# Electro- and Photoconductive Properties of the PVA/PAN-$I_2$ Blends

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**Summary:** The electrical conductivity of poly(vinylalcohol)/polyaniline-iodine blend (PVA/PAN-$I_2$) prepared by solution process was investigated. The FTIR spectroscopy revealed a structural change of both shape and intensity of the polyaniline (PAN) bands after doping with iodine, indicating the formation of a charge transfer complex. The *J-V* curves for pure PAN; PAN-$I_2$ and PVA/PAN-$I_2$ film obey the ohm law at lower voltages, deviate from the linear response at higher voltages and finally display the breakdown behavior. The PVA/PAN-$I_2$ exhibit photoconductivity by UV/visible irradiation as well as oscillations that may be attributed to a nonlinear behavior of the blend.

## Introduction

Polyaniline (PAN) in the form of emeraldine salt should be considered as one of the most interesting and attractive conductive polymer for industrial applications owing to its high electrical conductivity and unique electrochemical properties. Generally, the specific electrical and optical properties of the polyaniline, an organic conductor after doping, are of special interest in the absorption of light energy by the thin layers that can be converted into optical, chemical, electrical and thermal energy, leading to some interesting technological applications[1].

A major problem with intrinsically conductive polyaniline is the inability to process it by conventional methods as well as its inherently poor processability and mechanical properties[2].

Extensive works on the preparation of electrically conductive PAN blends containing a thermoplastic or elastomeric polymer having desirable physical and good mechanical characteristics have pointed as a promising route to overcome the PAN intractability and poor mechanical properties.[3].

This paper reports on the electrical and photoelectrical properties of the poly(vinyl

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alcohol)/polyaniline-iodine (PVA/PAN-$I_2$) blends. The biocompatibility properties of the PVA matrix such as the conductivity properties of polyaniline made the PVA/PAN-$I_2$ blend a promising material to use as conductive bioadhesive for bioelectrode applications in medicine.

## Experimental

Polyaniline (PAN) was chemically synthesized in the emeraldine salt form by the usual multi-step addition of the oxidant ammonium persulphate to an aqueous solution of aniline hydrochloride as reported in the literature[4]. PAN-$I_2$ charge transfer complexes were prepared by thermic reaction between PAN and $I_2$[5]. Thus, PAN (1 mole based on monomer) was mixed with 0.0772 mole of iodine and the mixture was heated at 90 °C until no further decrease in thiosulfate-titrable iodine occurred. The obtained doped iodine polyaniline (PAN-$I_2$) was then washed with a sufficient amount of propanol to remove all low molecular weight species. The product was then dried under vacuum at 70 °C for 24 h with a typical yield of 80-90 %. Poly(vinyl alcohol) (PVA) was used as received. The poly(vinyl alcohol)/polyaniline (PVA/PAN-$I_2$) films was obtained by casting technique with PAN-$I_2$ concentration of 30 % (wt). The current-voltage (J-V) characteristics in dark and illuminated conditions by the irradiation cavity either by polychromatic light (visible) or UV light (290 nm) were measured using High Voltage Source Measurement Unit Keithley 237 model.

The J-V characteristics were recorded in the temperature range of 295-380 K. Silver leaves were placed between the electrodes and the samples, ensuring good electrical contact. A voltage of 0-600 V was supplied to the samples and its bulk conductivity was measured. The microstructure of the blends was characterized by SEM (Phillips XL30). FTIR spectra of doped and undoped PAN were recorded using a Perkin Elmer 1750 spectrophotometer.

## Results and discussion

### Infrared Spectroscopy

Figure 1 shows the Fourier transform infrared (FTIR) spectra of polyaniline (PAN) and iodine doped polyaniline (PAN-$I_2$) samples in the range of 4000-400 $cm^{-1}$.

