

Electrochemical Characterization of Polypyrrole and Polypyrrole/EPDM Rubber Blends by Cyclic Voltammetry and Impedancimetry

*Rita A. Zoppi and Marco-A. De Paoli**

Instituto de Química, UNICAMP, C.P. 6154, 13083-970 Campinas - SP, Brazil

Eugène M. Genies

CENG, DRFMC/SESAM/LEM, 85x - F38041, Grenoble, France

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Polipirrol e a blenda elastomérica polipirrol/EPDM foram obtidos por oxidação química com FeCl_3 . As propriedades redox destes materiais foram estudadas por voltametria cíclica e por espectroscopia de impedância. Os resultados mostram uma relação proporcional entre a corrente de pico, i_p , e v^x (v = velocidade de varredura). O valor de x obtido para as blendas ($0,50 \pm 0,05$) não depende da espessura do filme de borracha (100, 200 ou 400 μm). Para o polipirrol puro obteve-se um valor de $0,96 \pm 0,05$. Estes resultados mostram nas blendas um comportamento de difusão linear semi-infinita e para o polipirrol a transferência de massa não está presente na reação redox. A espectroscopia de impedância foi usada para o polipirrol e para as blendas em diferentes estados de oxidação. Em todos os casos observa-se histerese e em todas as curvas está presente um semicírculo. No entanto, o diâmetro do semicírculo é maior para as blendas do que para o polipirrol puro. Observou-se uma distorção do gráfico de impedância, com relação ao semicírculo ideal com o aumento da espessura do filme de borracha.

Polypyrrole and polypyrrole/EPDM rubber blends were obtained by chemical oxidation with FeCl_3 . The redox properties of these materials were studied by cyclic voltammetry and impedance spectroscopy. The results show a proportional relationship between current peak, i_p , and v^x (v = scan rate). The x value obtained for the blends (0.5 ± 0.05) does not depend on the rubber film thickness (100, 200 or 400 μm). For pure polypyrrole the x value obtained was 0.96 ± 0.05 . These results show that the blends have a linear semi-infinite diffusion behavior, and for pure polypyrrole the mass transfer is not present in the redox reaction. Impedance spectroscopy was carried out with pure polypyrrole and the blends in different oxidation states. Hysteresis was always observed. In all experiments a semicircle is present. However, the semicircle diameter for the blends is larger than that for pure polypyrrole. A distortion of the impedance plot with respect to the ideal semicircle was observed when the rubber film thickness was increased.

Keywords: *polypyrrole, polypyrrole/EPDM, rubber blend, conductive rubber*

Introduction

The interest in the manufacture of polymeric blends considerably increased after 1970 when it was verified that new polymer production had become an expensive process. New techniques for obtaining polymeric materials were developed, such as copolymerization and the manufacture of blends. Polymeric blends can be defined as a physical mixture of two or more polymers without chemical bonds between these components. The initial motivation to study

the manufacture of blends was to try to eliminate the limitations that some polymers present, such as fragility, and poor processability and impact resistance. The main objective of the manufacture of blends is to obtain new materials that synergistically combine the properties of their components. Specifically, in conducting polymers there is a need to improve the mechanical properties and the processability, but the electrical conductivity and electrochemical properties must be retained. There are many methods for the synthesis of conducting blends, such as, (i)

the mechanical mixing of an insulating and a conducting polymer, (ii) evaporation of a solution containing the insulating and the conducting polymer, and (iii) the monomer polymerization into an insulating matrix (by electrochemical or chemical polymerization).

Little emphasis has been given to the electrochemical characterization of conducting polymers that are obtained by chemical synthesis. Some interesting pioneering papers are found in the literature¹⁻³. In this work, polypyrrole, PPy, and polypyrrole/EPDM rubber blends, PPy/EPDM, were obtained by chemical oxidation of pyrrole with FeCl₃. These materials were characterized by cyclic voltammetry and impedance spectroscopy.

