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Characterization of Conductive Natural Rubber by Cyclic Voltammetry and Electrochemical Impedance Spectroscopy

Natural rubber (NR) is an excellent insulator and is commonly used in the electric and electronic industry. On the other hand, a blending of NR with carbon black powder produces conductive materials with the qualities of the insulator composite. Studies of conductivity, cyclic voltammetry and electrochemical impedance spectroscopy were carried out to characterize the new material, showing good enhancement for the electron transfer processes. The charge-transfer resistances were 0.75 and 5.1 kΩ for the KPO and KPO, respectively. This values shows that the charge transfer resistance increases about 6.8 times.
Key words: *Natural rubber, Composite, Impedance spectroscopy*

1. INTRODUCTION

Natural rubber (NR) is an excellent insulator material, unsaturated elastomer with some good properties, such as high strength, outstanding resilience, high elongation at break and due to this fact is commonly used in electric and electronic industry. NR latex, a renewable polymeric material displaying excellent physical properties, is widely used in the manufacture of thin film products.

On the other hand, the blend of NR with a conductive composite, as carbon black powder, can produce a conductive material with the same qualities and properties of the rubber. This important technological process can be used to prepare materials with high performance, when compared to the individual constituents [1,2]. An adequate polymer-blend process requires precise information about the chemistry and physics of the constituents, aiming to promote good and homogeneous dispersion, as the control of the viscosity, elasticity and pressure are important for the optimization of the process [3].

As example, metallic powders [4,5] and metallic fibers have been used for promote and increase the electrical conductivity in polymers. The same procedure have been this kind of procedure could be used to promote the conductivity in NR.

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In this context, the Eeonomer® compost represents a new class of conducting additive used to promote *in-situ* polymerization processes, as the fabrication of polyaniline and polypyrrol with carbon black [6]. These composites, produced in neutral reaction, are thermally stable and compatible with the conditions of the blend process, presenting better electric and mechanical properties when compared with the traditional conducting additives. The high thermal stability of these composites is independent of pH and the electric conductivity remains relatively unaffected in a range of pH (0 to 8).

This kind of composites can be used in different applications, since that produces good electrochemical enhancement. Thus, for this case, electrochemical responses of the polymeric composites can be used satisfactorily to determine the redox processes of doped materials [7].

Some electrochemical processes depend directly of the pH and the electro-active species contained in solution [8,9], two important parameters to be observed in industrial processes. In a recent report, da Silva *et al.* [10] showed that the dependence of linear capacitive currents in function of the scan rate (v) could be used to determine the differential capacitance (C_d) in the interface electrode/solution and demonstrated that the cyclic voltammetry can be useful to determine the behavior of the capacitive currents.

The characterization of new polymeric materials has also carried out by cyclic voltammetry and impedance spectroscopy (EIS) techniques, aiming to determine the superficial electrochemical processes [11], charge transfer resistances on the interface solid/liquid [12] and double-layer capacitance [13].

In this context, the aim of this work is characterize conductive natural rubbers by conductivity measurement and study the electric and electrochemical properties of the materials by cyclic voltammetry and electrochemical impedance spectroscopy techniques.

2. EXPERIMENTAL

The natural rubber of Hevea Brasiliensis was provided by Borracha Paulista Indústria e Comércio. The carbon black from Degussa AG company was used as received. The particle size and specific surface area of CB was 40 nm and 1400 m^2/g, respectively. The conducting additive used KPO (15%) (Eeonomer® P20-5DB/S) and KP20 (25%) (Eeonomer® KP20-7DNF) by Eeonyx Co. (USA). This composite are a new generation of polymers modified with carbon black. The electrodes were prepared by mixing carbon black and respective composite conductor following the procedure reported elsewhere [8]. The processing conditions were temperature 70ºC, rotation 80 rpm and time of mixture 15 min. After 24 h, the molding was made by pressure (4 MPa) and hot (145ºC) during 20 min.