The 1579 and 1485 cm$^{-1}$ bands are assigned to non-symmetric aromatic ring stretching modes. The higher frequency vibration has a major contribution from the quinoid ring units, so that the relative intensity of these two bands gives an indication of the excitation state of the material[6]. The 1303 cm$^{-1}$ vibration is a C-N stretch, indicative of secondary aromatic amine groups. Besides the finger print region, bands are also seen in the N-H and C-H stretching regions, shown in Figure 1 between 3600-2800 cm$^{-1}$. This part of the spectrum has received less attention in the literature and has been investigated further.

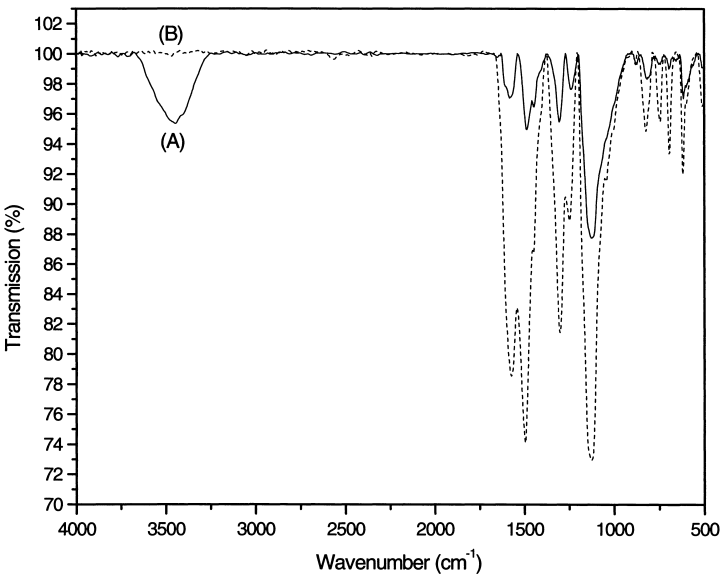

Figure 1. FTIR spectra of polyaniline (A) and polyaniline doped with iodine (B).

At higher wavenumbers an N-H vibration is observed at 3449 cm$^{-1}$ which is indicative of ν(NH) for the secondary amine[7]. This peak indicates hydrogen bonded amine groups. Comparing Figures 1 (A)-(B), the most striking difference is the loss of ν(NH) modes at 3449 cm$^{-1}$ after doping with iodine. The change in the intensity ratio of the N-H stretching modes is an evidence for the protonation process after doping with iodine and is indicative of the charge transfer complex formation. After PAN was doped with iodine the absorption peaks of the quinoid units shifted from 1126 $cm^{-1}$ and 1579 $cm^{-1}$ to 1119 and 1563 $cm^{-1}$, respectively. These shifts to lower frequencies may be due to the protonation of the benzoid units in the PAN-$I_2$[8].

## SEM Microscopy

To understand the changes occurring in the conductivity described below, it seemed to be of interest to investigate the morphological features, in particular, the distribution of polyaniline in PVA matrix.

Figures 2 and 3 show the micrographs of the polyaniline and PVA/PAN-$I_2$ blend. Polyaniline shows some tendency to form aggregates with particle sizes 3-50 μm (Fig.2). Thus, the distribution of PAN-$I_2$ (30% wt) in the host polymer (PVA) is not equal with distribution of visible spherical regions with size of 5-50 μm. These regions do not appear to be randomly distributed, but show some tendency to occur in "flocculated structures" in good accordance with SEM and TEM studies published earlier[9].

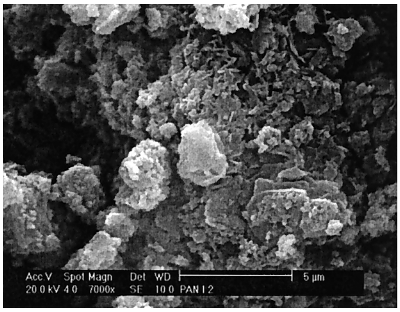

Figure 2. SEM micrographs of PAN-$I_2$ aggregates.

