



# CONDUCTIVITY STUDIES OF POLY (P-PHENYLENEDIAZOMETHINE)/PVC COMPOSITES

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**Abstract:** In-situ polymerization of Poly(p-phenylenediazomethine) from glyoxal and p-phenylenediamine in different solvents containing different amounts of PVC was done. The d.c. conductivity and microwave conductivity of each sample was measured. The effect of dopants like HClO<sub>4</sub>, HCl and I<sub>2</sub> on conductivity was also studied.

**Index Terms:** Poly(p-phenylenediazomethine), PVC, doping, d.c. conductivity and microwave conductivity

## I INTRODUCTION

Conducting polymer composites have drawn considerable interest in recent years because of their numerous applications in a variety of areas of electrical and electronic industry (Skotheim, 1986; Wessling, 1991; Margolis, 1993). In most of these applications, the main concern is to obtain sufficient level of conductivity in the material. Preparation of blends, composites and interpenetrating network has been widely used as an approach to combine electrical conductivity with desirable mechanical strength of polymers<sup>4</sup>. Several attempts have been described to produce conducting polymer composites with better physical properties by either chemically or electrochemically (Niwa and Tamamura, 1984; De Paoli, Waltman, Diaz and Bargon, 1984 & 1985; Niwa, Tamamura and Kakuchi, 1987; Kalaycioglu, Toppare and Akbulut, 1996). Charge transport mechanism in conducting polymer composites was reported by Radhakrishnan and Hande, 1995.

The present study involves In-situ polymerization of glyoxal and p-phenylenediamine in different solvents containing different amounts of PVC. The d.c. conductivity and microwave conductivity of each sample was measured. The effect of dopants like HClO<sub>4</sub>, HCl and I<sub>2</sub> on conductivity was also studied.

## 2. EXPERIMENTAL

### 2.1 Materials used

Paraphenylene diamine, Glyoxal hydrate (trimer), Polyvinylchloride, N,N-Dimethyl formamide, Toluene, Tetrahydrofuran, Methanol, Acetone, Hydrochloric acid, Perchloric acid, Iodine, and Carbon tetra chloride.

### 2.2 Synthesis of poly(p-phenylenediazomethine)–Polyvinylchloride blends

PVC (5g) was dissolved in 50 ml of Tetrahydrofuran. 0.1 mole of p-phenylene diamine was added to 300 ml of N,N-dimethylformamide and was dissolved in it by stirring. Then 0.1 mole of glyoxal was added to it and stirred well. The solution of PVC in THF was added to the above reaction mixture and stirred well. Then the temperature of the reaction medium was increased slowly to boiling, with continuous stirring, and was refluxed at the boiling temperature for 4 hours. By that time, the precipitation of the product takes place. It was then allowed to cool to room temperature and then poured into excess of ice-cold water with stirring. It was allowed to settle, filtered, washed with plenty of water until the filtrate was colourless. Then it was washed with methanol, and allowed to dry at room temperature in air for one day. Then the final drying of the sample was done at 70°C in vacuum.

The same procedure was repeated by varying the amount of PVC. For this, 10 gm of PVC was dissolved in 100ml of THF, 15 gm of PVC was dissolved in 150ml of THF, and 20 gm of PVC was dissolved in 200ml of THF and was added to the reaction mixture containing glyoxal and p-phenylenediamine in DMF.

The dried sample was powdered well, and, pelletized for the density and d.c. conductivity measurements. For the spectral and thermal studies, the sample was extracted with acetone until the extract was colorless, and dried well.

### 2.3 Doping

1g each of the sample was added to 50ml each of 1M HCl solution, 1M HClO<sub>4</sub> solution and saturated solution of I<sub>2</sub> in CCl<sub>4</sub> and kept for 24 hours. Then it was filtered, washed with a little amount of acetone and dried at 70<sup>0</sup> C in dynamic vacuum for one hour.

### 2.4 Measurements

#### 2.4.1 IR spectra

Particles of the polymer samples were flattened by means of cold compression between two diamond windows. IR spectra of the samples were recorded with a Biorad UMA 500infrared microscope, which is coupled to a Biorad FTS 6000 spectrometer. Spectra were recorded with a resolution of 4 cm<sup>-1</sup> co-adding 100 scans.

#### 2.4.2 D.C. conductivity

D.C. conductivity of the pressed pellets was determined by the two-probe technique. The samples were sandwiched between two copper electrodes and a constant voltage (6V) was applied to the sample. The current flowing through the sample was measured using a digital multimeter (APLAB model 1087). The conductivity of the sample was calculated using the equation,  $\sigma = t / RA$ , where 't' is the thickness of the pellet, 'R' is the resistance of the sample ( $R = E / I$ , where 'E' is the applied voltage and 'I' is the resulting current through the sample), and 'A' is the area of cross section of the pellet ( $A = \pi r^2$ , where 'r' is the diameter of the pellet).