Experimental

Polypyrrole was obtained as follows: an FeCl₃ solution in tetrahydrofuran (5% w/w) was deposited on a Pt electrode (0.5 cm²). This electrode was exposed to pyrrole vapors for different lengths of time (1-2, 10, 20 or 60 min.). The electrode was then completely rinsed with distilled water. Polypyrrole/EPDM rubber blends were obtained by the same procedure using a Pt electrode (0.5 cm²) covered by rubber films of different thicknesses (100, 200 or 400 μm). EPDM rubber is an ethylene-propylene-5-ethylidene-2-norbornene copolymer. The rubber film was obtained by the casting of a 40 g.L⁻¹ solution of EPDM in CHCl₃. The counter electrode was a Pt plate (0.5 cm²) and the reference electrode was a Saturated Calomel. An aqueous 1.0 M KCl solution was used as the electrolyte. During all experiments the cell atmosphere was maintained under argon flux. Cyclic voltammetry was done with a PAR EGG 273A potentiostat coupled to a Sefran X/Y recorder, in the -0.75 to 0.60 V range. Impedance experiments were done with a Transfer Function Analyzer (Solartron 1255H) connected to a PAR EGG 273A potentiostat and interfaced with a Victor V386 CX microcomputer. Impedance measurements were carried out between 10⁻² and 10⁴ Hz, at fixed potentials, corresponding to different redox states of the materials (0.40; 0.20; 0.0; -0.20 and -0.40 V). A sinusoidal perturbation of ± 0.010 V was applied after reaching a steady-state. Elemental analysis of the PPy/EPDM blends were made with a Perkin Elmer 2400 CHN. Scanning electron microscopy was conducted using a Jeol T-300 at an accelerator voltage of 20 kV after coating the PPy/EPDM blends with gold by sputtering.

Results and Discussion

The choice of synthesis conditions for obtaining PPy/EPDM blends and pure PPy were determined in previous experiments by changing the length of exposure time to pyrrole vapors (1-2, 10, 20 or 60 min.) and the concentration of the FeCl₃/THF solution (5 or 9% w/w). The films obtained from 5% solution and 20 min. present good elec-

troactivity. In these synthesis conditions the cyclic voltammograms are reproducible and clearly show defined redox peaks.

Figure 1 shows the cyclic voltammograms of pure PPy and the PPy/EPDM rubber blend (film thickness = 100 μm) at different scan rates. The behavior shown by the PPy/EPDM blend is similar to pure PPy. Oxidation peaks are anodically shifted when the scan rate increases. However, when the direction of the scan rate is reversed (cathodic sense), the blend response is slower. Further, for the blend, the peak currents (anodic and cathodic) are lower than pure PPy for the same scan rate. The same behavior was observed for blends with higher thicknesses (EPDM film thickness = 200 or 400 μm). The dependence of the anodic peak current with scan rate is expressed by $i_{pa} = Av^x$, as shown in Fig. 2. i_{pa} , A and v represent anodic peak current, a constant and the scan rate, respectively. The x value was 0.50 ± 0.05 for the blends independent of the EPDM film thickness. For pure PPy, x was 0.96 ± 0.05 . These results show that for pure PPy the electroactive material is located on the electrode surface and is not involved in a diffusion process (thin layer behavior). For the PPy/EPDM blends the redox reaction is controlled by the linear semi-infinite diffusion.

Figure 3 shows the variation of the anodic peak potential as a function of anodic peak current. We always observed straight lines. Their slopes represent the ohmic drop created by the electrolyte and the ohmic resistance of the

