

INVESTIGATION OF ELECTRICAL CONDUCTION IN EUDRAGIT RS-100

* Dr. Imrana Siddiqui **N. Dubey

Polymers' exhibit structures covering the entire range from amorphous to crystalline. By virtue of their high insulating properties and high concentration of deep traps, polymers are good charge storing materials and therefore yield the best electrets for practical applications. The complicated architecture of atomic arrangements and fine textures are vital factors, which affect the structure, properties and chemistry of solid polymers. The intrinsic charge carries generation, at room temperatures, in polymer is very low. Polymers contain many impurities, additives and imperfections; their amorphous structure is complex. Due to these reasons not much information is available on the nature of charge carriers and the charge transfer mechanism operating through and dielectric metal boundary. As a consequence different workers have reported different conduction mechanisms for the same material.¹⁻⁵ Therefore the study of electrical conduction has become important in the investigation of conduction mechanism in the solids.

Factors Affecting Conductivity-Factors which affects the electrical conductivity of polymer are given below:

Pressure-Akamotu and Inokuchi⁶ found that conductivity increases with increases in pressure upto 80 atmosphere, after that the conductivity remains constant.

Field-Poole⁷ has reported exponential variation of conductivity with field, while Joffe⁸ states that it is only the steady state conductivity which increases with field and the true conductivity is independent of field.

Temperature-Organic polymers being semiconductors show a rise in their electrical conductivity with increase of temperature.⁹

Thickness-Wright¹⁰ found that current varies as the inverse cube of the thickness.

$$I = a (l/d^3)$$

where, a – constant
d – thickness

Basara and Dotty¹¹ suggested the space charge limited currents increases with thickness.

Humidity-Many workers^{12,13} have found that humidity cause the conductivity to increase with field strength.

Impurity-The electrical conductivity of organic

compounds is extremely sensitive to the presence of impurities. The conductivity itself could be used as a measure of purity provided the absolute value for a given material is known.

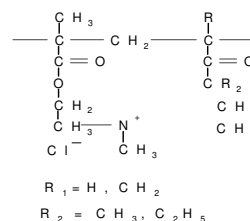
Electrode material-Values of the measured current and conductivity have a great dependence on the nature of the electrodes. Electrodes are considered ideal if they do not react chemically with material and are unaffected by variations of temperatures, field. It should introduce no resistance of the flow of current.

Electrical Circuit Arrangement-Fig. 1 and Fig. 2 shows the circuit and block diagram of the experimental set up used for D.C. conductivity measurements.

Present Investigation-For the study of Electrical conduction, samples were prepared as described. The electrical conductivity measurements were carried out by measuring the steady state current, with electrometer, as a function of voltage at different temperatures.

After making proper electrical connections as shown in Fig. 1 and Fig. 2, the sandwiched sample of Eudragit RS 100 mounted on electrode assembly was placed inside the thermostat and allowed to attain required temperature. It takes about 3-4 hrs. The sample was allowed to remain on the same temperature for about 2 hrs to attain thermal equilibrium. Then a constant D.C. field was applied. The current was recorded at regular intervals and in about 2 hrs it attained a steady value. Then the field was increased in steps at the same constant temperature upto 100 volts to record steady current. While in the second part the temperature was increased in steps at the same constant field upto 85°C. Further, sample was changed and fresh sample was used in each case.

EXPERIMENTAL -The work reported in this paper has been carried out on Eudragit RS 100 of commercial grade supplied by Rohm Pharma GMBH weiterstadt (west Germany). Eudragit RS is a copolymer synthesized from acrylic and methacrylic acid esters with a low



content of quaternary ammonium groups.

The molar ratio of these ammonium groups to the remaining natural (meth) acrylic acid is 1:40 with Eudragit RS. The mean molecular weight is approximately 150000. The letter RS relate to the initial letter of the German word 'schwerdurchlassig' (slightly permeable).

The solvent is made ready and the granules are added, with vigorous stirring, at room temperatures. 15 gm of material in 100 gm of solvent at 20°C on a magnetic stirrer was dissolved according to the following data:

Solvent	Dissolution Time
1. Methylene chloride	10 min.
2. Chloroform	15 min.
3. Acetone	20 min.
4. Methyl alcohol	25 min.
5. Ethanol	105 min.

