Electrochemical characterization of electroactive poly(aniline)/EPDM rubber blends obtained chemically on Ag substrates for corrosion protection

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Abstract

Sensor devices, such as pressure gauges and membrane keyboards, contain Ag paths built from colloidal serigraphy. One of the steps in the manufacture of such devices is the deposition of graphite carbon to form a protective barrier that prevents the corrosion of the metallic paths. Nonetheless, several shortcomings are associated with such an approach. Corrosion protection requires the use of specialized high-valued materials to prevent even higher maintenance costs later on. The present work will address the possibility to replace graphite carbon coatings by conductive polymers. In this sense, Poly(aniline)/EPDM blends were prepared by casting rubber matrixes containing different oxidant agents and dodecylbenzene sulfonic acid in an organic solution exposed afterwards to aniline vapors to allow chemical polymerization. Secondary doping of the obtained blends was conducted with xylene. The influence of the nature of oxidant and the concentration of conductive polymer on the electroactivity of the blends as surface coatings on Ag were studied by Cyclic Voltammetry, Electrochemical Impedance Spectroscopy and Optic Microscopy.

1 Introduction

Intrinsically conducting polymers are an extensively studied class of materials due to their interesting properties, including electrical conductivity, electrochromism and electroactivity [1]. However, their mechanical properties preclude their use in the polymer industry. Since the first studies concerning their

main goal of the preparation of blends is to obtain new materials that combine the properties of their components. As intrinsically conductive polymers is concerned, it is necessary to improve their mechanical properties and processing, without loss of electrical conductivity and electrochemical properties. The preparation of polymer mixtures can be carried out by different ways. Usually, it is preferred chemical or electrochemical polymerization of the monomer into an insulating matrix. For polypyrrole preparation, different kinds of insulating organic polymers have been employed, such as, poly(vinyl chloride) [2], poly(vinylene fluoride) [3], polyurethane [5], poly(tetrafluorethene) [6] and others. It was also reported the use of $CuCl_2$ or $FeCl_3$ as oxidant in the preparation of mixtures of polypyrrole and EPDM rubber [7-8]. In addition, polymer blends and composites of polyaniline and conventional polymers such as poly(vinyl alcohol) [4], poly(methyl methacrylate) [9], polyethylene [10], polycarbonate, polystyrene, polysulfonate, poly(vinyl acetate), polypropylene [11], poly(vinyl chloride), acrylonitrile-butadiene-styrene copolymer (ABS) [12-13] and nitrile rubber [14-15] are also reported in literature. Chemical synthesis can offer advantages if one consider the necessity of large-scale production, but the conducting polymers are generally obtained as a powder and their characterization by electrochemical techniques is an arduous task. Concerning to the field of sensor materials, the final properties depend of a careful and adequate preparation and a good choice of materials. Such devices are commonly built depositing colloidal silver layers on polyesther substrates, followed by the deposition of graphite carbon layers. However, they present some limitations such as short lifetime due mainly to the loss of adherence between the metallic components and to the corrosion of the basic substrate. In this work, an alternative to improve the properties of such sensor devices, by using mixtures of polyaniline and EPDM rubber as replacing materials of graphite carbon layers, is presented. Those blends act not only as sensor materials but also as protective coatings against the corrosion of the metallic substrate. Polyaniline was chosen due to the low cost of the monomer and easy synthesis. On the other hand, EPDM rubber presents low density, high stability to chemical attack, atmospheric and ozone oxidation, and to hydrolysis, associated with excellent mechanical properties.

2 Experimental procedures

Reagents and Solutions: For the preparation of the polymeric blends, the following chemicals were used: aniline (without previous purification), EPDM rubber (terpolymer of ethylene-propylene-5-ethylidene-2-norbornene, EP57 Nitriflex). As oxidant agents were employed $(NH_4)_2S_2O_8$ and KIO_3. Acid doping of polyaniline (PAni) was performed with dodecylbenzene sulfonic acid (HDBSA), and for vapor-phase secondary doping xilene was used. Chloroform was employed to solubilize the rubber component. Cyclic voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) experiments were carried out in 1 M and 0.1 M $LiClO_4$ aqueous solution, respectively. All reagents were of analytical grade.

