Effects of Electron Beam Irradiation on Electrical Properties of Poly (Ethylene-co-Vinyl Acetate) (EVA) doped conductive PPy polymer blends

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Abstract.

A series of thin films from poly(ethylene-co-vinyl acetate) (EVA) blends with different amounts of Polypyrrole (PPy) / carbon nano-particles were subjected to various integral irradiation dose levels, up to 100 kGy. The irradiation dose levels were 10, 25, 50, 75 and 100 KGy respectively at room temperature in air.
The electrical conductivity has been measured at room temperature (300K) by studying the *I–V* characteristics at various loading conductive PPy and Dose dependence. 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. All samples show a nonlinear increase in the current with applied voltage and does not follow a power law, $I=KV^m$. The applicable conduction mechanism for all samples was found to be Schottky- Richardson mechanism. The analysis of these results suggests that Schottky and Richardson mechanisms are primarily responsible for the observed conduction which does not affected by electron-beam irradiation. A modified equation of the percolation model which describes well the PPy/EVA composites into the percolation region is proposed.

Keywords. Electron Beam Irradiation, Dose dependence, Electrical conductivity, (EVA), **conductive PPy and polymer blend.**

Introduction

The importance of polymeric blends has been increased in recent years because of the preparation of the polymeric materials with desired properties, low basic cost, and improved processability. Polymeric blends are physical mixtures of structurally different polymers or copolymers which interact with secondary forces with no covalent bonding such as hydrogen bonding, dipole–dipole forces and charge-transfer complexes for homo polymer mixtures [(1)].

Conductive polymers are becoming an increasingly important class of material for a variety of applications in the electronic and electrical industries.Polymer composites are materials made up of two or

more components and consisting of two or more phases [2]. These composites have recently drawn considerable attention, due to the ease with which polymer propertiescan be modified to achieve characteristics that cannot be achieved by a single polymer system [3].

The reinforcement of polymer blends with carbon black [4] serves the purpose of not only reinforcing these materials but also of imparting to them some mechanical and electrical properties. The modified properties of these composites are very complicated depending on a large number of parameters such as size, surface area, structure and dispersion of the carbon particles.

Now days, one of the most important methods of obtaining new materials with new properties is to irradiate it with electron beam, the effects of high-energy irradiation on polymers can lead to changes in their properties, and their interaction with high-energy electrons is a complex and random process. The changes resulting from irradiation are mainly a consequence of electron absorption followed by bond cleavage to give radicals, radical recombination leading to the formation of crosslinks and end-links or disproportionation to give chain scission and gas evolution, mainly by radical recombination [5, 6]. The final result depends on the nature of the material, on the dosage, dosage rate and the radiation energy. Thus, there are many ways to exploit these processes technologically, such as cross-linking [7-10] and surface modification [11-13].

Following the previous work [14], the present investigation is concerned with detailed studies on the electrical properties of EVA composites filled with conductive PPy nano filler (loaded with constant concentration (40phr) of HAF black) under the effect of electron beam irradiation doses. Finally d.c.-conduction of mixed polymers 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 Arrehenius plots to examine the applicability of these models to the present systems and its modification owing to the electron beam irradiation doses.

2. Experimental

2.1 Materials and *Preparation of sample*

EVA, containg 12% VA which used throughout this work was supplied by Aldrich Company in the form of pellets. Polypyrrole / carbon nano-particles used for the study was supplied from Aldrich Company also. EVA was melt-mixed in a Brabender Plasticorder PLE-319 (Brabender co., Germany) at a temperature 80^{o}C and 80 rpm rotor speed for 5 minutes which was followed by the addition of polypyrrole / carbon nano-particles and the mixing lasted for another swing. The formulations of the mixes are given in Table (1). The resultant mixtures were sheeted on a two roll mill at ambient temperature. The sheets were then compression moulded between smooth teflon sheets at a temperature of 110^{o}C and a pressure of 5 MPa in an electrically heated press (type carver M-154). In order to ensure predetermined sheet size, the hot pressed sheet was cold pressed afterward in another press at the same pressure and cooled with water.

Table (1): Shows the composition of the blend

Ingredients	Phr*					
EVA	100	95	90	85	80	70
PPY	0	5	10	15	20	30

* Parts per hundred parts by weight of rubber.

2.2*Electrode coating*

The electrode coating on the film of measured thickness was done by using quick drying and highly conducting silver paint supplied by TAAB. A mask of circular aperture of 1.0 cm diameter was used while coating, to ensure uniformity in the size of the coated silver electrode.

2.3*Measurements*

The circuit used incorporated a digital auto ranging picoammeter type (Keithley 485), with a range varying from 10^{-13} to 10^{-1}A, and a smoothly variable power supply. The test samples were in the form of disks of 0.2-0.3 cm thick and 1.0 cm in diameter. The sample holder consists of two parallel plates of brass electrodes which were isolated from each other using Teflon.

The dc-electrical conductivity, σ was determined from the relation:

$$\sigma = \frac{d}{VA} I \qquad (1)$$

where:

V: is the applied voltage across the sample in volts and

I: is the current in amperes flowing through the sample of the materials.

2.4 Electron-beam Irradiation:

The electron irradiation was performed in air at room temperature using a 1.5 MeV electron beam from the ICT-type electron accelerator (NCRRT, AEA, Cairo, Egypt). The conveyer was attached to a cooling system in order to avoid temperature heating of the samples. The films were subjected to various integral irradiation dose levels, up to 100 kGy. The irradiation dose levels were 10, 25, 50, 75 and 100 KGy respectively. The dose determined by the FWT 60-00 dosimeter that was calibrated using the CERIC/CEROUS dosimeter. The uncertainty in the delivered dose was estimated to be 1.15%.

3. Results and discussion

Studies of the transport mechanisms in intrinsically conductive polymers and polymer blends have gained importance in recent years owing to the potential applications in various devices technologies [15--17]. Polypyrrole is one of the most widely studied conducting polymers. It exhibits relatively high conductivity and good environmental stability like other polymers. Polypyrrole is electroactive and can acts as an anion exchanger. During the synthesis of PPy, dopant anions are incorporated in the structure of PPy to balance the positive charge developed on the oxidized polymer chain [18].

3.1. Effect of electron-beam Irradiation on the d.c electrical properties.

Interaction of radiant energy with substance is extremely important from the view point of theory and practice. This interaction may be considered from various aspects. When radiant energy acts on a metal its electrical properties may change and new electrical phenomena may develop on it, furthermore, strength, optical properties, etc… [19].

Irradiation of different types of polymers was studied by R. J. Woods and A. K. Pikeav [20]. The effect of the radiation on the polymer composition induced crosslinking was studied by many workers [21-22]. It is well known that the electrical conduction in polymer can be considerably enhanced by irradiation [23].

a. Dose dependence of the electrical conductivity.

Figure (1) shows the relation between the electrical conductivity, σ_{dc}, measured at 300 K and the irradiation doses (Φ in KGy) for EVA loaded withdifferent concentration of conductive PPy (in phr). It may be presumed that the polymer sample. Meanwhile a slight decrease in σ_{dc} at relatively high electron-beam dose (≥50 KGy) was detected for most samples. Figure (2) displays the resistivity composition plot of the loaded EVA with different weight (in phr) of conductive PPy at different electron-beam doses. According to the percolation theory, one expects a scaling law and the percolation threshold is slightly changed with electron-beam doses as tabulated in Table (2).

Table (2): The relation between the electron-beam doses and percolation threshold forall samples.

Electron-beam dose	Percolation Threshold
0 KGy	0.11
10 KGy	0.1
25 KGy	0.092
50 KGy	0.09
75 KGy	0.09
100 KGy	0.09

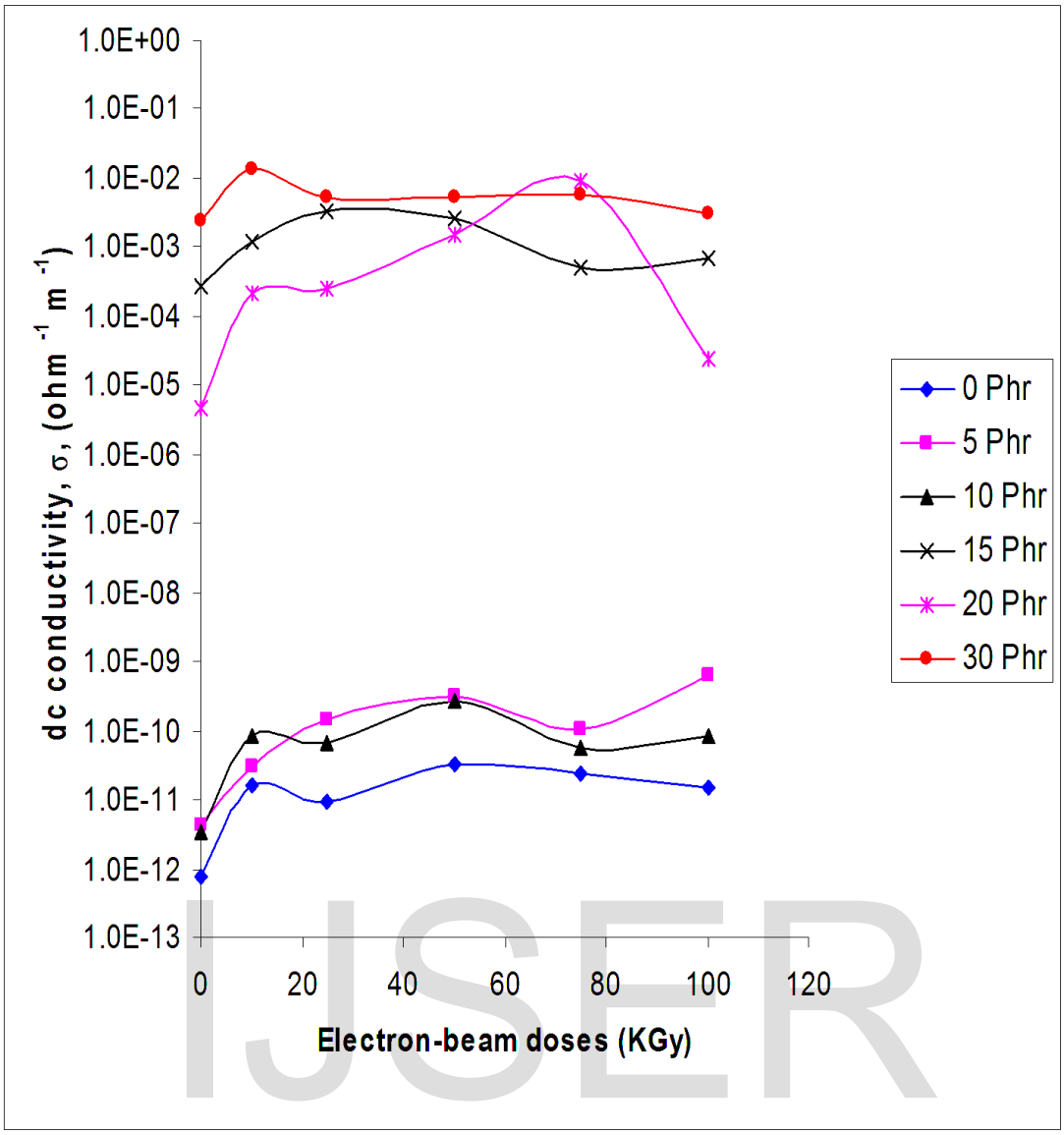


Figure (1): The relation between dc conductivity and radiation doses of EVA loaded with conductive PPy samples at room temperature (300K) for irradiated and un-irradiated samples.

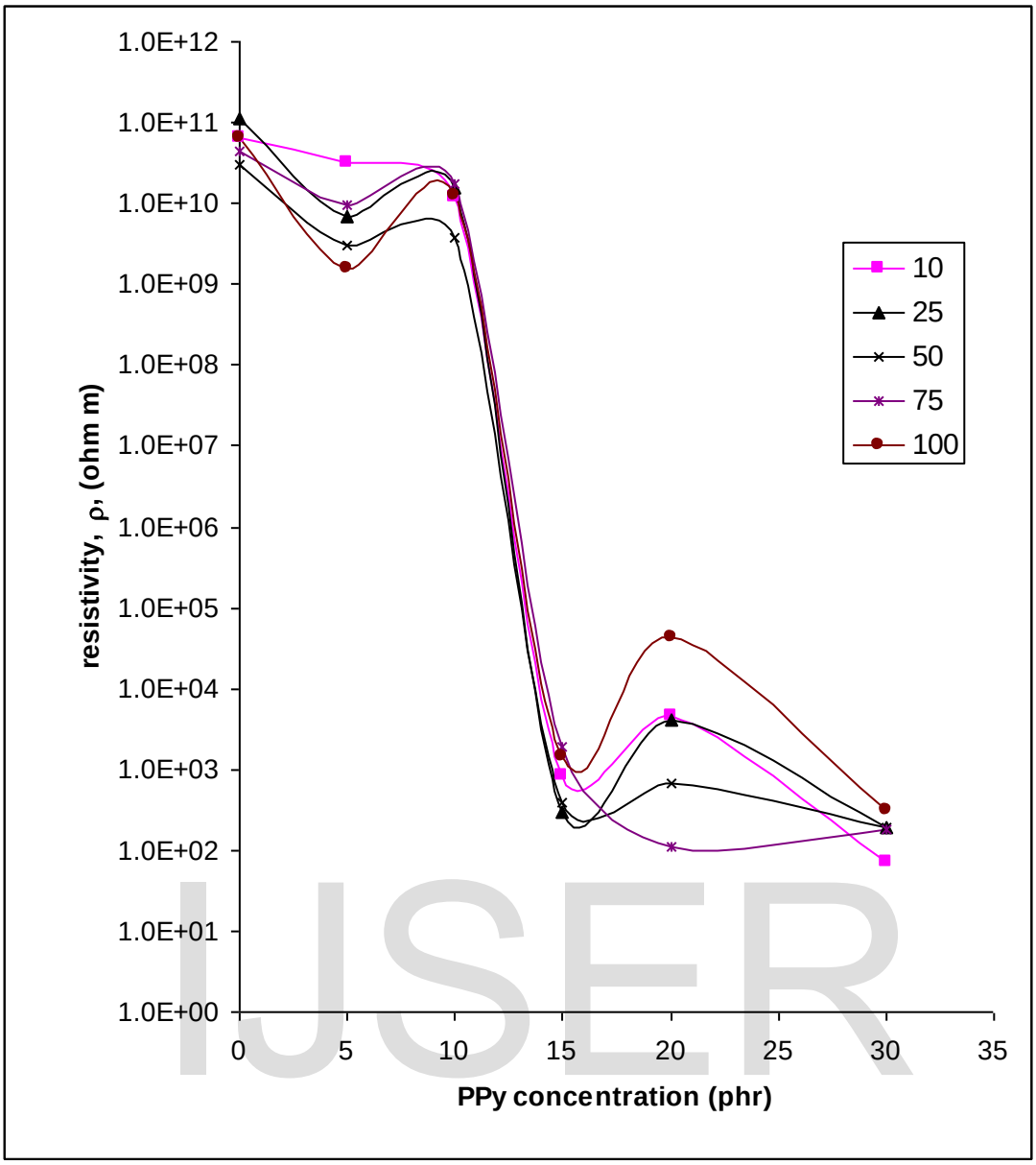


Figure (2): The relation between dc resistivity and PPy concentration with different electron-beam doses at room temperature (300K).