The polymer was in the form of solid substance (granules). Polymer has been kept in a dessicator in which freshly dehydrated calcium chloride was kept. The dessicator was covered with a freshly greased lid and kept in a cool place, so that humidity could not affect it. The polymer has been crushed and meshed (160 no.) many times.

Preparation of pellets for electric conduction measurements

300 mg of this polymer was weighed precisely and carefully with the help of electronic weighing machine. After weighing, pellets of 300 mg each with the help of Perkin Elemer press were formed. Polymer was crushed under ten (10) tons pressure. The vacuum pump was run for three minutes, and the pellets of thickness 0.18 cm and diameter 1.30 cm were obtained. The surfaces of the pellets were made conducting by painting them with silver paint obtained from National physical Laboratory (NPL) Delhi. These samples were then dried in a dessicator and they become ready for electrical conduction measurement.

Details of measuring instruments for electrical conduction measurements

The various instruments used for electrical conduction measurements were as follows: Sample Holding Assembly, Power Supply, Temperature Controller, Electrometer, Amplifier etc.

**TABLE-1
POWER 'm'ASESTIMATEDFROM
FIGURES 03 AND 04**

S. No.	Temperature (°C)	'm' value
1.	50°C	0.391
2.	60°C	0.523
3.	70°C	0.538
4.	75°C	0.638
5.	80°C	0.872

6.	85°C	0.759
7.	90°C	2.4

**TABLE-2
ACTIVATION ENERGY, E (ev) ASESTIMATED
FROM FIGS. 07 TO 10**

S. No.	Field (volts)	E ₁ Lower Region ev	E ₂ Upper Region ev
1.	45	1.383	1.702
2.	70	1.023	1.702
3.	75	1.113	1.677
4.	80	1.138	1.778
5.	85	1.319	1.827

RESULT AND DISCUSSION-The isothermal I-V characteristics plotted in the form of log I-log V are shown in figs. 3 and 4. It is to be seen from the graphs that in the low voltage regions the current rises at a faster rate with voltage while at higher voltage the current varies linearly with voltage. In higher field regions current shows approximately saturation in most cases. The magnitude of current (90°C) is of the order of 10⁻⁵ amp. An abrupt rise in the current is observed between 60-70°C shows possibility of some phase transition in the polymeric matrix. The polymeric chains may undergo some transitional changes between these temperatures and the current therefore, show abrupt increase. The reason of getting some downward trend of current at 75°C isothermal is very obvious. The polymer matrix undergoes glass like to rubber like transition and therefore the macromolecules start losing their preferred orientation during transition of phase. The initial stage of change in phase is very sensitive of course. Above 75°C, current again shows rapid increasing trend. Once the chains are mobilized the current will certainly shows greater increment Fig. (5 and 6).

Now for the confirmation of the different natures of conduction mechanism, values of m i.e. power (from the slopes of I-V characteristics) were calculated and are collected in Table 1. In case where values of m is approximately equal to unity, there is an agreement with ohm's law. M > 1 or m < 1 shows departure from ohm's law. In the first case there is a faster than linear in current and in the second case there is a slower

**TABLE-3
THEORETICAL AND EXPERIMENTAL VALUES OF β**

S. No.	Temperature (K)	Theoretical		From SR graph β (experimental)	From PF graph β (experimental)
		β _{SR}	β _{PF}		
1.	313	0.0534	0.1068	0.223	0.143
2.	318	0.526	0.1052	0.050	0.032
3.	323	0.0517	0.1034	0.154	0.071
4.	328	0.0509	0.1018	1.815	0.038
5.	333	0.0502	0.1004	0.154	0.071
6.	338	0.0494	0.0988	0.220	0.143
7.	343	0.0487	0.0974	0.165	0.082
8.	348	0.0480	0.0960	0.193	0.108
9.	353	0.0474	0.0948	0.248	0.103
10.	358	0.0467	0.0934	0.247	0.247

than linear increase in current. The values of m increase from 50°C to 80°C but above 80°C to 85°C it decreases and becomes 0.759 and once again it increases suddenly till 2.4 at 90°C. On the basis of slope values, it seems that current-voltage relationship is non-ohmic as slope value for this mechanism should be around 1. In the higher temperature region the slope value greater than 2 at higher fields suggest that current is governed by space charge mechanism. Slope values less than one suggest that the charge carriers have probably been supplied by impurity atoms. To study, the variation of conductivity with temperature at different fields, the graphs are drawn between log of conductivity and reciprocal of temperature and are shown in Figs. (7 to 10).