Blend preparation: The rubber component and the oxidant were primarily milled in an analytical mill (Janke&Junkel – A10 IKA Labortechnik). A rubber matrix containing the oxidant agent and the dopant acid was first prepared by dissolution of 0.2 g of the elastomer in 15 ml of $CHCl_3$. A

containing the oxidant agent and the dopant acid was first prepared by dissolution of 0.2 g of the elastomer in 15 ml of $CHCl_3$, under stirring at 60°C. A solution of 1M HDBSA in chloroform was added to the rubber solution and stirred after complete dissolution. Further on, the oxidant agent was added and stirred for 30 min. Specimens containing 5, 15 and 25% of each type of oxidant were prepared by this method. The solution containing the dopant and the oxidant was then deposited on a glass sheet already coated by Ag and then placed into a casting box in a solvent saturated atmosphere, during 24h. Films of approximately 100 μm of thickness (φ) were obtained by using a guide wire. The polymer matrix was then exposed to the monomer vapors, in a closed saturated vapor atmosphere during 24h, to allow the polymerization of aniline. The polymer mixtures cast from chloroform, were additionally exposed to xilene vapors, during 5h, to perform vapor-phase secondary doping of polyaniline. The samples were then stored under vacuum atmosphere previous to characterization.

Electrodes: The electrochemical properties of the polymer blends were studied using a three-electrode cell with a saturated calomel electrode (E = 0.241 V vs NHE) as reference, and a platinum sheet (14.25 cm²) as counter electrode. The working electrode was a glass sheet (18.75 cm²), with one face coated by Ag. The coating with Ag was carried out by firstly cleaning the glass sheet in an isopropylic alcohol bath and then placing it in a high vacuum evaporation device. The thickness of the Ag layers was accurately controlled with an oscillating quartz crystal. In the interior of the chamber an ionic discharge was applied in order to remove aggregated particles on the glass surface. Next, a tungsten crucible containing Ag was heated with an applied electrical current up to complete fusion of the Ag. Silver vapors were condensed on the glass surface due to pressure difference, up to a thickness of 1500 Å has been reached. After this step, the polymer blend was deposited on the Ag coated glass sheet, at 25 °C.

Cyclic voltammetry: CV was performed using a potentiostat (EG&G PAR 283) at different scanning rates (0.5 to 5 mV/s), in a range of -0.5 to 0.8 V_{SCE}.

Electrochemical Impedance Spectroscopy: A frequency response analyzer (Solartron SI 1255) coupled to a potentiostat/galvanostat PAR 273A was used for the impedance measurements. These experiments were carried out during exposure the polymer blends to the electrolyte, up to 72h. Experiments were performed with a sinusoidal perturbation of 20 mV, in a frequency range of 100 kHz to 10 mHz, at 25 °C.

Optic microscopy: An Optic Microscope (Jenaval – Carl Zeiss) was employed to observe the distribution of poly(aniline) into the elastomeric matrixes.