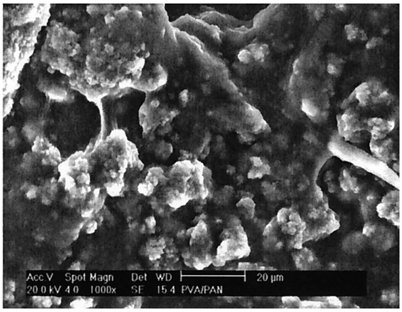

Figure 3. SEM micrographs of PVA/PAN-$I_2$ blend.

**Electrical Conductivity**

The *J-V* characteristics of PVA matrix, PAN-$I_2$ and PVA/PAN-$I_2$ blend at different temperatures are shown in Figures 4 - 6. It is evident from the Figures that the electric current in this material increases with the increase in temperature.

Assuming the trapping of the charge carrier between the chains can be expressed in the form of Arrhenius equation, the conductivity $\sigma$ may be expressed as a function of temperature T

$$\sigma = \sigma_o e^{-Ea/kT} \tag{1}$$

where $\sigma_o$ is a constant, $E_a$ is thermal activation energy, and k is the Boltzmann constant. The activation energies calculated from Figures 4 - 6 for PVA matrix, PAN-$I_2$ and PVA/PAN-$I_2$ blend are 1.14 eV, 0.01 eV and 0.46 eV, respectively.

A probable explanation for the difference in the $E_a$ for the conductivity process may be due to the process used for the blend preparation that does not destroy the PAN-$I_2$ aggregates, as shown in SEM micrographs (Figures 2 and 3). Therefore, the conducting particles are larger, favoring the touching of each other and consequently the conducting phenomenon is influenced.

As expected, the blending of the PAN-$I_2$ with nonconducting PVA results in a substantial decrease in the conductivity at room temperature. Surprisingly, the conductivity of the PVA/ PAN-$I_2$ blends at room temperature exhibit photoconductivity, an increase of conductivity caused by UV/visible radiation, as shown in Figure 7.

In spite of the large number of investigations about the photoconductivity of polymers with conjugated C=C, C=N and -N=N- double bonds in the main chain [10], as far as the authors are aware, photocurrent generation in PAN-$I_2$ or PVA/PAN-$I_2$ blends was not reported until now.

From the *J-V* measurements in the dark and UV/visible illuminated conditions of the PVA/PAN-$I_2$ striking pulse-like self-oscillations were observed (Fig. 8) that may be attributed to a nonlinear behavior of the blend.

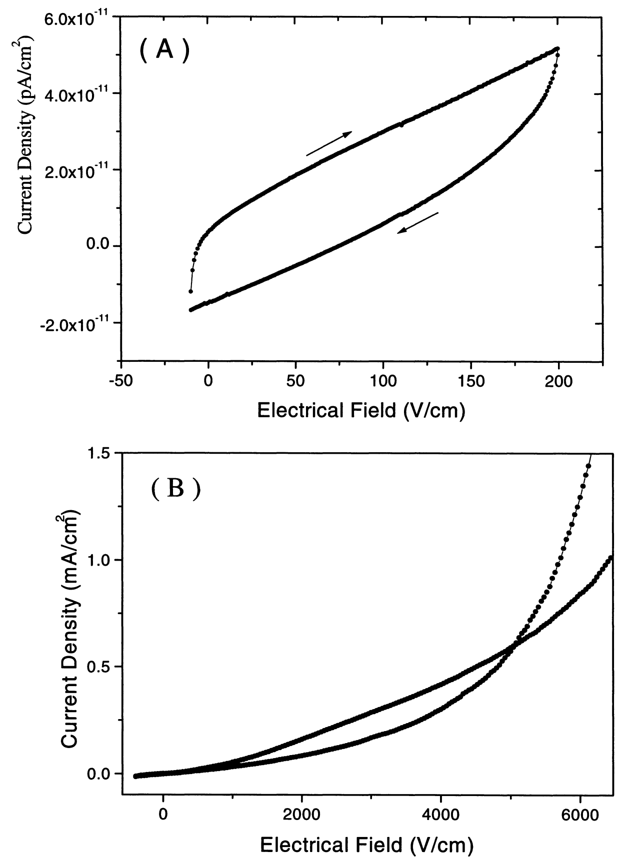

Figure 4. *J x V* characteristics for PVA matrix at room temperature, 20 °C (A), and at 70 °C (B).