The important features of these curves are: 1. The conductivity rises with temperature at each field being of the range of 10^{-13} to 10^{-9} mho cm^{-1} . 2. Curves are found to have two regions. Higher temperature region and lower temperature region. At all the voltages except 85 volts, 65°C temperature (transition temperature) separates the curves into two regions. At 85 volt the curve was divided by 75°C temperature. 3. The straight line curves in higher temperature region are steeper than that of low temperature region at all voltages. This represents that the conductivity varies rapidly in the high temperature region as compared to low temperature region. 4. Transition temperature which separates the two straight lines is sharp and has same value for all the cases except at highest voltage. 5. Two straight lines in these plots also show that there are two activation energies for the two regions of temperatures. The activation energy for both these region have been calculated and are given in the Table 2.

From the Table-2 it is observed that

1. The values of activation energy at lower temperature region are always smaller than those for higher temperature region in all the cases. 2. The values of activation energy at low temperature region seemed to be centered around 1.2 eV while at higher temperature region around 1.7 eV. Now for the confirmation of different natures of conduction mechanism graph between J Vs $E^{1/2}$ and s Vs $E^{1/2}$ have been plotted and are shown in Figs. 11 and 12. The plots are seen to be linear. This is naturally taken as evidence of either Schottky or Poole-Frenkel mechanism. The slope of the curve 11 or 12 gives the b_{exp} value and the values of b_{SR} calculated theoretically using following equation –

$$b_{\text{SR}} = \frac{1}{kT} \left[\frac{e^3}{4\pi\epsilon'\epsilon_{\text{od}}} \right]^{1/2}$$

Where,

b_{SR} = Schottky field lowering constant

e = Electronic charge

ϵ_{od} = Permittivity of free space

ϵ' = High frequency dielectric constant of the material

k = Boltzmann constant

T = Absolute temperature

The value of dielectric constant used in the calculation is 0.038 (in cgs). All these values are shown in the Table No. 3. The Table-3 gives the impression that the theoretical and experimental values of b show marked departures. This complicates the interpretation in terms of either of the simple models because a temperature dependence is not provided in both the Schottky and Poole-Frenkel mechanism.

References-

1. Fleming and Ranicar J. Macromol; Sci. Chem. A 4(5), 1223 (1970).
2. Hogarfch, R. and Iqbal, T., Phys. Stat. Sol. (A), 65, 11 (1981).
3. Alan J., Heeger, Alan G. MacDiarmid and Hideki Shirakawa, Kungl. Vetenskapsakademien, The Royal Swedish Academy of Sciences (2000).
4. Chantasiriwan, S., International Communications in Heat and Mass Transfer. Vol. 29, 811-819 (2002).
5. Chantasiriwan, S. KMUTT Research and development Journal, Vol. 24, No. 1, pp. 17-29 (2001).
6. Akamotu, H. and Inokuchi, I., J. Chem. Phys., 18, 810 (1950).
7. Poole, H., Phil. Mag., 32, 112 (1916).
8. Joffe, A., Zeits. F., Physik, 48, 288 (1928).
9. Gamal, G.A., The conduction mechanism and thermoelectric phenomenon in In_2S_3 layer crystals, Semicond. Sci. Technol. 12 1106-1110 (1997).
10. Wright, G., Solid state electronics, 2, 2 (1961).
11. Basara, N.H. and Doty, C.T., J. Appl. Phys., 35, 3494 (1964).
12. Hartshorn, I. and Rushton, J., I.E.E., 75, 631 (1934).
13. Katnani, A.D., Matienzo, L.J., Emmi, F. (IBM Corp. Endicott, N.Y., USA), J. Mater. Sci. Lett. (UK), Vol. 8, No. 10, p. 1177-8, (1989).