Electrical conductivity of Poly (Ethylene-co-Vinyl Acetate) (EVA) doped conductive PPy polymer blends

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Abstract: The electrical conductivity Poly (Ethylene-co-Vinyl Acetate) (EVA) doped conductive PPy polymer blends thin films has been measured at room temperature (300K) by studying the *I*–*V* characteristics at various loading conductive PPy. The results are presented in the form of *I*–*V* characteristics and analysis has been made by interpretation of Poole–Frenkel, Fowler–Nordheim, Schottky, Richardson and Arrhenius plots. Most samples except (5, 15, 20 phr), 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.

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1. Introduction

High molecular weight compounds constitute one of the major fields of modern technology. Thus high polymers either natural or synthetic participate in a wide range of industrial applications. Very few natural polymers which can be used in industry only through mechanical technology, but the majority of them, on the other hand, are subjected to both mechanical and chemical technology in order to realize a polymeric article good enough for industrial applications (1).

Since the end of the second world war, the annual production of industrially used synthetic polymers are in continues increase, these industries cover the industry of plastic materials, synthetic fibers, synthetic rubbers, insulator materials for electrical cables and many other industries.Today many constructive materials have been prepared from synthetic polymers; also many of industrial reactors are made from plastic materials.

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.

Thermal stability, mechanical properties and electrical conduction of nylon-6/polypyrrole composite films were reported by Kelkar *et al.*(5). The results show that there is an improvement in the electrical properties of the composite films. The anisotropy of electrical conductivity in polypyrrole deposited on poly (ethylene oxide)-copper (II) chloride complex films deposited by the dip-coating technique were studied by Khedkar *et al.*(6). Schmeiβer *et al.*(7) reported on the electronic and magnetic properties of Polypyrrole films with a one-dimensional and two-dimensional microstructure. Costa *et al.*(8) prepared new composite materials in order to optimise the Radar electromagnetic absorption, based on polystyrene (PS) and polypyrrole (PPy) particles.

To study the effect of Poly (Ethylene-co-Vinyl Acetate) (EVA) doped conductive PPy polymer blends. In the present study, 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. The X-ray diffractogram (XRD) shows that the crystallinity is almost negligible showing the sample is amorphous.

2. Experimental

2.1 Materials and Preparation of sample

EVA, containing 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°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°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. Structural characterization

For structural characterization the x-ray diffractograms of films were obtained on XPERT – PRO – PAN analytical – Netherland. The x-ray diffractograms of all the samples ensures the amorphous nature.

2.4 *Measurements*

The circuit used incorporated a digital autorangingpicoammeter 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:

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

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.

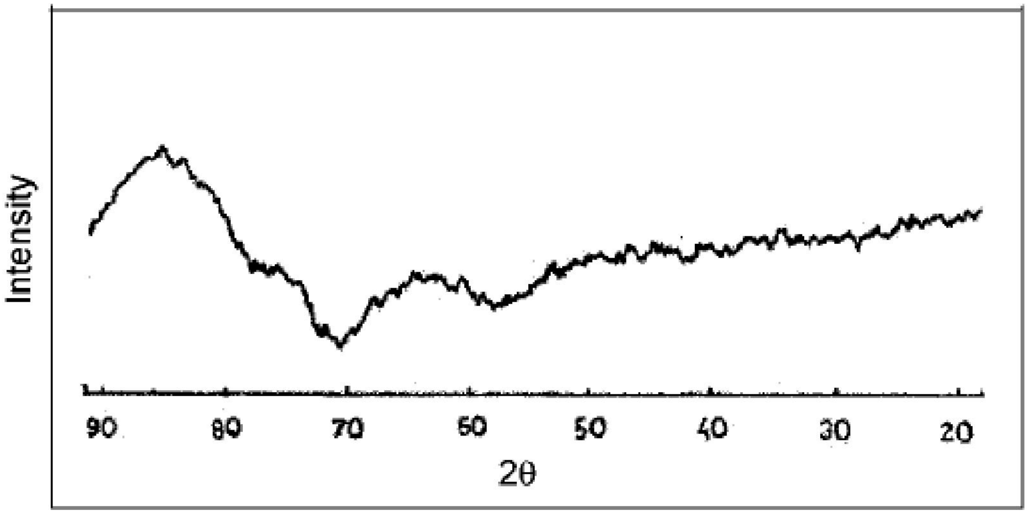

Figure (1). X-ray diffractogram of sample, of Poly (Ethylene-co-Vinyl Acetate) (EVA) doped conductive PPy polymer blend.