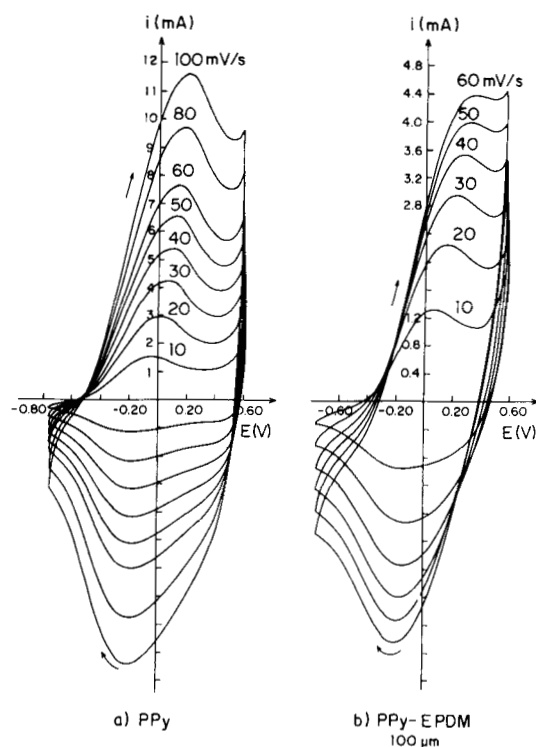


Figure 1. Cyclic voltammeteries at different scan rates for: a) pure PPy, and b) PPy/EPDM rubber blend (EPDM film thickness = 100 μm).

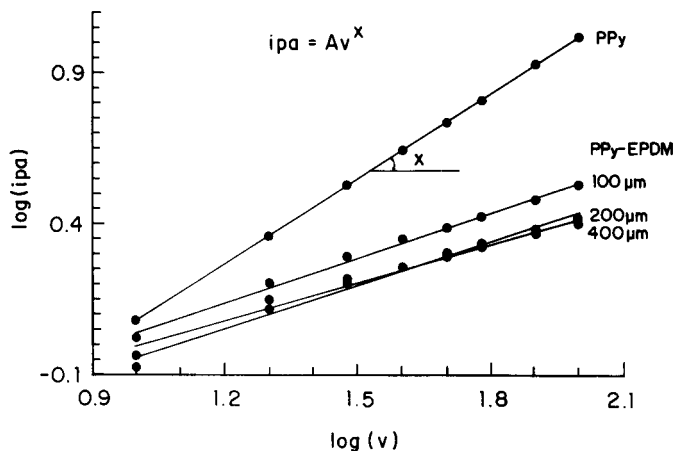


Figure 2. Log(*i*_{pa}) vs. log(*v*) for pure PPy and PPy/EPDM blends with different EPDM film thickness.

polymer. We observed that the resistance for pure PPy ($37 \pm 7 \Omega$) is lower than for blends. When the EPDM film thickness increases from 100 to 200 μm , the resistance increases from 135 ± 50 to $211 \pm 20 \Omega$. It is important to note that the increase in EPDM film thickness from 200 to 400 μm ($209 \pm 10 \Omega$) does not change the resistance value.

The results obtained by impedance spectroscopy are presented in a Nyquist diagram (imaginary part as a function of the real part of the impedance). The experiments were carried out with blends (different EPDM film thicknesses) and pure PPy in different oxidation states (in forward and reverse direction). We always observe hysteresis, as shown for pure PPy, and a semicircle in the high frequencies range, as shown in Fig. 4. The hysteresis in the electrochemical process of conducting polymers has been associated with the conformational changes in the polymer backbone⁴, solvent and electrolyte movement into the film⁴, mechanical properties of

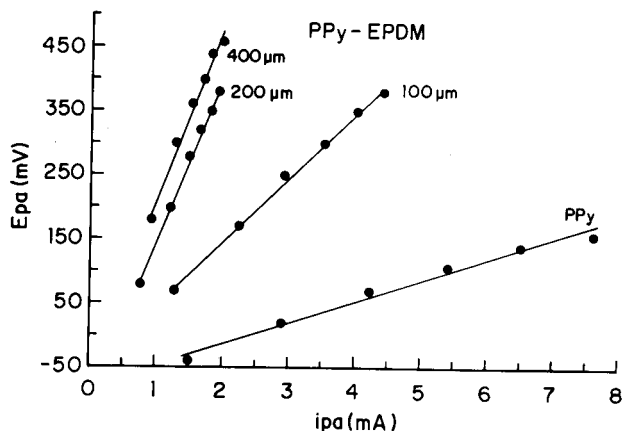


Figure 3. Anodic peak potential as a function of anodic peak current for pure PPy and PPy/EPDM blends with different EPDM film thickness.