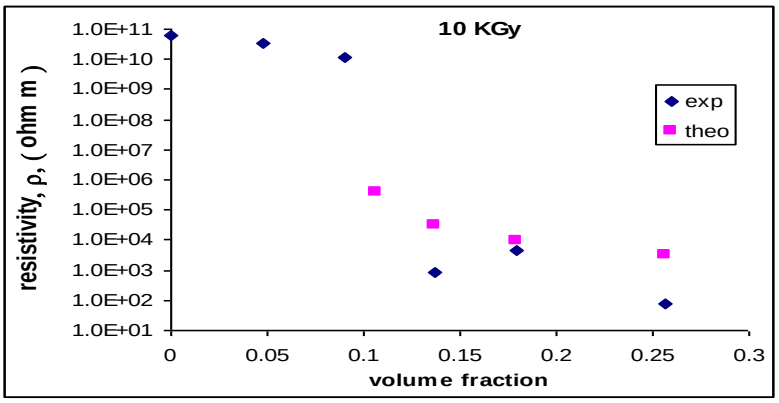
The dependence of the percolation threshold on the electron-beam dose is presented graphically in Figure (3 a-b), which could be fitted by the equation:

$$\Phi_c = \Phi_{co}\,(A\text{-}BD) \qquad (1)$$

Where Φ_{co} is the percolation threshold for un-irradiated samples, A, B are fitting parameters and D is the electron-beam irradiation dose in KGy. Substituting equation (1) in the scaling law equation [14] one can get a direct relation between the sample resistivity and the electron-beam dose.

$$\rho = \rho_0\,[\Phi - \Phi_{co}\,(A\text{-}BD)]^{-t} \qquad (2)$$

Figures (3 a, b) represent the modified equation of the percolation model which describes well the PPy/EVA composites well into the percolation region.



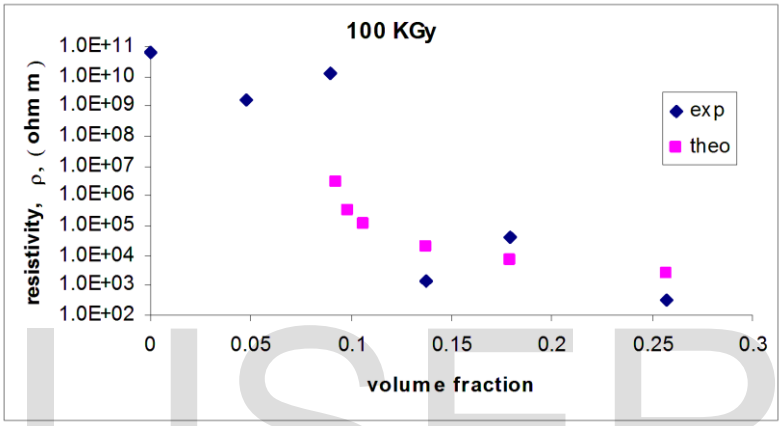


Figure (3 a): The PPy volume fraction dependence on the dc resistivity with different electron-beam doses at room temperature (300K).

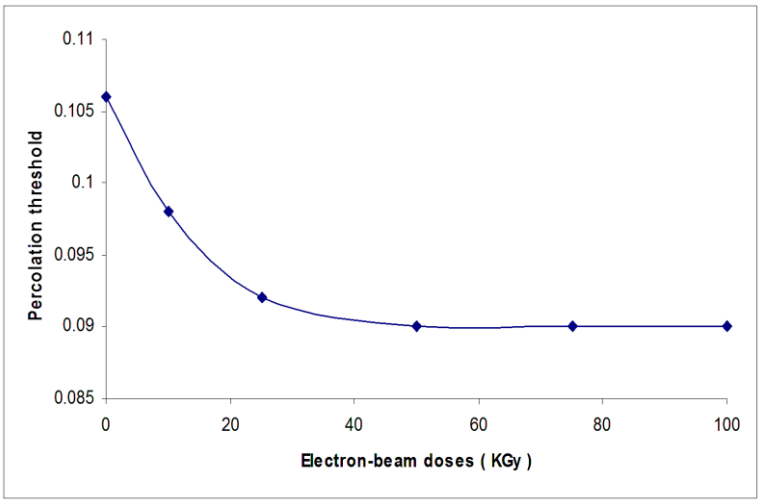
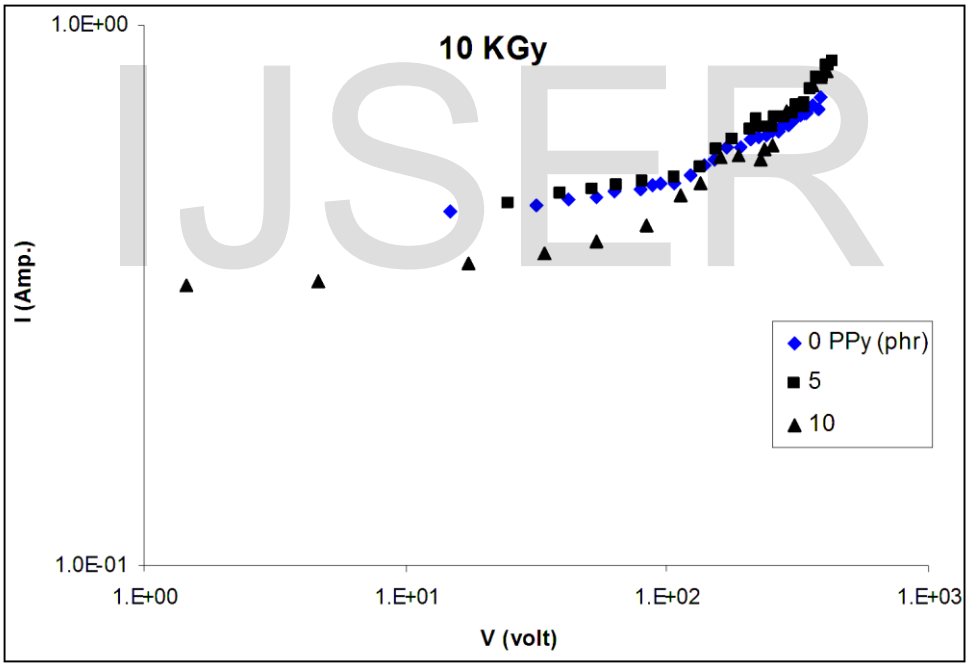


Figure (3 b): The percolation threshold dependence on electron-beam doses at room temperature (300K).

b. I-V characteristic curves of irradiated samples.

Concerning the ln (I) versus ln (V) plots of EVA loaded with conductive PPy samples at room temperature (300K) and different electron-beam doses are shown in Figure (4 a-e). For all samples, the current increases none 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 behavior of I-V characteristics of these samples. This is also evident from the fact that Ohm's law follows from the free electron model of a metal. in the present case the constituents of composites are itself have an insulator phase and the rubber phase 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 freeable a charge carrier density, space charge limited conduction seems a remote possibility.



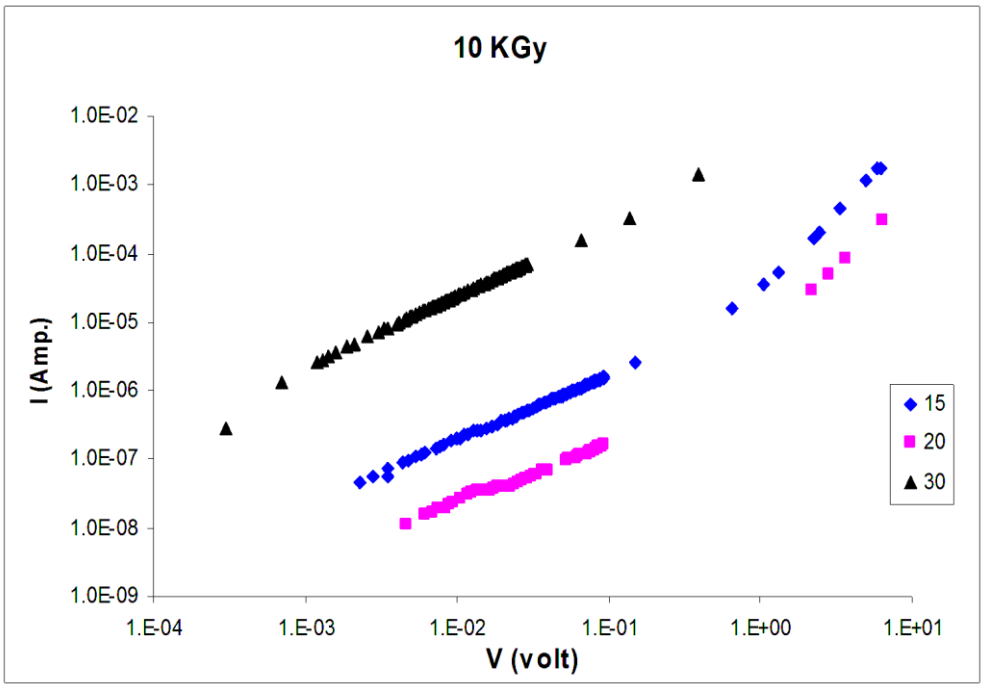
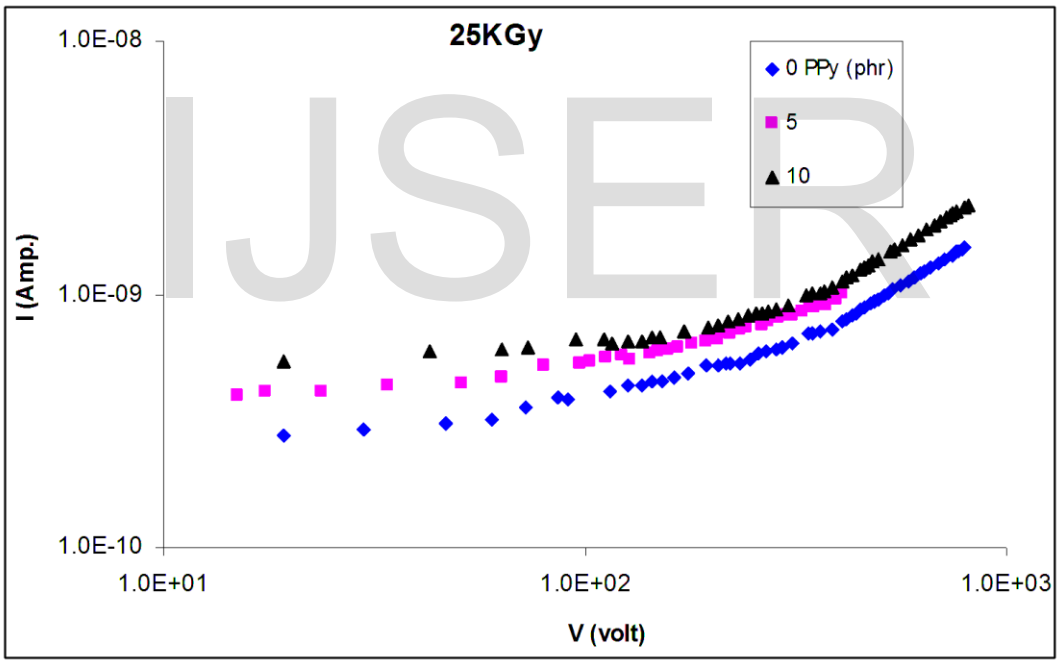
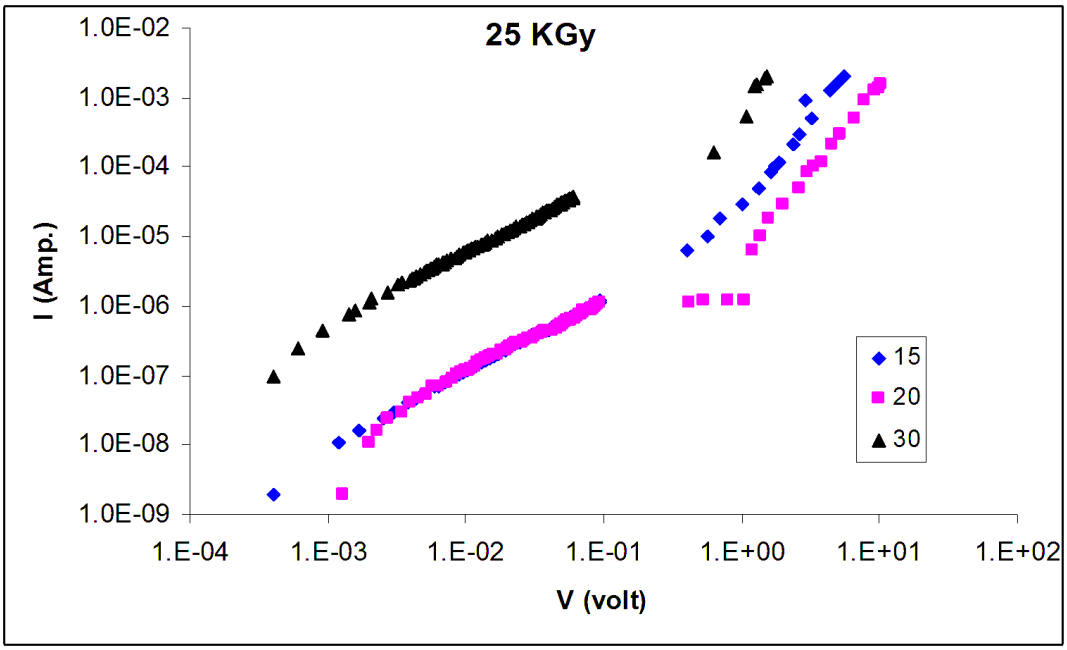