3 Results and Discussion

The cyclic voltammograms of PAni.DBSA/EPDM rubber mixtures, prepared with different concentrations and types of oxidant, are shown in Figures 1 and 2. Two well defined peaks related to the oxidation and reduction of the conductive polymer were observed in all experiments.
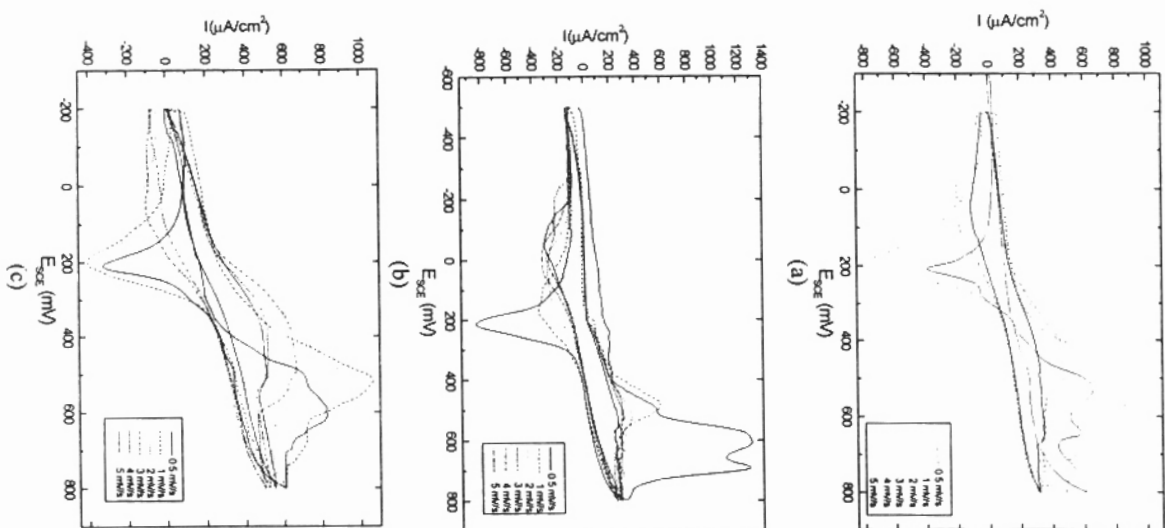
Figure 1: Cyclic voltammograms of PAni:DBSA/EPDM rubber blends on Ag electrode. Blends prepared with: (a) 5%; (b) 15%; (c) 25% of KIO₃. Scanning rate: 0.5 mV/s, in LiClO₄ 1 M.
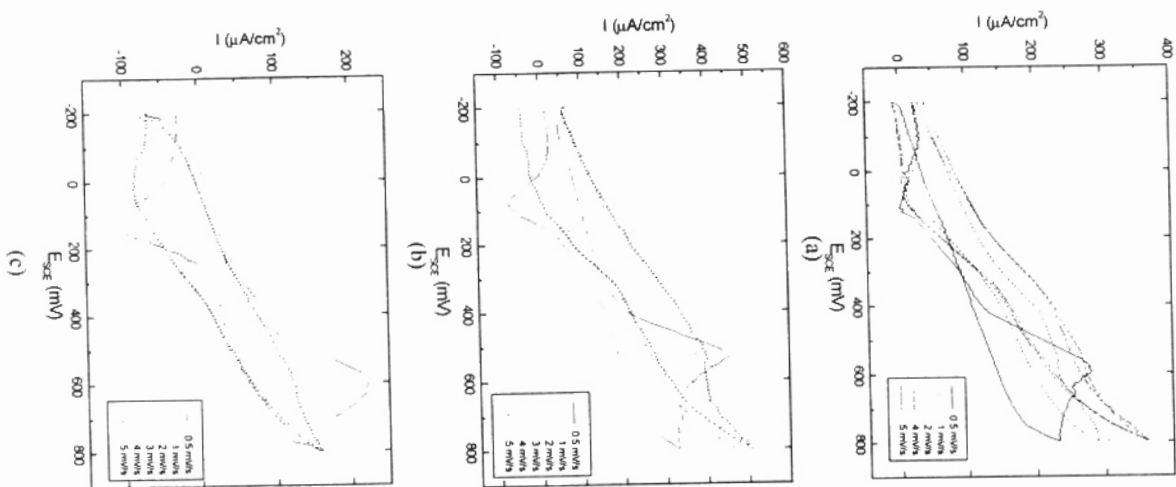

Figure 2: Cyclic voltammograms of PAni:DBSA/EPDM rubber blends on Ag electrode. Blends prepared with: (a) 5%; (b) 15%; (c) 25% of (NH₄)₂S₂O₈. Scanning rate: 0.5 mV/s, in LiClO₄ 1 M.

