Application of Cyclicvoltammetry Method in Determination of Extremely Lower Percolation Threshold Electroactivity of the Blend of PVC/Polyaniline Doped with Sulphosalicylic Acid

Hassan Namazi¹, Roya Kabiri² and Ali Akbar Entezami²(∗)
(1) Laboratory of Biopolymer and Carbohydrates, Faculty of Chemistry, Tabriz University 51664, Tabriz, I.R. Iran
(2) Laboratory of Polymer Chemistry, Faculty of Chemistry, Tabriz University 51664, Tabriz, I.R. Iran

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ABSTRACT

The cyclicvoltammetry method was utilized for the determination of percolation threshold of electroactivity of polyvinylchloride (PVC) and doped polyaniline through sulphosalicylic acid (SSA) blend. The blends were prepared from N-methylpyrrolidone (NMP) solutions and PVC/PANI-SSA blend with weight fractions from 0.1 to 0.006 of polyaniline. The films from the blends were provided by casting the above polymer solutions on a GC electrode. Voltammograms were recorded by using a one-compartment cell fitted with a GC as working electrode, Pt as auxiliary electrode and SCE as reference electrode, in 1M perchloric acid electrolyte solution. The obtained results from cyclicvoltammetry showed that PANI-SSA/PVC on and above 0.008 percent weight from polyaniline is electroactive.

Key Words: cyclicvoltammetry, percolation threshold, polyaniline, PVC, sulphosalicylic acid

INTRODUCTION

Among conducting polymers, polyaniline(PANI) is of particular interest due to its excellent air stability, low cost, ease of polymerization, making it a potential candidate for many advanced technological applications and its numerous applications [1-2]. One of the key problems related to the potential application of polyaniline is its difficult processability. With a rigid π-conjugated backbone molecular structure, polyaniline decomposes without melting when heated.

Therefore, it is impossible to process polyaniline by conventional methods such as extrusion or injection moulding. Due to the insolubility of conductive form of the polyaniline in common solvents its processability is difficult [3].

In recent years, many efforts have been made to improve the solubility and processability of polyaniline. These approaches include the polymerization of ring or N-substituted aniline derivatives [4-5], the use of functionalized protonic acids as the dopants [6-7], electrochemical polymerization of aniline in

(∗) To whom correspondence should be addressed. E-mail: a.entezami@proxi.ipi.ac.ir
polymer matrix [8] and blending of polyaniline with a host polymer in which it could produce desirable properties which are promoted by enhanced compatibility and homogeneity of the two components. The host polymers such as polymethyl methacrylate, nylon 6, polyvinyl alcohol and other thermoplastics have been used for this purpose [9-12].

The determination of percolation threshold electroactivity in four-probe method for a few polymeric blends has been reported. Yang and et al. have determined the percolation threshold of 0.48 percent weight of polyaniline in PANI-CSA/PMMA blend [9] and Zilberman et al. have determined the percolation threshold of 5 percent weight of polyaniline in PANI-DBSA/PS blend with four-probe method [13].

In this work the preparation of blends PVC/PANI-SSA, and for the first time the application of cyclic voltammetry method for the measurement of lower percolation threshold electroactivity of these polymers are reported. The structure and morphology of prepared blends were also investigated by FTIR spectra and optical microscope and the conductivity of blends were measured with two-point probe method.

EXPERIMENTAL

Materials
Aniline was purified by double distillation under vacuum before use. Ammonium persulphate was used without purification. N-Methylpyrrolidone (NMP) from Riedel-de Haën, PVC (36,000) from Fluka and sulphosalicylic acid (Fluka) were used as received.

Preparation of Polyaniline
Polyaniline was prepared by oxidative polymerization of aniline in 1.7 M aqueous HCl using ammonium persulphate as oxidant (1:1 mol ratio) at 5 °C for 2 h.

Polyaniline as a green powder was formed and it was filtered, washed several times with methanol and finally a colourless filtrate was obtained. The collected green polyaniline salts were added into ammonia solution (% 3) and stirred for 30 min. The undoped polyaniline was filtered and then it was washed several times with water and methanol. The resulted blue powder polyaniline was dried under vacuum at 40 °C for about 4 days. For doping the PANI-EB with sulphosalicylic acid, 32 mg SSA and 40 mg PANI-EB were dissolved in 15 mL NMP and stirred for 30 min under inert nitrogen and solution was filtered over 0.50 μm (Watman).

Preparation of Blends
For the preparation of blends, 0.5 g of emeraldine base was dissolved in 20 mL of N-methylpyrrolidone by vigorous shaking. The undissolved portion was removed by filtration, then this solution was doped with sulphosalicylic acid. A solution of 2.5 g PVC powder in 20 mL, NMP was prepared separately.