Figure (4 a)





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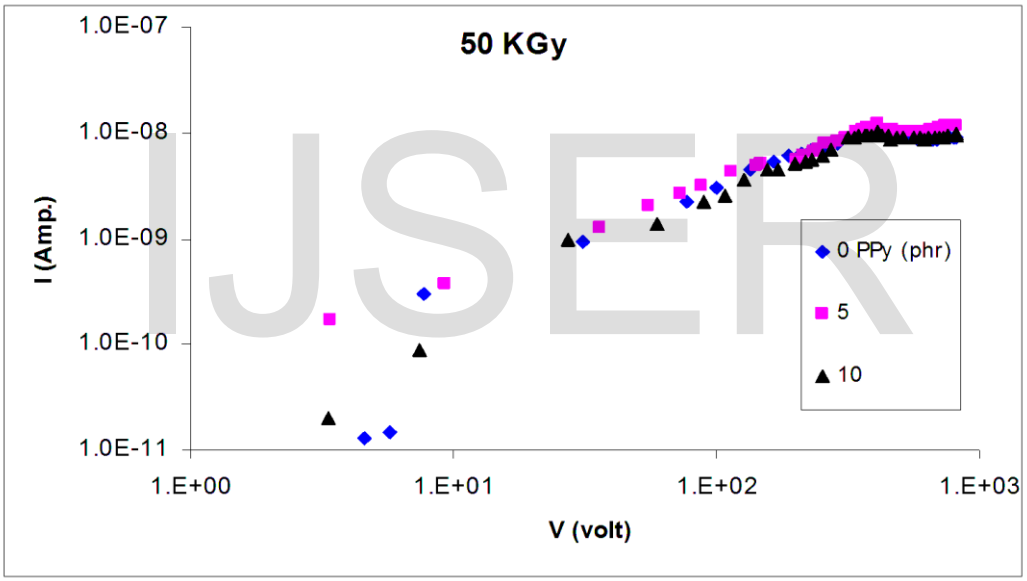


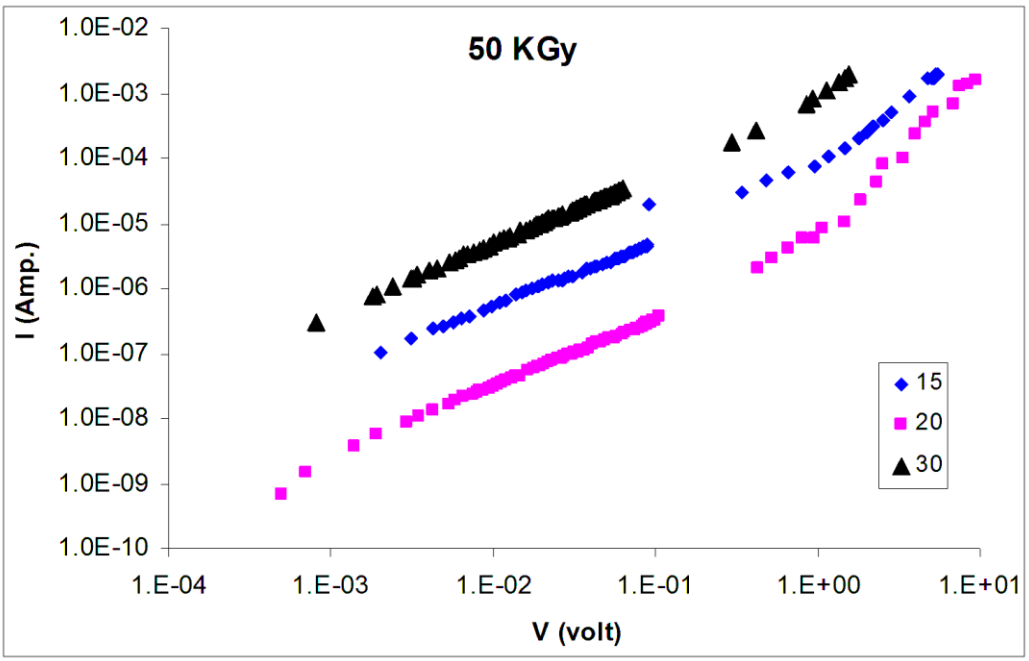
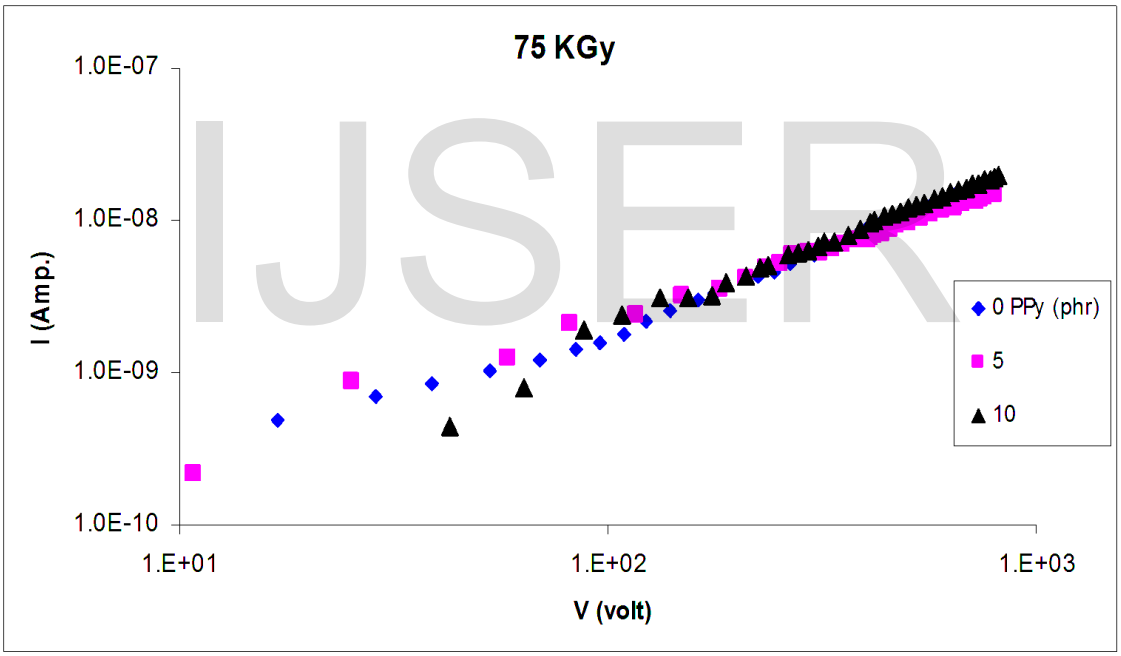


Figure (4 c)



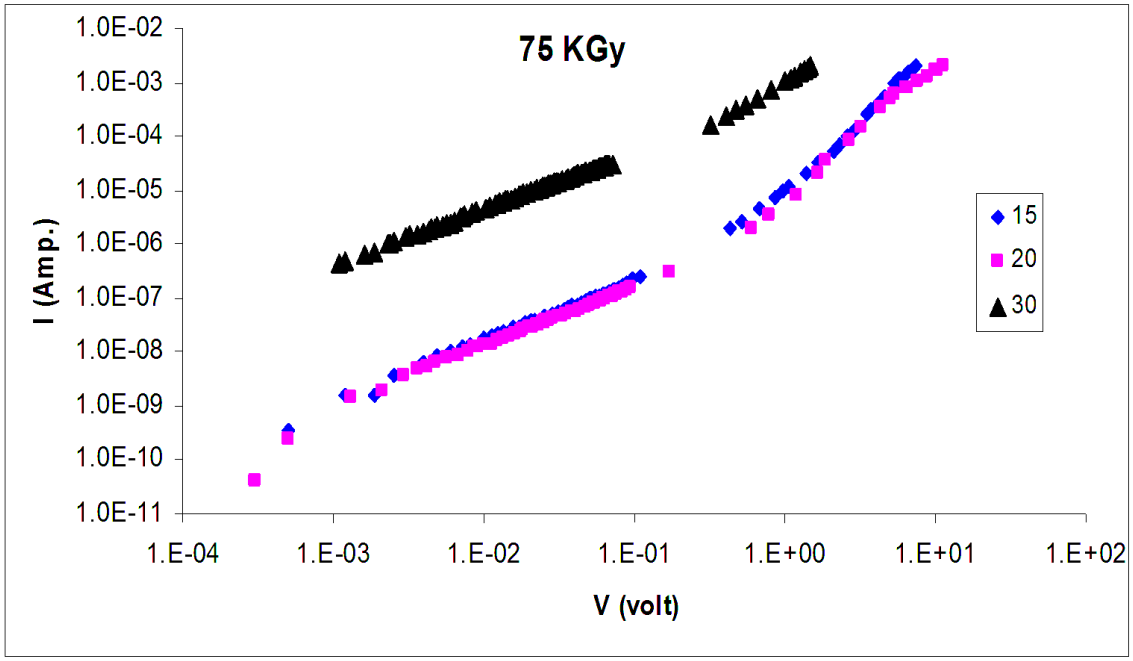
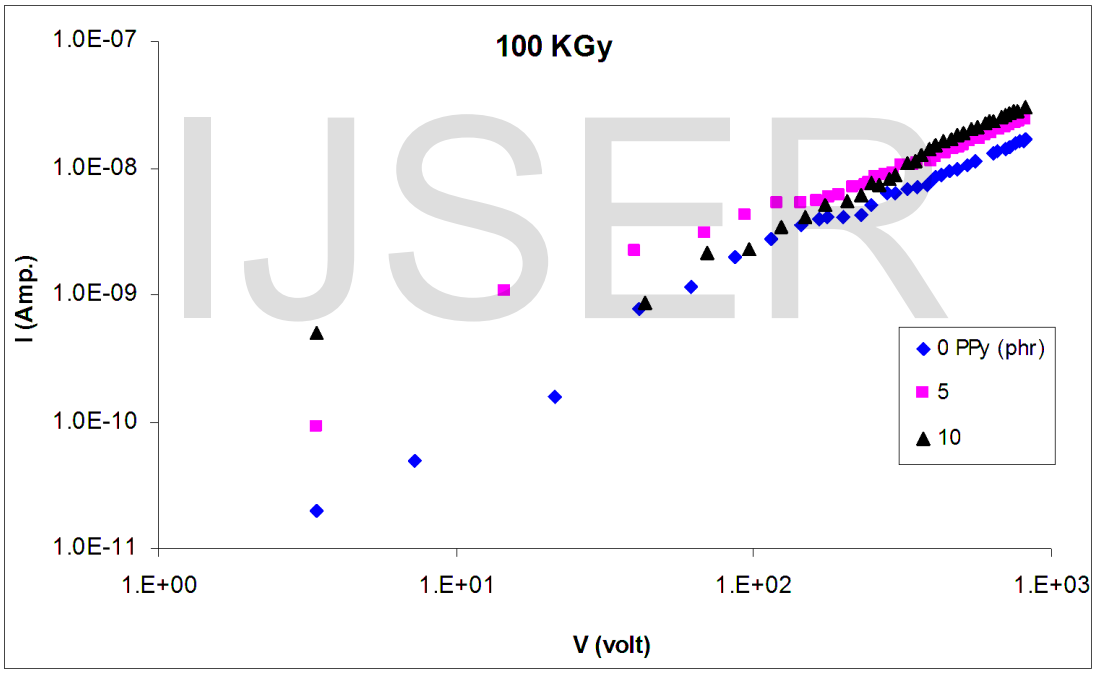


Figure (4 d)



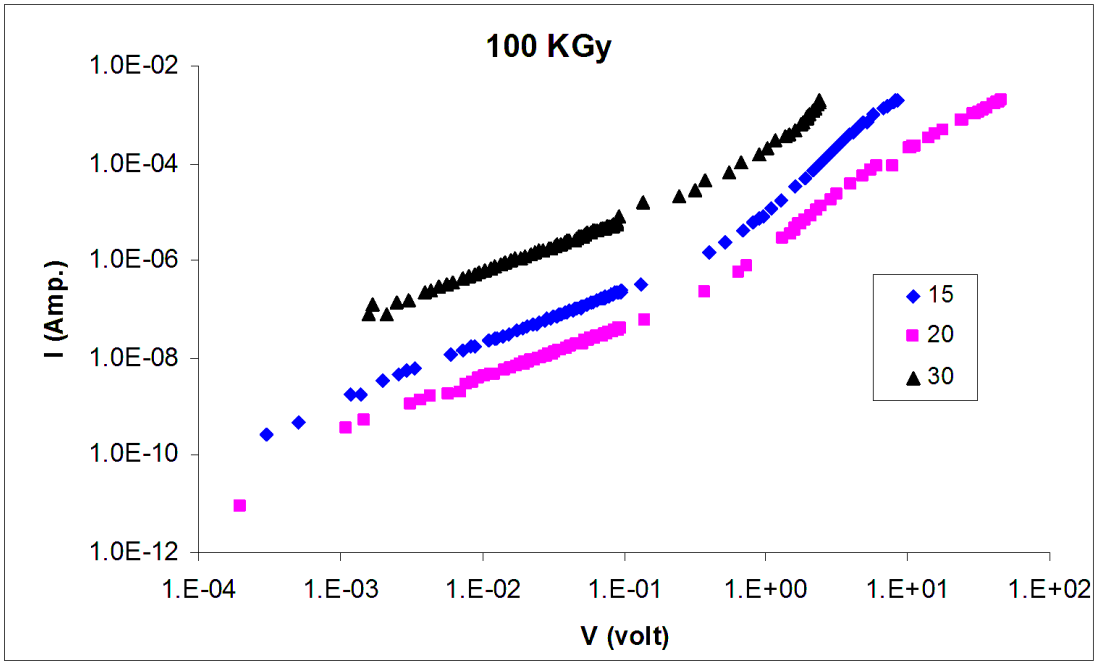


Figure (4 a-e): The ln (I) versus ln (V) characteristics of EVA loaded with conductive PPy samples at room temperature (300K) with different electron-beam doses.

