

New Composite Biopolymer with Conductive Properties Obtained from Cassava and Poly Starch (3, 4-Ethylenedioxythiophene)

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Abstract

Objectives: To use of cassava (*Manihot esculenta Crantz*) starch to prepare a new composite biopolymer from starch and poly (3,4-ethylenedioxythiophene) starch/PEDOT with conducting properties and redox activity. **Methods/Analysis:** The synthesis of the composite biopolymer starch/PEDOT was carried out by thermochemical process. Its electrochemical properties were studied by means of cyclic voltammetry and the structural characteristics were determined with infrared spectroscopy. **Findings:** The results showed excellent redox behavior of the composite biopolymer starch/PEDOT, with oxidation and reduction of the polymer at 0.38 V and - 0.43 V potential, respectively. In addition, the kinetic of the composite biopolymer films shows to be faster and more sensitive response than the pure starch and pure PEDOT films. Moreover, a study was conducted with infrared spectroscopy to determine possible interactions or structural changes in the polymer chains of starch when combined with PEDOT. The results of these studies showed that there is an interaction between the molecules of both polymers and an improvement in the conductivity of the starch polymer. **Novelty/Improvement:** In this way, a composite conductive biopolymer stable from cassava starch and PEDOT was obtained, which has excellent electrochemical properties, which makes it a material with technological potential in chemical sensor or charge storage.

Keywords: Composite Biopolymer, Conducting Polymer, Cassava Starch, Electrochemistry, Poly (3, 4-ethylenedioxythiophene)

1. Introduction

Conductive polymers are materials of great scientific and technological interest, because they bring together representative properties of traditional polymers such as corrosion resistance and flexibility, with the ability to conduct electric current of the metals. The good stability and conductivity of the polymers with the monomeric

aromatic or heteroaromatic have made them materials with excellent technological expectations, giving rise to their application in multiple applications, among them the most outstanding are, their use as electromagnetic shields, intelligent windows, Anti-corrosion coatings, solar cells, LEDs, biosensors, artificial muscles, chemical sensors, etc¹⁻⁶.

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The ability of the conducting polymers to conduct electricity is due to its molecular architecture with the conjugate bonds that along the polymer chains allow the movement of charges generated by oxidation or reduction. The conjugate structures of the conducting polymers have the fundamental property of having π orbitals extended over the entire structure. An electron located at one of these levels is characterized by being displaced, that is, it has freedom of movement. However, this fact is not sufficient for a polymer to conduct the electric current; it is necessary to cause in your chain a distortion in the conjugation system. This alteration consists of extra electrons (oxidation) or insertion of electrons (reduction) in the polymer chain, by means of a doping process^{7,8}. The more studied polymers for their good conductivity, stability and processability in polypyrrole (PPy), poly 3-methylthiophene (P3MT), polyaniline (PANI), polyacetylene (PA) and poly 3,4-ethylenedioxythiophene (PEDOT)^{3,8,9}.

PEDOT is an insoluble conductive polymer that has widely demonstrated its ability to form flexible films with thermal, atmospheric stability and has excellent electrical conductivity. This polymer may be synthesized by a number of methods, the most common being chemical polymerization through the use of an oxidizing agent such as ammonium sulfate, hydrogen peroxide or ferric chloride and electrochemical polymerization through the application of a stream anodic oxidation. Despite its interesting electrochemical properties and good stability, its applications are restricted by its mechanical properties, which in most cases limit its industrial use.

In the quest to expand the technological possibilities of PEDOT, this polymer has been synthesized in combination with other traditional polymers of petrochemical origin such as Polystyrene Sulfonate (PSS), Polystyrene (PS) and Polyvinyl Alcohol (PVC) among others, presented in most of the cases improvements in its properties and the preservation of the high conductivity and electro activity. In addition, the search for non-polluting and low environmental impact polymer materials has led to

the use of biopolymers to prepare composites with conductive polymers^{8,10}. On this wise, the combination of materials of synthetic origin as the conductive polymers with the biopolymers has opened the possibility to obtain new materials that combine the advantages of both. The combination of conductive polymers with biopolymers is a recent issue and has been reported work combining conductive polymers with starch, cellulose, dextrans and chitosan¹¹⁻¹³. In the particular case of PEDOT, it has been combined in a composite material with lignin, DNA, hyaluronic acid, and dextran^{12,13}.