Polymer blends of PANI-SSA/PVC with: 0.8/99.2, 1/99, 4/96, 5/95, and 10/90 by weight ratios were prepared by mixing the above solutions. The resulted well-mixed solution was transferred to a glass dish and dried under vacuum at 40 °C for about 4 days. When the films were visually dried, they were peeled off from the glass substrate by wetting with cold deionized water. The film was washed carefully with cold water to remove traces of NMP and subsequently dried in vacuum at 50 °C for a week. FTIR spectroscopy, conductivity measurements and optical microscopy have been carried out on the prepared polymeric films.

For the recording of voltammograms the polymer films from the above solutions were cast on a glass, carbon (GC) electrode by removing the solvent and drying in vacuum for 24 h.

Characterization
Cyclic voltammograms were recorded with a digital potentiostat DP 8R (home-made). All electrical measurements were performed in a single-compartment three-electrode cell under an argon atmosphere. The working electrode was a glass carbon, which had been coated with blends, the auxiliary electrode was Pt and the reference electrode was a saturated calomel electrode. The infrared spectra of films were obtained using a Shimadzu DR-408 FTIR spectrophotometer. Photomicrographs of the films were obtained using an Olamposcope microscope BH2 UMA. Conductivity measurements of the films were carried out on a two
point probe. All measurements were carried out in air at room temperature and the conductivity was calculated by the following equation:

\[ \sigma = \frac{I \times d}{V \times A} \]

where, \( \sigma \) is conductivity (S/cm), \( V \) is potential difference (V), \( I \) is applied current (A) and \( d \) is thickness of the film (cm) and \( A \) is area (cm\(^2\)).

RESULTS AND DISCUSSION

Cyclic Voltammograms

Determination of electroactivity percolation threshold for polymeric blends was investigated for the first time by cyclicvoltammetry method. The blends were formed from \( N \)-methylpyrrolidone (NMP) solutions of PVC/PANI-SSA having weight fractions from 0.1% to 0.008%. Then the films were cast on a glass carbon (GC) electrode from prepared solutions.

Voltammograms were recorded by using a one-compartment cell fitted with a film which had been cast on a GC electrode, Pt electrode, and SCE as work, auxiliary and reference electrodes, respectively in perchloric acid as electrolytic solution by scanning the potential from -800 mV to 1000 mV. Cyclic voltammograms of the polymer blend for PVC/ PANI-

\[ E \quad \text{(mV)} \]

Figure 1. Cyclic voltammograms of PVC/PANI-SSA (90/10) film on the GC electrode in 1 M perchloric acid electrolyte solution in different scan rates.

SSA (90/10) were obtained at various scan rates (50, 70, 90 and 110 mV/s) and they are shown in Figure 1. The current is increased by gradual increases of the scan rate. Two anodic peaks at 141 and 597 V, and two cathodic peaks at -131 and 355 V are clearly appeared on the voltammograms. The secondary anodic peaks (i\(_{pa}\)) and the secondary cathodic peaks (i\(_{pc}\)) currents are directly proportional to the potential scan rate \( v \) in the range of 50 to 110 mV/s and the peaks formed are characteristic for an adsorption-limited process (Figure 2). The slopes value obtained from these curves are proportional to the electroactivity of polymer blend. The obtained polymers are significantly electroactive, because the polymer films deposited on the electrode surface can electropoly-

\[ \text{Peak current (arbitrary units)} \]

\[ \text{Scan rate (mV/s)} \]

Figure 2. The curve of secondary anodic and cathodic peaks current vs scan rate of PVC/PANI-SSA(90/10) film.

\[ V=110 \quad V=90 \quad V=70 \quad V=50 \]

\[ I (\mu A) \]

\[ E (mV) \]

Figure 3. Cyclic voltammograms of PVC/PANI-SSA (90/10) film on the GC electrode in 1 M perchloric acid electrolyte solution in different scan rates after growth of polyaniline on the polymeric film.
merize the aniline in a solution containing 1 M perchloric acid and 0.1 M aniline with applied potential range from -800 to 1000 mV with scan rate of 50 mV/s for 10 cycles. The electroactive sites of polyaniline, dispersed in blend matrix, are responsible for the growth of polyaniline (see micrographs). The cyclic voltammograms of the polymer blend after growth of polyaniline on the polymeric film at the various scan rates (50, 70, 90 and 110 mV/s) in the solution of perchloric acid free from aniline are shown in Figure 3.