Let us now discuss the probable mechanisms of conduction in our samples [24].

i) Poole -Frenkel conduction

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

$$J=B \exp(-\Phi/KT + \beta_{PF} E^{1/2}), \quad (3)$$

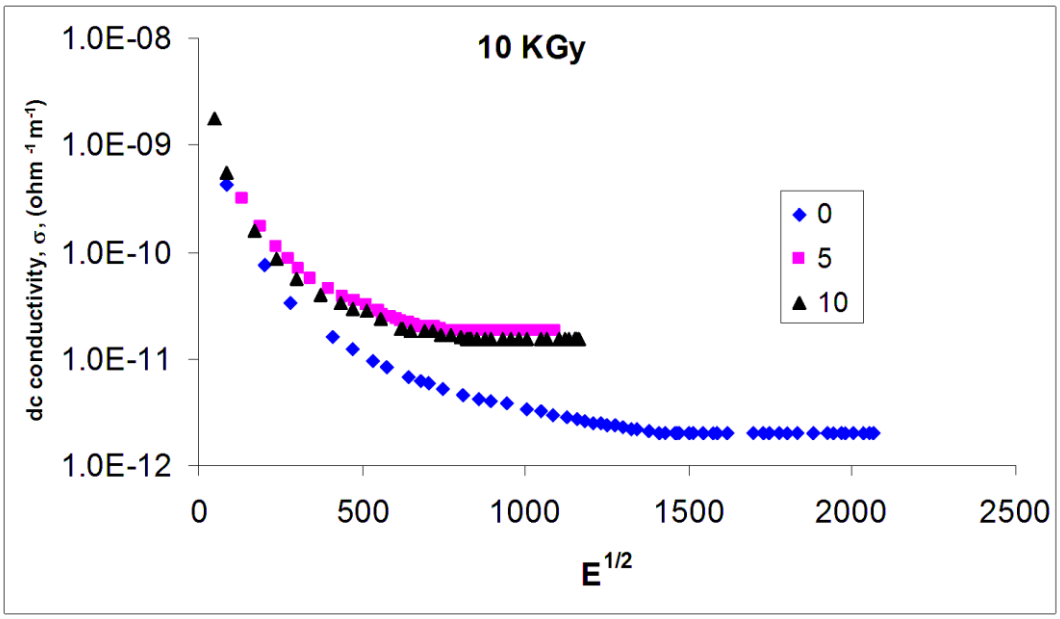
Where $$\beta_{PF} = \left(\frac{e}{kT}\right)\left(\frac{e}{\pi\varepsilon_o\varepsilon'}\right)^{1/2} = \text{constant} \quad (4)$$

Where β is a constant and all other symbols have their useful meanings. The poole- Frenkel mechanism predicts a field dependent conductivity as:

$$\sigma = \sigma_o \exp\left(\frac{B_{PF} E^{1/2}}{2kT}\right) \quad (5)$$

Or $$\ln\sigma = \ln\sigma_o + (\beta_{PF} E^{1/2} / 2KT) \quad (6)$$

So that the Poole – Frenkel mechanism is characterized by the linearity of lnσ versus $E^{1/2}$ i.e Poole – Frenkel plots predicted by equation (6) are linear with a positive slope. It can be noticed from Figure (5 a-e) which represents the Poole – Frenkel plots, that this mechanism does not contribute significantly to the conduction as lnσ does not show appreciable dependence on $E^{1/2}$ axis, indicating absence of Poole – Frenkel mechanism.



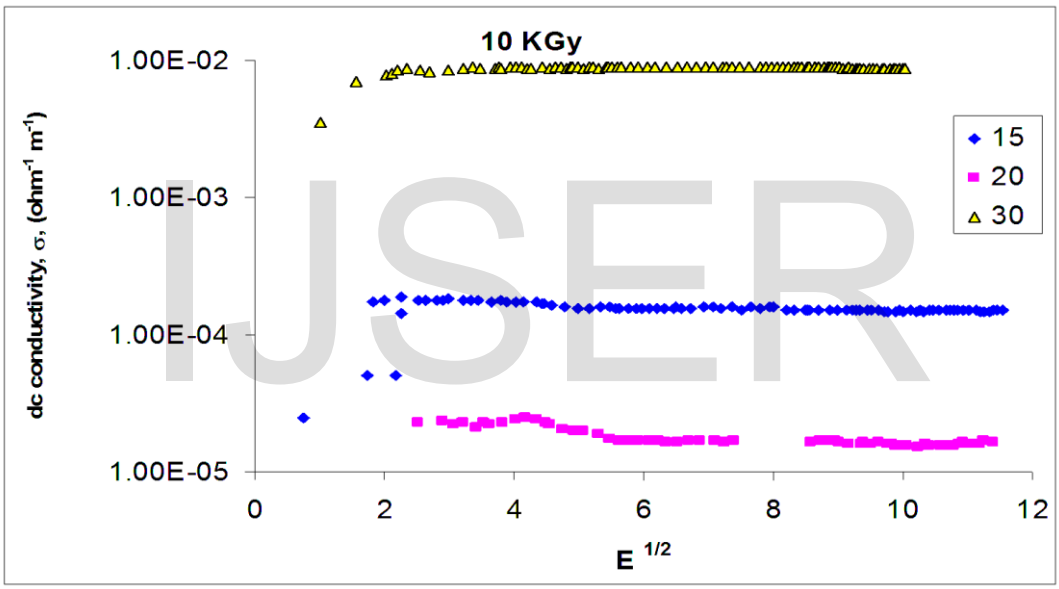
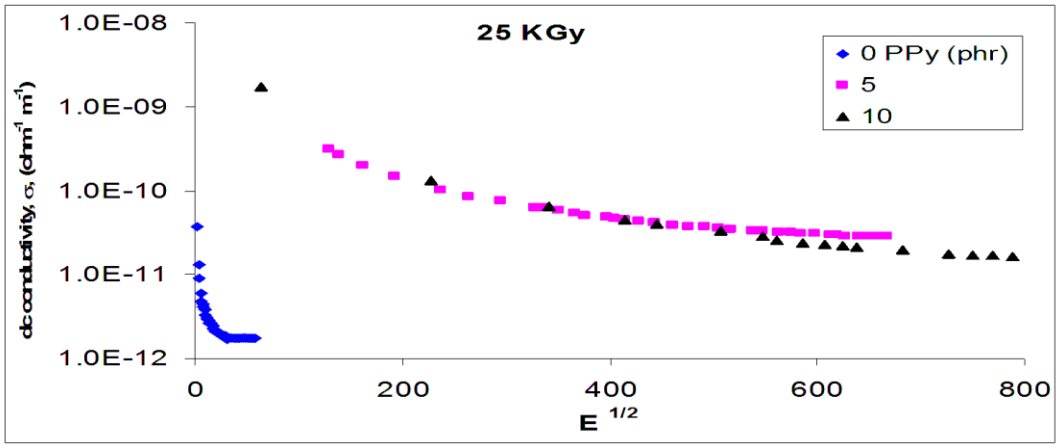
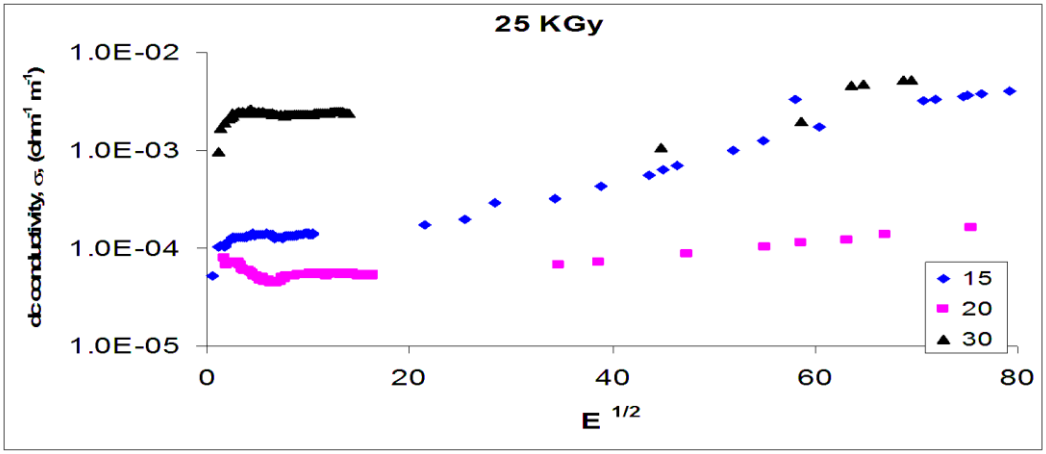


Figure (5 a)





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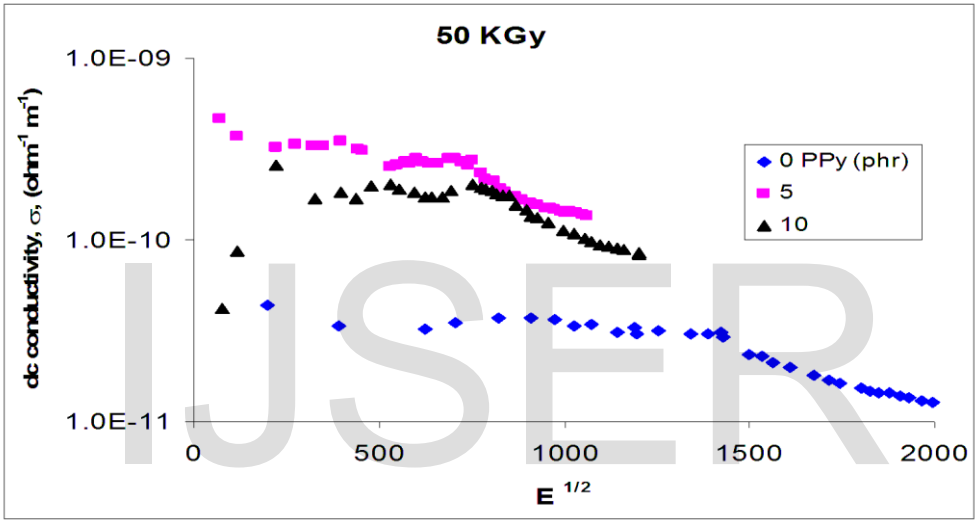


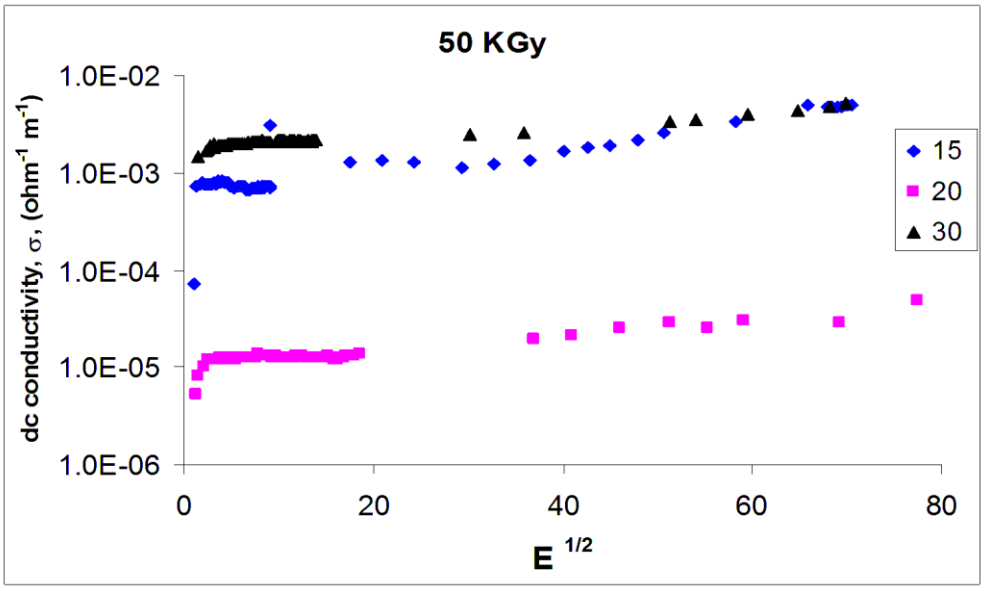
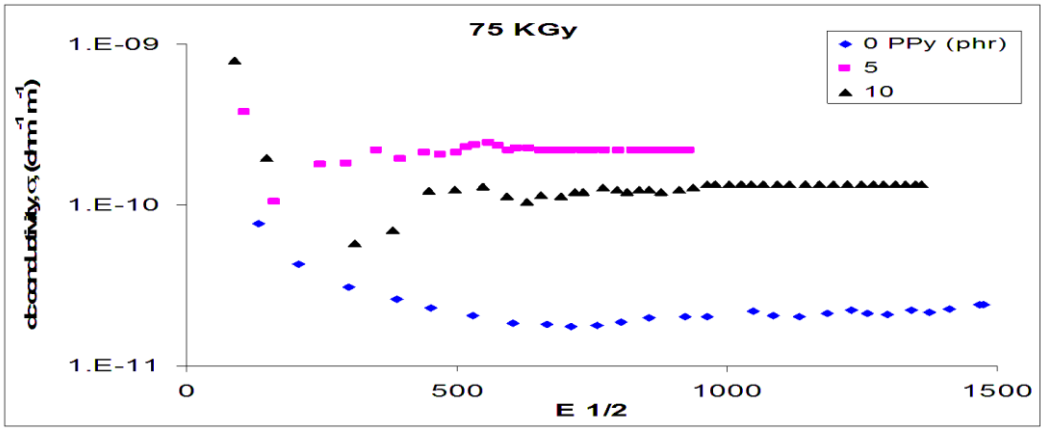