The electrochemical parameters calculated from figures 1c and 2c are shown in Table 1. The cyclic voltammograms of PAni/EPDM blends obtained at 0.5 mV/s show more defined peaks and smaller separation between cathodic and anodic peaks (ΔE) than those performed at higher scanning rates. The peaks became broader and poorly defined as the scanning rates increased. This behavior was observed for both oxidants used. Higher current densities were produced by the samples prepared with KIO₃. It could be related to a better distribution of this oxidant in the rubber matrix, comparatively to $(NH_4)_2S_2O_8$, thus creating good conductive ways, as the micrographs will later show. In addition, as peroxidissulfate is a strong oxidant, it could cause secondary reactions (over oxidation) during polymerization of polyaniline, decreasing the electroactivity of the polymer.

Table 1. Voltammetric data for PAni.DBSA/EPDM blends, calculated from voltammograms 1(c) and 2(c). (I_{pa} and I_{pc} stand for anodic peak current density and cathodic peak current density, respectively).

Specimen	Scan rate (mV/s)	I_{pa} ($\mu A/cm^2$)	I_{pc} ($\mu A/cm^2$)	ΔE (mV)
PAni.DBSA/EPDM blend (25% $(NH_4)_2S_2O_8$)	0.5	150.0	-86.3	448.8
	1	86.1	-54.3	478.1
	2	81.4	-49.6	531.6
	3	67.3	-25.7	596.0
	4	36.7	-11.6	609.5
	5	20.2	-6.0	620.1
PAni.DBSA/EPDM blend (25% KIO₃)	0.5	476.2	-495.5	388.9
	1	709.7	-549.7	319.9
	2	540.6	-350.3	392.9
	3	279.5	-177.4	428.4
	4	133.3	-70.8	386.1
	5	114.9	-42.3	370.0

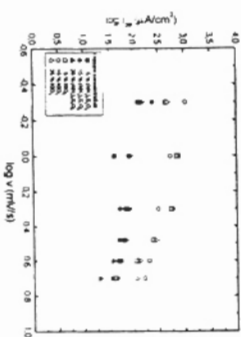The dependence of I_{pa} with scanning rate was expressed by $y = A + Bx$ (Figure 3).

Figure 3: Log of anodic peak current density (I_{pa}) vs log of scanning rate in LiClO₄ aqueous solution of PAni.DBSA/EPDM blends prepared with oxidants of different nature at increasing concentrations.

The slopes of the curves changed from − 0.33 ± 0.19 to − 0.72 ± 0.02 as the concentration of $(NH_4)_2S_2O_8$ increased, and from − 0.72 ± 0.02 to − 1.21 ± 0.23 with increasing concentration of KIO₃. These results suggest that at high concentration of conductive polymer, the samples behave as pure polyaniline films, that mean, the electroactive material is located mainly on the electrode surface, like a thin layer. However, for the samples prepared with lower concentrations of oxidant, the redox reaction of polyaniline is controlled by a diffusion process. The higher slopes obtained for the blends prepared with KIO₃ are also indicative of a better distribution of the conductive polymer into the rubber matrix, and good electroactivity.

