



Composite material elaborated from conducting biopolymer cassava starch and polyaniline

Material compuesto elaborado de biopolímero conductor de almidón de casava y polianilina

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Abstract

This paper presents the preparation of a composite material synthesized from a conducting biopolymer of cassava starch and polyaniline. The composite material was made from the addition of aniline to the synthetic mixture of a conducting biopolymer of cassava starch with plasticizers (glycerol, glutaraldehyde and polyethylene glycol) and lithium perchlorate. The resulting composite material was a dark colored film with flexible and stable consistency. FTIR-ATR spectroscopy showed that there is a possible interaction by hydrogen bonds between the structures of the origin polymers, established between the OH groups of the starch and the NH group of the polyaniline. On the other hand, the electrochemical response of the composite material presented redox activity, with oxidation and reduction process well marked and intense in its signals. Additionally, the electrochemical signals of the composite material were stable when recording 50 consecutive cycles. From the above, it could be concluded that it is possible to make a composite material with electrochemical properties from conductive films of starch and polyaniline. Due to the excellent electrochemical properties, this type of composite materials can be applied in the development of devices such as electrochemical accumulators, solar cells, sensors, etc.

Keywords: Solid biopolymer electrolyte, cassava, starch, polyaniline, composite material.

Resumen

En este trabajo se presenta la elaboración de un material compuesto sintetizado a partir de un biopolímero conductor de almidón de yuca y polianilina. El material compuesto fue elaborado a partir de la adición de anilina a la mezcla de síntesis de un biopolímero conductor de almidón de yuca con plastificantes (glicerol, glutaraldehído y polietilenglicol) y perclorato de litio. El material compuesto resultante fue una película de color oscuro con consistencia flexible y estable. La espectroscopia FTIR-ATR mostró que existe una posible interacción por puentes de hidrogeno entre las estructuras de los polímeros de origen, establecidos entre los grupos OH del almidón y el grupo NH de la polianilina. Por otra parte, la respuesta electroquímica del material compuesto presentó actividad redox, con proceso de oxidación y reducción bien marcados e intensos en sus señales. Adicionalmente, las señales electroquímicas del material compuesto mostraron ser estables al registrar 50 ciclos consecutivos. De lo anterior, pudo ser concluido que es posible elaborar un material compuesto con propiedades electroquímicas a partir películas conductoras de almidón y polianilina. Debido a las excelentes propiedades electroquímicas, este tipo de materiales compuestos pueden ser aplicados en el desarrollo de dispositivos como acumuladores electroquímicos, celdas solares, sensores, etc.

Palabras clave: Electrolito de biopolímero sólido, yuca, almidón, polianilina, material compuesto.

1 Introduction

Polymers are characterized by being materials with high strength/density ratio, excellent thermal insulation properties, good resistance to acids, alkalis and solvents and plasticity comparable to

that of metals. From the point of view of their electrical properties, the main characteristic that has distinguished these materials from metals has been their low capacity to conduct electric current; while metals have traditionally been identified as excellent electrical conductors, polymers are characterized as insulating materials.

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However, this perspective began to change when, in the late 1970s, A.G. MacDiarmid, H. Shirakawa and A.J. Heeger synthesized a polymer with conductive characteristics (MacDiarmid, 2001; Shirakawa, 2001; Heeger, 2001). In general terms, conducting polymers are materials formed by long hydrocarbon chains with alternating single and double bonds (conjugated bonds). This architecture allows them to conduct the electric current when they have been doped by oxidation or reduction, such materials are known as intrinsically conductive polymers (ICP) (MacDiarmid, 2001; Shirakawa, 2001; Heeger, 2001; Lu *et al.*, 2018). Among the intrinsic conducting polymers highlight, polyaniline, polypyrrole, poly 3-methylthiophene, due to its easy synthesis process, excellent optical and electrochemical properties and its good stability.