3. Results and Discussion

Studies of the transport mechanisms in intrinsically conductive polymers and polymer blends have gained importance owing to the potential applications in various devices technologies (9-11). 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 (12).

3.1 The effect of conductive PPy loading on dc resistivity:

The resistivity of a compound strongly depends upon the conductive filler loading. Figure (2) shows the effect of PPy loading on the volume resistivity of the conductive PPy filled EVA composites. It was observed that when the quantity of the PPy was low, the resistivity of the composites was only slightly different from that of the base polymer. However, beyond a certain critical PPy loading (10 Phr) a significant drop in resistivity was observed. In this region a relatively small increase in filler loading produced a large increase in conductivity (decrease in resistivity). This region of rapid resistivity decrease is called the percolation region. Further increasing the filler loading beyond the percolation region causes a marginal change in the conductivity of the composites.

The conduction in a composite of an insulation filled with conductive particles is explained by percolation theory. The conduction through the bulk of the compound is controlled by conduction over a number of paths of a randomly formed chain of particles. As the number of particles increases the number of continues chains or conduction paths through the matrix increases.

The total resistance for any chains consists of the sum of the individual resistances at each point of contact. If the resistances at each point of contact remain constant, the resitivity of the composites at volume loading Φ follows the form:

$$\rho=\rho_0\,(\Phi-\Phi_c)^{-t} \qquad (2)$$

Where Φ_c is the volume fraction of the filler at the percolation point, ρ_0 is the scale factor and t is a geometric factor, the value of t commonly is (1.6-2). The percolation model usually describes compound performance well into the percolation region (13) as shown in Figure (2).

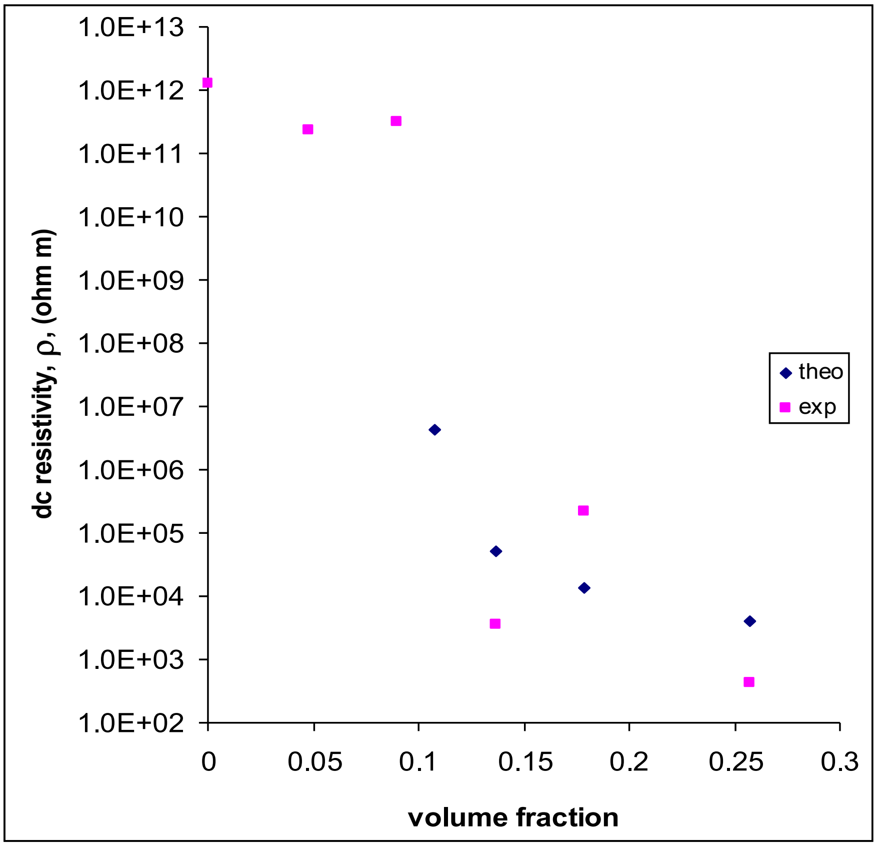

Figure (2): The volume fraction dependence of PPy on the electrical resistivity for all samples.