Figure (5 c)



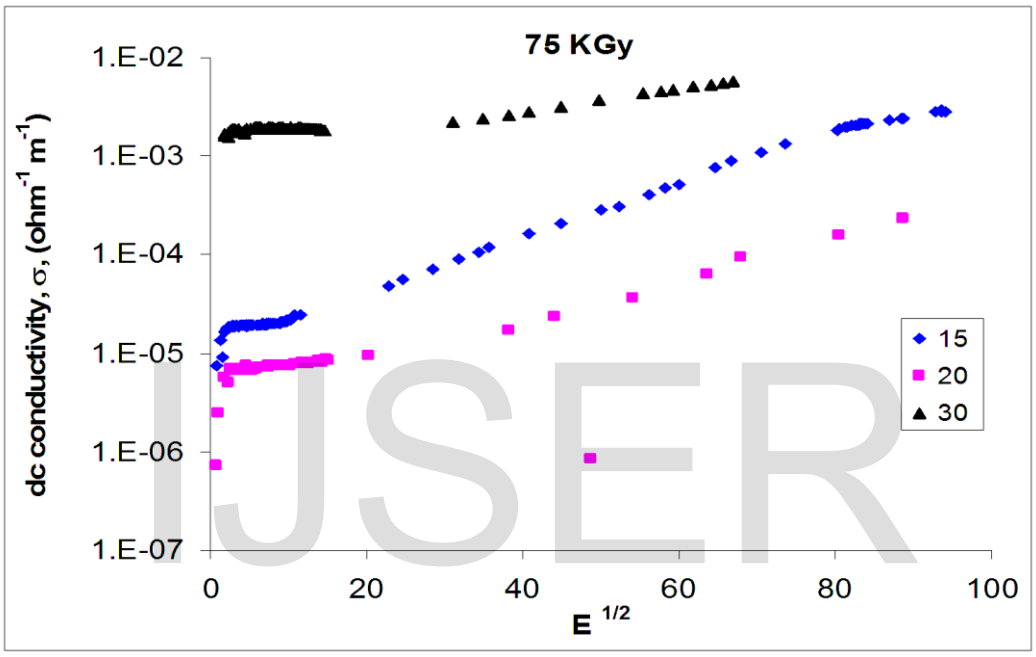


Figure (5 d)

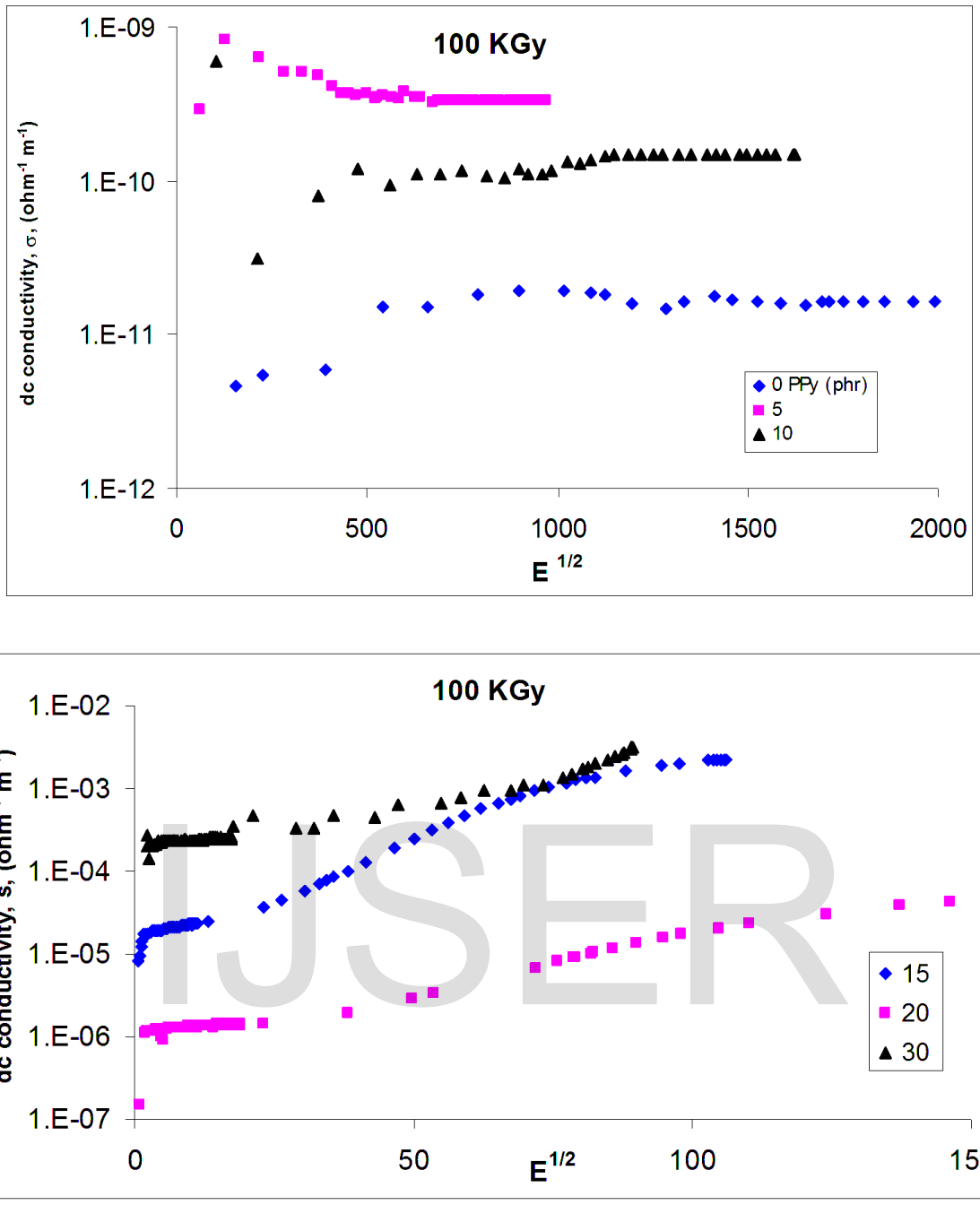


Figure (5 e): The Poole-Frenkel plots at room temperature (300K) with different electron-beam doses.

ii) Fowler - Nordheim mechanism.

TheFowler- Nordheim relation [25] for current density is

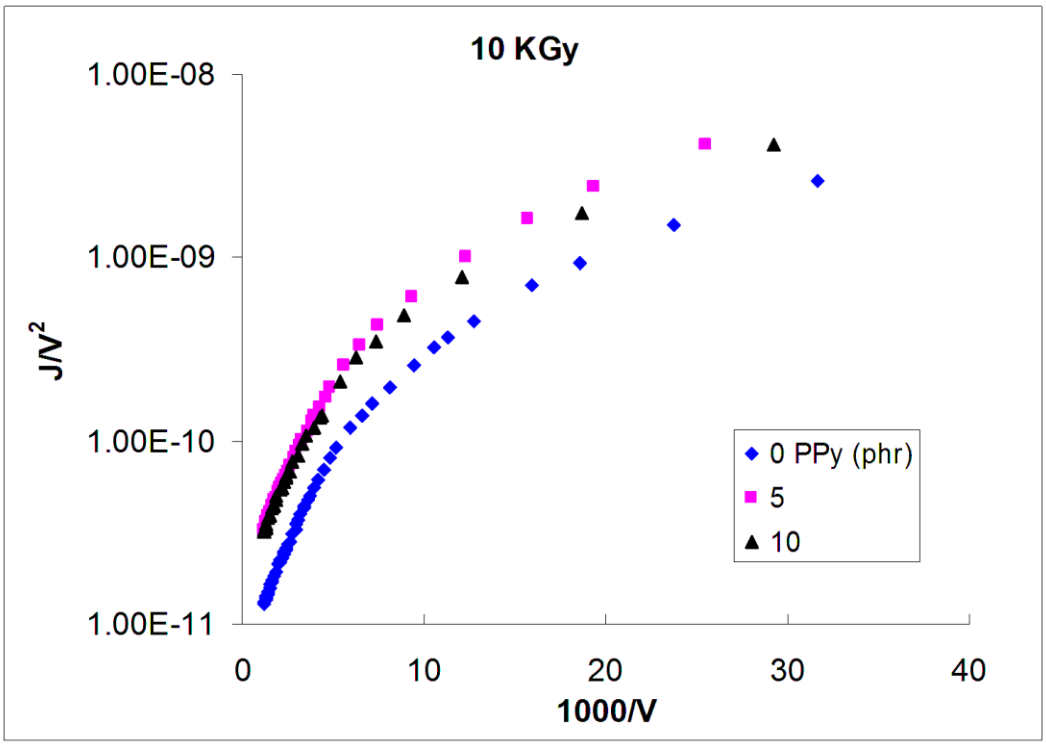
$$J=AV^2\exp(-\Phi/V) \quad (7)$$

so that

$$\ln(J/V^2) = \ln A - (\Phi/V) \quad (8)$$

And the $\ln(J/V^2)$ versus 1000/V plots is expected to be a linear straight line relation with a negative slope.In the present case, the $\ln(J/V^2)$ versus 1000/ V plots for the sample are presented in Figure (6 a-e) which are

nearly straight lines with a positive slope for higher as well as for lower values of V indicating the absence of tunneling current as suggested by Fowler- Nordheim relation.



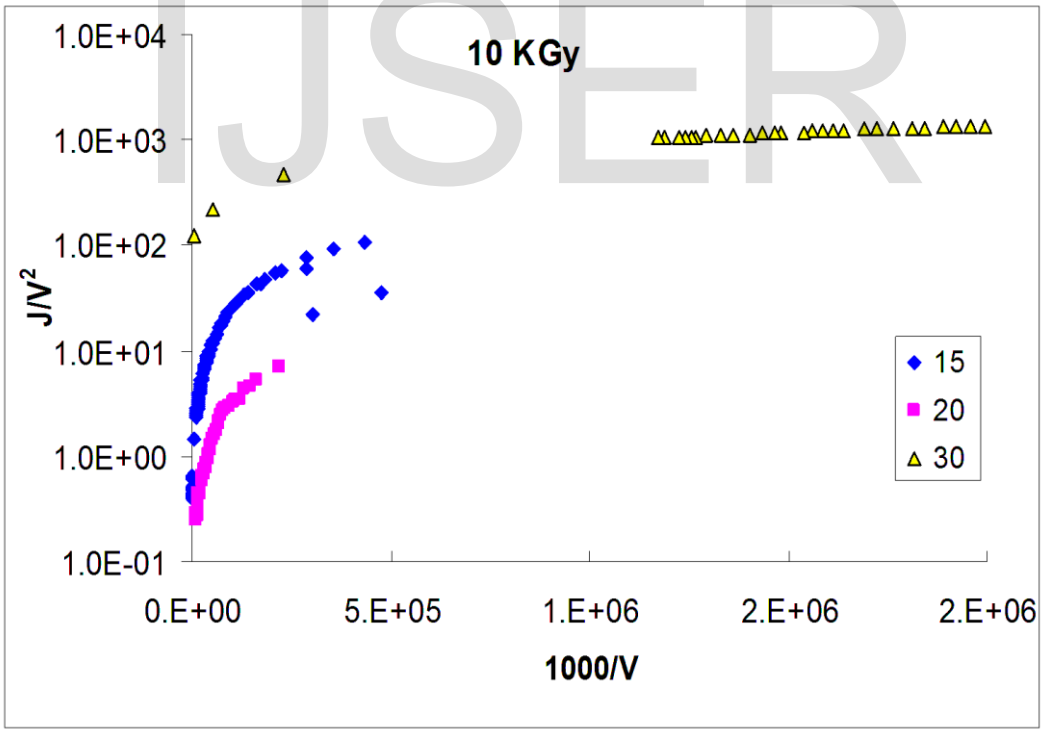
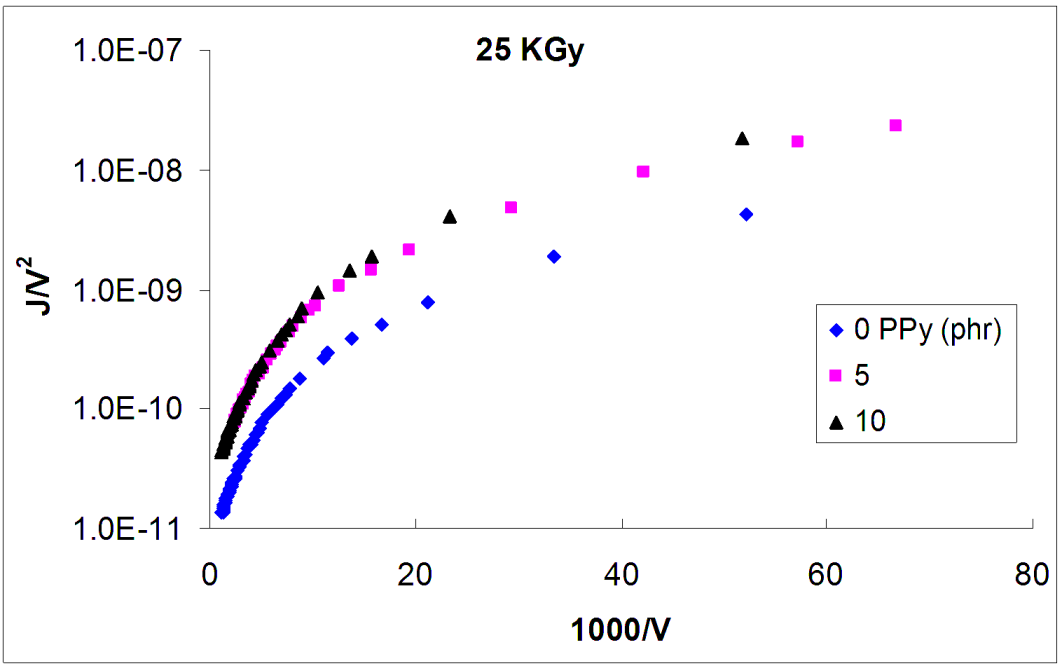