The polyaniline (PANI) is synthesized from aniline, a substituted aromatic compounds whose oxidation produces its polymerization, the polyaniline is therefore a chain of phenylene rings joined together by a group NH that can be protonated and deprotonated to through oxidation and reduction processes. This structure allows the polyaniline to conduct the electric current and reach conductivity values of the order of 10^4 S cm^{-1} , very close to those registered for some metals such as Cu and Ag, which can have values of the order of 10^6 S cm^{-1} (MacDiarmid, 2001). The oxidation/reduction states (redox processes) shown by the polyaniline strongly depend on the pH of the medium (Scotto *et al.*, 2017; Liao *et al.*, 2019). Therefore, the peaks of the electroactivity corresponding to oxidation/reduction are observed by voltammetry in acid solutions. Neutral or basic media interfere with the electroactivity of polyaniline and limit its applications (Liao *et al.*, 2019; Arrieta *et al.*, 2004). In order to improve the electrochemical properties and maintain the electroactivity of polyaniline in non-acidic media, some strategies have been tested, among which the synthesis of composite materials stands out. In this way, polyaniline has been combined with inorganic and organic materials such as carbon nanotubes, graphene, molybdenum disulfide, zeolite, among others, with the aim of generating composite materials with better properties (Zhang *et al.*, 2019; Ji *et al.*, 2018; Yellappa *et al.*, 2019; Jevremović *et al.*, 2019; Meng *et al.*, 2019).

Composite materials are made to combine properties of different materials. The purpose of combining a polymer of natural origin, biodegradable and environmentally friendly with polymers of synthetic origin with electrochemical properties is

relatively new and can generate materials with new properties and a large number of applications. In this sense, polyaniline has been combined with biopolymers such as chitosan, starch, cellulose, among others (Gautam *et al.*, 2015; Janaki *et al.*, 2012; Gautam *et al.*, 2016). One of the common characteristics of the biopolymers used is that they are not electrical conductors. In this investigation we have synthesized a composite material made from polyaniline and a solid biopolymeric electrolyte (SBE) made from cassava starch capable of conducting electric current (Arrieta *et al.*, 2011).

Starch is a very abundant natural polymer and easy to synthesize. It consists of amylase molecules formed by linear chains of glucose and amylopectin, formed by branched chains of glucose. This biopolymer has been used in various applications through its modification and synthesis as a composite material (Gautam *et al.*, 2015; Gautam *et al.*, 2016; Cheng, 2019; Arrieta *et al.*, 2016; Wang *et al.*, 2018; Guz *et al.*, 2017; López-Hernández *et al.*, 2018). The majority of biopolymers elaborated from starch reported in the literature are made from corn starch and are not conductive. The development of cassava starch biopolymers capable of conducting electric current has been recently reported and has been applied in the development of an artificial muscle and an electrochemical accumulator (Nuñez *et al.*, 2016; Arrieta *et al.*, 2019).

Solid biopolymeric electrolytes (SBE), are materials capable of conducting electricity through the movement of ions along the polymer matrix. The combination of this type of new electrolytic conducting biopolymers with polyaniline has not been reported in the literature. Due to the above, the study of the electrochemical behavior of a composite material based on a solid biopolymer electrolyte (SBE) of cassava starch and an intrinsic conducting polymer (polyaniline) is reported.

2 Materials and methods

2.1 Materials and reagents

All reagents used (glycerin, glutaraldehyde, polyethylene glycol, lithium perchlorate, sodium hydroxide, aniline and ammonium persulfate) were analytical grade. The aniline was distilled before being used. The water used was milli-Q (ultrapure) quality and all solutions were prepared with ultrapure water.

The starch was extracted from cassava roots, of the *Manihot esculenta* variety. The extraction process was carried out through the following stages; washing and peeling the roots of cassava, disintegrating the roots by liquefying, sieving with fine sieve (silk cloth) three times, decanting the solution and washing the decanted solid three times with ultrapure water, drying the decanting to 40 °C for 24 hours, pulverized and sieved in a 300 μm sieve. The purity of the starch obtained was determined according to the official method of the AOAC (Association of official analytical chemists) (AOAC, 1995).

2.2 Synthesis of composite material from conducting starch biopolymer and polyaniline

3.0 g of starch in 100 ml of water (with pH 9, adjusted by the addition of 0.1 M NaOH) was added. 2 g of lithium perchlorate salt were added, stirring was maintained for 5 minutes and the plasticizers, glycerin (2 g), glutaraldehyde (5g), polyethylene glycol (1 g) were added little by little. To the mixture was added aniline monomer (2 mL) and ammonium persulfate (0.2 mL), which allowed the polymerization of aniline. The mixture was heated at 70 °C with constant stirring for 15 minutes. The heating was then suspended and immediately the contents were poured into a petri dish (100 x 15 mm) which was then taken to the oven at 70 °C for 48 hours to obtain the composite film. In order to compare the results of the studies carried out on the composite material, a starch film was synthesized without the addition of aniline and oxidizing agent (ammonium persulfate). In addition, the synthesis of a polyaniline film was performed by electrogeneration on a steel plate (1 cm x 1 cm) in a three electrode electrochemical cell; reference electrode of saturated calomel, auxiliary platinum electrode and as a working electrode (substrate), the steel plate for electrodepositing polyaniline. The polymerization solution consisted of an aqueous solution of aniline (0.1 M) and hydrochloric acid (0.1 M). The film was detached from the steel sheet by ultrasound application.

