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European Polymer Journal 38 (2002) 771–777

EUROPEAN POLYMER JOURNAL

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Determination of extremely low percolation threshold electroactivity of the blend polyvinyl chloride/polyaniline doped with camphorsulfonic acid by cyclic voltammetry method

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Received 24 November 2000; received in revised form 25 June 2001; accepted 31 August 2001

Abstract

The percolation threshold of prepared blends of poly(vinyl chloride) (PVC) with doped polyaniline (PANi) from camphorsulfonic acid (CSA) was investigated by cyclic voltammetry. The blends were formed from *N*-methyl pyrrolidone (NMP) solutions and PANi–CSA/PVC with weight fractions from 0.1% to 0.005%. The film of blends were prepared by casting the above polymer solutions on a glass carbon (GC) electrode. Voltammograms were drew in a one-compartment cell fitted with a GC electrode, Pt electrode and SCE as working, auxiliary and reference electrode respectively, in 1 M perchloric acid as electrolytic solution. The obtained results showed that PANi–CSA/PVC blend onto 0.007% weight from PANi is electroactive. The structure and morphology of prepared blends were investigated by FT-IR spectra and optic microscope. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Percolation threshold; Polyaniline; Polyvinylchloride; Cyclic voltammetry

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1. Introduction

Polyaniline (PANi) has received considerable attention due to its simple synthesis, good environmental stability and adequate level of electrical conductivity [1]. The reversible control of its electrical properties by either changing the oxidation state of the backbone or via protonation of the immune nitrogen atoms makes PANi unique polymer among the conducting polymers [2]. However, major problems relating to the successful utilization of PANi such as its poor mechanical property and solubility remain unsolved problem. PANi could not be processed in the melt, since polymer decomposes at the temperatures below a softening or melting point. In recent years, much efforts have been made to improve the solubility and processability of PANi. These works are included as follows:

(a) Structural modification of PANi by ring or *N*-substitution [3,4].
(b) Electrochemical polymerization of aniline in polymer matrix [5].
(c) Doping PANi with functionalized protonic acids in place of inorganic acids such as HCl [6].
(d) Blending with other polymers using a cosolvent [7].

A lot of work carried out on the preparation of electrically conductive polymer blends containing PANi. The most of such blends were obtained in situ by chemical or electrochemical oxidation of aniline in the presence of thermoplastic polymers. The methods for

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PII: S0014-3057(01)00232-4

polymerization of aniline in the presence of polyvinyl chloride (PVC) [8], polyolefins, Nylon 6 [9] or PVC [10] have been reported. PANi is dispersed in the matrix of above polymers.

Recently Stockton and Rubner [11] reported the miscibility of PANi/poly(*N*-vinyl-2-pyrrolidone) (PVP) blends. Undoped PANi was mixed with PVP by solution casting. The studies showed that each of the blends containing 3–30% of the undoped PANi exhibited a single glass transition temperature (T_g) indicating miscibility, however, for blends formed from doped PANi, some level of phase segregation was observed [12] Goh et al. has reported a miscible and electroactive component polymer blend comprising PANi as the conductive component and polyvinylacetate as the thermoplastic component. Blends containing 50 w/w% or less of PANi–PSA which were miscible [13].

The determination of percolation threshold electroactivity in four-probe method for a few polymeric blends has been reported. Yang et al. have determined the percolation threshold of 0.48% weight of PANi in PANi–camphorsulfonic acid (CSA)/PMMA blend [14] and Zilberman and Titelman have determined the percolation threshold of 5% weight of PANi in PANi–DBSA/PS blend with four-probe method [15].

In this work we prepared the blends of PVC/PANi–CSA and for the first time the measurement of lower percolation threshold electroactivity of these polymers with cyclic voltammetry method is reported. The structure and morphology of prepared blends were investigated by FT-IR spectra and optic microscope and the conductivity of blends also were measured with two point probe method.