The use of natural polymers has attracted attention due to its great environmental advantages, low cost, availability and biodegradability. All these properties have made them the object of numerous research and industrial developments. Polysaccharides such as starch have been used to develop packages, pouches, edible coatings. Recently the use of maize and cassava starches has been reported in the elaboration of composites with PPy¹⁴. In this sense, it is important to say that although in the literature we find work that describes the combination of cornstarch to form aerogels with PEDOT, The use of cassava starch for the formation of films in combination with PEDOT has not been reported.

In this article, we present the preparation of composite biopolymer films obtained from the use of cassava starch and poly 3,4-ethylenedioxythiophene. The generation of the films has been carried out by thermochemical synthesis and their conductive properties and electrochemical activity have been studied using cyclic voltammetry techniques. In addition, a study was also performed with infrared spectroscopy to determine the structural characteristics of the films.

2. Materials and Methods

2.1 Reagents and Materials

The reagents, lithium perchlorate, glycerol, polyethylene glycol, glutaraldehyde and 3,4-ethylenedioxythiophene

were analytical grade and purchased from Sigma-Aldrich. The solutions were prepared with milli-Q water. The cassava starch used in this study was obtained from the variety *Manihot esculenta* Crantz, through the traditional method of washing, peeling, grating, and screening, decantation, drying and spraying. The purity of the starch was determined by difference, taking into account the content of proteins, fats, ash and raw fiber, through the application of the official methods of AOAC¹⁵.

2.2 Films Synthesis

The cassava starch conducting films were prepared by thermochemical synthesis¹⁶. For this, starch (3.0 g) was dissolved in 100 mL of water at pH 9 at 70 °C, and then were auditioned 2 g of glycerol, 1.5 g of polyethylene glycol and 1 g of lithium perchlorate. The solution was again heated to 75°C with constant stirring for 15 min and subsequently deposited in teflon containers and dried in an oven at 70°C for 48 h to obtain the starch biopolymer films. Under this same procedure, unplasticized starch biopolymer films were prepared. For the synthesis of composite biopolymer starch/PEDOT, the synthesis was carried out in a manner similar to the plasticized films (glycerol and polyethylene glycol) and the salt (lithium perchlorate), adding 3 g of 3, 4-ethylenedioxythiophene. The thickness of the films was measured with a micrometer to ensure that in all cases they were worked with similar thicknesses.

In addition, PEDOT films were synthesized to make the comparative studies with the composite biopolymer films starch/PEDOT. This synthesis was performed by electrochemical oxidation in a cell of three electrodes; saturated calomel reference electrode, auxiliary platinum electrode and a platinum working electrode where the electrodeposition of the PEDOT was carried out. The electrosynthesis was made from a 0.1 M solution of lithium perchlorate and 0.2 M of 3,4-ethylenedioxythiophene by chronoamperometry applying 1.1 V of potential

for 500 s. Once generated, the film was detached from the substrate with ultrasound for 5 s.

2.3 Films Characterization

The infrared spectroscopic characterization was performed with a Shimadzu IRTracer 100 spectrometer with ATR (Total Attenuated Reflectance) type IIA with diamond crystal, at 25 °C, with a wave number range between 4000-550 cm⁻¹ and a resolution of 4 cm⁻¹. All spectra were recorded with 100 scans. The electrochemical characterization was carried out by Electrochemical Impedance Spectroscopy (EIS) and cyclic voltammetry using a potentiostat/galvanostat FRA 2263 PARSTAT (Princeton Applied Research) controlled by PowerSuite software. Electrochemical impedance measurements were performed on one-cm² samples at room temperature in a frequency range of 1 Hz to 0.1 MHz and 10 mV (rms). Studies with cyclic voltammetry were recorded with a potential scanning speed of 100 mV s⁻¹, in a potential range of -1.0 V to 1.0 V. In all cases, 10 replicates were performed. All potentials were measured in relation to the Open Circuit Potential (OCP), which had a value of 0.15 V. The measurement cell, both for cyclic voltammetry and for the spectroscopy of Impedance, consisted of a solid sample cell composed of two 2 x 2 cm stainless steel sheets fixed on acrylic plates, which were closed, by a system of nuts¹⁴. To carry out the measurements, the films were cut into samples of 1 x 1 cm and placed between the steel sheets of the sample holder.