b. I-V characteristic curves:

Concerning the ln (I) versus ln (V) plots of EVA loaded with conductive PPy samples at room temperature (300K) are shown in Figure (3). For most samples except (5, 15, 20 phr), 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 Ohmicconduction 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 except for the samples that includes higher concentration of conductive PPy that has the same sort of regular structure and Ohmic conduction is applied.

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.

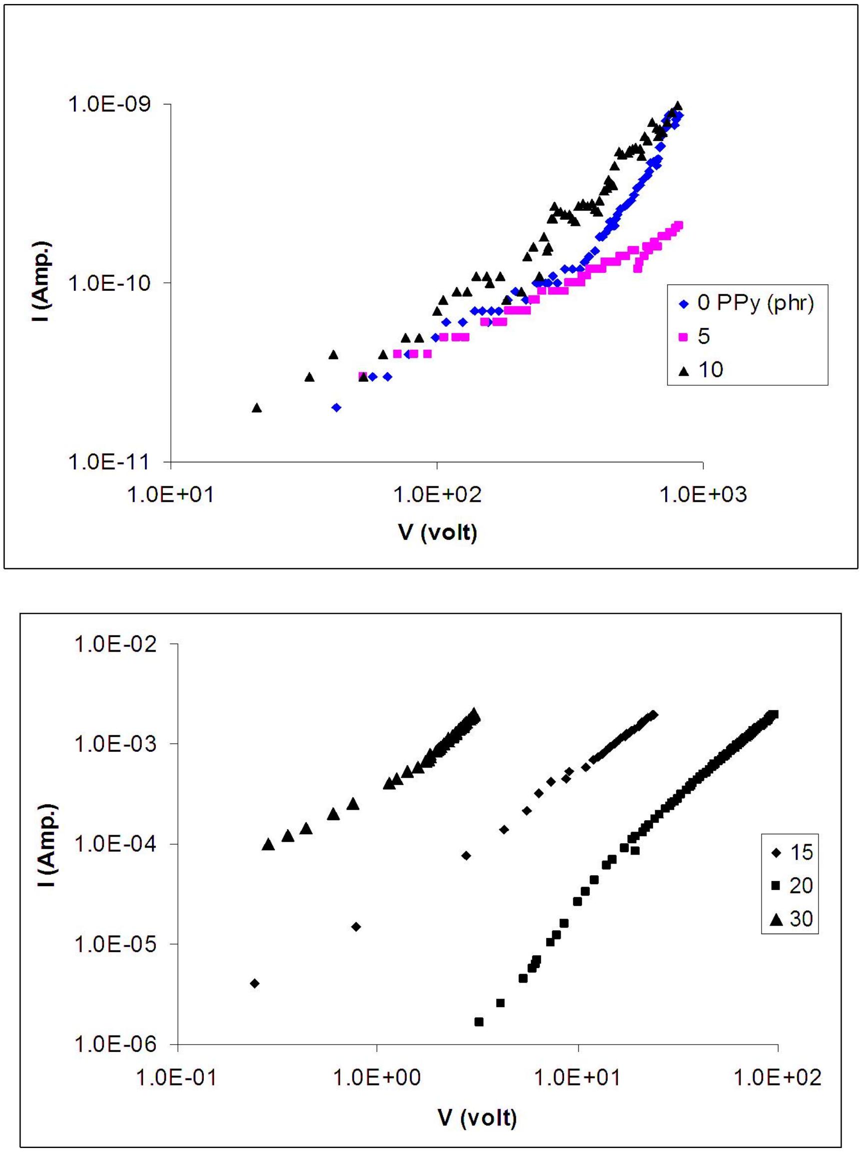

Figure (3): The ln (I) versus ln (V) characteristic curves of EVA loaded with conductive PPy samples at room temperature (300K) for all samples.