2. Experimental

Aniline from Aldrich was double distilled under vacuum before use. Ammonium persulfate was used without purification. *N*-methyl pyrrolidone (NMP) from Redel, PVC (36,000) from Fluka and (±) camphorsulfonic acid (CSA) 98% from Aldrich were used as received. PANi was prepared by oxidative polymerization of aniline in 1.7 M aqueous HCl using ammonium persulfate as oxidant (1:1 mole ratio) at 5 °C for 2 h. The green powder PANi formed and was filtered, washed several times with methanol and finally the colorless filtrate was obtained. The collected green PANi salts was added into ammonia solution (3%) and stirred for 30 min. The undoped PANi was filtrated then washed several times with water and methanol. The resulted blue powder PANi was dried under vacuum at 40 °C for about four days. For doping the PANi–EB with CSA, 30 mg CSA and 40 mg PANi–EB were dissolved in 15 ml NMP and stirred for 30 min under inert nitrogen and solution was filtrated over 0.50 μm (Watman).

To the preparation of blends 0.5 g of emeraldine base was dissolved in 20 ml of NMP by vigorous shaking. The undissolved portion was removed by filtering then this solution doped with CSA. A solution of 2.5 g PVC powder in 20 ml NMP was prepared separately.

Polymer blends of PANi–CSA/PVC with 0.7/99.3, 1/99, 2/98, 4/96, 6/94, 8/92 and 10/90 ratio weight 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 four days. When the films were visually dry, they 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. FT-IR spectroscopic, conductivity measurements and optic microscopy has been carried out on the prepared polymeric films. For the recording of voltammograms the polymer films from above solutions were casted on a glass carbon (GC) electrode by removing the solvent and drying in vacuum for 24 h.

2.1. Methods and instrumentations

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 GC which has been coated with blends, the auxiliary electrode was Pt and the reference electrode was a saturated calomel electrode. The infra-red spectra of films were obtained using a Shimadzu DR-408 FT-IR spectrophotometer. Photomicrographs of the films were obtained using a microscopy Olampose BH2 UMA. Conductivity measurements of the films were carried out on a two point probe. All measurements were done in air at room temperature and conductivity was calculated by the following equation:

$$\sigma = I\frac{d}{V}A$$

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

3. Results and discussion

3.1. Cyclic voltammograms

Determination of electroactivity percolation threshold for polymeric blends were investigated for the first

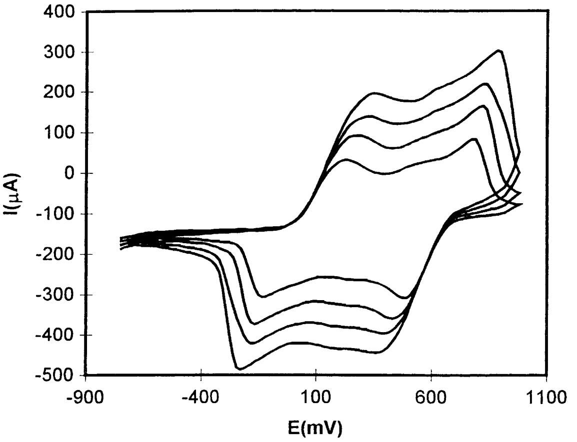

Fig. 1. Cyclic voltammograms of PVC/PANi–CSA (90/10) film on the GC electrode in 1 M perchloric acid as electrolytic solution at various scan rates.

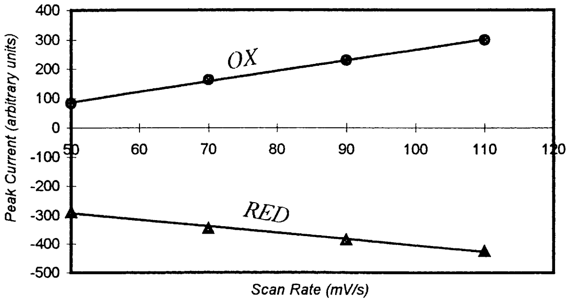

Fig. 2. Plot of secondary anodic and cathodic peaks current vs scan rate for PVC/PANi–CSA (90/10) film.

