,4]. The complex conduction behavior can be explained in terms of electron emission from cathode i.e. Schottky - Richardson mechanism [4] or by liberating electron from the traps in the bulk material, i.e. Poole–Frenkel mechanism [5]. In addition to there is also possibility of tunneling [6] or Fowler–Nordheim mechanism [7], space charge limited conduction [8], etc occurs. In case of polymer films space charge limited conduction, Poole-Frankel and Richardson-Schottky emission and tunneling mechanism generally discussed. When the applied field is sufficiently high and the electrode makes ohmic current with the polymer then the charge carriers are injected into the polymer by lowering of the barrier at the metal – insulator interface, this effect is known as Richardson-Schottky (RS) emission.

PVC is a polar molecule and one of the most important commercially available polymer due to its light, electrical & chemical resistant and it has the ability to get mixed with other to produce verity of compounds which has a wide range of physical & chemical properties.

PMMA is strongly polar and it is a hard, rigid and transparent polymer which has good outdoor weatherability and it has more impact resistance than glass. PMMA is a versatile polymer showing plenty of application. Blends of these two polymers are expected to yield strong and long lived electrets useful for industrial application. Both PVC-PMMA are rigid polymers but by blending PVC with PMMA make the resultant blend soft & open to make useful applications. Many researchers reported the electrical conductivity and experimental observations in PS-PMMA [9], PVC-PMMA blends [10], [11], [12]. The conductivity studies on PVC-PMMA polymer blends electrolytes shows stability [10].

In the present study, the electrical conductivity of PVC-PMMA blends doped with Oxalic acid was measured to identify the mechanism of electrical conduction in the polyblends. The electrical conduction mechanism discussed by various models such as Poole–Frenkel, Fowler–Nordheim, Schottky ln(J) Vs T plots, Richardson and Arrhenius Plots.

2. Experimental

The polymers, PVC (Aldrich) and PMMA (Otto kemi, Mumbai) in 1:4 weight proportions were dissolved in 20 ml solvent cyclohexanone (SD Fine Chemicals, Mumbai) respectively. Oxalic acid used as a dopant in these selected polymers. The dopant & polymer mixture were mixed together and this mixed solution was kept in a stand for three days so as to get the complete homogenous dissolution of blends. After three days, the solution mixture was poured on perfectly plane and chemically clean glass plate, which is kept floating freely in a pool of mercury for perfect horizontal leveling. It was, thereafter, allowed to evaporate in air at room temperature. Further, it was dried for 48 hrs. to remove any traces of solvent.

The dried film was removed from the plate and cut into small pieces (samples) of desired size, which were then coated on both sides with silver paste (Eltecks Corporation, Bangalore) so that electrical contact hold very well. The polyblends films of PVC-PMMA doped with 5%, 10%, 15% Oxalic acid (wt. percentage) were prepared by the same method given above but the results are only interpreted for doping of 15% Oxalic acid due to the significant change in conduction of blends. The thickness of the polyblends film was measured

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by using Digital Micrometer screw gauge (Mitutoyo Corporation, Japan, Least Count 0.001mm) is found to be 56 µm. These polyblends films were kept between the electrodes of a specially designed sample holder having gold plating. The variation between current and voltage measured by using Keithley 6487 Picoammeter / Voltage source meter instruments at various constant temperature.

3. Results & Discussion

3.1. I-V characteristics of Polyblends

The I-V characteristics of 1: 4 **(**PVC-PMMA) doped with 15% Oxalic acid is represented by lnI - lnV plots at various temperatures 313K, 323K, 333K, 343K, 353K, 363K and 373K are shown in figure 3.1. The current increases non-linearly with the applied voltage and does not follow a Power law I = kV^{m} where, k and m are constant.