#### 2.4.3 Density

Density of the pressed pellets were determined using the equation,  $D = M/V$ , where 'M' is the mass of the pellet and 'V' is the volume of the pellet .

## 3. RESULTS AND DISCUSSION

Figure 1 gives the IR spectrum of the conducting polymer- polyp-phenylenediazomethine- blends with PVC. A broad band existed between 3200 and 2400 cm<sup>-1</sup>. These bands can be assigned to the -(N-H<sub>x</sub>)-Cl stretching vibration of amine salts. Other spectral bands were due to the conducting polymer. Some more absorption bands can be ascribed to the PVC spectrum. Figure 2 compares the IR spectrum of the conducting polymer with that of the blend. Some of the spectral bands were common in both of the spectra. From these, we can conclude that conducting polymer was incorporated into the PVC matrix.

As the amount of PVC was increased in the blends, the solubility of the polymer was increased. This may be due to the effect of two solvents, THF and DMF, in the reaction medium, or, it may be due to the removal of HCl from PVC by the action of heat during the course of the reaction. The presence of acid was found to increase the solubility of the conducting polymer. In concentrated acids, the polymer was soluble at high temperature. So the processability of the conducting polymer can be improved by making its blends with PVC without any chemical change in the polymer structure.

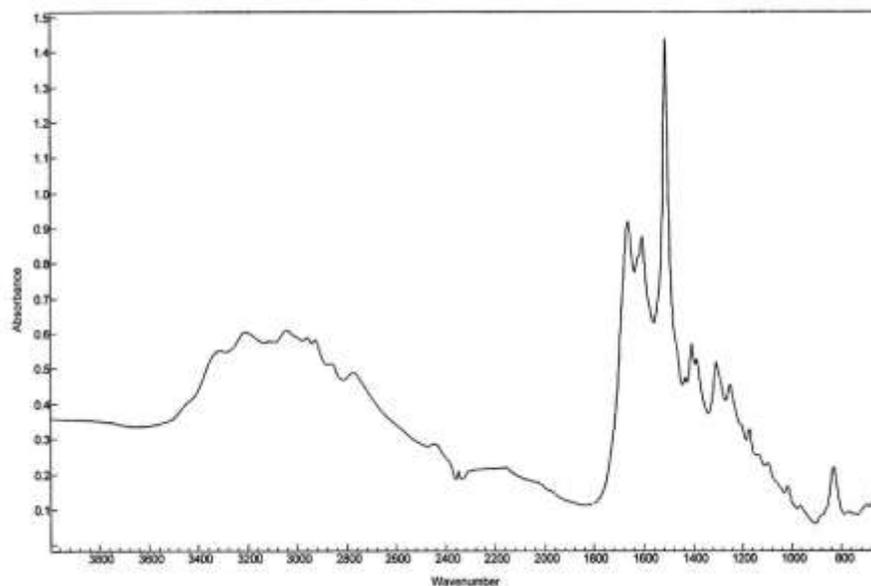
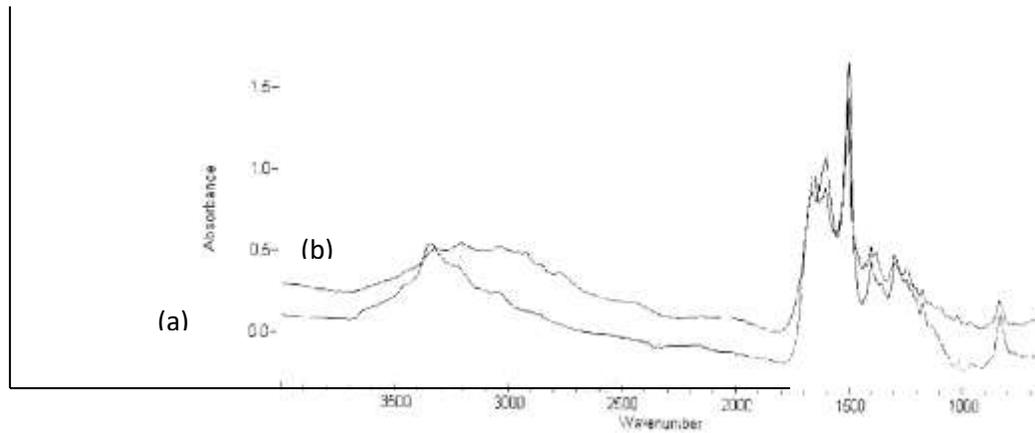
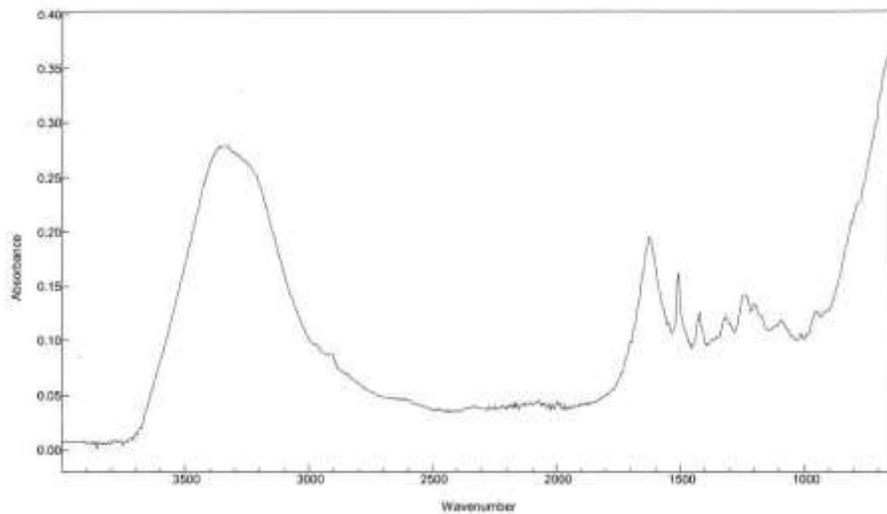


