

# Electrical Properties and Transport Conduction Mechanism of Nitrile Rubber/Poly(vinyl chloride) Blend

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**ABSTRACT:** The current–voltage characteristics of acrylonitrile butadiene rubber (NBR)/poly(vinyl chloride) (PVC) blends are studied as a function of sample temperature and PVC content. These samples showed ohmic behavior up to (225 V), after this value the behavior become SCLC (space charge limited conduction). The results obtained show that the charge carriers are generated by Richardson–Schottky

emission from the electrode as well as from trapped ionic impurities at high fields. The activation energy of the prepared samples was calculated by using Arrhenius equation. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 3134–3139, 2010

**Key words:** activation energy; blends; charge transport; molding; poly(vinyl chloride)

## INTRODUCTION

In recent years, the investigations on the electronic transport properties of organic polymers have been much intensified. Electrical conduction in polymers studies are aimed at understanding the origin of the charge carrying species, their numbers, and the way in which they move through the bulk of the material. Various mechanisms, such as Schottky emission,<sup>1–4</sup> Poole–Frenkel emission,<sup>5,6</sup> space charge limited conduction,<sup>7</sup> and hopping conduction,<sup>8,9</sup> have been suggested for the charge transport. More recently, considerable interest has been shown on the effect of doping on the transport properties of polymers.<sup>10,11</sup> Depending on their chemical nature and the way in which they react with the host matrix, the doping substances alter the transport properties to different degrees. The physical mixing or blending of two polymers produces an alloy with quite different properties, which can be potentially useful. A good amount of work has been reported on the conduction mechanism in polymeric materials. Less has been reported on charge carrier injection and its transport in the blends.<sup>12–14</sup> In this article, results of electrical conduction in blends of acrylonitrile butadiene rubber (NBR) and poly(vinyl chloride) (PVC) have been reported to give an understanding of charge carrier generation and transport through the bulk of these materials.

## MATERIALS AND METHODS

### Preparation

NBR [density 0.98 g/cm<sup>3</sup> and acrylonitrile content 34%, Mooney viscosity ML (1 + 4) at 100°C of NBR is 45 + 5 (ASTM D 1646), average molecular weight 163,376, glass temperature is –36°C] and suspension polymerized PVC in powder form [density = 1.38 g/cm<sup>3</sup>, K-value (molecular mass) is 66–69, melting point is 80°C, and the glass temperature is 87°C], was supplied by the Transport and Engineering Company (TRENCO, Alexandria, Egypt). The blends of NBR/PVC were prepared on a home made two-roll mixing mill (length 0.3 m, radius 0.15 m, speed of slow roll 18 rpm). The compound formulations are presented in Table I. The mixing occurred for 40 min at a temperature of 298 K and left 24 h before being vulcanized in a heated press (Karl Kolb, Germany) at 425 K, and pressure about 0.4 MPa was fixed for an optimum time of 30 min.

### Measurements

#### DC measurements

The current (*I*)–voltage (*V*) measurements were done at various temperatures from 303 to 423 K using simple power supply Pasco scientific model 1030 A as voltage source (USA), Keithley digital electrometer model 616 (Keithley Inst) for current measurements and Digi-sense temperature controller (R/S) Model 89,000-15 (Eutech Instruments) with On/Off or PID Control, and several modes in between and temperature range from –99.9° to 999.9° (Resolution

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**TABLE I**  
**The Formulations of PVC/NBR Blend**

Materials	Blends (phr)					
	Pure PVC	N30	N40	N50	N60	Pure NBR
NBR	–	30	40	50	60	100
PVC	100	70	60	50	40	–
Stearic acid <sup>a</sup>	–	0.6	0.8	1	1.2	2
Zinc oxide <sup>a</sup>	–	1.5	2	2.5	3	5
(DOP) <sup>b</sup>	–	X	X	X	X	15
MBTS <sup>a</sup>	–	0.45	0.6	0.75	0.9	1.5
TMTD <sup>a</sup>	–	0.15	0.2	0.25	0.3	0.5
PBN <sup>a</sup>	–	0.3	0.4	0.5	0.6	1.0
Sulfur <sup>a</sup>	–	0.6	0.8	1	1.2	2

<sup>a</sup> Means all ingredients in (phr) relative to NBR.

<sup>b</sup> X means the weight of DOP equals 50% of the weight of PVC.

0.1°). Before taking measurements, each sample was heated at 343 K for about 1 h to remove absorbed moisture. The Specimens (diameter, 1 cm and thickness, 40 μm) with silver electrodes was sandwiched between two brass electrodes of a special home made “sample holder” (multipurpose cell) for electrical measurements. The cell was calibrated in National Institute of Standards NIS-Egypt. This formed the metal–insulator (polymer)–metal (M–P–M) system, which was placed in the furnace.