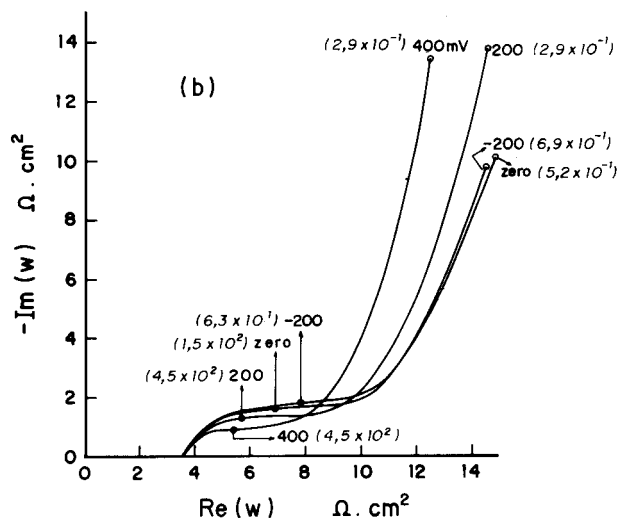
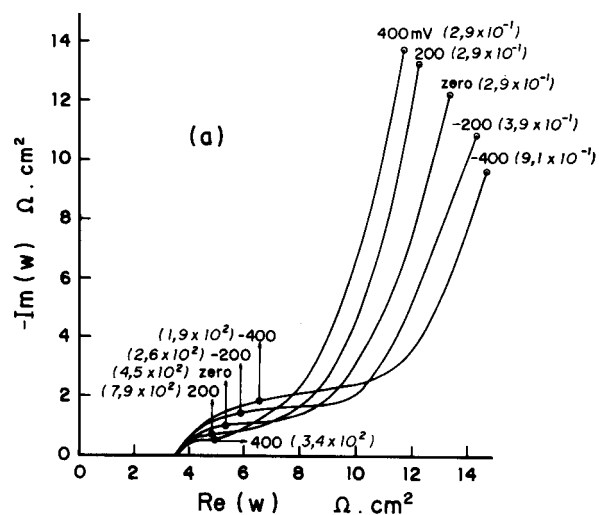


Figure 4. Impedance diagrams for pure PPy under different potentials: (a) forward direction (from 0.40 to -0.40 V), and b) reverse direction (from -0.40 to 0.40 V). The numbers in parentheses represent the frequency (Hz) at the respective points.

conducting polymers⁵, or electrical conductivity evolution between the reduced and oxidized states⁶. The semicircle is characteristic of a charge transfer resistance of the redox reaction, R_{ct} , parallel with the double layer capacitance of the electrode, C_{dl} . The semicircle intersection with the real axis is shifted to 4-5 $\Omega \cdot \text{cm}^2$. This point provides the electrolyte resistance value, R_o . R_{ct} is given by the distance between the two intersection points of the semicircle with the real axis. C_{dl} can be calculated from the frequency corresponding to the maximum of the semicircle. The low frequency part of the diagram, characterized by a nearly vertical line, reveals the existence of limiting capacitance, C_l . In Fig. 4, when PPy is reduced (the potential decreases) the diameter of the semicircle increases. This behavior is explained by an increase of the charge transfer resistance. When the