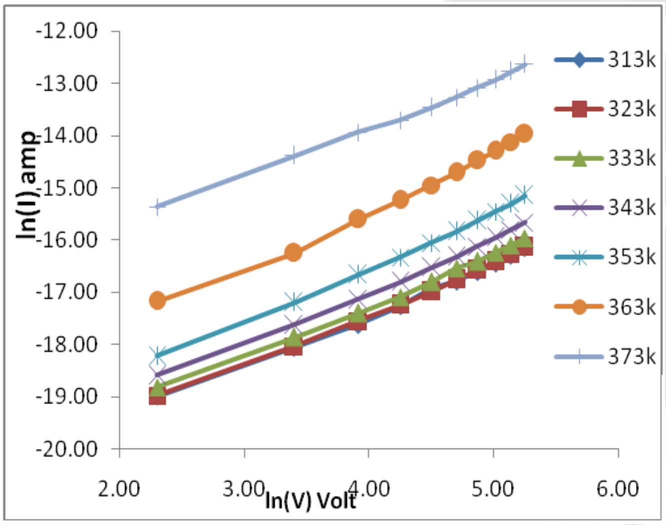

Figure 3.1: I-V characteristics

It is seen from the figure 3.1 that, the current increases nonlinearly with applied voltage at constant temperature and also the current increases with increase in temperature at constant applied voltage). The possibility of ohmic conductions as well as space charge limited conduction is ruled out from the observed behavior of *I–V* characteristics. As we know the compositions of blends are insulators and blends are almost non-crystalline, which give rise to wide scope for irregularities in the structure therefore there is absence of ohmic conduction.

3.2. Poole–Frenkel Mechanism

The Poole-Frenkel relation [5] for the current density is given by the equation 3.1 ,

$$J=B\exp\left(\frac{-\phi}{kT}+\beta_{PF}E^{\frac{1}{2}}\right) \qquad (3.1)$$

Where, $\beta_{PF}=\frac{e}{kT}\left(\frac{e}{\pi\varepsilon\varepsilon_0 d}\right)^{\frac{1}{2}}$ = constant

and e = electronic charge which predicts a field -dependent conductivity as,

$\sigma=\sigma_0\, e^{\frac{\beta_{PF}E^{\frac{1}{2}}}{2kT}}$ or

$$\log\sigma=\log\sigma_0+\frac{\beta_{PF}}{2kT}E^{\frac{1}{2}} \qquad (3.2)$$

So that, the Poole -Frenkl mechanism is characterized by linearity of logσ Vs $E^{\frac{1}{2}}$ plots with positive slope. In this present case of 1: 4 **(**PVC-PMMA) doped with 15% Oxalic acid the lnσ Vs $E^{\frac{1}{2}}$ plots are linear with negative slope (figure 3.2) indicating the absence of Poole-Frenkl mechanism.

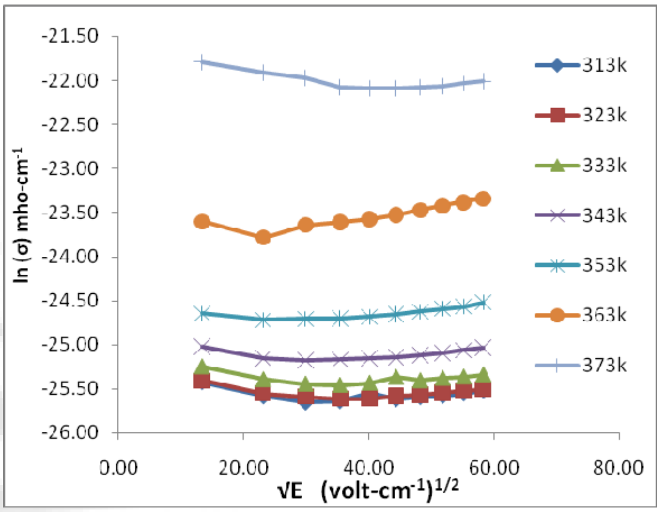

Figure 3.2: Poole-Frenkel Plot

3.3. Fowler– Nordheim Mechanism:

The Fowler -Nordheim Relation for [7] current density J can be expressed by equation 3.3.

$$\log\frac{J}{V^2}=\log A-\frac{\phi}{V} \qquad (3.3)$$

and $\log\frac{J}{V^2}$ Vs $\frac{1}{V}$

Plots is expected to be a linear With a negative slope .

In this present case the log $\frac{J}{V^2}$ Vs $\frac{1}{V}$ plots for 1: 4 **(**PVC-PMMA) doped with 15% Oxalic acid is represented by figure 3.3. Excepting few plots which have strayed away the graph are nearly straight lines with a positive slope indicates the absence of tunneling current as is suggested by Fowler -Nordheim mechanism.