time by cyclic voltammetry method. The blends were formed from NMP solutions of PVC/PANi–CSA having weight fractions from 0.1% to 0.007%. Voltammograms were drew in a one-compartment cell fitted with a film which casted on a GC electrode, Pt electrode and SCE as working, auxiliary and reference electrode respectively in perchloric acid as electrolytic solution by scanning the potential from −800 to 1000 mV. Cyclic voltammograms of the polymer blend for PVC/PANi–CSA (90/10, w/w) obtained at the various scan rates (50, 70, 90 and 110 mV/S) are shown in Fig. 1. The current is increased by the gradual increases of scan rate. Two anodic peaks at 146 and 719 mV, and two cathodic peaks at −235 and 379 mV are clearly appear on the voltammograms. The secondary anodic peaks (i_{pa}) and cathodic peaks (i_{pc}) currents are directly proportional to v in the potential scan range between 50 and 110 mV/s and the peaks forms are characteristic for an adsorption-limited process (Fig. 2). It could be resulted that the slopes value obtained from the curves (Figs. 2 and 4 and Tables 1 and 2) are proportional to the electroactivity of polymer blends. The obtained polymers are significantly electroactive, because the polymer film deposited on the electrode surface can electropolymerized the aniline in the 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 cycle. The electroactive sites of PANi which has been dispersed in blend matrix are responsible to the growth of aniline. After preparation of PANi on the polymer film deposited on the working electrode surface, it was removed from the cell, washed with CH_3CN and finally placed in the cell without monomer and scanned with scan rate 50–110 mV/s in the same range −800 to 1000 mV in the solution of perchloric acid (Fig. 3). As seen two anodic peaks at 151 and 714 mV, and two cathodic peaks at −250 and 371 mV are clearly appear on the voltammograms.

Table 1
Slope value of PVC/PANi–CSA for secondary anodic peaks with various percent of PANi obtained from cyclic voltammograms

PVC/PANi–CSA	90/10	93/7	95/5	96/4	97/3	99/1	99.3/0.7
Slope*	3.5	2.13	2.0	1.6	0.33	0.08	0.04
Slope**	5.0	3.25	2.88	1.8	0.45	0.09	0.04

Slope value before (*) and after (**) growth of PANi on the electrode surface coated with blend film.

Table 2
Slope value of PVC/PANi–CSA for secondary cathodic peaks with various percent of PANi obtained from cyclic voltammograms

PVC/PANi–CSA	90/10	93/7	95/5	96/4	97/3	99/1	99.3/0.7
Slope*	−2.4	−1.0	−0.50	−0.18	−0.09	−0.03	−0.02
Slope**	−4.2	−1.78	−0.72	−0.31	−0.11	−0.05	−0.02

Slope value before (*) and after (**) growth of PANi on the electrode surface coated with blend film.

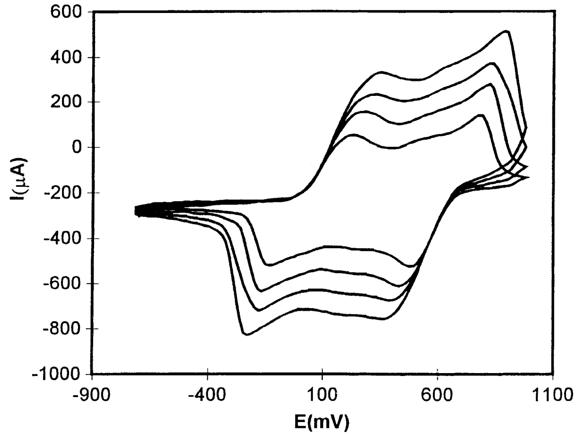

Fig. 3. Cyclic voltammograms of PVC/PANi–CSA (90/10) film on the GC electrode in 1 M perchloric acid as electrolytic solution at various scan rates after growth of aniline on the polymeric film.

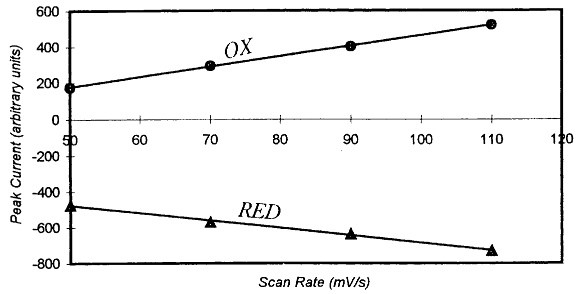

Fig. 4. Plot of secondary anodic and cathodic peaks current vs scan rate for PVC/PANi–CSA (90/10) film, after growth of aniline on the polymeric film.