Figure 9 shows a typical trace of a pulse train in the stable regime. Since the contact between polymer chains ranges from good to poor, it is natural to assume that some contacts will break down at different electric fields, which broadens the shoulder and the *J*-*V* curves may be reminiscent of the avalanche discharge or break down processes. However oscillations can be caused by external "accidental" positive feed back, with identical apparatus, no oscillations were observed when the sample was replaced with pure PAN-$I_2$ which had similar d.c. resistance.

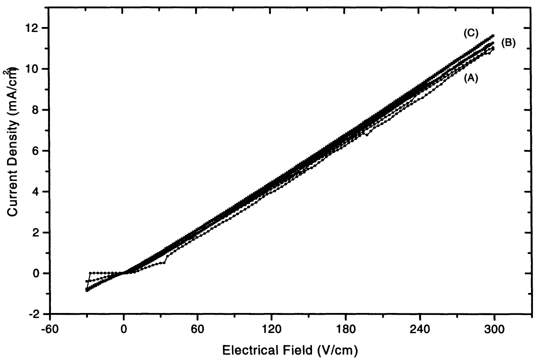

Figure 5. $J$ x $V$ characteristics for doped PAN-$I_2$ at: 293 K (A), 316 K (B) and 378 K (C).

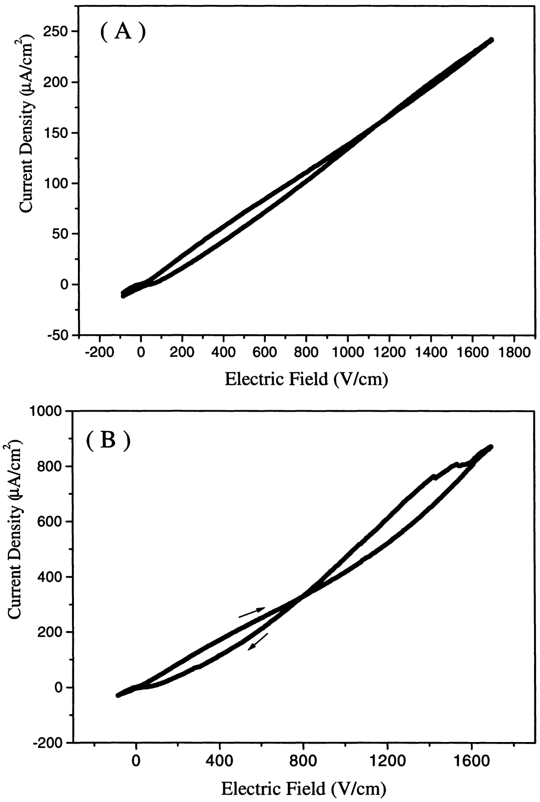

Figure 6. $J$ x $V$ characteristics for PVA/PAN-$I_2$ at room temperature (A), and at 42 °C (B).

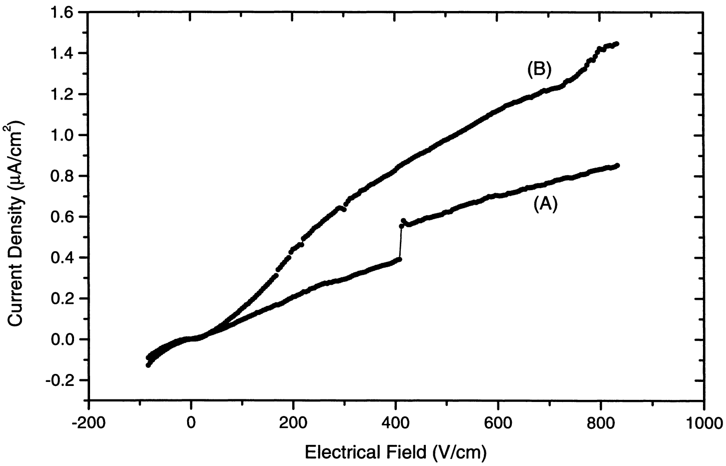

Figure 7. $J$ $x$ $V$ characteristics for PVA/PAN-$I_2$ blend: before (A) and after (B) UV irradiation at room temperature. $\lambda = 410$ μm.