Figure (6 a)



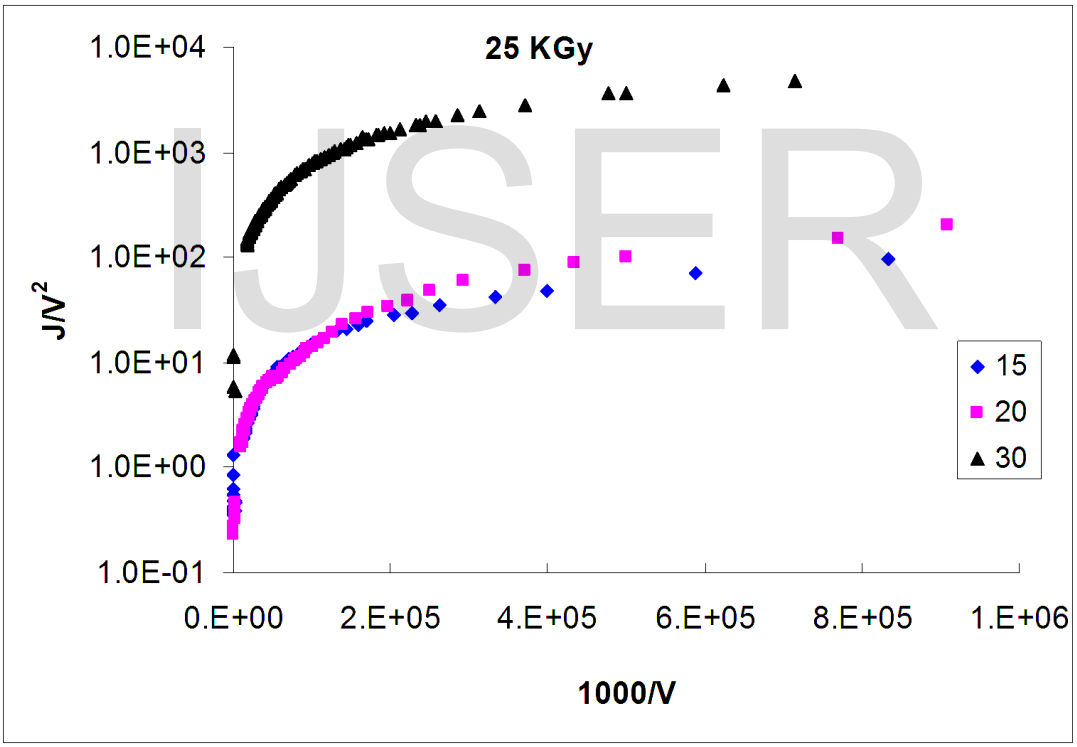
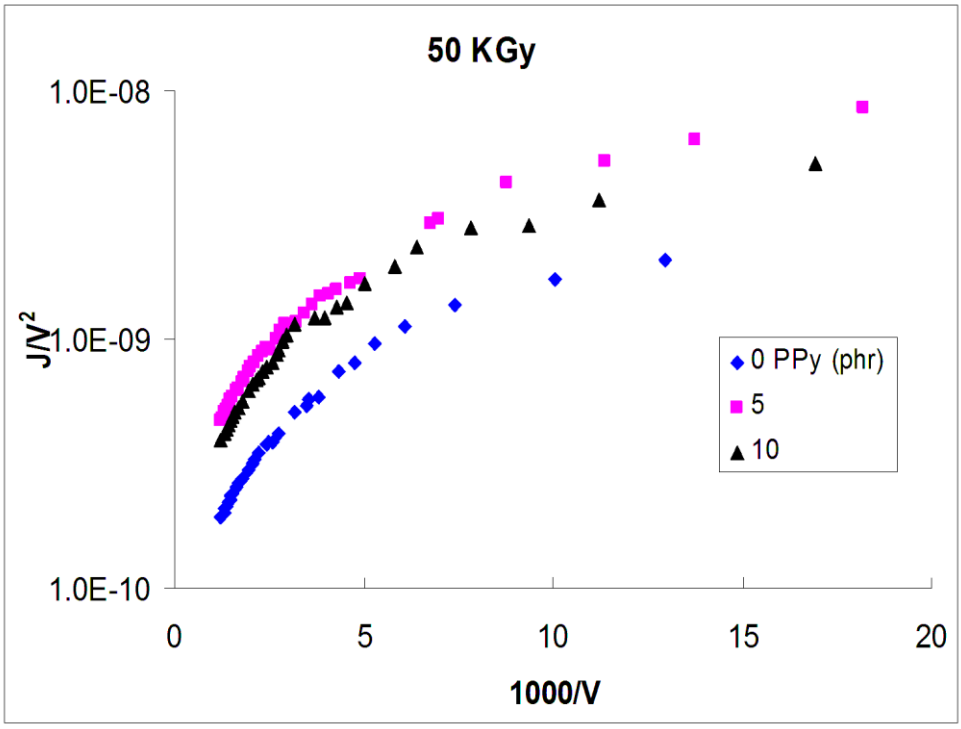


Figure (6 b)



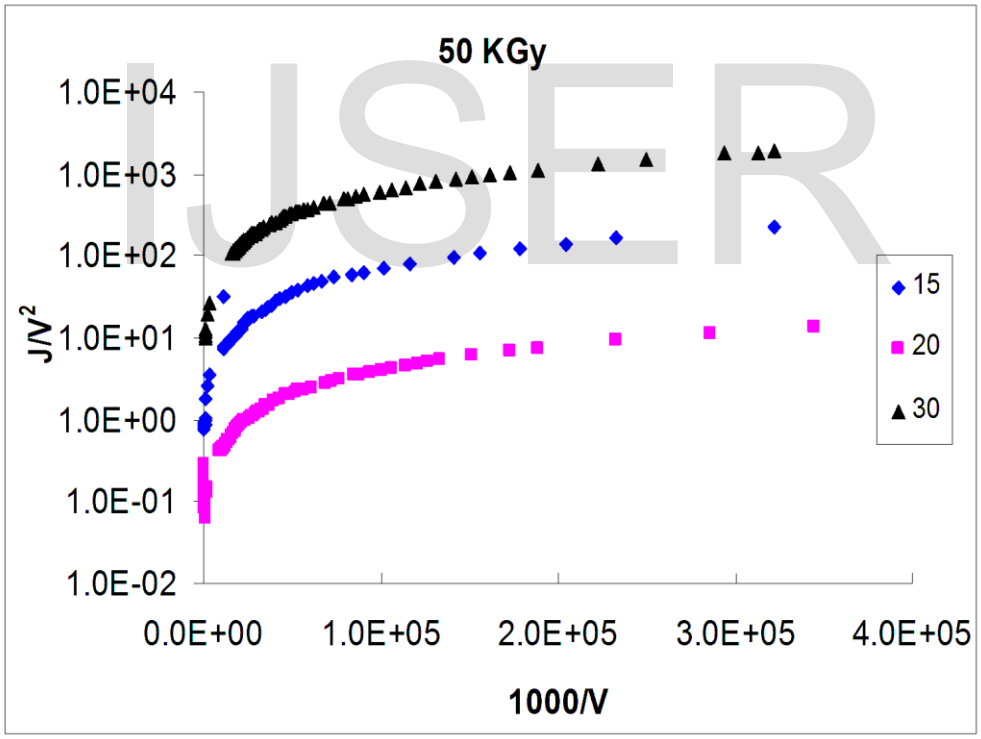
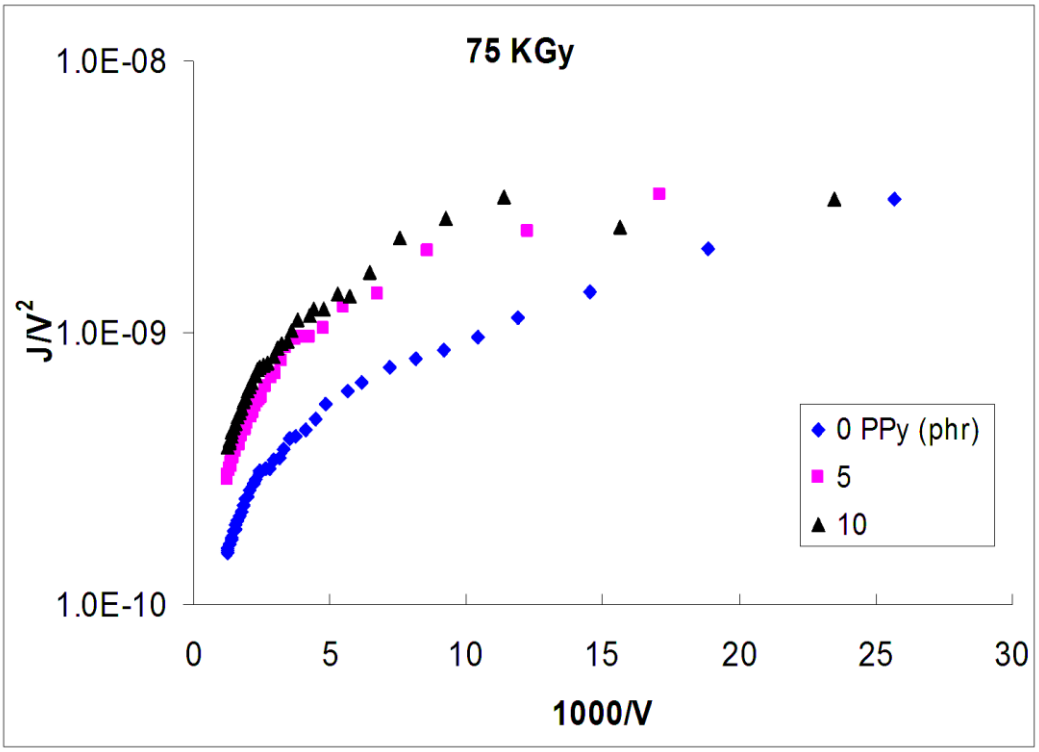


Figure (6 c)



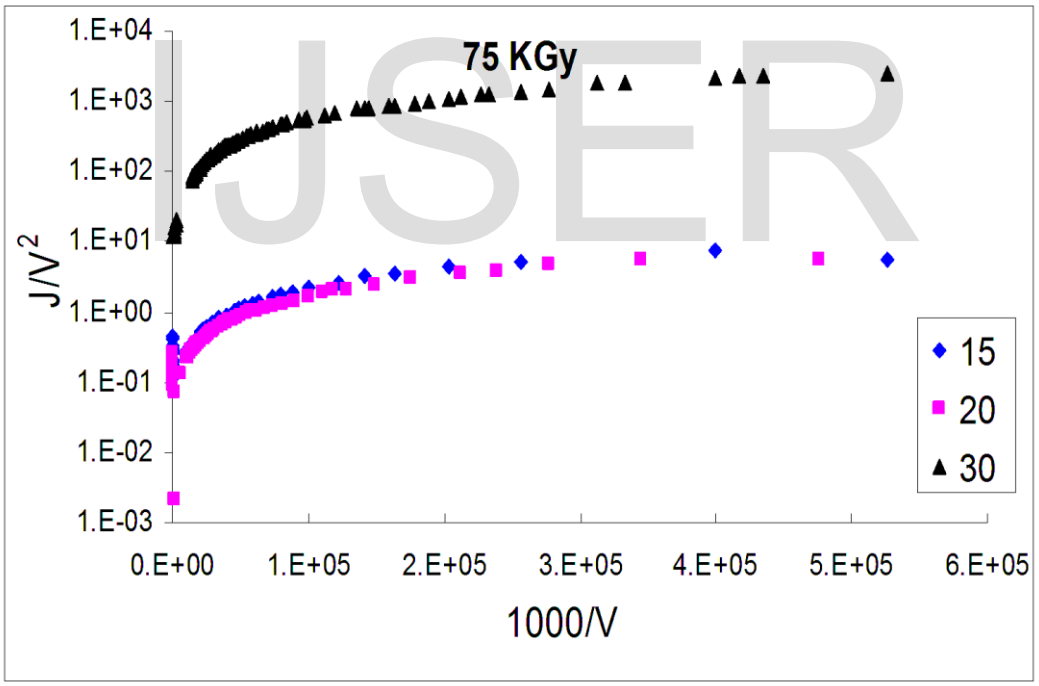
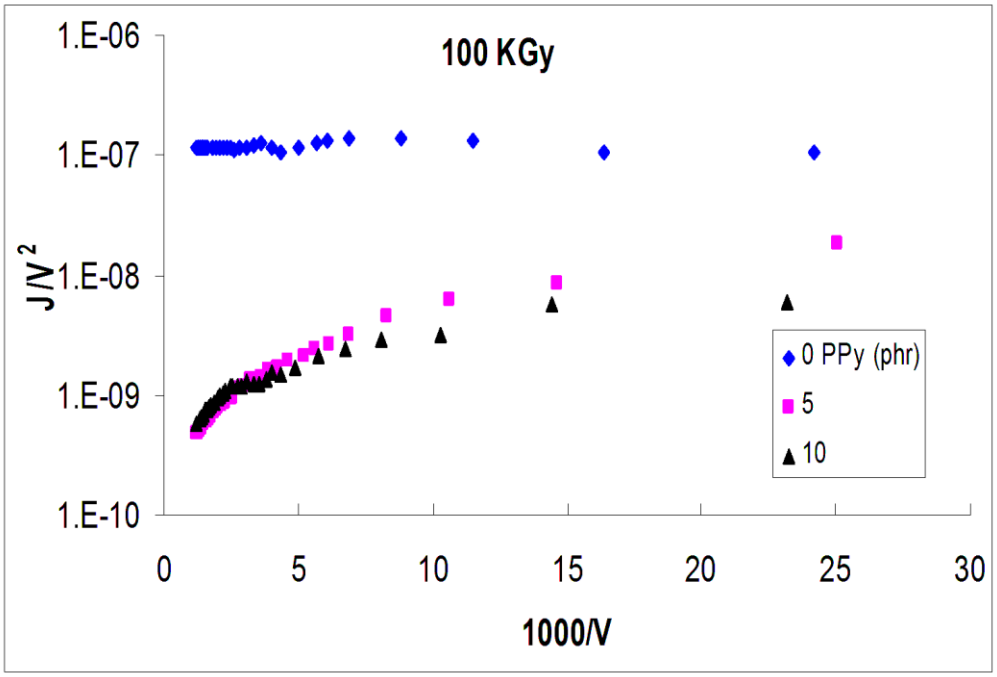