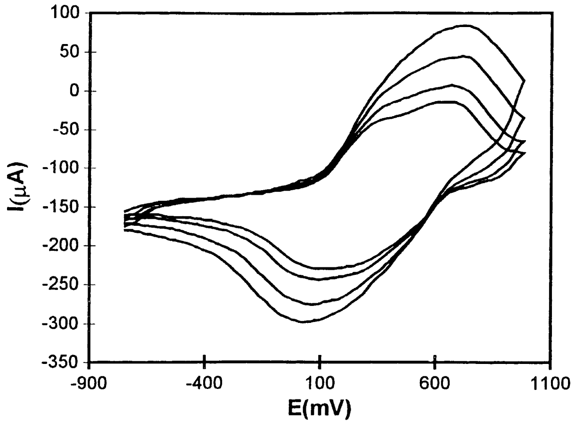

Fig. 5. Cyclic voltammograms of PVC/PANi–CSA (96/4) film on the GC electrode in 1 M perchloric acid as electrolytic solution at various scan rates.

From comparison of the Figs. 1 and 3 it is clear that, the separation between two peaks was reduced after growth of aniline by electropolymerization on the film. In addition current in the scan rate 110 mV/s is 322 μA while in the scan rate 110 mV/s after growth of aniline on the film current is 550 μA. It has been found that the electroactivity of blend film on the working electrode after growth of aniline on the blend film was increase. The secondary anodic peaks (i_{pa}) and secondary cathodic peaks (i_{pc}) currents are directly proportional to v in the potential scan range between 50 and 110 mV/s (Fig. 4). From comparison of slopes in Figs. 2 and 4, it can be concluded that after growth of the PANi on the film, the electroactivity was increased. In another experiment, we investigated the electroactivity of polymer blend for PVC/PANi–CSA (96/4 w/w) at the abovementioned conditions. The cyclic voltammograms of this polymer blend is shown in Fig. 5. Although the scan rate 50 mV/s of the anodic peaks is clearly observed however, the cathodic peaks are not resolved. Similarly at scan rates of 70, 90 and 110 mV/s two anodic peaks are not very well resolved. The reason for these observations is related to the percent of PANi in the blend film. The distortion of the cyclic voltammograms in Fig. 5 in comparison with cyclic voltammograms in Fig. 1 also is related to the percentage of aniline in the blend film. After the growth of aniline on the blend film by electrochemical polymerization both the anodic and cathodic peaks are clearly appeared again (Fig. 6). Electroactivity of the blends with less percentages of

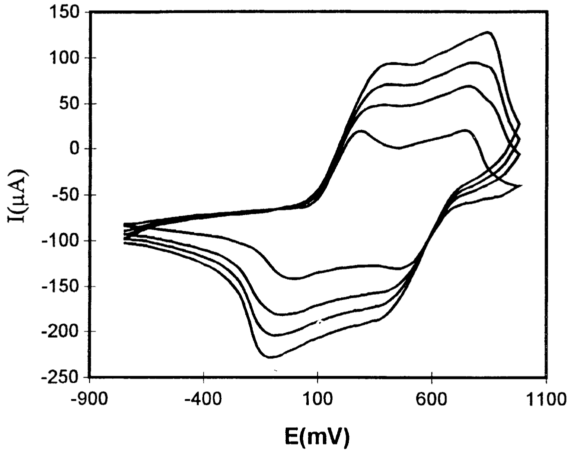

Fig. 6. Cyclic voltammograms of PVC/PANi–CSA (96/4) film on the GC electrode in 1 M perchloric acid as electrolytic solution at various scan rates after growth of aniline on the polymeric film.