The electric conductive of the electrodes was measured for the method of four points. The electrochemical experiments were performed in a three-electrode Pyrex® glass cell having degassing facilities for bubbling N_2. The auxiliary electrode was a 2-cm^2 Pt foil and, unless otherwise stated, all measurements were carried out using as reference a Hydrogen Electrode in the Same Solution (HESS). All reagents used in this work were Merck P.A. quality and the water was purified by a Milli-Q system from Millipore. Steady-state polarisation curves and cyclic voltammetry were carried out using a mod. 273 EG&G PARC electrochemical instrument. Electrochemical impedance spectroscopy (EIS) experiments were carried out in a 0.5 mol L^{-1} H_2SO_4 solution using a Voltalab potentiostat mod. PGZ 402, controlled by the Voltamaster 4.0 Software.

3. RESULTS AND DISCUSSION

Figure 1 showed the curves of the electrical conductivity *vs* quantitative of composite that the incorporation of composite conductive promoted an increase of 1 S/cm in the electrical conductivity. The KPO composite presented the low limit of percolation (10^{-2} S/cm for 10 phr). The literature reports [14, 15] that the percolation behaviour of natural rubber is depended of the superficial area. Natural rubber with high superficial area presented the low limit percolation possessing high liquid superficial accessible and better exhausted. It is observed that the composites KPO showed high conductivity followed by KP20 (25%). These results are quite promising when compared carbon black with natural rubber [14,16,17] and of some conductive blend of polyaniline and polypirrol [18-20]. In first case it is necessary a great amount of carbon black to obtain a reasonable electric conductivity being caused damage in the mechanic properties. In the second case, the literature [21, 22] demonstrated that there is great difficulty in the processing of blends conductive polymer tends like these quite inferior values to those found. The values obtained in this work are in the wide of semiconductors, with a wide band of application for these composites, as static waste of charge and electromagnetic interference protection.

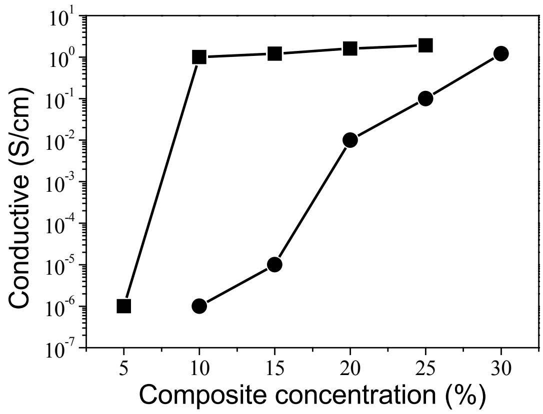
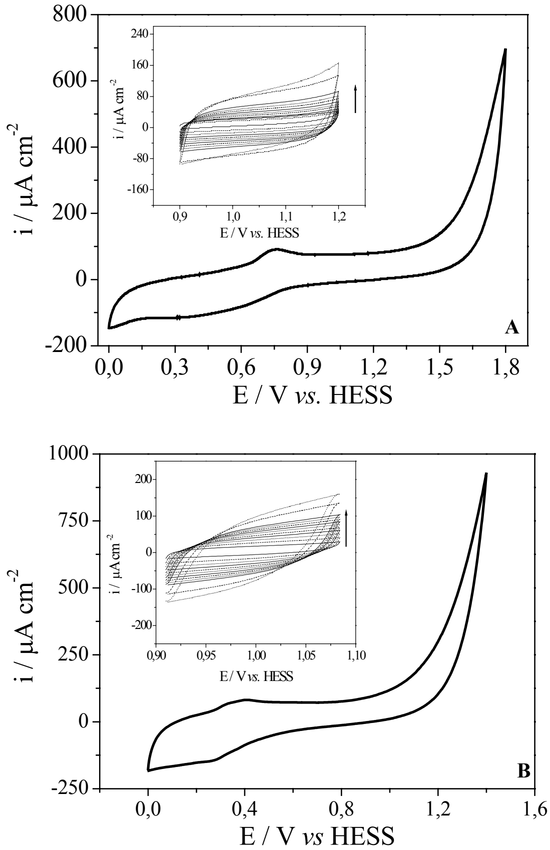


Figure 1 - Electric conductivity curves vs *composition concentration for KPO (■) and KP20 (●)*

The electrochemical behavior of the composites, KPO e KP20 was studied by cyclic voltammetry and the curves are presented on Fig.2. For both materials, a redox process can be observed and it could be related to the quinine/hydroquinone or poly(methoxyaniline) electrochemical reaction [8]. The potential peak diference (ΔE_p) to the KPO (15%) is about 98 mV (a cathodic peak near of 0.75V and an anodic undefined peak in around 0.69 V). For the KP20, the difference of ΔE_p is about 78 mV (a chatodic undefined peak in 0.35V and an anodic undefined peak in 0.28 V).