Figure (6 d)



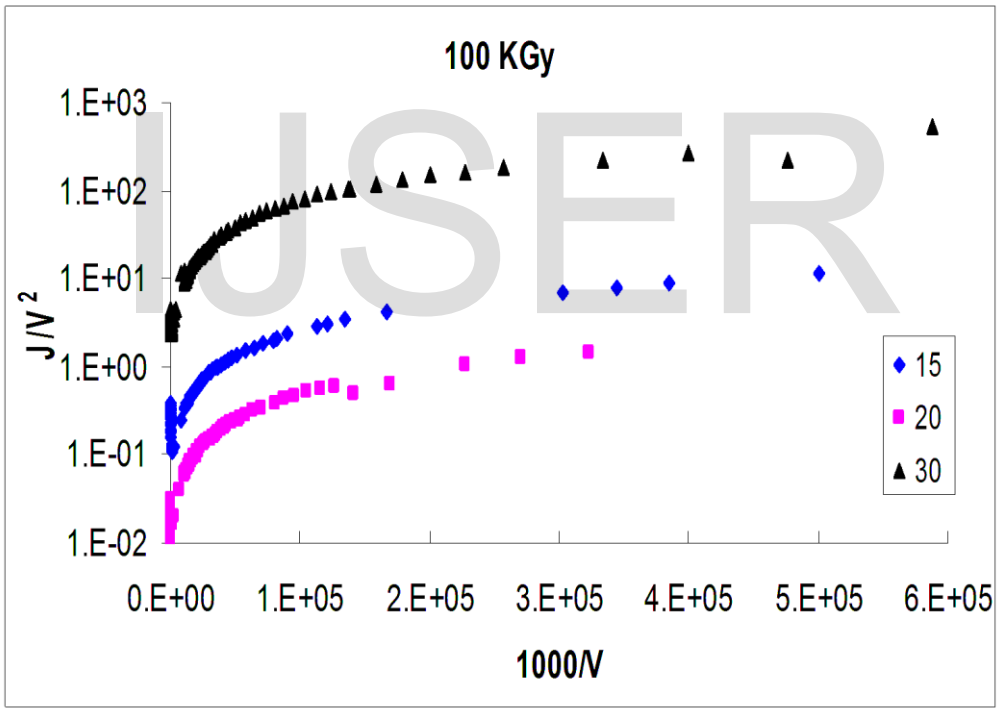


Figure (6 a-e): The Fowler-Nordheim plots at room temperature (300K) for irradiated samples with different electron-beam doses.

iii) Schottky plots:

The Schottky- Richardson current voltage relationship is expressed as:

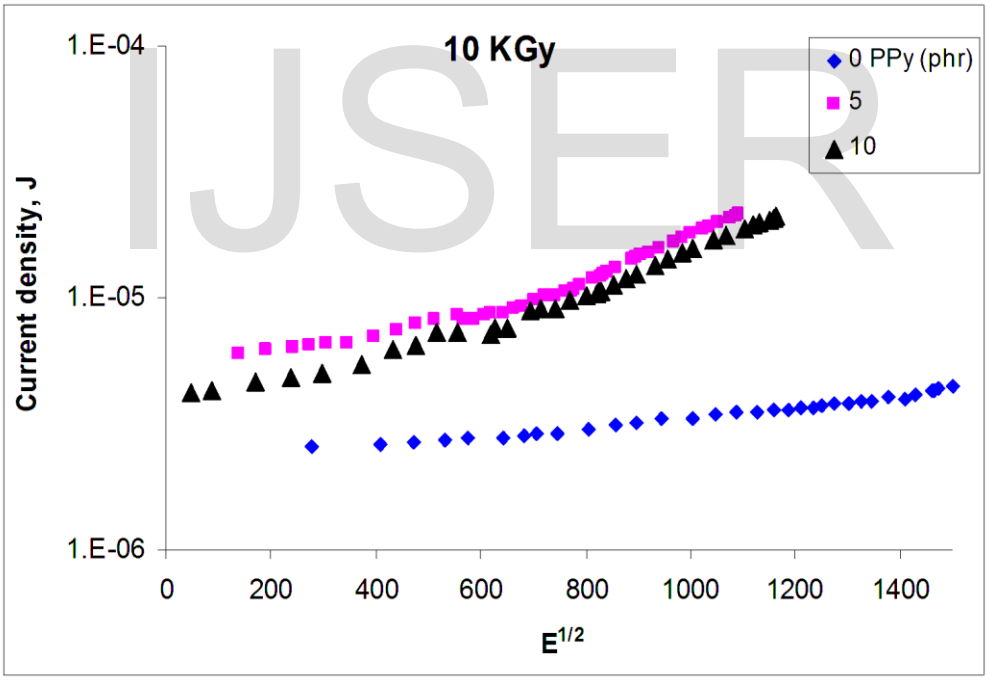
$$J = A\,T^2 \exp\left[\left(\frac{-\phi s}{KT}\right) + \beta_{SR} E^{1/2}\right] \qquad (9)$$

β_{RS} being the field lowering constant given by:

$$\beta_{SR} = \left(\frac{e}{kT}\right)\left(\frac{e}{4\pi\varepsilon_o \varepsilon' d}\right)^{1/2} \qquad (10)$$

and hence $$\ln J = \ln A\,T^2 - \left(\frac{\varphi_s}{kT}\right) + \beta_{SR}\,E^{1/2} \qquad (11)$$

and thatln J versus $E^{1/2}$ plots should be a straight line with a positive slope. The results plotted with axes marked in this way are referred to as Schotky plots and linear positive slope on Schottky plots generally characterize Schottky- Richardson mechanism. Schottky plots for the case (Figure 7 a-e) are straight lines 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 Poole – Frenkel mechanism.



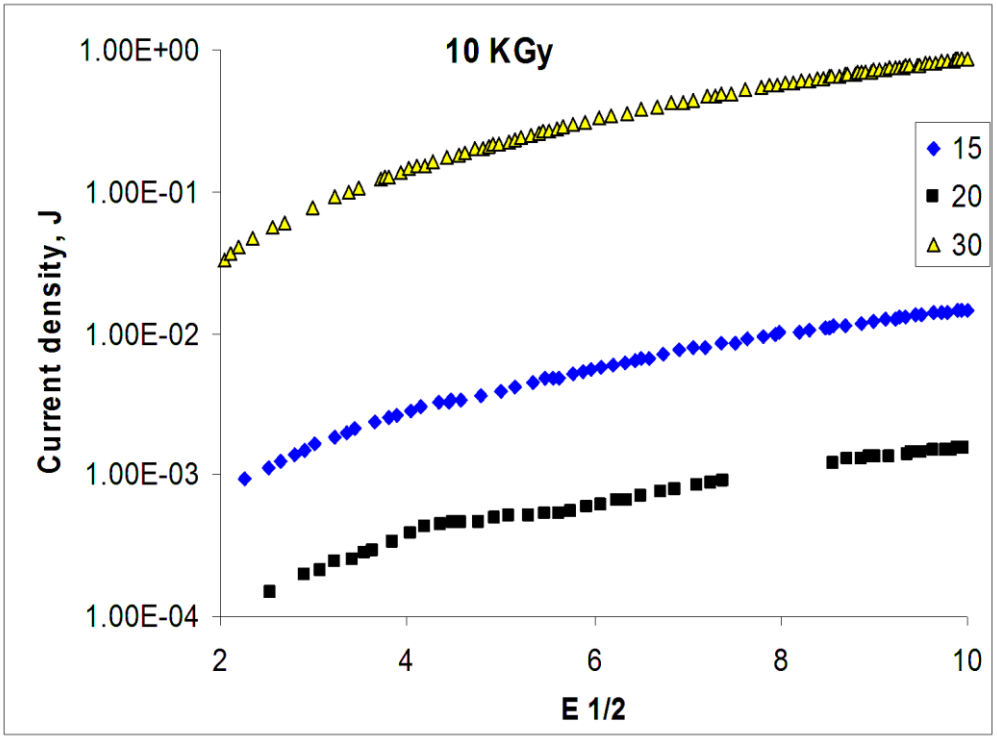
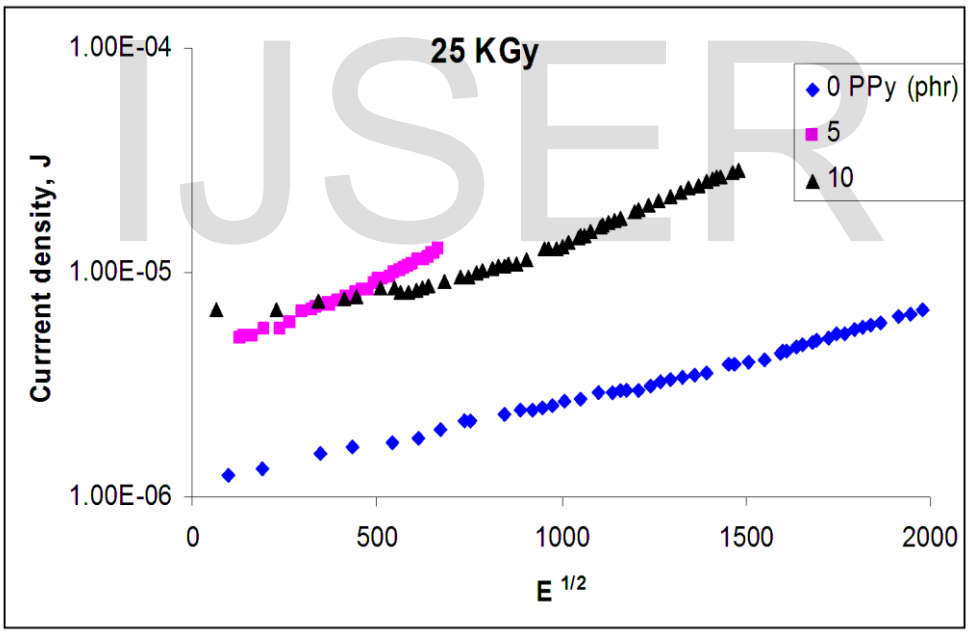


Figure (7 a)



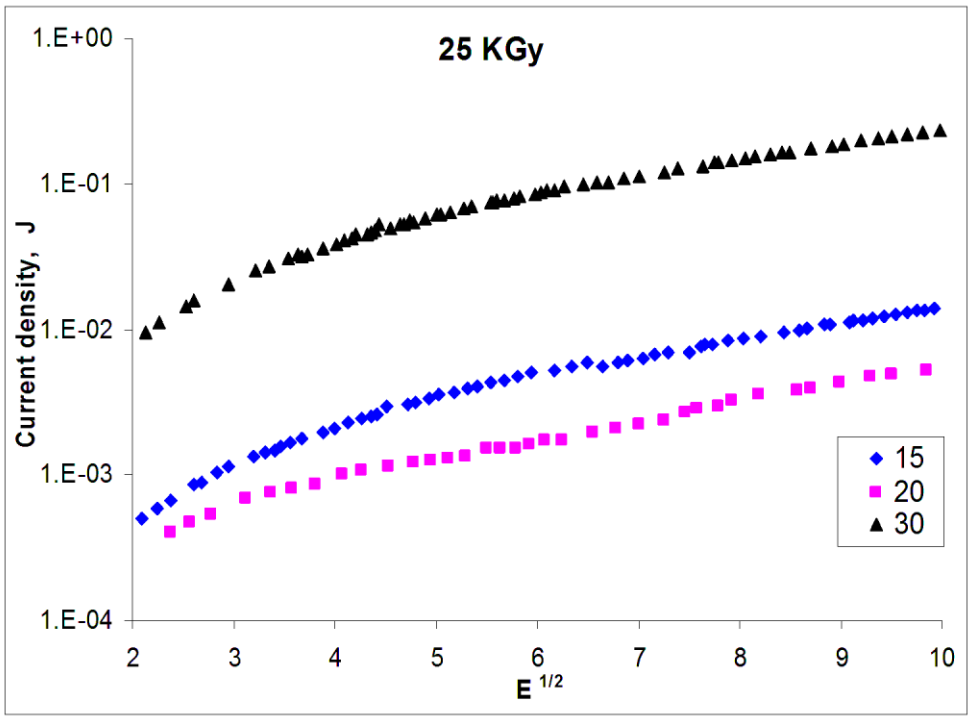
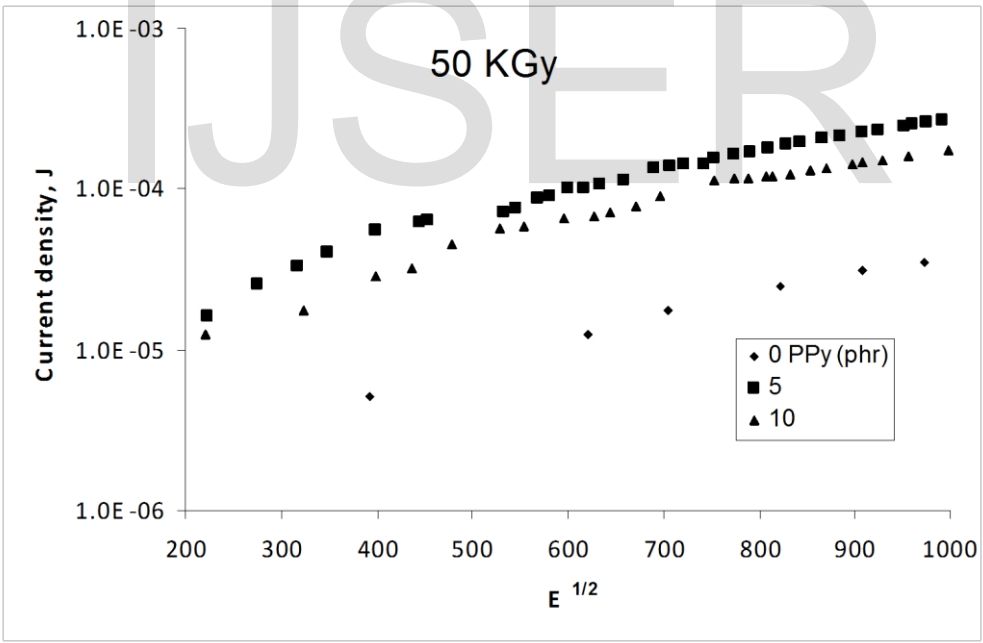