3. Results and Discussion

The starch extraction process of the cassava tubers allowed isolating starch as a bright white powder in a yield of 12.3% and the purity determined by the AOAC method was 99.1%. This starch was used to prepare the biopolymers films.

To analyze the different results obtained, it was necessary to prepare pure PEDOT and pure starch films, which

allowed us to compare their behavior as individual polymers and as a composite biopolymer starch/PEDOT. The starch and composite biopolymer films were prepared following the same procedure, which was described in the experimental section. On the other hand, the PEDOT films were made by electrochemical polymerization from a solution of EDOT and lithium perchlorate as detailed above.

The starch films showed a white color and became opaque, whereas the starch films containing PEDOT (starch/PEDOT) turned light brown, which darkened until the 5 days of preparation. The darkening allows evidencing the polymerization process, which was slow because in the synthesis mixture there was no strong oxidant. In this case, the heating promotes the formation of the 3,4-ethylenedioxythiophene cation radical and consequent thermo-polymerization of PEDOT¹⁷.

Figure 1 shows the recorded infrared spectra of the films obtained and the cassava powder starch spectrum. When comparing the powder starch spectrum (Figure 1 (a)) with the starch film made with plasticizers without PEDOT (Figure 1 (b)), it can be seen that there is no significant difference in the characteristic bands for this biopolymer. However, a displacement of some of its main bands is observed. This phenomenon of band shift is caused by the difference in molecular organization of the polymer chains, which affects the crystallinity of the same; this fact has been reported in the literature by different authors^{14,18}. Recently it has been proposed that the position of the bands can be used and correlated with the crystallinity of the starch molecules¹⁹.

In the powder starch spectrum (Figure 1(a)), a broad band at 3379 cm^{-1} corresponding to the vibration of the OH bonds is observed, bands at 2931 cm^{-1} and 1651 cm^{-1}

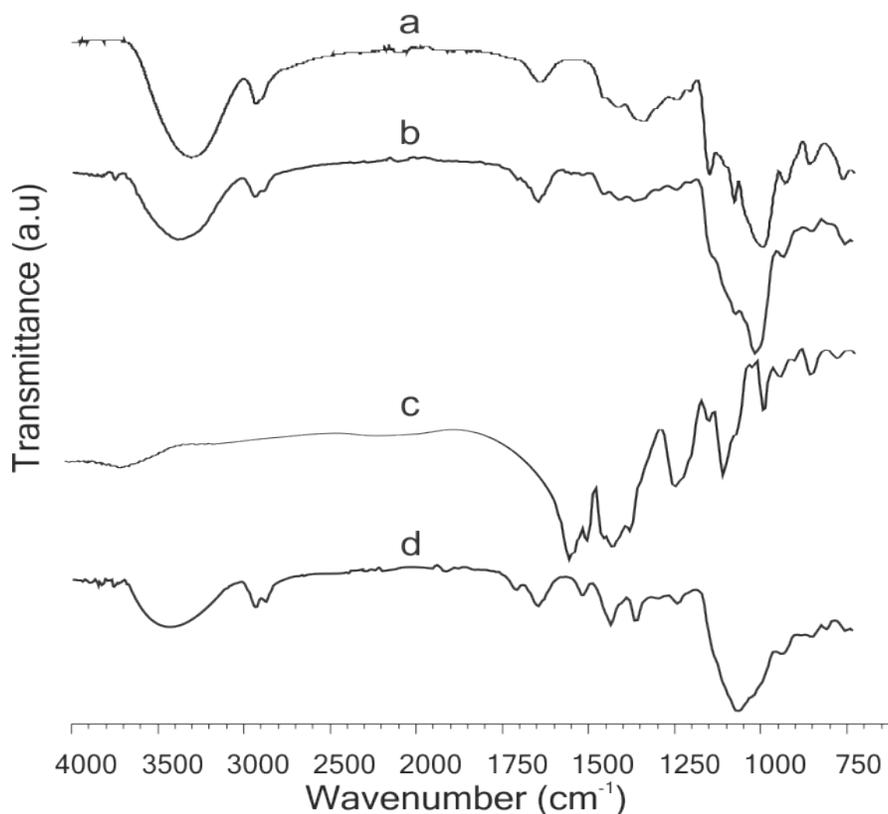


Figure 1. FTIR spectra of. (a) Cassava starch powder. (b) Cassava starch film. (c) Starch film/PEDOT. (d) PEDOT film.