2.3 Characterization of composite material

Electrochemical characterization was performed using the cyclic voltammetry technique. The voltage curves were recorded in a potential window of -2 V to 2 V at a scan rate of 100 mV s⁻¹. The measurements were

carried out on the films without immersion in liquid cell (electrolyte), using a solid-state cell consisting of two stainless steel plates adhered each to an acrylic plate. The samples to be analyzed were placed in the middle of the steel plates and the four terminals were connected to a IVIUM brand potentiostat/galvanostat. The measurements were made using the open-circuit potential (OCP) as a reference potential, which corresponded to 0.11 V.

Additionally, infrared spectrometry measurements were made to determine the possible molecular interactions between starch polymers and polyaniline. Infrared spectroscopy was performed directly on the films, through the application of an ATR (Attenuated Total Reflectance) Type II accessory on a Shimadzu IRTracer 100 spectrometer. All spectra were recorded with a wavelength range of 4000-550 cm⁻¹, a spectra resolution of 4 cm⁻¹ and 100 scans.

3 Results and discussion

The preparation of the films was carried out simultaneously. Three films of each specimen were made to compare the repeatability of the synthesis method. The films prepared with starch without aniline were transparent and of flexible consistency. On the other hand, the composite material films synthesized from the mixture of cassava starch and polyaniline, turned green at the beginning of the drying process and after 48 hours, turned a dark hue. The color change in composite material films may be related to the polymerization process of the polyaniline that continues to occur during this period. An image of the two types of films generated is presented in Figure 1; Figure 1a, starch biopolymer film without polyaniline; Figure 1b, composite material film. In both cases the films presented a flexible consistency, with good mechanical stability to manual handling.

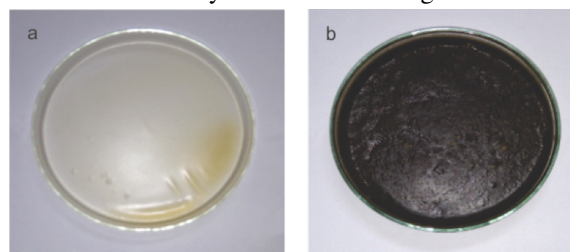


Fig. 1. Film image of: a) cassava starch film and b) composite material film.

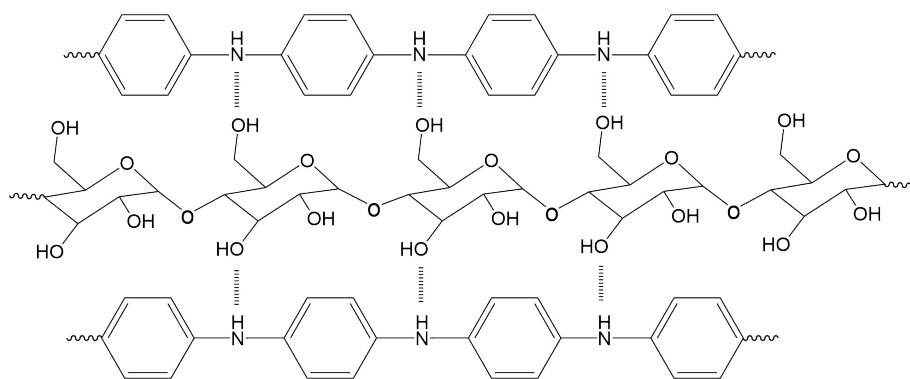


Fig. 2. Possible scheme of hydrogen bonds formed between starch and polyaniline.