EIS results for Ag film and PAni/EPDM blend on Ag substrate, at different immersion on the electrolyte solution are presented as Nyquist and Bode Phase diagrams in figure 4 (a) and (b), respectively. The experimental parameters obtained by EIS experiments are shown in Table 2.
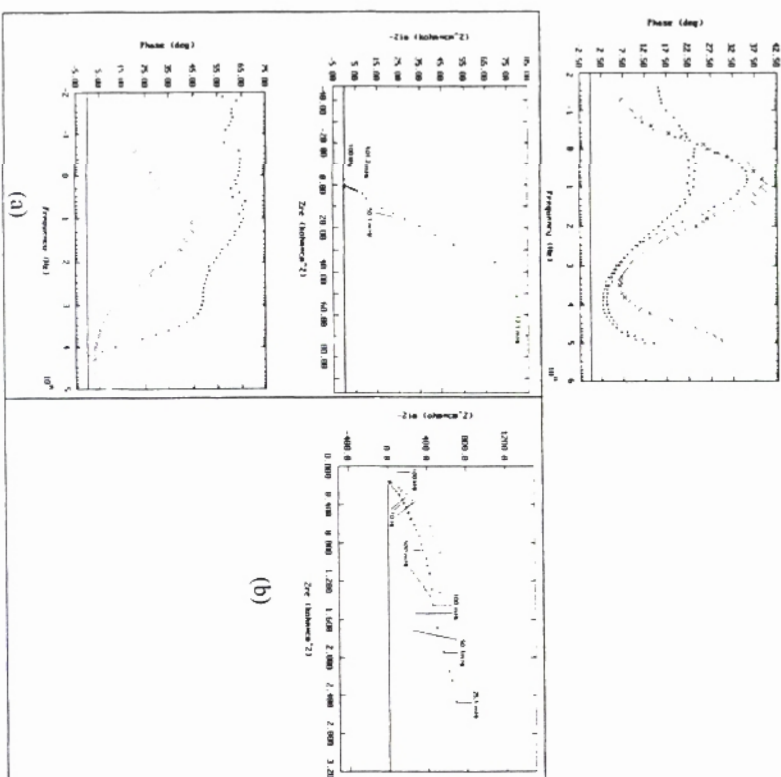
(a)

(b)

Figure 4: Nyquist and Bode Phase diagrams obtained for :(a) Ag film (thickness = 1500 Å); (b) PAni.DBSA/EPDM film (prepared with 5% of $(NH_4)_2S_2O_8$) on Ag substrate. Symbols: After (□) 1h; (+) 3h; (*) 5h; (◊) 24h; (X) 72h of immersion in LiClO₄ 0.1 M.

From the EIS data's were stablished the equivalent circuits for non coated Ag and for PAni/EPDM –Ag systems shown in Figure 5.
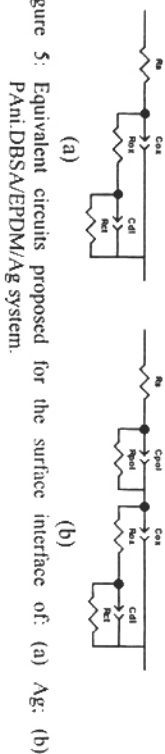
Figure 5: Equivalent circuits proposed for the surface interface of: (a) Ag; (b) PAni.DBSA/EPDM/Ag system.

Table 2. Estimated values from the circuit element extracted from EIS of pure Ag and PAni.DBSA/EPDM blend (prepared with 5% $(NH_4)_2S_2O_8$ on Ag) at different times of exposure.

Time (h)	C_{pol} (μF/cm²)	R_{pol} (Ω/cm²)	C_{ox} (μF/cm²)	R_{ox} (Ω/cm²)	C_{dl} (μF/cm²)	R_{ct} (Ω/cm²)
1 (Ag)	----	----	524.9	7.4	751.2	39887.0
1	0.0205	18,92	2302.1	343.7	144.4	106.1
24	0.0019	513.6	913.0	319.0	145140.0	35.08

C_{pol} and C_{ox} stand to the capacitances of the polymer blend and silver oxide layer, respectively.