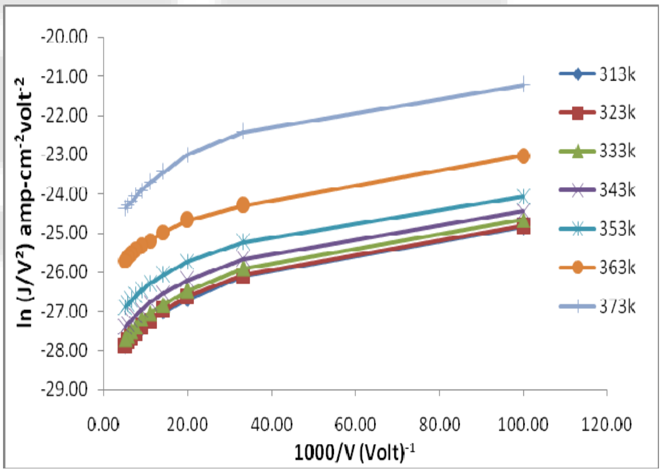

Figure 3.3: Fowler-Nordheim Plot

3.4. Schottky – Richardson Mechanism

The Schottky – Richardson current voltage relationship is expressed by the equation 3.4.,

$$\log J = \log AT^2 - \frac{\phi_s}{kT} + \beta_{sc} E^{\frac{1}{2}} \qquad (3.4)$$

and that log J Vs $\sqrt{E}$ Plot referred to a Schottky Plots should be a straight line with positive slope.

For the present case, Schottky plot are shown in figure 3.4.1 below. The linear positive slope indicates that Schottky - Richardson mechanism is applicable to the process in 1:4 (PVC-PMMA) with 15% O.A.

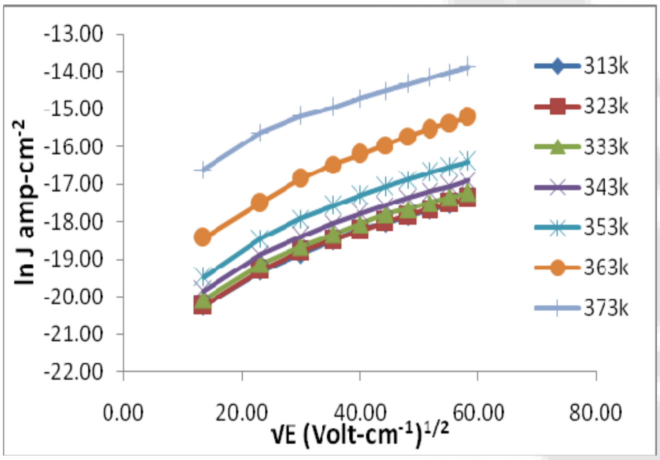

Figure 3.4.1: Schottky Plot

Further, in the 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 temperature dependence of current density is represented plot of ln (J) verses temperature shown in the figure 3.4.2, observed that ln (J) increases almost linearly with change in the temperature. The temperature dependence is great agreement with the Schottky -Richardson Mechanism. Further that the slopes of all the lines are nearly same for all the fields, shows that, no thermodynamic transition occurs in the temperature range studied.

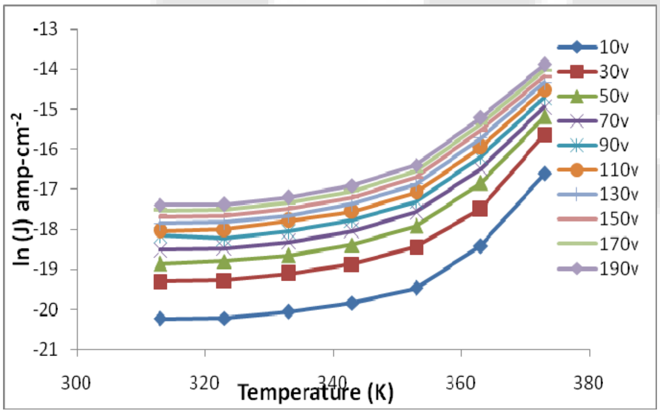

Figure 3.4.2: Current density Ln (J)Vs Temperature Plot

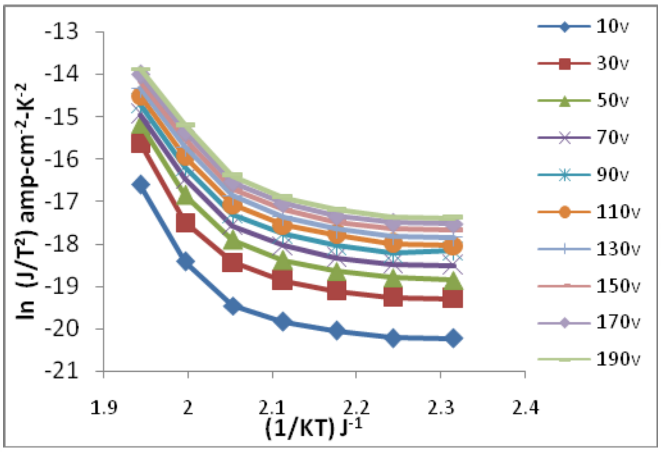

Figure 3.4.3: Richardson Plot

From the relation 3.4 we can plot the variation between Ln(J/T^2) versus (1/KT) shown in fig. 3.4.3 Richardson Plot, it is observed from plot, it should be a straight line with a negative slope. In our case such a straight line graph have been obtained with a negative slope. This shows the linearity of the plot which supports to Schottky- Richardson Mechanism.