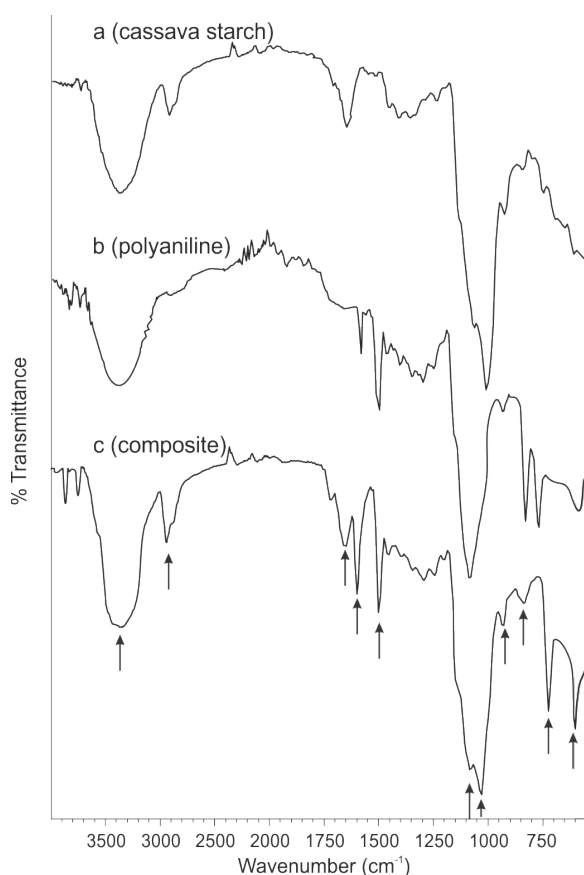


Fig. 3. FTIR-ATR film spectra for; a) cassava starch film; b) polyaniline film and c) composite material.

During the starch film generation process, the amylose and amylopectin chains rearrange their structure due to the presence of plasticizers (glycerol, polyethylene glycol and glutaraldehyde). The presence of functional groups formed by oxygen atoms (OH, C=O), both in the plasticizers and

in the amylose and amylopectin chains, allow the generation of hydrogen bonds between them, with the consequent opening of the crystalline structure of starch (Sun *et al.*, 2014; Dankar *et al.*, 2018). This makes it possible for the polyaniline, through its NH group, to interact more easily with the OH groups of the starch and establish hydrogen bonds, which allow a strong interaction between the starch chains and the polyaniline that is formed in the mixture of synthesis during the manufacturing process of the composite polymer. A similar phenomenon was reported for the synthesis of polypyrrole and starch (Arrieta *et al.*, 2016; Vasques *et al.*, 2010). Figure 2 shows a schematic representation of the biopolymer interactions of starch with polyaniline by hydrogen bonds established between both polymers.

Figure 2. Possible scheme of hydrogen bonds formed between starch and polyaniline. In order to demonstrate the interactions and behavior of the functional groups specific to starch and polyaniline in the composite material, an infrared spectroscopy analysis was performed. In Figure 3, the FTIR-ATR spectra recorded with starch films without polyaniline (figure 3a), polyaniline (figure 3b) and composite material cassava starch/polyaniline (figure 3c) are presented.

In figure 3a, the spectrum of the starch film is shown, which shows the typical bands of this biopolymer (Vasques *et al.*, 2010; Dai *et al.*, 2019). In the spectrum, the characteristic bending band OH at 3375 cm^{-1} can be seen, with its respective OH stretching at 1650 cm^{-1} , which corresponds to the hydroxyl of the starch structure, the CO bending bands at 2932 cm^{-1} and CH at 2878 cm^{-1} , the bands associated with CO, CC, COH are observed in the region of 1200 cm^{-1} at 900 cm^{-1} .

Table 1. Assignment of infrared spectra bands (FTIR-ATR) of films of cassava starch biopolymer, composite material and polyaniline.

Assignments	Wavenumber (cm ⁻¹)		
	Starch	Starch/Polyaniline	Polyaniline
Bending N-H	-	3441	3481
Bending O-H	3375	3371	-
Bending C-O	2932	2932	-
Bending C-H	2878	2884	2881
Bending C=O	-	1712	1712
Stretching O-H	1650	1651	-
Stretching C-C	1552	1597	1575
Bending C-N	-	1496	1499
Deformation in the plane C-H	1458	1458	1457
Deformation in the plane C-N	-	1285	1248
Stretching C-O	1151	1149	-
Bending out of plane N-H	-	1080	1085
Deformation C-OH	1017	1026	-
Deformation out of plane C-C	933	925	947
Deformation N-H	-	822	822
Ring deformation C-H	-	748	785
CCC ring in-plane deformation	-	587	587