AC measurements

The permittivity (ε') and dielectric loss (ε'') of the investigated samples were measured using LCR Hioki 3531z Hitester, Japan, which is fully computerized with guard electrodes. The samples were in the form of disks of about 15-mm diameter and 3-mm thickness.

**RESULTS AND DISCUSSION**

**I–V characteristics**

Figure 1 shows ln(I) versus ln(V) plots of PVC–NBR blend (N30) at various temperatures 303, 323, 343, 363, 383, 403, and 423 K. The current increases 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. This is also evident from the fact that Ohm’s law follows from the free electron model of a metal.<sup>15</sup> 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 (defects such as impurity atoms and also atoms temporarily out of place as they vibrate) in the crystal structure. In the present case, the constituents of blends are themselves insulators and blends almost

amorphous, giving wide scope for irregularities in the structure and so ruling out Ohmic conduction.

Activation energy measurements

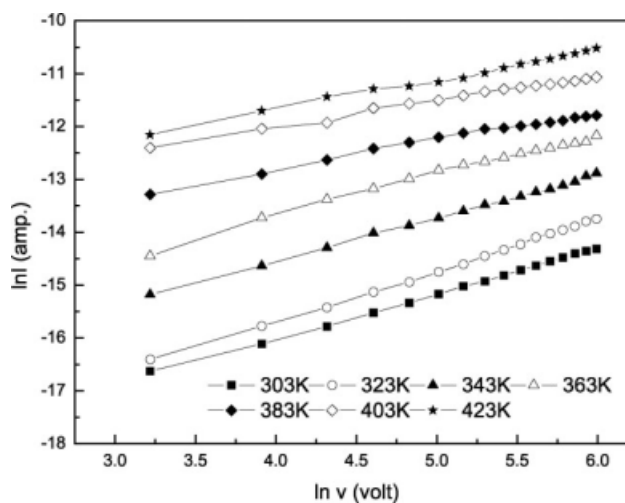
The dependence of the DC conductivity σ on temperature is given by arrhenius equation<sup>16</sup>:

$$\sigma = \sigma_0 e^{\frac{-E_a}{kT}}$$

where σ<sub>0</sub> is the maximum conductivity and E<sub>a</sub> is the activation energy. The activation energy values for the blends were calculated from the slope ln(σ) versus 1000/T plot (Fig. 2) and are given in Table II. These activation energy values are typical of electronic conduction.<sup>17,18</sup>

Electrical conductivity-concentration dependence

The dependence of the DC electrical conductivity on the PVC content is illustrated in Figure 3, it is clear



**Figure 1** Current–voltage characteristics.

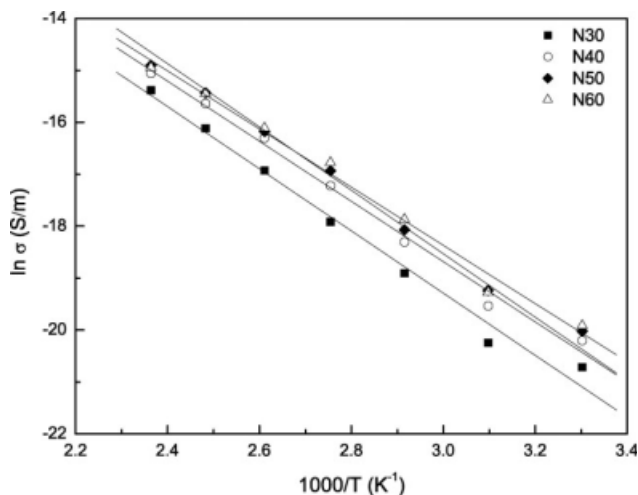


Figure 2 Arrhenius plots for PVC/NBR blends.

from this figure that,  $\sigma$  decrease with an increasing PVC content. The decrease in  $\sigma$  with increasing PVC content may be due to partial blockage of conductive path by the PVC molecules embedded in the NBR matrix.<sup>19</sup>

**Model fitting of the experimental I–V data**

Regarding space charge limited conduction; it follows that electrical conduction may occur through the movement of either electrons or ions.<sup>20</sup> 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. Several conduction mechanisms such as the Schottky effect, the Pool-Frenkel effect, thermally assisted tunneling (Fowler–Nordheim effect), ionic current, and space charge limited current are examined to explain the non-linear dependence of the current on voltage at high electric fields. Among those conduction mechanisms, the Fowler–Nordheim tunneling conduction mechanism will not be considered because the sample thickness is much thicker (~40  $\mu\text{m}$ ) for applying the Fowler–Nordheim tunneling conduction mechanism (~10 nm).<sup>21</sup> In this study, the overall features of the graphs for all blends have quite similar nature; therefore, only representative graphs for sample PVC/NBR (N30) have been included in the script.