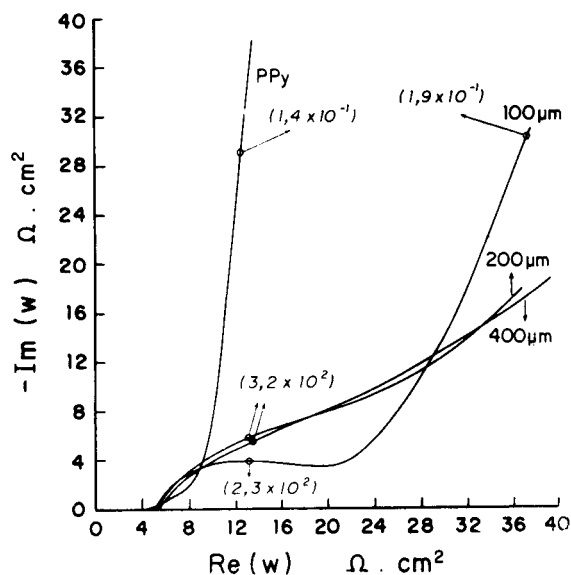
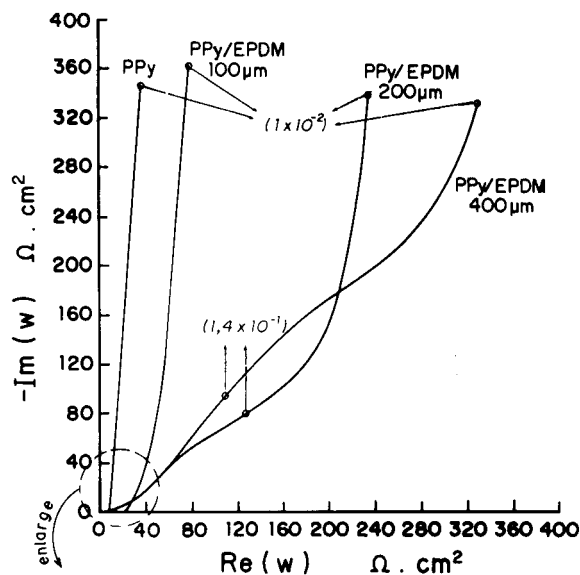
Table 1. R_{ct} for pure PPy as a function of applied potential.

Direction	R_{ct} ($\Omega \cdot \text{cm}^2$)	E (V)
Forward	1.5 ± 0.5	0.40
	1.8 ± 0.5	0.20
	2.2 ± 0.6	0
	2.8 ± 0.8	-0.20
Reverse	3.5 ± 0.9	-0.40
	3.2 ± 0.8	-0.20
	2.8 ± 0.6	0
	2.3 ± 0.9	0.20
	2.0 ± 0.8	0.40

potential decreases, reduction occurs, the exchange current of the reaction decreases and R_{ct} increases, as shown in Table 1. For blends with EPDM film thickness = 100 μm , the impedance behavior is similar to pure PPy, but here the diameter of the semicircle is larger.

When the EPDM film thickness is increased from 100 to 200 or 400 μm , the behavior of the impedance diagrams deviates from the ideal behavior, and shows a tendency to present two semicircles, as in Fig. 5. This behavior might be associated with the morphological differences that these materials present, as Fig. 6 indicates. The morphology of the blends changes from a very porous to a compact and smooth structure when the EPDM film thickness increases from 100 to 400 μm . Further, for the blend with a 400 μm thickness we verify clear phase segregation. We believe that this phase segregation could cause the differences observed in the impedance diagrams.

Table 2 shows the different parameters obtained for pure PPy and the blends with different EPDM film thickness, at 0.20 V. The magnitude of the uncompensated ohmic resistance is almost the same in all cases, and shows the small influence of EPDM film thickness on R_o . R_{ct}

**Figure 5.** Impedance diagrams for pure PPy and PPy/EPDM blends with different EPDM film thickness, at 0.20 V. The lower curves represent an enlargement of the high frequency region of the upper curves. The numbers in parentheses represent the frequency (Hz) at the respective points.**Table 2.** Parameter values for pure PPy and PPy/EPDM blends with different thickness, at 0.20 V (vs. SCE).

Parameter	PPy	PPy/EPDM		
		100 μm	200 μm^*	400 μm^*
R_o ($\Omega \cdot \text{cm}^2$)	3.9 ± 0.3	5.3 ± 0.8	5.1 ± 0.2	5.8 ± 0.6
R_{ct} ($\Omega \cdot \text{cm}^2$)	4 ± 1	16 ± 3	80 ± 20	80 ± 40
C_{dl} ($\text{F} \cdot \text{cm}^{-2}$) $\times 10^4$	1.6 ± 0.5	1.1 ± 0.3	1.7 ± 0.6	1.0 ± 0.3
C_l^{**} ($\text{F} \cdot \text{cm}^{-2}$) $\times 10^2$	4.8 ± 0.4	5.4 ± 0.3	4.1 ± 0.5	3.6 ± 0.4

*The parameters R_o , R_{ct} and C_{dl} were obtained by considering the semicircle at high frequencies.