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

i) Poole -Frenkel conduction

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

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

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

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

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

$$\text{Or} \ln\sigma=\ln\sigma_{o}+(\beta_{PF}E^{1/2}/2KT) \qquad (6)$$

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 (4) 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.

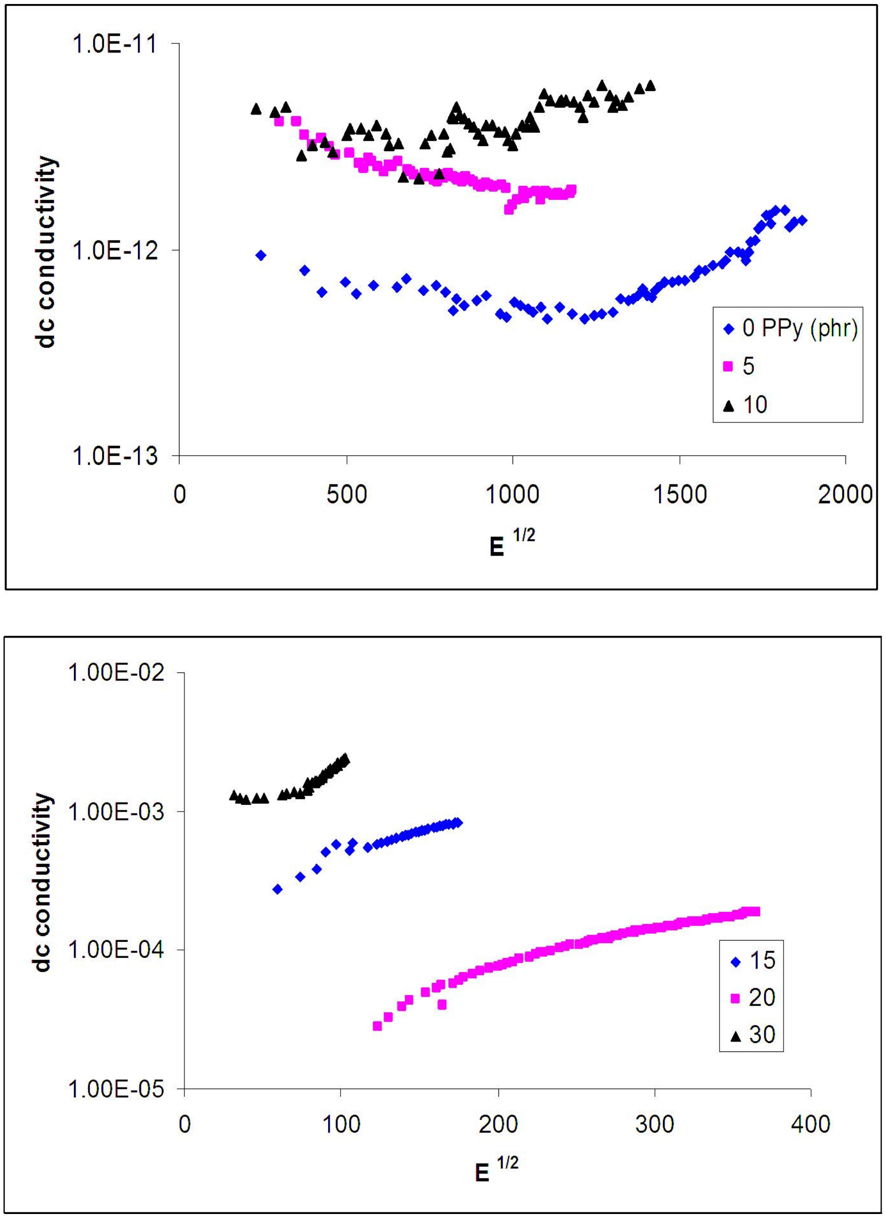

Figure (4): The Poole-Frenkel plots at room temperature (300K) for all samples.

ii) Fowler - Nordheim mechanism.