Figure (7 b)



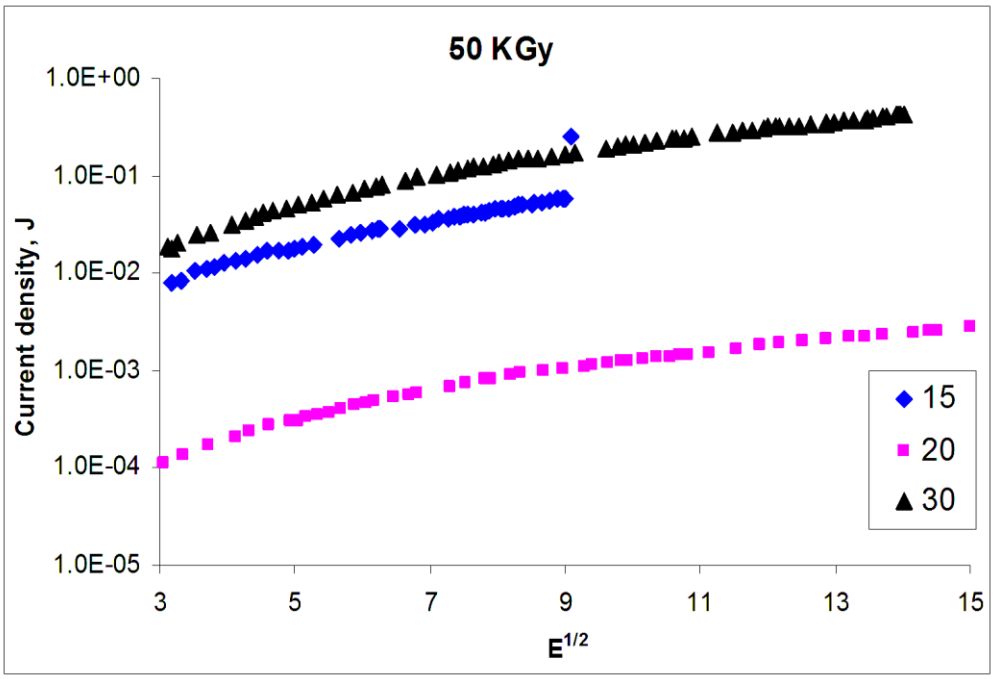
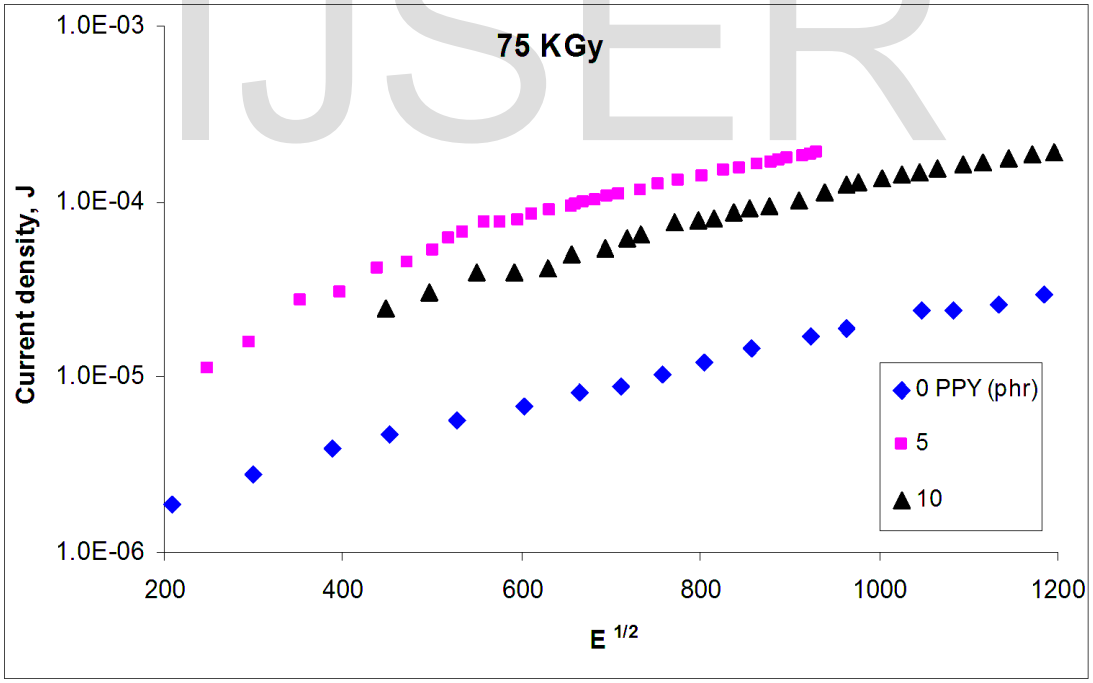


Figure (7 c)



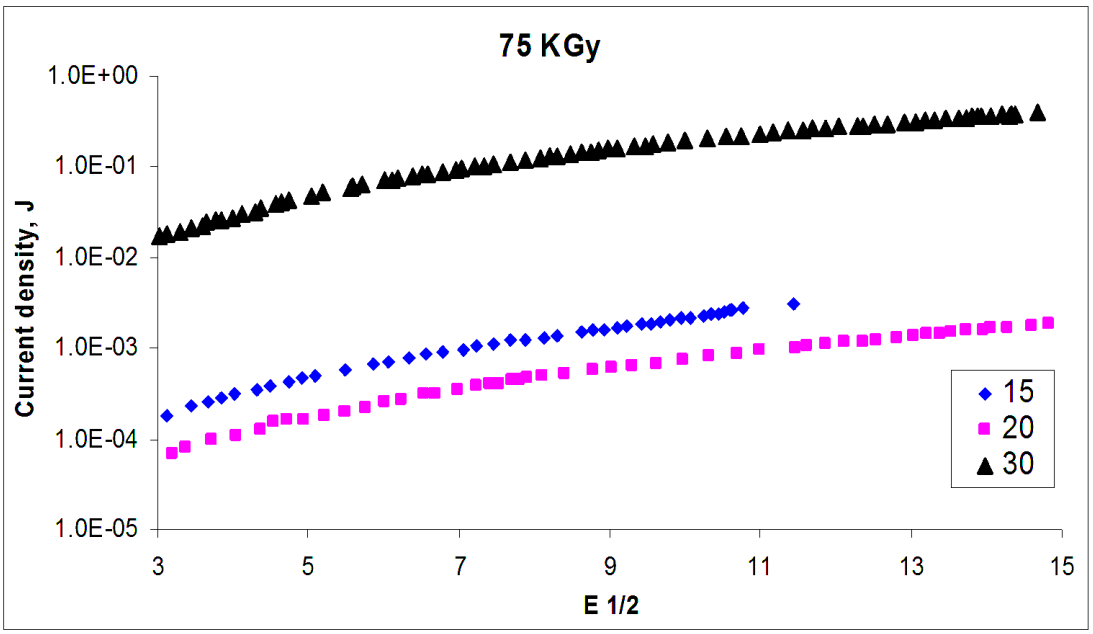
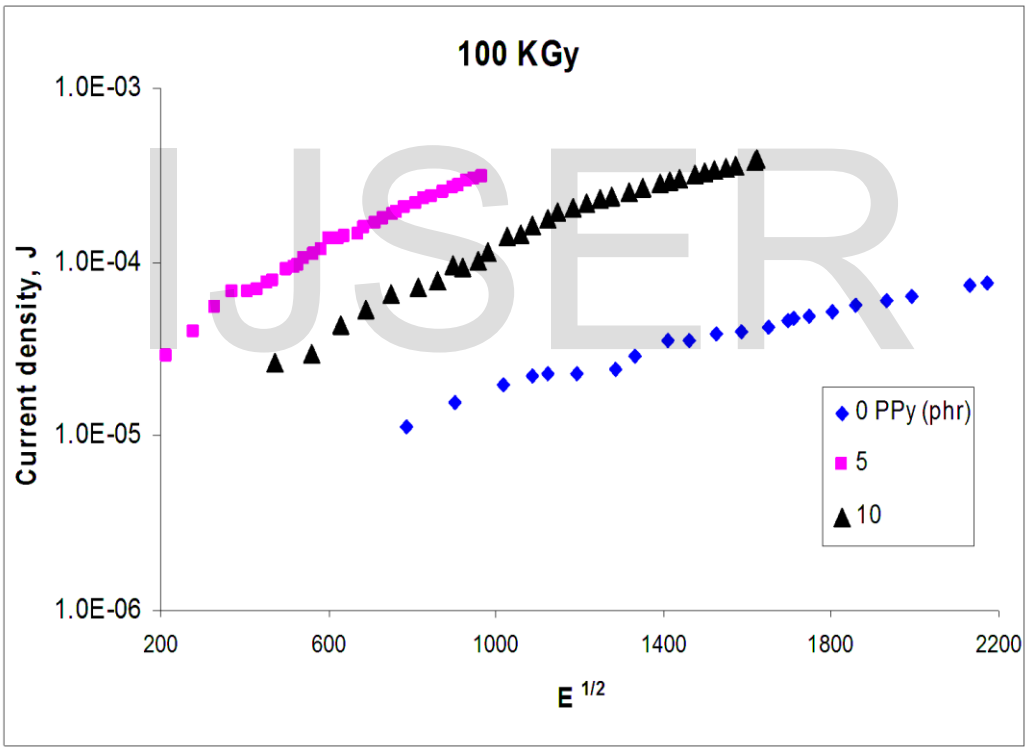


Figure (7 d)



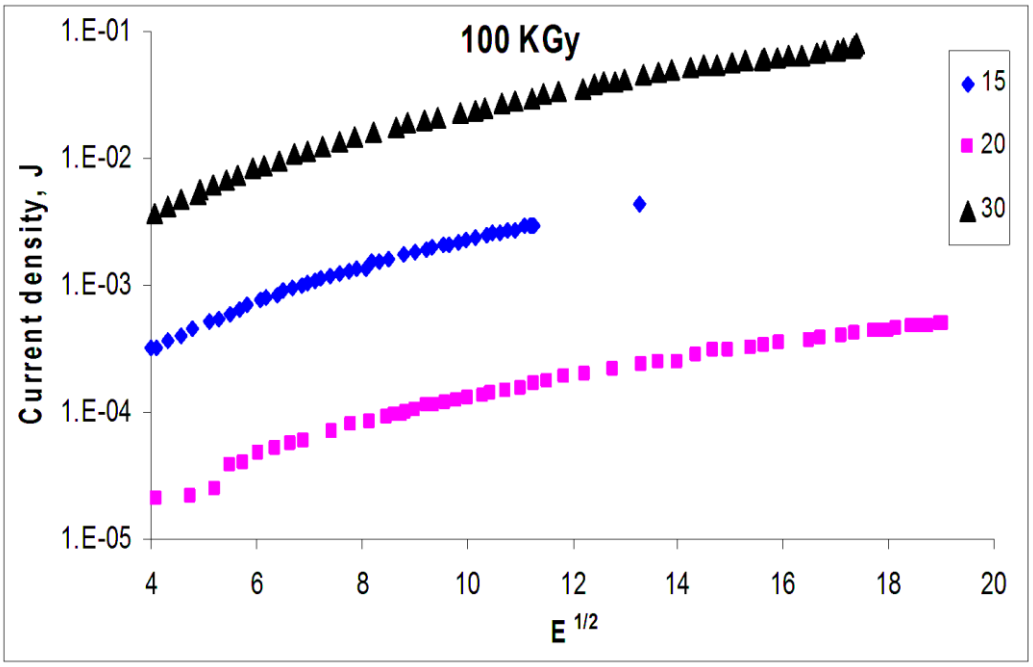


Figure (7 a-e): The Schottky plots at room temperature (300K) for irradiated samples with different electron-beam doses

4. Conclusions

After studying electrical conduction through the PPy/EVA samples under various existing mechanisms, it is observed that in the present case, the behavior cannot be described by P- F and F-N mechanisms but can closely described by Schottky and Richardson mechanism and this mechanism isn't altered with electron-beam irradiation. The concentration dependence of the electrical conductivity, σ, for EVA mixed with conductive PPy satisfied the scaling law of percolation clusters within the range of $\Phi c \leq \Phi \leq 0.23$.the percolation threshold for these composites is 0.106 and changes with the electron-beam irradiation dose of 100 KGy to 0.09. A modified equation of the percolation model which describes well the PPy/EVA composites into the percolation region is proposed.

Acknowledgement

The authors are thankful to and express their sincere gratitude to Prof. G. M. Nasr, Professor of Solid State, Phys. Dept., Faculty of Science, Cairo University, for providing necessary laboratory facilities during the course of this work, supervision, encouragement and fruitful discussion.

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