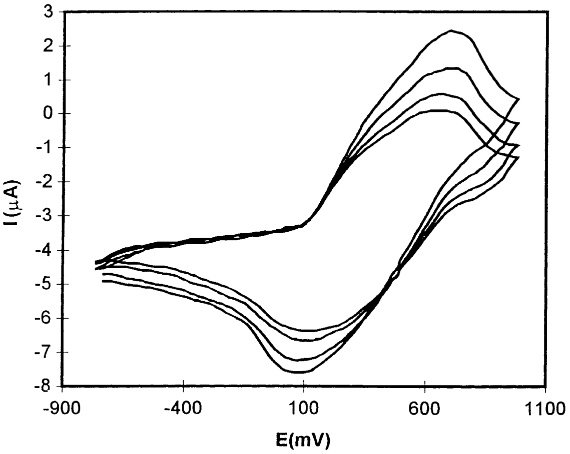

Fig. 7. Cyclic voltammograms of PVC/PANi–CSA (99.3/0.7) film on the GC electrode in 1 M perchloric acid as electrolytic solution at various scan rates.

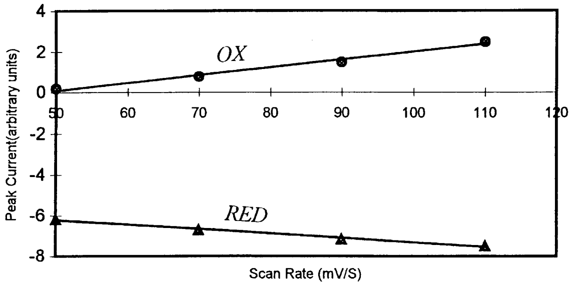

Fig. 8. Plot of secondary anodic and cathodic peaks current vs scan rate for PVC/PANi–CSA (99.3/0.7) film.

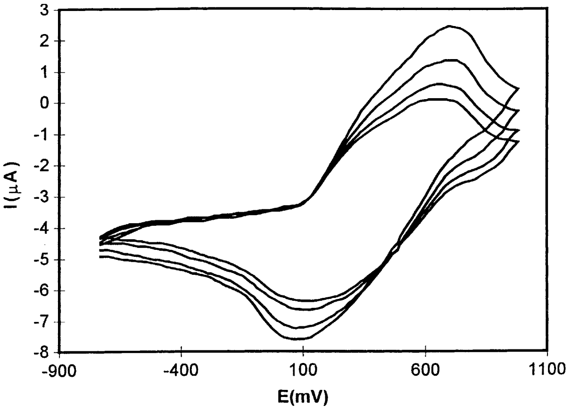

Fig. 9. Cyclic voltammograms of PVC/PANi–CSA (99.3/0.7) film on the GC electrode in 1 M perchloric acid as electrolytic solution at various scan rates after growth of aniline on the polymeric film.

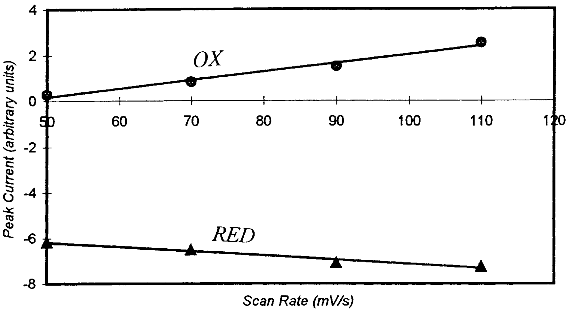

Fig. 10. Plot of secondary anodic and cathodic peaks current vs scan rate for PVC/PANi–CSA (99.3/0.7) film, after growth of aniline on the polymeric film.

PANi in PVC/PANi–CSA blends were showed that until 0.007% weight of PANi–CSA, the blends are electroactive (Figs. 7–10) and lower than this percent weight the cyclic voltammograms do not show any electoactivity. Therefore, we conclude that the extremely low percolation threshold of PVC/PANi–CSA blend with cyclic voltammeter is 0.007% weight of PANi–CSA. In the morphology studies method of HCl-doped PANi–PVC blend, Banerjee and Mandal have been reported that 0.035 and 0.045 wt.% PANi–HCl is the extremely low percolation threshold [8]. The slope values obtained from the curves of the anodic peaks currents versus of various scan rate for the PVC/PANi–CSA blend with different weight percent of PANi–CSA have been collected in Tables 1 and 2. These slopes values can be attributed to the electroactivity of PVC/PANi–CSA. Therefore, with preparing of blend film of PANi–CSA/PVC with solution method it is possible to growth of aniline on the blend by the electropolymerization method in order to access the desired electroactivities.