The Fowler- Nordheim relation (14) for current density is

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

so that $\ln(J/V^2) = \ln A - (\Phi/V)$ (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 (5) 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.

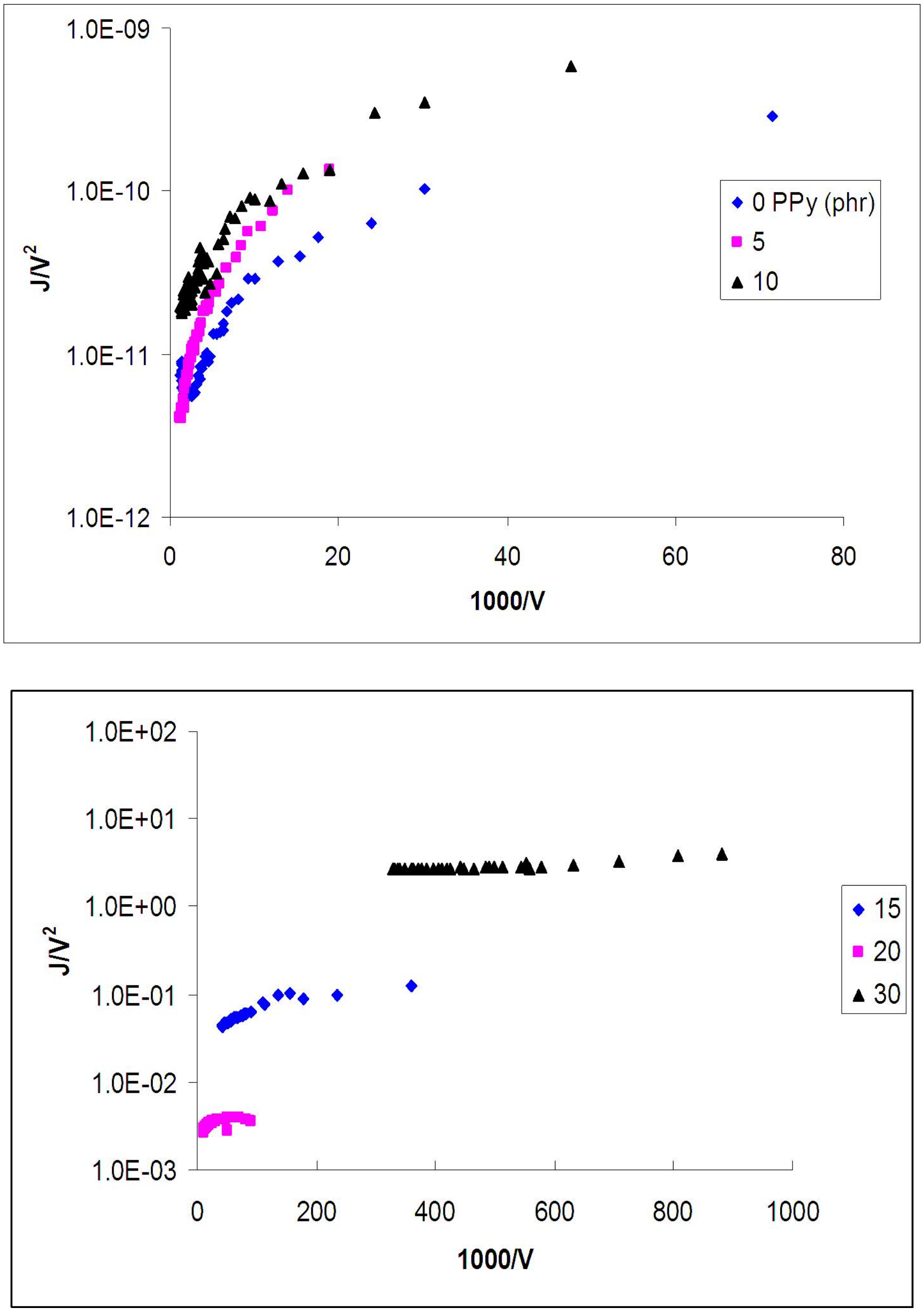

Figure (5): The Folwer-Nordheim plots at room temperature (300K) for all samples.