Anodic ($i_{pa}$) and cathodic peaks ($i_{pc}$) currents are directly proportional to potential scan rate in the range between 50 to 110 mV/s (Figure 4). From comparison of the slopes in Figures 2 and 4, it can be concluded that after growth of polyaniline on the film, the electroactivity was increased. Electroactivity of the blends with less percentages of PANI in PVC/PANI-SSA blends were shown to be electroactive until 0.008 percent by weight of PANI-SSA (Figures 5 and 6), and lower than this weight percent of the cyclic voltammograms do not show any electroactivity. Therefore, we conclude that the extremely low percolation threshold of PVC/PANI-SSA blend with cyclic voltammetry is 0.008 percent by weight of PANI-SSA.

In morphology studies method of HCl-doped polyaniline-PVC blend, Banerjee et al. have reported that 0.035 and 0.045 weight percent of PANI-HCl is the extremely low percolation threshold with transmission of electron microscopy method [14]. The slope values obtained from the curves of the anodic and cathodic peaks currents versus various scan rates for the PVC/PANI-SSA blend with different weight percentages of PANI-SSA are shown in Figures 7 and 8. These slopes values can be attributed to the electroactivity of PVC/PANI-SSA.

**Conductivity Measurements**

The conductivity measurement with common instruments for very low electroactivity is not a suitable method. However, the cyclic voltammetric method is a suitable method for the determination of lower electroactivity of conducting polymers. The result of conductivity measurements on the PVC/PANI-SSA blends at room temperature with a two-point probe method is listed in Table 1.
Table 1. Conductivity of PVC/PANI-SSA blends at room temperature.

<table>
<thead>
<tr>
<th>Blend composition</th>
<th>90/10</th>
<th>93/7</th>
<th>95/5</th>
<th>96/4</th>
<th>97/3</th>
<th>99/1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity (Scm⁻¹)</td>
<td>5.6×10⁻⁴</td>
<td>1×10⁻⁴</td>
<td>6.3×10⁻⁵</td>
<td>3.1×10⁻⁵</td>
<td>1×10⁻⁵</td>
<td>1.5×10⁻⁶</td>
</tr>
</tbody>
</table>

FTIR Studies

Figure 9 shows the FTIR spectra of blends PVC/PANI-SSA weight ratios 90/10(a), 95/5(b) and 99/1(c). The absence of the absorption peak in region of the carbonyl group related to the NMP proves that there is not any trace of solvent in the films. There are characteristic peaks at 1688 cm⁻¹ due to C=O stretch vibration, and 3225 cm⁻¹ related to O–H stretch vibration of sulphosalicylic acid.

As shown in Figure 7 the quinoid and benzenoid absorptions for a, b and c blends appeared approximately at 1433–1443 cm⁻¹ and 1595–1603 cm⁻¹, respectively. Therefore, we could conclude that polyaniline was dispersed in PVC matrix. The absence of the absorption peak in the region of the carbonyl group related to the NMP proves that there is not any trace of the solvent in the films.

Optical Microscopic Studies

The observations of micrographs obtained from the optical microscopy showed that PANI completely has

![Figure 7](image1.png)

**Figure 7.** The slope obtained for the curve of ipα vs scan rate, and the plot of slope vs percent of polyaniline. Before and after polyaniline growth on the polymeric film.

![Figure 8](image2.png)

**Figure 8.** The slope obtained for the curve of ipc vs scan rate, and the plot of slope vs percent of polyaniline. Before and after growth of polyaniline on the polymeric film.

![Figure 9](image3.png)

**Figure 9.** FTIR absorption of PVC/PANI-SSA blends of: (a) PVC/PANI-SSA= 90/10, (b) PVC/PANI-SSA= 95/5 and (c) PVC/ PANI-SSA= 99/1.
Figure 10. Micrograph of PVC/PANI-SSA films with ×100 magnification. (a) PVC/PANI-SSA = 90/10 and (b) PVC/PANI-SSA = 95/5.

Figure 11. Micrograph of PVC/PANI-SSA films after growth of polyaniline on the polymeric film with ×100 magnification. (a) PVC/PANI-SSA = 90/10 and (b) PVC/PANI-SSA = 95/5.

been dispersed in the matrix of PVC (Figure 10). These results are in agreement with the concluded results in FTIR studies. Also Figure 11 shows that polyaniline has been grown on the surface of blend films and has been completely dispersed in PVC matrix.

CONCLUSION

The blends of PVC/PANI-SSA were prepared and for the first time the lower percolation threshold electroactivity of the polymers with cyclicvoltammetry method was investigated with 0.008 weight percent of PANI content. The morphology and structure of prepared blends were characterized with optical microscope and FTIR spectroscopy. The conductivity of blends also was measured with two-point probe method.

REFERENCES