3.5. Arrhenius Mechanism

The ln (σ) verses 1/T plots at all values of applied voltage is shown in figure 3.5., the conductivity of polymer is mostly dependent on the temperature. As the temperature increases polymer becomes soft and mobility of the main chain segment as well as the rotation of the side group becomes easier [13]. Thus at higher temperature more & more dipoles are oriented resulting in the higher equivalent surface charge density i,e. as the temperature increases conductivity also increases in accordance with the Arrhenius equation given by relation 3.5.

$$\sigma = \sigma_0 \exp^{\left(\frac{-E_a}{kT}\right)} \qquad (3.5)$$

where , σ_0 - is the pre-exponential factor, E_a- is activation energy and K- Boltzmann constant

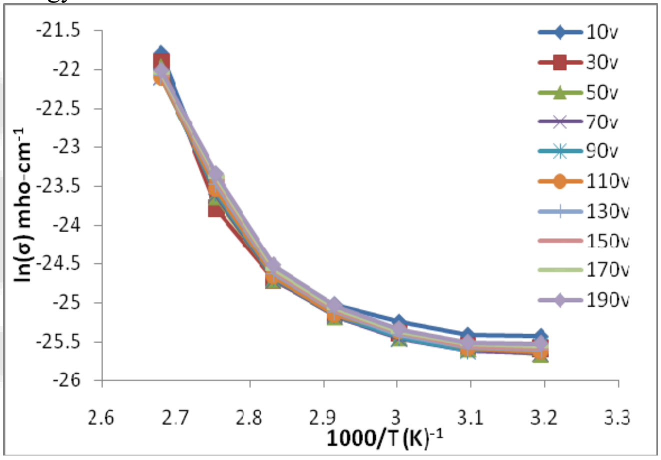

Figure 3.5: Arrhenius plot

From the slope of straight line the activation energy is calculated & is found to be in the neighbored of 0.1eV.This is in good agreement with the reported earlier.

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4. Conclusions

The observed conduction nature at higher fields and temperatures is found to be Richardson-Schottky emission. Due to the formation of charge transfer complex, there exist a link between the dopant molecules and polymer molecules in amorphous region. Schottky and Richardson mechanism of conduction predominates over other mechanism in the doped sample. The applied field seems to be insufficient to liberate electrons from the trapping centers (dopant molecules) showing absence of the Poole–Frenkel mechanism.

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Author Profile

Ms. Archana B. Dakre has received her B.Sc. degree in 1996, M.Sc. degree in 1998 from Sant Gadge Baba Amravati University, Amravati, Maharashtra State, India. Recently she is registered for Ph. D. degree in the Sant Gadge Baba Amravati University, Amrvati. Presently she is working as Assistant Professor at Department of Physics, P.R. Pote (Patil) College of Engineering & Management, Amravati since last four years and she has also ten years teaching experience in the UG and PG level. She has published two research papers in reputed international journals and two research papers presented in conference. Her current interests of research are synthesis and characterization of Polymers, polyblends, polymer electrolyte and gas sensors etc.

Dr. G. T. Lamdhade has received his B.Sc. and M. Sc. Degrees from Sant Gadge Baba Amravati University, Amravati, Maharashtra State, India. in the years 1996 and 1998 respectively. He obtained his Ph.D. degree in year 2003 from Sant Gadge Baba Amravati University, Amravati. Currently he is an Associate Professor in the Department of Physics, Vidya Bharati Mahavidyalaya, Amravati. He has fifteen years teaching experience at UG and PG Level classes, currently five students are working for Ph.D. Degree under his guidance and five students have been awarded by M.Phil. Degree under his guidance. He is also supervised fourteen M.Sc. Physics students for completion of dissertation/project. He is working as members on various committees of college administrative and university administrative also. He is working as a editorial board member, review members, referee, expert, members on many international/national journals and he has completed one research project sanctioned by UGC and one major research project is in progress. He has published more than thirty five research papers in reputed international journals and conferences. His current interests of research are in synthesis of metal oxides nanoparticles, Polymers, polyblends, polymer electrolyte, nanocomposites, Humidity sensors etc., characterizations and their applications as chemical gas sensors, thin and thick film sensors etc.

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