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

and that ln 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 Schottky plots and linear positive slope on Schottky plots generally characterize Schottky- Richardson mechanism. Schottky plots for the case (Figure 6) 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.

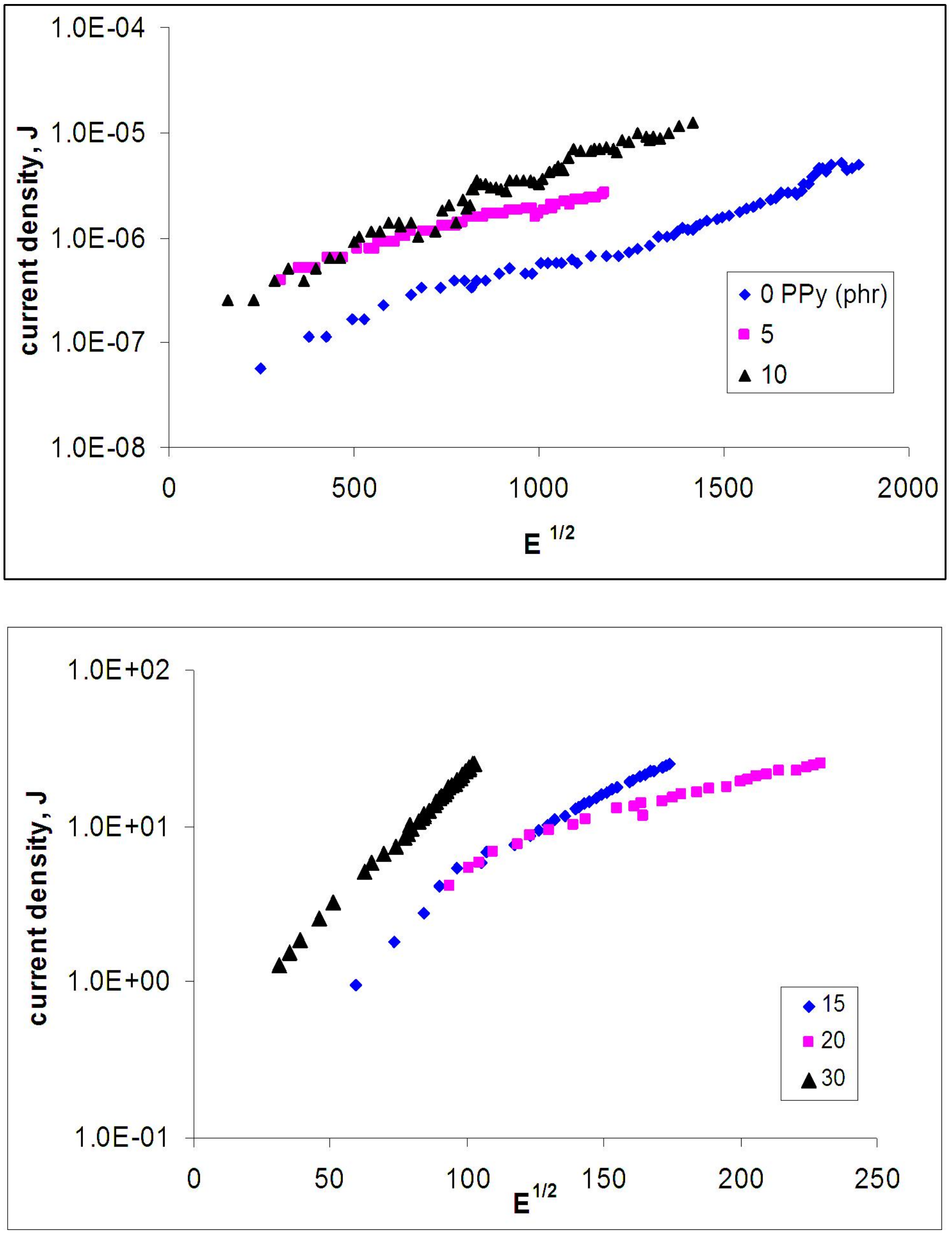

Figure (6): The Schottky plots at room temperature (300K) for all samples.

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. 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 $\Phi c \leq \Phi \leq 0.23$.

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