Fig. 1 IR spectrum of the conducting polymer- PVC blend

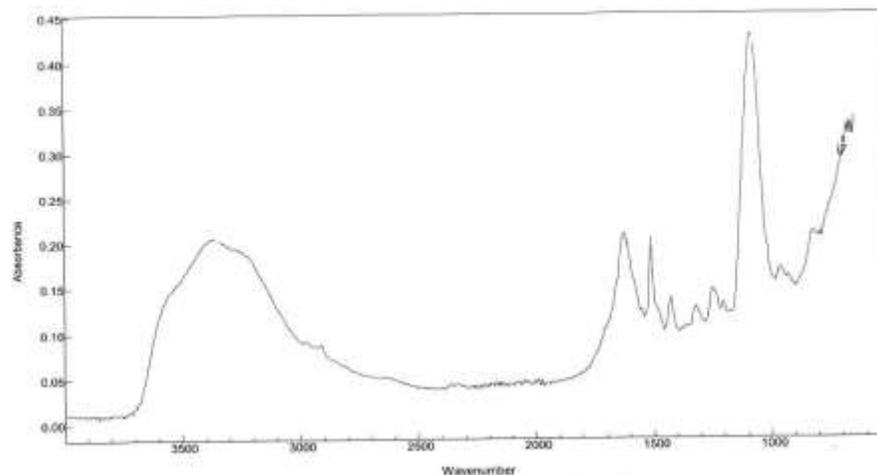


**Fig. 2 IR spectra of (a) conducting polymer prepared in DMF and (b) its blend with PVC**

Figures 3 and 4 show the IR spectra of the conducting polymer /PVC blends doped with HCl and HClO<sub>4</sub>. The absorption peak at 3345 cm<sup>-1</sup> in the undoped polymer was shifted to a broad band in the region of 3338 and 3360 cm<sup>-1</sup> in HCl and HClO<sub>4</sub> doped samples respectively. The strong peak at 1628 cm<sup>-1</sup> was characteristic of C=N bond in conjugated polymers. The bands at 1094 and 1084 cm<sup>-1</sup> were due to the dopant molecules HCl and HClO<sub>4</sub>. The bands at 1512 and 1425 cm<sup>-1</sup> showed the benzenoid and quinoid rings attached to N atom. Other bands were same in undoped and doped samples.



**Fig. 3 IR spectrum of the conducting polymer/PVC blends doped with HCl**



**Fig. 4 IR spectrum of the conducting polymer/PVC blend doped with HClO<sub>4</sub>**

D.C. conductivity of the blends of the conducting polymer based on glyoxal, p-phenylene diamine and varying amounts of polyvinyl chloride is shown in the figure5.