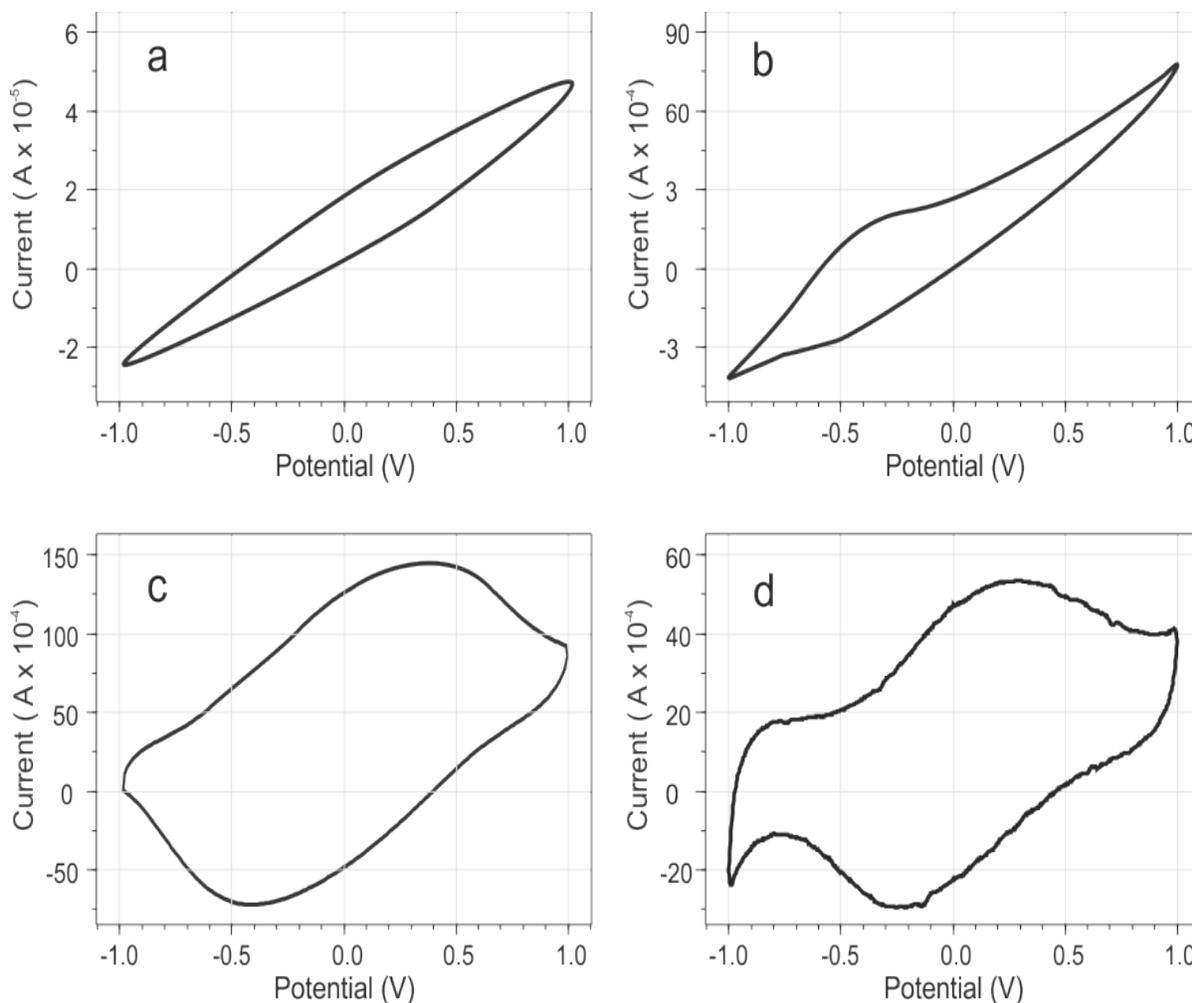


Figure 2. Cyclic voltammetry of polymeric films. (a) Unplasticized starch. (b) Plasticized starch. (c) Biopolymer composite starch/PEDOT. (d) PEDOT. Scan rate: 0.1 V s⁻¹.