** C_l values were obtained by considering the 10^{-2} Hz frequency, in all cases.

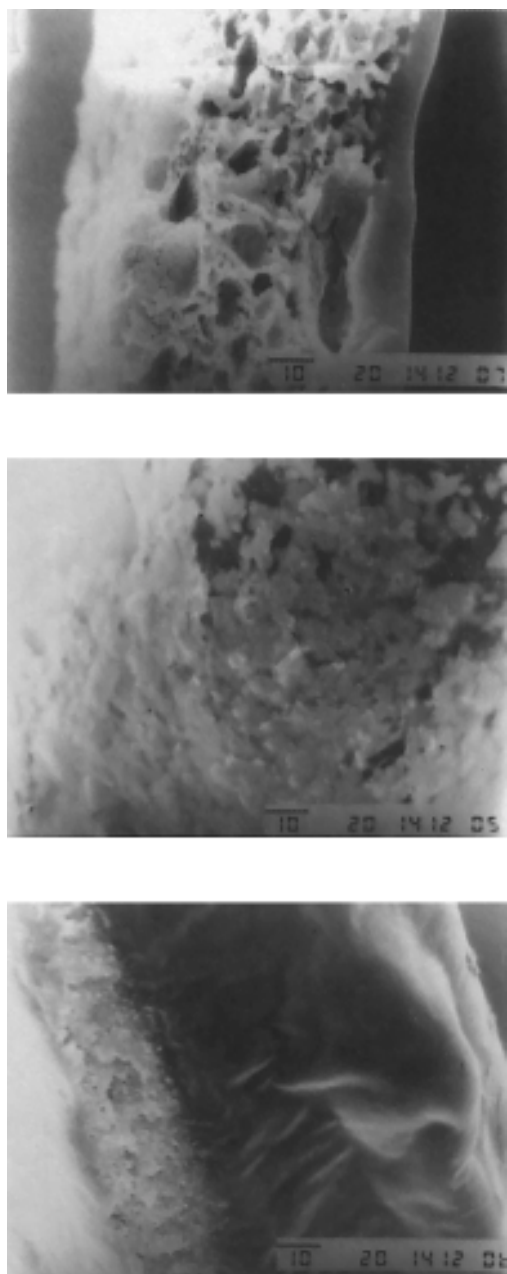


Figure 6. Scanning electron microscopy of PPy/EPDM blends with different EPDM thicknesses: a) 100, b) 200, and c) 400 μm .

increases when the EPDM film thickness increases, showing that the electronic transfer is weaker and confirming the lower electroactivity of the thicker blends. C_{dl} obtained in all cases are near $100 \mu\text{F}\cdot\text{cm}^{-2}$, and agrees with the C_{dl} values observed by other authors⁷. The C_1 values decrease slowly when the EPDM film thickness increases. These results agree with the elemental analysis for the blends. The polypyrrole weight fractions in the blends, X_{PPy} , were as follows: PPy/EPDM (100 μm) = $13 \pm 2\%$, PPy/EPDM (200 μm) = $10 \pm 3\%$ and PPy/EPDM (400 μm) = $6 \pm 1\%$. Thicker blends containing less PPy show lower C_1 values, as expected.

Conclusions

It was verified that PPy obtained by pyrrole oxidation with FeCl_3 present a redox behavior similar to PPy prepared by electrochemical synthesis. PPy/EPDM rubber blends are self-supported films, with good mechanical properties and electroactivity. Thicker blends (EPDM film thickness = 200 or 400 μm) have a characteristic impedance diagram that will be studied in more detail in future work.

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