A)

B)

Figure 2 - Cyclic voltammetry studies for (A) KPO and (B) KP20 composites in 0.5 mol L^{-1} H_2SO_4 solution. v = *10 mVs^{-1}. The inserts shows the double-layer responses for both materials*

The inserts of the Fig 2 shows the capacitive cyclic voltammetry profiles, carried out in a 0.5 mol L^{-1} H_2SO_4 solution. The insert of the Fig. 2(A) and 2(B) presents the dependence of capacitive currents in function of the scan rates for a KPO and KP20 composite respectively. These two graphics present a tendency to a steady state behavior. It observed that in 0.90 and 1.2 V vs. HESS KPO and in 0.9 and 1.1 V vs. HESS to KPO the current value is independent of the scan rate. This behavior is a typical response of a porous material, according to previous reports [10,23].

This kind of capacitive responses can be represented by an equivalent circuit (EC) that contains a resistance (R), representing all resistive contributions in the system (i.e, resistance of the solution, of the porous and of the materials) and a capacitor, representing the electrode/solution interface (double-layer capacitance).

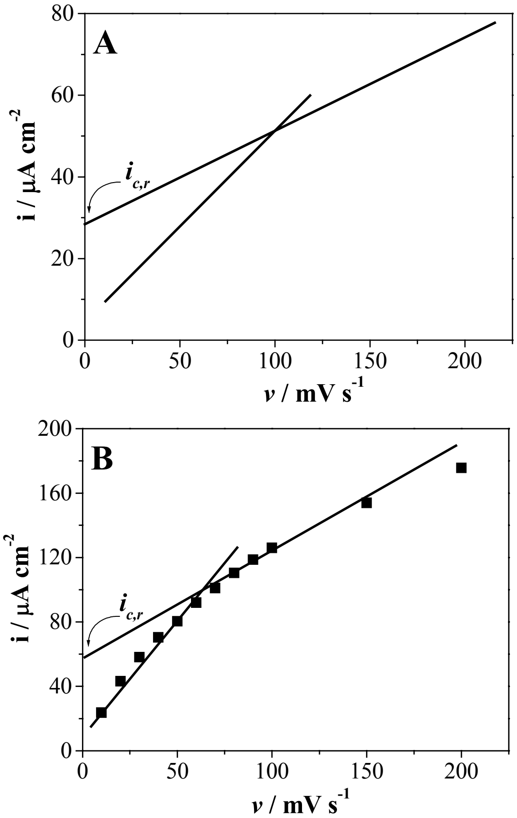
According to the Kirchhoff's law, the capacitive current for electric circuit can be expressed by a dependence of the currents in function of the potential, as follow [10].

$$i_c = C_d v + \left(\frac{E^*}{R} - C_d v \right) exp \left[\frac{-\left(E - E^*\right)}{RC_d v} \right] \quad (1)$$

Retyping the equation in function of the time and considering that $E^* = E_{\text{inicial}} = 0$, the approximation is:

$$i_c = C_d v \left[1 - exp \left(\frac{-E}{RC_d v} \right) \right] \quad (2)$$

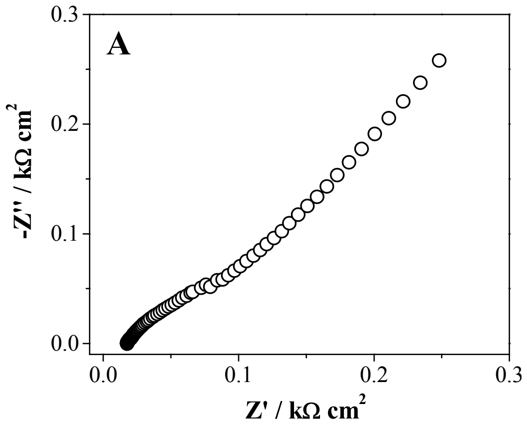
It is valid for a homogeneous material that contains porosities. This model is complex and it was exhaustively described by Xianbo and Juntao [23], when the authors described that the approximation $i_c \sim C_d v$ is valid. The Fig. 3 (A) and (B) show the i_c vs. v behavior for both studied materials. The graphics behavior present two linear regions that were obtained in high and low scan rates. Da Silva [10] discussed that the two distinct slopes were obtained in this kind of experiment: The first slop is related to the low scan rates and information about capacitance values can be obtained and the second slope and generally presents a capacitance value 20% higher than that first one, due to is related charge accumulation processes.



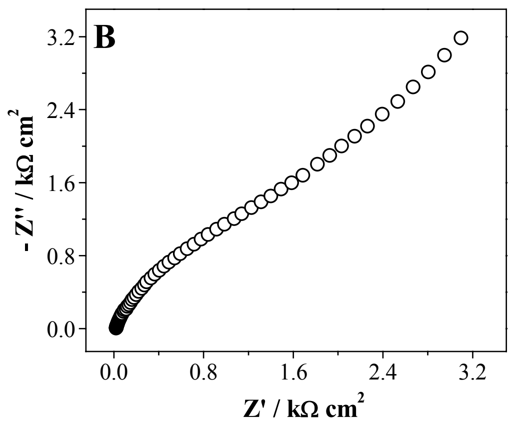
A)

B)

Figure 3 - Linear dependence of the capacitive currents in function of the scan rates for (A) KPO and (B) KP20 composites. The capacitive current values were obtained directly by the Fig. 2.



A)



B)

Figure 4 - Nyquist plots for (A) KPO and (B) KP20 in 10^{-3} mol L^{-1} $K_4Fe(CN)_6$ + 0,5 mol L^{-1} H_2SO_4 solution. The measurements were carried out with fixed potentials of 0,7 V and 0,3 V for KP20 and KP20.

4. CONCLUSION

Natural rubber modified with carbon black composites were studied in this work by conductivity, cyclic voltammetry and electrochemical spectroscopy impedance techniques. The conductivity studies showed that the KPO composite presented a higher conductivity, if compared with the KP20 composite (the materials is a typical conductivity of semi-conductors), probably, due to the formation of a inactive polymer in the electrode surface during to the polarization.

The initial cyclic voltammetry studies show the presence of quinone in the synthesized composites and the study of the dependence of the scan rates in function of the capacitive currents for the KPO and KP20 returns values of 4.6 and 0.12 mF cm^{-2} respectively. This behavior can be related to the charge of carbon black and polyanilyne in the samples. The relevance of this measurement can be related to the active electrochemical surface, directly proportional with the capacitance in an electrochemical study. The electrochemical impedance spectroscopy studies show that increasing the amount of carbon black in the sample, the charge transfer resistance increases 6.8 times in agreement with the conductivity studies.

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REZIME

KARAKTERIZACIJA PROVODNOG PRIRODNOG KAUČUKA CIKLIČNOM VOLTAMETRIJOM I ELEKTROHEMIJSKOM IMPEDANCNOM SPEKTROSKOPIJOM

Prirodni kaučuk je odličan izolator i koristi se u elektroindustriji i elektronici. Mešanjem prirodnog kaučuka i crnog ugljeničnog praha mogu se proizvesti provodni materijali. U ovom radu su ispitivani takvi materijali korišćenjem ciklične voltametrije i elektrohemijske impedancne spektroskopije, pri čemu je nađen dobar prenos elektrona u tim kompozitima. Otpor prenosu elektrona je bio 0,75 i 5,1 kΩ za KPO i KP2O, respektivno. Ove vrednosti pokazuju da otpor prenosu elektrona je oko 6,8 puta veći kod KP2O.

Ključne reči: *prirodna guma, kompozit, Impedancna spektroskopija*