3.2. Conductivity measurements

The conductivity measurement with common instruments to the very lower electroactivity is not suitable method. However, the cyclic voltammometric method is a suitable method for the determination of lower electroactivity of conducting polymers. The result of conductivity measurements on the PVC/PANi–CSA blends at room temperature with two point probe method are listed in Table 3.

3.3. FT-IR studies

Fig. 11 shows the FT-IR spectra of blends PVC/PANi–CSA ratio weight 90/10 (a), 95/5 (b) and 99/1

Table 3
Conductivity of PVC/PANi–CSA blends at room temperature

Blend composition	90/10	93/7	95/5	96/4	97/3	99/1
Conductivity (S/cm)	7.9×10^{-4}	4.5×10^{-4}	9.9×10^{-5}	5.4×10^{-5}	2.1×10^{-5}	6.5×10^{-6}

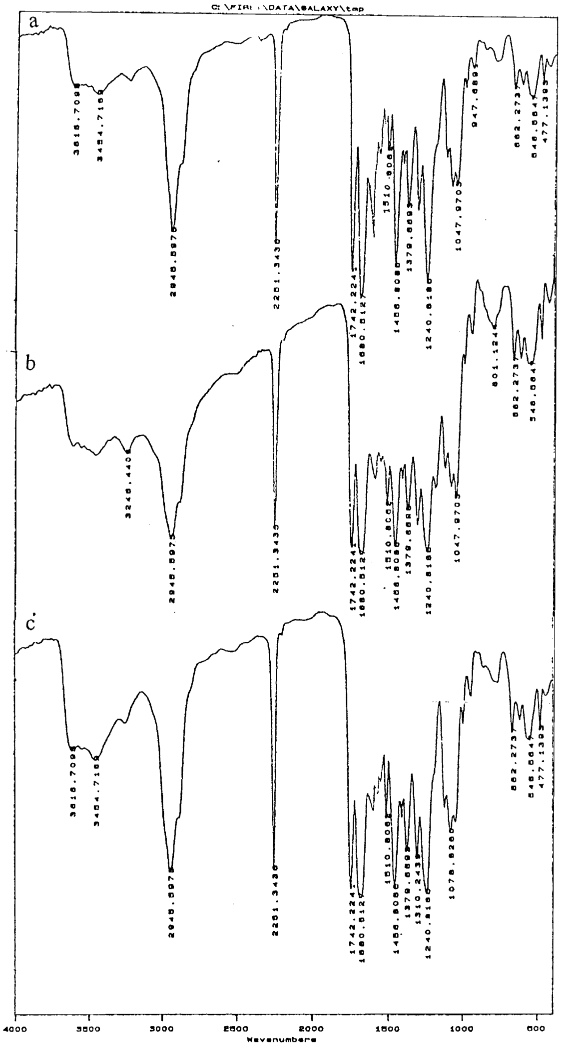

Fig. 11. FT-IR absorption of PVC/PANi–CSA blends of the (a) PVC/PANi–CSA = 90/10, (b) 95/5, (c) 99/1.