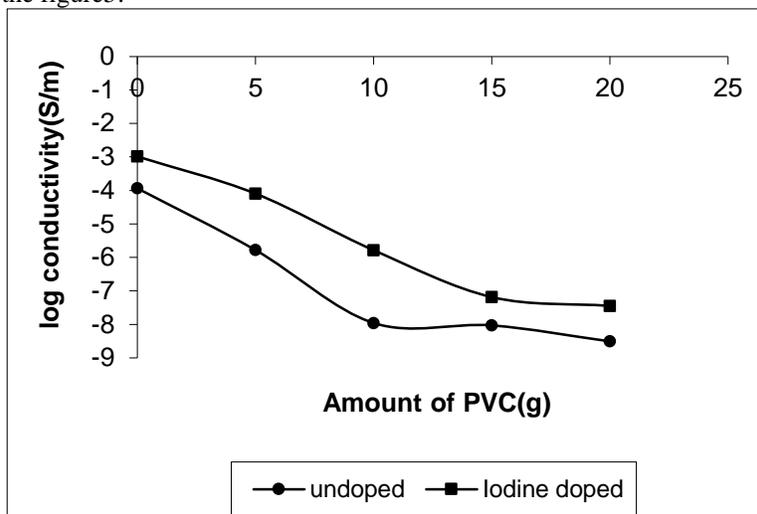


Fig. 5 D.C. Conductivity of the conducting polymer/PVC blends

The d.c. conductivity of the undoped blends decreased with increase in the amount of PVC. It was because, PVC is an insulator and the presence of nonconducting PVC in the composite prevented the free movement of electrons through the conducting polymer chain. Here, the conducting region was separated by a nonconducting region, so that the jumping of electrons from one conducting region to other became difficult. Hence the conductivity was decreased as in the case of polyethylene blends.

The variation in d.c. conductivity of the doped samples with the amount of PVC is given in figure6. The d.c. conductivity of the doped samples was more than that of the undoped samples. This was because, after doping, more charge carriers were introduced into the polymer chain, which helped to increase the conductivity. Conductivity of perchloric acid doped samples containing higher amount of PVC were more than that of other doped samples. HClO<sub>4</sub> was found to be the better doping agent because, of the large size of ClO<sub>4</sub><sup>-</sup> counter ion, which helped to tightly attach the dopant to the polymer chain. Hence the removal of the dopant was difficult. This may be due to the attachment of H<sup>+</sup> ions to the N atom of the polymer using the lone pair of electrons to increase the charge delocalization as it is clear from the IR spectra. Conductivity of the I<sub>2</sub> doped samples were lower than that of other samples doped with HCl and HClO<sub>4</sub>. It may be due to the fact that charge delocalization due to iodine on the polymer chain was very low. Also, on drying the samples, the action of heat and vacuum may be removing the iodine easily, compared to acid dopants.

The d.c. conductivity of perchloric acid doped blends were more than that of the pure conducting polymer doped with perchloric acid. As the amount of PVC was increased, d.c. conductivity was increased and remained almost constant at higher amount of PVC. This was because, PVC present in the blend is polar in nature, and the charge delocalization and oxidation takes place with the conducting polymer as well as with PVC molecules as shown in the IR spectra. So the removal of the dopant molecule may be difficult during the drying process and since the charge carriers were not lost, the conductivity was higher for the blends. After a saturation point was reached, the increase in conductivity was negligible because, the amount of insulating region of PVC was increased in the blend.

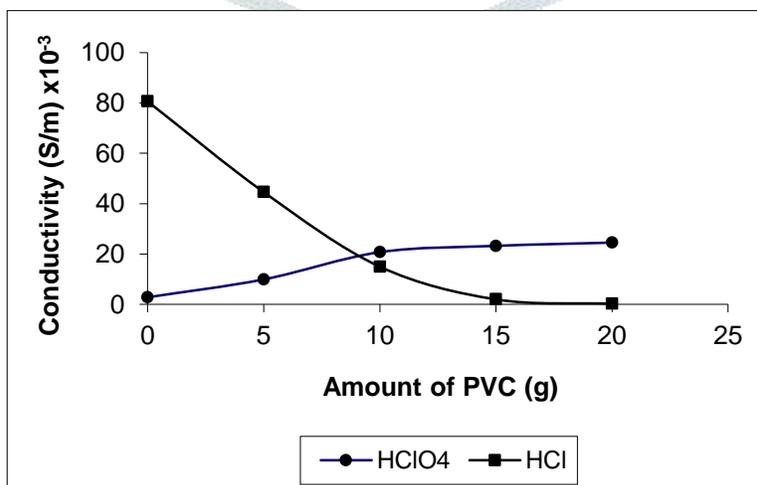


Fig.6 D.C. Conductivity of HCl and HClO<sub>4</sub> doped conducting polymer/ PVC blends

#### 4. CONCLUSIONS

1. The d.c. conductivity of the undoped conducting polymer blends was lower than the d.c. conductivity of the conducting polymer.
2. The d.c. conductivity of the undoped polymer blends was decreased with increase in the amount of PVC.
3. The d.c. conductivity of the conducting polymer blends was increased on doping with HCl, HClO<sub>4</sub> and iodine.
4. The d.c. conductivity of the blends of conducting polymer with PVC doped with HCl and iodine was decreased with increase in the amount of PVC, but it was increased on doping with HClO<sub>4</sub> and it remained constant at higher concentration of PVC.

#### 5. REFERENCES

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