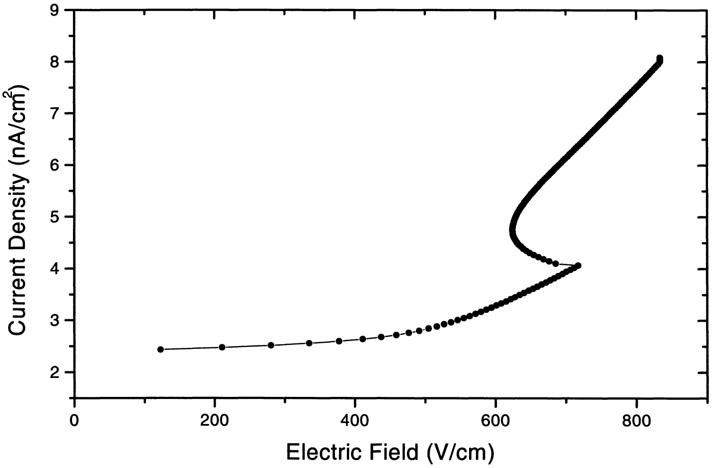

Figure 8. $J$ $x$ $V$ characteristics for PVA/PAN – $I_2$ blend at room temperature (295 K).

A strong evidence exists that the observed oscillations might be similar to the Gunn effect[11] observed for some semi-conductors because the samples not only have the characteristic oscillations but they also showed a negative resistance regime.

If the oscillations are due to the Gunn effect, it would be the lowest frequency ever measured for such a system. Thus, the period of the oscillation $\tau$ is proportional to the distance between the voltage leads $l$ divided by the drift velocity of the charge carriers $v$. From $v$ the mobility $\mu$ of the charge carriers is

$$\mu = \frac{v}{E} \tag{2}$$

where E is the electric field felt by the charge carriers.

The Hall constant $R_H$ may be deduced as

$$R_H = \frac{\mu}{\sigma} = \frac{1}{qn} \tag{3}$$

where $n$ is the carriers concentration and $q$ is the carrier charge. In this moment we are in the process of directly measuring the Hall resistance as an independent check of the Gunn theory or any other mechanism to explicate the observed oscillations in the PVA/PAN-$I_2$ blend.

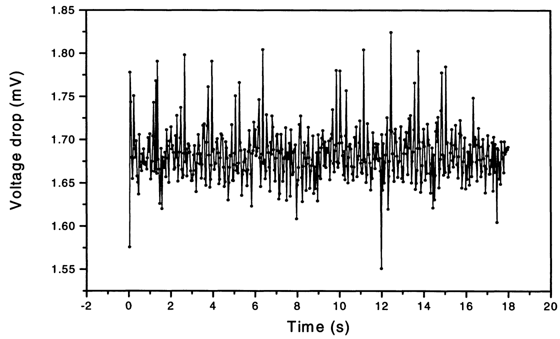

Figure 9. Typical pulse trains at room temperature for PVA/PAN-$I_2$ blend. The bias current is 0.166 nA.

## Conclusions

From the *J-V* measurements in the dark and UV/visible illuminated conditions of the PVA/PAN-$I_2$ it has been shown that PVA/PAN-$I_2$ blend exhibit oscillations that may be attributed to a nonlinear behaviour of the blend. The activation energies calculated from for PVA matrix, PAN-$I_2$ and PVA/PAN-$I_2$ blend are 1.14 eV, 0.010 eV and 0.46 eV, respectively.

The diminution on the activation energy with the incorporation of the PAN-$I_2$ to the PVA matrix may be attributed to the increase in the conducting particle size which may favour the contacts between the particles and consequently affect the conducting phenomenon.

## Acknowledgements

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