The Nyquist diagram obtained for the Ag film after 1h of exposure shows a Warburg like behaviour typical of a porous material. This could be due to the formation of a porous oxide layer, as a result of Ag oxidation. After 3h of exposure, the diagrams present a semicircle which indicates a capacitive behavior. In the case of the polymer blend, the electrolytic solution penetrated into the polymeric film in the first hours of exposure, and the electrode potential became stable. The plot obtained for the PAni.DBSA/EPDM film on Ag substrate after 1h of immersion also shows a linear behavior indicative of a diffusion controlled regime at the whole frequency range tested. It might be due to the quite porous nature of the film, as Figure 6 illustrates. It also shows the surface of the polymer blends, obtained with different types of oxidant, and the porous nature of the polymer is clearly seen. The high ionic conductivity of the polymeric film in the first hours of immersion might have also contributed to this result. For longer immersion periods (3h to 72h) a semicircle depressed from the real axis. This behavior is related in literature as characteristic of porous specimens, with varying pore size [16]. This capacitive arc is likely related to the polymer/electrolyte interface. From the length of the arc on the real axis, the charge transfer resistance (R$_{ct}$), can be estimated. R$_{ct}$ is the resistance associated with the transfer of ions across the polymer/electrolyte interface. From 1 to 5 hours of exposure, the observed increase of the length of the depressed arc is associated with the loss of the conductive characteristics of the polymer film, resulting from swelling. A significant loss of adherence of the rubbery film on the substrate was clearly seen by visual observation after 24h of exposure, which leads us to conclude that after 24h of exposure, the drastic diminution of the length of the depressed arc, could be mainly related with the electrochemical

behavior of the metallic substrate. From 24h to 72h of solution exposure, the length of the depressed arc (R$_r$) increases. The formation of corrosion products, causing the scaling off some pores of the Ag oxide film must have contributed to this result. In both micrographs a good distribution of the conductive polymer in the rubbery matrix was observed. Polymer blends produced with $(NH_4)_2S_2O_8$ had polyaniline particles of approximately 3 μm of diameter, while those blends prepared with KIO$_3$, showed particles size of around 1 μm. These differences in the particle size might be responsible for the higher current densities observed in the cyclic voltammograms of the samples prepared with KIO$_3$.
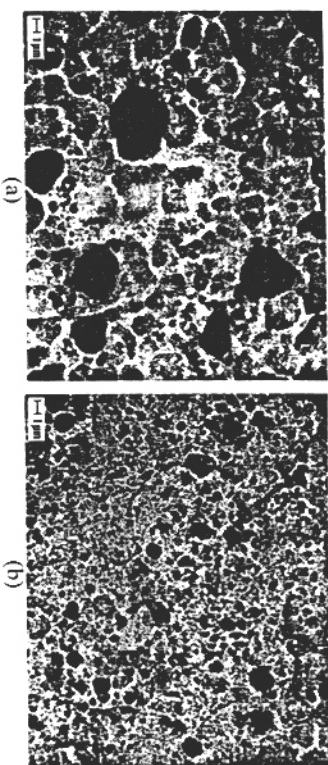
Figure 6 : Optical micrographs of PAni.DBSA/EPDM blends prepared with: (a) 25 % $(NH_4)_2S_2O_8$; (b) 25 % KIO$_3$.

Conclusions

Cyclic voltammetry experiments revealed that the conductive polymer is present in the polymer blend, and it is electrochemically active, showing typical redox processes in LiClO$_4$, independently of the oxidant agent used. The increase of scanning rate diminishes the reversible character of the conductive polymer. Although all specimens analyzed were electro active, blends produced with KIO$_3$ presented better response, indicating a better distribution of the conductive polymer into the rubber matrix that favors probably the conduction of charges through out the film. EIS results indicated that the system is primarily formed by a polymer film that acts as a barrier to the diffusion of ions across the polymer/electrolyte interface related with the transfer of ions across the polymer/electrolyte interface increased from 1h to 5h, and this was related to swelling/degradation of the polymer film with immersion time producing a decrease of the film conductivity, and consequently an increase in R$_{ct}$. After some exposure time, the electrolyte diffuse totally in the polymer film and a layer of silver oxide starts to grow up in the interface silver-polymer. The growing oxide eventually cause the blockage of the pores in the oxide layer. Optical micrographs showed the presence of the conductive polymer as well distributed particles. The lowest particle size (~1 μm) was observed for the blends produced with KIO$_3$. This could be related with the better electrochemical response observed in these specimens. The use of a polymer blend of PAni.DBSA/EPDM seems to act as a

protective coating against the corrosion of the Ag substrate, without loosing its electroactive characteristics.

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