On the other hand, the polyaniline spectrum (figure 3b) presents the characteristic signals (Melánová *et al.*, 2019; Song *et al.*, 2016), with bands in 1712 cm⁻¹ corresponding to the bending of the C = O bond, which is assigned to the over-oxidation of polyaniline occurred during the synthesis process by nucleophilic attack of the water, band at 1499 cm⁻¹ corresponding to the bending of the CN bonds, the planar deformation of the CN bonds of the polyaniline at 1248 cm⁻¹, the bending out of plane of NH at 1085 cm⁻¹, its NH deformation at 822 cm⁻¹ typical of the disubstituted amines, and the deformation of the aromatic rings at 785 cm⁻¹.

The composite material film presented a spectrum formed mainly by the combination of the bands of starch and polyaniline (Figure 3c), with small variations in the position of some bands, possibly due to changes in the arrangement and structural crystallinity of the polymers of origin. Thus, it can be observed the characteristic bands of cassava starch at 1026 cm⁻¹, 1149 cm⁻¹, 1650 cm⁻¹ and 2932 cm⁻¹ that correspond to deformation C-OH, stretching C-O, stretching O-H and bending C-O respectively, and also polyaniline characteristic bands such as the deformation band N-H at 822 cm⁻¹, bending out of plane N-H at 1080 cm⁻¹, deformation in the C-N plane at 1285 cm⁻¹, C-N bending at 1496 cm⁻¹. In the Figure 3c indicates with arrows the main bands

of the polymers of origin in the composite material. Additionally, the possible interaction by hydrogen bonds between the OH groups of the starch with the NH groups of the polyaniline is observed due to the stretching of the bands between 3000-3700 cm⁻¹, which were more intense than those observed in the corresponding spectra to the polymers of origin. Table 1 summarizes the values of the bands observed in the spectra of the films analyzed.

The electrochemical analysis of the composite material was performed using cyclic voltammetry technique. As mentioned earlier, the characterization was carried out in solid phase (without immersing the samples in any type of electrolyte), to know the real electrochemical behavior of the material. The voltammetric response of the composite material film (starch/polyaniline) is presented in Figure 4a. To compare the behavior of the composite material, voltammetric records of the origin polymers were made. Thus, the response of cassava starch films is presented in Figure 4b and the response of the polyaniline film is shown in Figure 4c.

In Figure 4a, it can be seen that composite film has good electroactivity; two oxidation peaks in the anodic sweep with potentials of 0.13 V and 1.69 V and three reduction peaks in the cathodic sweep at -1.24 V, -0.23 V and 0.73 V.

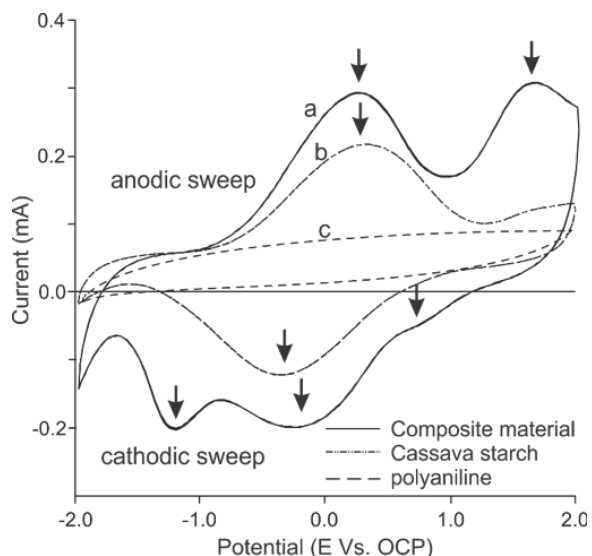


Fig. 4. Voltammetric response of films for: a) composite material, b) cassava starch and c) polyaniline.