are observed. Vibration of the CH bonds and the flexion of the OH (absorbed water). In addition, bands at 1458 cm⁻¹, 1411 cm⁻¹ and 1142 cm⁻¹ are present, which can be assigned to the C-H deformation of the CH₂, C-O and C-C respectively. The stretching of the C-O-H, C-OH and C-O-C bonds, causes the bands 1072 cm⁻¹, 1018 cm⁻¹ and 933 cm⁻¹. The modes of vibration of the groups C-H and CH₂ are present in 848 cm⁻¹ and 756 cm⁻¹. The bands of the starch film are similar to those of the starch powder. However, as mentioned above the positions of some of the principal bands are in positions somewhat displaced due

to the crystallinity of the polymer structure. In Figure 1 c, the PEDOT spectrum is observed. The bands observed at approximately 1512 and 1301 cm⁻¹ are assigned to the tension mode of C=C and the tension in the C-C ring, respectively. The vibration of C-O-C in the ethylenedioxy can be seen at 1196, 1134 and 1053 cm⁻¹. The vibration bands of C-S-C on the thiophene ring are observed at approximately 940, 910, 825 and 678 cm⁻¹. On the other hand, when comparing the starch and PEDOT films with those of the composite biopolymer starch/PEDOT (Figure 1 (d)); it is observed that in the spectrum of the compos-

Table 1. Assignment of infrared spectra bands (FTIR) of films of starch powder, plasticizer-free starch biopolymer, starch biopolymer with plasticizer, composite biopolymer starch/PEDOT and PEDOT.

Assignments	Wavenumber (cm ⁻¹)			
	Starch powder	Starch film	Starch/PEDOT film	PEDOT film
ν O-H	3248	3379	3501	
γ C-O	2930	2931	2920	
γ C-H	2903	2905	2892	
ν O-H	1651	1651	1651	
ν C=C			1523	1512
δ C-H	1415	1419	1408	1398
ν C-C	1335	1341	1347	1349
δ C-O	1141	1142	1142	
δ C-O-C	11020	1141	1175	1185, 1132, 1075
ν C-O-H	1087	1072	1059	
δ C-OH	1003	1018	1013	
ν C-S-C			1005	975, 917, 840
δ C-H	849	848	859	
δ CH ₂	756	756	761	

ν represents stretching, γ out-of-plane deformation and δ in-plane deformation

ite biopolymer the starch characteristic bands prevail. However, typical PEDOT bands are also observed, for example those related to the vibrations of C=C, C-O-C and C-S-C at 1523 cm⁻¹, 1175 cm⁻¹ and 1005 cm⁻¹, respectively. Table 1 summarizes the main bands observed in the FTIR spectra of starch powder, starch films, PEDOT

and starch/PEDOT biopolymer and their corresponding allocation.

The electrochemistry of the biopolymers films was studied by cyclic voltammetry. The results obtained from the composite biopolymer starch/PEDOT films were contrasted with those of PEDOT films, starch

films unplasticized, and starch films plasticized without PEDOT. Figure 2 shows the voltammograms obtained from each of the films studied.

In the Figure 2 can be observed that in the case of starch films unplasticized, no redox activity was generated, and non-faradic current was recorded, since the voltammogram lacks peaks. In contrast, in starch films plasticized if they exhibit redox activity, with an oxidation process at - 0.38 V and the reduction located at approximately - 0.52 V. To discard that the redox activity was produced by any of the compounds used as plasticizers, voltammetry measurements were made to each of them individually and none had redox activity. Thus, redox activity occurs only when the starch polymer film is generated with starch and plasticizers. This behavior may be due to the plasticizer compounds generating a rearrangement of charges in the polymer chain, causing possible structural changes and in consequence of their electrochemical properties. Additionally, the presence of lithium ions from lithium perchlorate generates greater charge mobility, affecting the conductivity and therefore its response to electrochemical stimuli.

The conductivity in the starch films may be due to the movement of Na^+ and Li^+ positive ions along the nega-

tively charged starch polymer chains by the reaction of some hydroxyl groups ($-\text{OH}$) in the films with the NaOH used to facilitate the dissolution of the starch and the LiClO_4 used in the synthesis (Figure 3).

The voltammetric response of the composite biopolymer starch/PEDOT films was drastically different from that of starch and was rather similar to that of the PEDOT film. With two peaks, one of oxidation at 0.38 V and one of reduction at -0.43 V. The peaks observed in the plasticized starch are completely masked by the peaks of the PEDOT reduction and oxidation processes. As a result, the voltammogram recorded in the composite biopolymer starch/PEDOT films is similar to that recorded in pure PEDOT films. In the curves obtained from the PEDOT films two peaks are observed, a peak that shows an oxidation process at 0.31 V and one product of the reduction at - 0.28 V. The curves of both types of films, PEDOT and composite biopolymer starch/PEDOT are similar in shape, however their redox potentials vary slightly.