TABLE II  
Activation Energy of the Blends

Sample name	Activation energy (eV)
N30	0.52
N40	0.50
N50	0.49
N60	0.48

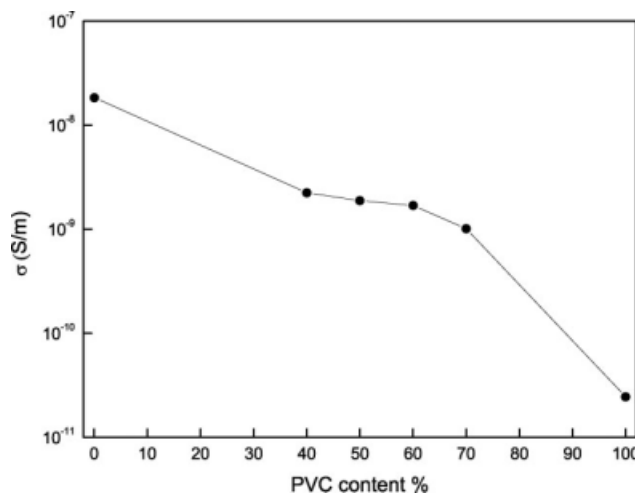


Figure 3 PVC content dependence of the DC conductivity.

Poole–Frenkel mechanism

The Poole–Frenkel relation for current density is<sup>5,6</sup>:

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

where  $\beta_{PF} = \frac{e}{kT} \left(\frac{e}{\pi\epsilon\epsilon_0 d}\right)^{1/2}$  = constant,  $\beta$  is a constant and all other symbols have their usual meanings. The Poole–Frenkel mechanism predicts a field dependent conductivity as:

$$\log \sigma = \log \sigma_0 + \frac{\beta_{PF} E^{1/2}}{2kT}$$

so that the Poole–Frenkel mechanism is characterized by the linearity of  $\log \sigma$  versus  $E^{1/2}$  plots with a positive slope. In this case of PVC/NBR blend,  $\log \sigma$  versus  $E^{1/2}$  plots are linear but with a negative slope (Fig. 4) indicating the absence of PF mechanism.

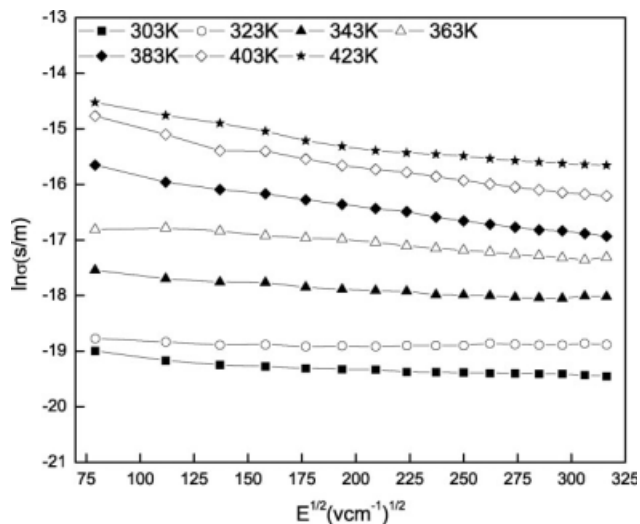


Figure 4 Poole–Frenkel plots.

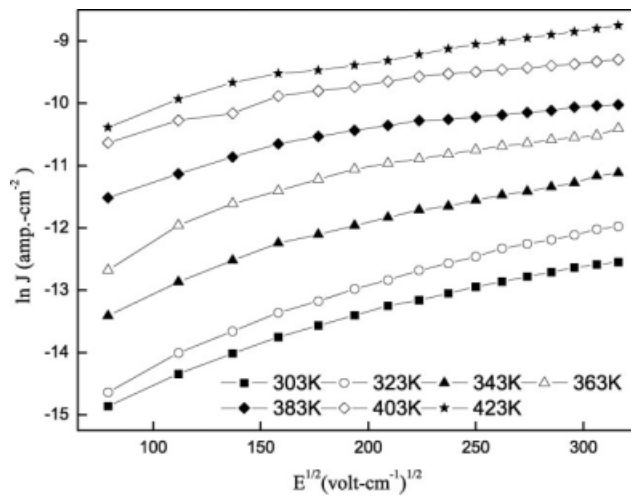


Figure 5 Schottky plots.