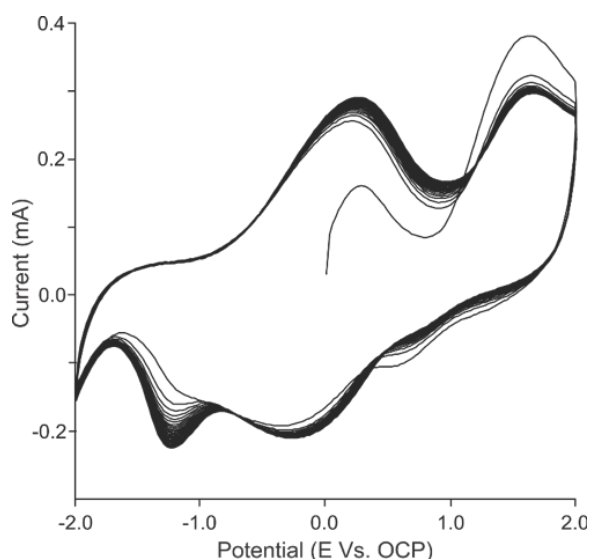


Fig. 5. Voltammetric signal of composite material recorded for 50 consecutive cycles.

On the other hand, the voltammetric signal of the film of starch, presented a well-defined redox process, with an oxidation peak in the anodic sweep at 0.33 V and a reduction peak in the cathodic sweep at -0.37 V. In the case of polyaniline, it did not record redox electrochemical activity, because the electroactivity of this intrinsically conducting polymer is dependent on the presence of mobile H^+ ions in the aqueous phase and the measurement conditions used were in the solid phase. Therefore, the absence of electroactivity

of polyaniline film may be due to the lack of sufficient moisture in the film and the absence of mobile H^+ ions. This dependence between polyaniline electroactivity and pH has been reported in several previous studies (Scotto *et al.*, 2017; Liao *et al.*, 2019; Arrieta *et al.*, 2004; Prakash, 2001; Su *et al.*, 2016). On the other hand, there is a marked difference in the currents recorded in the voltammograms; composite material signal show maximum current values of 0.257 mA, cassava starch of 0.79 mA and polyaniline of 0.05 mA. The current values in cyclic voltammetry are related to the conductivity of the analyzed medium, so it could be inferred that the composite material has a conductivity of approximately twice that recorded in cassava starch and almost 5 times that of the polyaniline in the absence of H^+ ions.

Thus, it could be established that the composite material shows redox electrochemical activity in which starch processes predominate. However, in the composite material there is a greater number of processes (peaks) that may be related to the electivity of polyaniline as a compound present in its structure. In addition, the peaks were better defined and more intense than those recorded in the cassava starch film, which may suggest that the incorporation of polyaniline can improve ionic mobility and generate greater electroactivity of the material. This result contrasts with that obtained by combining cassava starch with another type of intrinsic conductive polymer (polypyrrole) in a cassava starch/polypyrrole composite material, where the predominant oxidation/reduction peaks are those of polypyrrole (Arrieta *et al.*, 2016). This difference in the voltammetric behavior of the cassava starch/polyaniline and cassava starch/polypyrrole composite materials may be due to the fact that voltammetric measurements were not carried out in an acid medium and the electrochemical activity of the polyaniline is dependent on the presence of the ions (H^+), while the electroactivity of polypyrrole is independent of this factor.

The stability of the electrochemical response of the composite material was evaluated. To do this, successive measurements were made to see if there was signal variability after generating continuous reduction oxidation cycles. Figure 5 shows the record of 50 consecutive cycles of the composite material. It can be observed that, in the first six cycles, there is loss of signal intensity, possibly due to conditioning processes in the film structure. In consecutive cycles, the loss of intensity is minimal, showing a stable electrochemical behavior.

Conclusions

From the results of this work it can be concluded that it is possible to obtain a composite material from the combination of a solid byopolymer electrolyte of cassava starch and an intrinsic conducting polymer (polyaniline). Cassava starch and polyaniline molecules can interact in the composite material by establishing hydrogen bonds formed between the hydroxyl groups (OH) of glucose units in the cassava starch structure and the amine group (NH) present in the polyaniline structure. The infrared spectrum recorded in the composite material showed the combination of characteristic bands of its origin components and also the band corresponding to the bending of hydrogen bonds was more intense than that recorded in the conducting polymer of cassava starch and polyaniline in an isolated way.

The electrochemical behavior of the composite material showed excellent electroactivity, showing well defined oxidation and reduction peaks. The signal of the composite material was more intense than that recorded in the cassava starch films and the peaks corresponding to the redox processes were better defined in the composite material. The polyaniline voltammetric signal did not show any type of redox activity due to the measurement conditions, which were in the solid phase and in the absence of hydrogen ions (H^+). Additionally, the voltammetric signals of the composite material were repetitive for 50 cycles, which reflected a good electrochemical stability.

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