The similarity in the PEDOT curves and the composite biopolymer starch/PEDOT may be because the PEDOT is a polymer with a much greater redox activity than the conductive starch (plasticized starch). In such

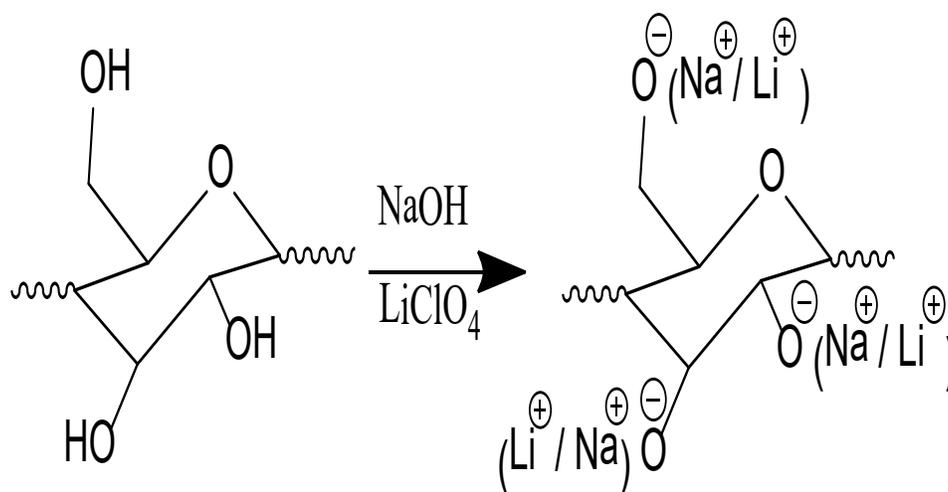


Figure 3. Alkalization reaction of starch with sodium hydroxide.

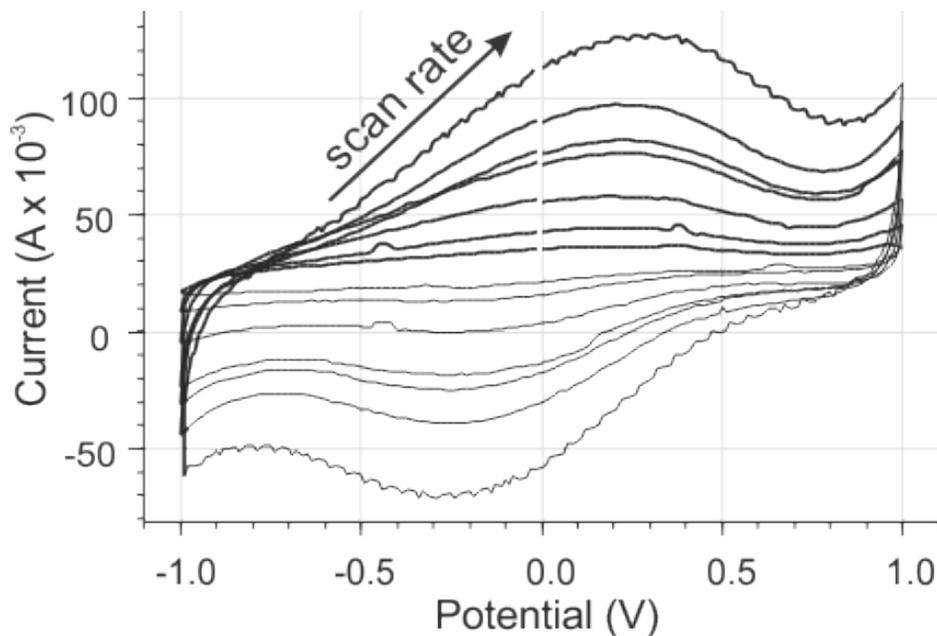


Figure 4. Cyclic voltammetry of composite biopolymer starch/PEDOT at different scan rate (10 mV/s to 500 mV/s).

a way that its greater intensity masks the processes of starch, making similar the responses of PEDOT and the composite biopolymer starch/PEDOT.