Schottky–Richardson mechanism

Schottky–Richardson current–voltage relationship is expressed as<sup>1–4</sup>:

$$J = AT^2 \exp\left(\frac{-\Phi_s}{kT} + \beta_{SR}E^{1/2}\right)$$

$\beta_{SR}$  being the field lowering constant given by,

$$\beta_{SR} = \frac{e}{kT} \left( \frac{e}{4\pi \epsilon \epsilon_0 d} \right)$$

and hence

$$\ln J = \left( \ln AT^2 + \frac{-\Phi_s}{kT} \right) + \beta_{SR}E^{1/2}$$

and that  $\ln J$  versus  $E^{1/2}$  plots (Schottky plots) should be a straight line with a positive slope. Schottky plots for the sample N30 (Fig. 5) are straight lines with positive slopes, indicating the applicability of the Schottky–Richardson mechanism. The value of  $\beta$ ; here  $\beta_{exp}$ ; calculated from the slope of  $\log I$  versus  $E^{1/2}$  plot, along with the theoretically calculated values of  $\beta_{SR}$  and  $\beta_{PF}$  are given in Table III for PVC/NBR blends. The values of the dielectric constant at different temperatures, if used in the calculation of  $\beta$ , are the experimentally measured high-frequency (1 MHz) dielectric constants of the blends. The  $\beta_{exp}$  value lies intermediate to that of  $\beta_{SR}$  and  $\beta_{PF}$  and is more close to  $\beta_{PF}$ . Moreover from Figure 6, it is clear that the current is temperature

TABLE III  
Theoretical and Experimental Values of  $\beta$  and Slopes of Lines for (PVC–NBR) at Different Temperature

Sample	Temperature (K)	Slope ( $\times 10^{-4}$ )	$\beta$ Experimental [eV (Vm <sup>-1</sup> ) <sup>1/2</sup> $\times 10^{-5}$ ]	$\beta_{PF}$ Theoretical [eV (Vm <sup>-1</sup> ) <sup>1/2</sup> $\times 10^{-5}$ ]	$\beta_{sc}$ Theoretical [eV (Vm <sup>-1</sup> ) <sup>1/2</sup> $\times 10^{-6}$ ]
N30	308	6.8	1.8	7.4	1.5
	323	8.0	2.2	7.3	1.5
	343	6.6	1.9	7.0	1.4
	363	4.9	1.5	6.9	1.4
	383	3.1	1.0	6.8	1.4
	403	3.0	1.1	6.7	1.3
	423	5.1	1.9	6.5	1.3
N40	308	8.1	2.1	6.8	1.4
	323	9.3	2.6	6.7	1.3
	343	7.1	2.1	6.6	1.3
	363	4.8	1.5	6.5	1.3
	383	4.2	1.4	6.4	1.3
	403	4.5	1.6	6.3	1.3
	423	4.5	1.6	6.2	1.2
N50	308	6.8	1.8	6.2	1.2
	323	6.8	1.9	6.1	1.2
	343	5.1	1.5	6.0	1.2
	363	4.2	1.3	5.9	1.2
	383	4.9	1.6	5.9	1.2
	403	5.1	1.8	5.8	1.2
	423	3.8	1.4	5.7	1.1
N60	308	6.4	1.7	6.5	1.3
	323	6.7	1.9	6.4	1.3
	343	6.6	1.9	6.3	1.3
	363	5.8	1.8	6.2	1.2
	383	4.5	1.5	6.2	1.2
	403	3.2	1.1	6.1	1.2
	423	3.3	1.2	6.0	1.2

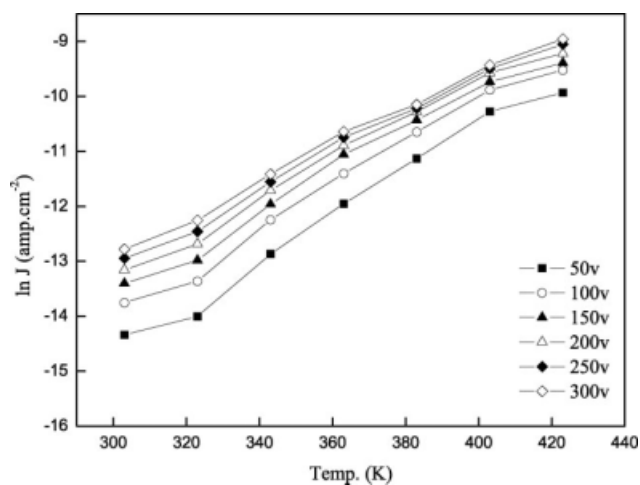


Figure 6 Current density versus temperature plots.