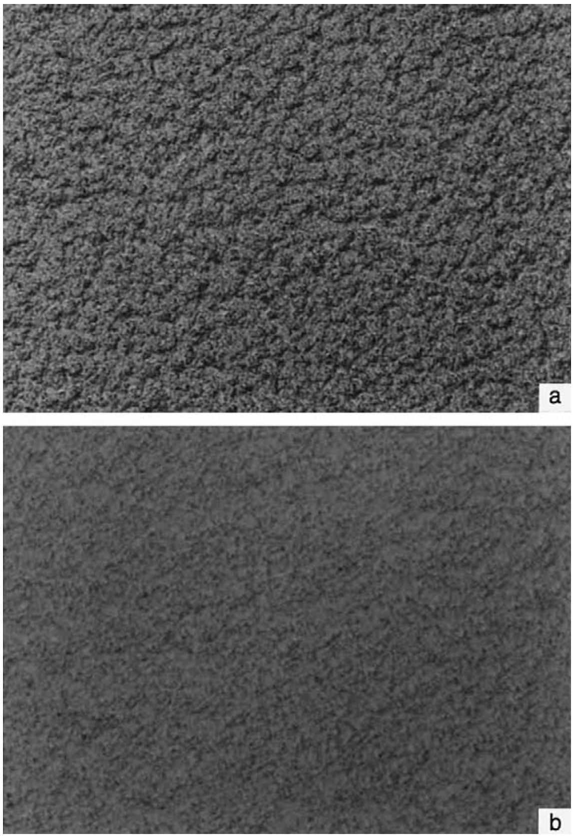

Fig. 12. Micrograph of PVC/PANi–CSA films with 100 times magnification. (a) PVC/PANi–CSA = 90/10, (b) 95/5.

(c). There are characteristic peaks at 1704 cm^{-1} due to C=O stretch vibration of CSA, 3245 cm^{-1} related to O–H stretch vibration of CSA. As shown in Fig. 9 the quinoid and benzenoid absorption for a, b and c blends were appeared approximately at 1433–1443 and 1595–1603 cm^{-1}, respectively. Because the characteristic peaks did not showed significant shifting, as the literature [10] we could concluded that PANi was dispersed in PVC matrix.

3.4. Optic microscopic studies

The micrographs of the optic microscope showed that PANi completely has been dispersed in the matrix of PVC (Fig. 12). This result is in agreement with the concluded results in FT-IR studies. Also Fig. 13 shows that aniline has been grown in the surface of blend films and completely has been dispersed in PVC matrix.

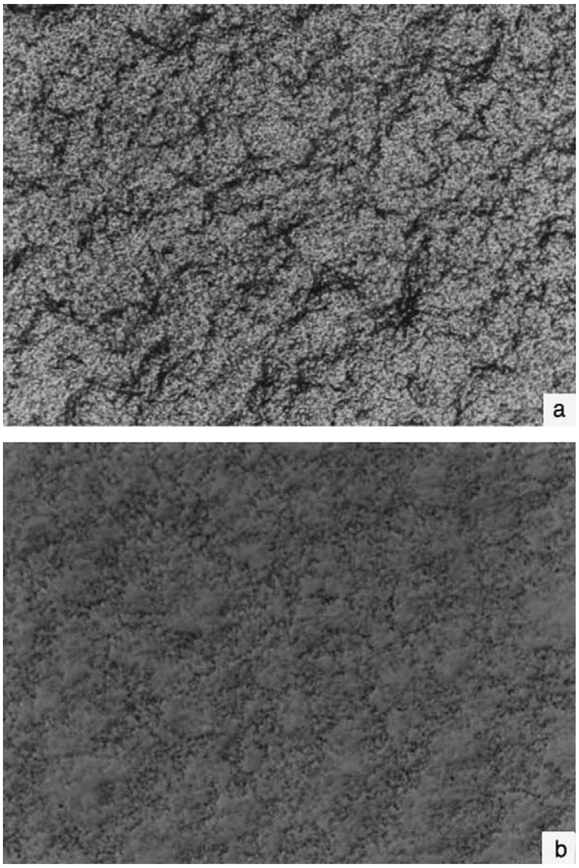

Fig. 13. Micrograph of PVC/PANi–CSA films after growth of aniline on the polymeric film with 100 times magnification. (a) PVC/PANi–CSA = 90/10, (b) 95/5.

4. Conclusions

The blends of PVC/PANi–CSA were prepared and for the first time the lower percolation threshold electroactivity of the polymers with cyclic voltammetery method was investigated. The morphology and structure of prepared blends were characterized with optic microscope and FT-IR spectra. The conductivity of blends also were measured with two point probe method.

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