Additionally, the electrochemical dynamics of the films were studied by determining the relationship of the voltammetric sweep velocity (scan rate) and the current intensities of the oxidation and reduction peaks. In Figure 4, the voltammetric response of the composite biopolymer films starch/PEDOT is presented at different scanning rates (dE/dt). An increase in the intensity of the redox peaks can be observed as the scan rate increases.

By plotting the current intensities of the redox peaks recorded against scan rate, a linear relationship was obtained indicating a non-diffusion controlled process (Figure 5). This makes sense since the measurements were made in solid phase, in such a way that the charges that are displaced are the charges of the contractions trapped in the polymers and the movement of these dominates in the conduction process of the films. Figure 5 shows the dependence with the scanning rate of the redox peaks for

the composite biopolymer films starch/PEDOT (Figure 5 (a)). Dependency of the redox peak current on the PEDOT films was also observed (Figure 5 (b)). However, it is worth noting that in the case of composite biopolymer starch/PEDOT films, the linear relationship between the redox peak current and the sweep velocity was approximately 0.5 times higher and therefore faster than the PEDOT films. This result indicates that, in comparison with PEDOT films, the starch/PEDOT films show excellent dynamic character in redox processes and facilitate the transfer of charge within them and/or through the interface with the electrode cell. This behavior must be related to molecular ordering in the configuration and distribution of charges along the polymer chains of the composite biopolymer. It can be concluded that the electrochemical response of films depends on their ability to allow the movement of ions in their structure, which in turn is affected by their morphology and porosity. In addition, the dynamic behavior of the composite biopolymer films starch / PEDOT suggests the possibility of a

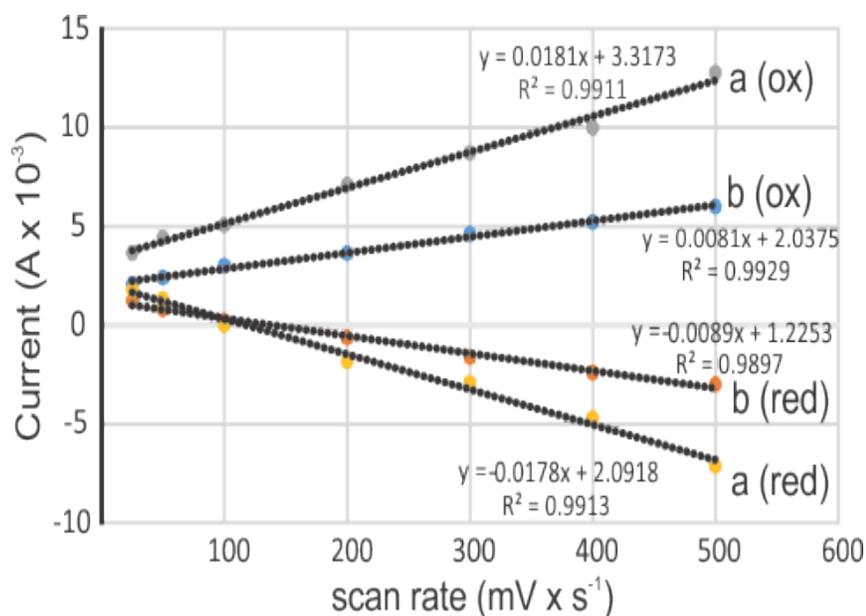


Figure 4. Dependence of the oxidation (ox) and reduction (red) current peaks on scan rate for: (a) starch/PEDOT polymer. (b) PEDOT.

faster and more sensitive response in chemical detection and charge storage applications.

4. Conclusions

A composite polymer can be made by thermochemical synthesis using cassava starch and PEDOT. Composite films are stable and have conductive properties. Studies by infrared spectroscopy showed that there is an interaction between the polymer chains of starch and the PEDOT chains. In addition to the degree of crystallinity of the starch is affected by the addition of plasticizers in the synthesis mixture. Cyclic voltammetry shows that starch films unplasticized lack electrochemical activity, while plasticized films exhibit an activity due to the interactions of starch molecules with plasticizers. The composite biopolymer starch/PEDOT, presents a rich electrochemical activity with dominant oxidation and reduction peaks due to PEDOT. The kinetics of the films show that the dynamics of the composite biopolymer starch/PEDOT

films is much larger than those of PEDOT, suggesting their potential as a sensitive material or of charge storage.

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6. References

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