dependent. This suggests that the dominant charge carrier mechanism in the blends is the Schottky–Richardson type along with trapping of injected charge carriers and their subsequent release following the Poole–Frenkel mechanism. In fact this type of mechanism has also been observed in other types of polymers.<sup>22,23</sup> The  $\beta_{\text{exp}}$  for these blends were, however, found to be much higher than that for  $\beta_{\text{SR}}$  and  $\beta_{\text{PF}}$ . This suggests that the conduction process is governed not only by SR or PF mechanisms but there is a possibility of ionic conduction by hopping mechanism.<sup>8,9</sup> AC conductivity ( $\sigma_{\text{ac}} = \omega \epsilon_0 \epsilon''$ ) was calculated from the ac dielectric measurements for blend samples and the results were plotted versus frequency ( $f$ ) at 303 K (Fig. 7). The ac conductivity was higher than the dc conductivity and increased with an increase in the frequency. The noted weak temperature dependence in all samples (Fig. 8) indicates that charge carriers are transported through

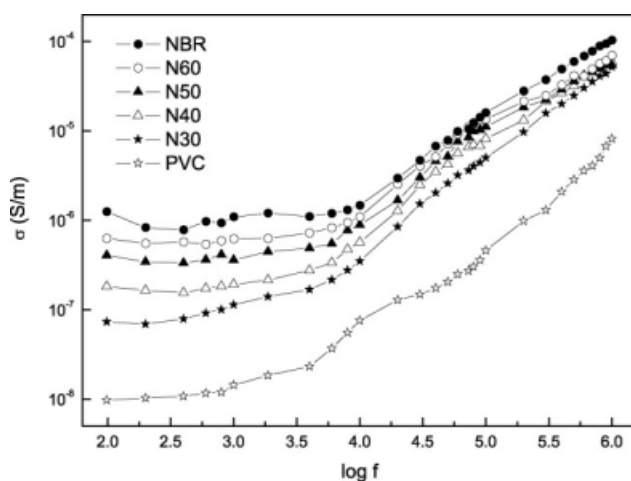


Figure 7  $\sigma_{\text{ac}}$  versus  $\log f$  plots for different blends at 303 K.

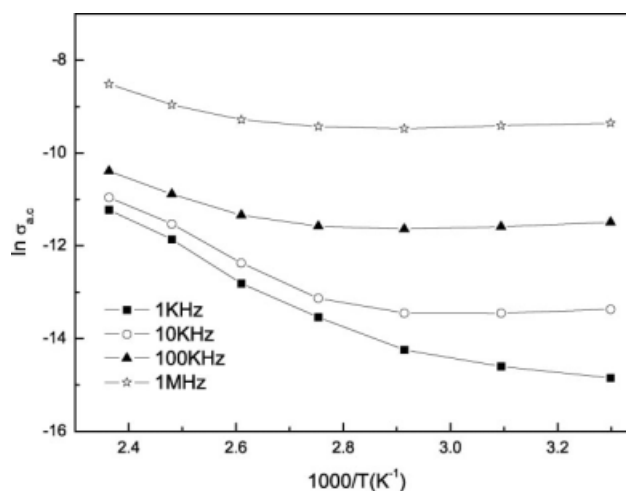


Figure 8  $\ln \sigma_{\text{ac}}$  versus  $1000/T$  plots for different frequencies.

the bulk by hopping conduction, through the defect sites along the chains.<sup>24</sup>

The theoretical values of  $\beta$  were calculated for the Poole–Frenkel and Schottky mechanisms<sup>14</sup>:

$$\beta_{\text{PF}} = (e/\pi\epsilon'\epsilon_0)^{1/2} \quad \text{and} \quad \beta_{\text{RS}} = (\beta_{\text{PF}}/2)$$

## CONCLUSIONS

The increase in PVC content decreases the conductivity of the blend. The prepared samples show Ohmic behavior up to 225 V, after which the  $I$ – $V$  curves, deviated from linearity which indicated SCLC mechanism. It was found that these samples obey both Poole–Frenkel and Schottky–Richardson conduction mechanism; charge carriers are generated by thermionic emission from the electrode by the lowering of the interface barrier by high fields as well as from trapped ionic impurities at such field values and are then conducted by a hopping process through the defect sites along the chains in the bulk of the material. The activation energy of the prepared samples were calculated by using Arrhenius equation, which give activation energy about  $0.50 \pm 0.02$  eV, which lies in the semi conducting range.

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