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PROPRIEDADES TÉRMICAS E ELETROQUÍMICAS DE ELETRÓLITOS SÓLIDOS DE BIOPOLÍMEROS DE AMIDO DE DIFERENTES ORIGENS BOTÂNICAS

THERMAL AND ELECTROCHEMICAL PROPERTIES OF SOLID BIOPOLYMER ELECTROLYTES FROM STARCH OF DIFFERENT BOTANICAL ORIGIN

PROPIEDADES TÉRMICAS Y ELECTROQUÍMICAS DE ELECTROLITOS SÓLIDOS DE BIOPOLÍMEROS DE ALMIDÓN DE DIFERENTE ORIGEN BOTÁNICO

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RESUMO

Introdução: Eletrólitos de biopolímero sólido são um tipo de material com alto potencial tecnológico utilizado no desenvolvimento de células solares, baterias, células a combustível, entre outros, devido à sua natureza biodegradável e baixo impacto ambiental. Objetivo: Este estudo teve como objetivo avaliar o efeito da origem botânica do amido utilizado na preparação de filmes eletrolíticos sólidos biopoliméricos sobre suas propriedades eletroquímicas e térmicas e estabelecer as variacões nas temperaturas de decomposição térmica e potenciais redox em função da origem botânica do amido utilizado. Métodos: Filmes de eletrólito de biopolímero sólido foram feitos por processos de síntese termoquímica utilizando amido de milho, amido de mandioca, amido de batata, glicerol, polietilenoglicol e glutaraldeído como plastificantes e sal perclorato de lítio. As soluções de síntese foram levadas à estufa a 70 °C por 48 horas. Os filmes foram caracterizados eletroquimicamente por voltametria cíclica em célula eletroquímica seca e termicamente por calorimetria exploratória diferencial e análise termogravimétrica. Resultados e Discussão: Os resultados mostraram que o comportamento eletroquímico dos filmes foi semelhante em termos de processos redox registrados. Entretanto, os valores potenciais de oxidação e redução foram diferentes, assim como a estabilidade e intensidade dos processos. Por outro lado, a análise térmica permitiu estabelecer dois processos de decomposição em cada um dos filmes estudados; o primeiro processo foi devido aos fenômenos de desidratação e despolimerização nos filmes. As temperaturas registradas foram 59,0 °C, 58,9 °C e 89,9 °C para os filmes de amido de batata, amido de mandioca e amido de milho, respectivamente. O segundo processo evidenciou a decomposição térmica que ocorreu em diferentes temperaturas, 267,7 °C nos filmes de amido de batata, 280,6 °C nos filmes de amido de milho e 287,1 °C nos filmes de amido de mandioca. Conclusões: Pode-se concluir que a origem botânica do amido utilizado na síntese de filmes eletrolíticos de biopolímero sólido afeta seu comportamento e estabilidade eletroquímica e térmica.

Palavras-chave: Estabilidade, Voltametria cíclica, Milho, Mandioca, Batata.

ABSTRACT

Background: Solid biopolymer electrolytes are a type of material with high technological potential used in the development of solar cells, batteries, fuel cells, among others, due to their biodegradable nature and low environmental impact. **Aim:** This study aimed to evaluate the effect of the botanical origin of the starch used to prepare solid biopolymeric electrolyte films on its electrochemical and thermal properties and to establish the variations in thermal decomposition temperatures and redox potentials depending on the botanical origin of the starch used. **Methods:** Films of solid biopolymer electrolyte were made by thermochemical synthesis processes using corn starch, cassava starch, potato starch, glycerol, polyethylene glycol, and glutaraldehyde as plasticizers and lithium perchlorate salt. The synthesis solutions were taken to an oven at 70 °C for 48 hours. The films were characterized electrochemically by cyclic voltammetry using a dry electrochemical cell and thermally by differential scanning calorimetry and thermogravimetric analysis. **Results and Discussion**: The results showed that the

Periódico Tchê Química. ISSN 2179-0302. (2021); vol.18 (n°38) Downloaded from www.periodico.tchequimica.com. © *The Author(s)* 2021 DOI: 10.52571/PTQ.v18.n38.2021.10_ARRIETA_pgs_137_148.pdf electrochemical behavior of the films was similar in terms of registered redox processes. However, the potential values of the oxidation and reduction were different, as are the stability and intensity of the processes. On the other hand, the thermal analysis allowed establishing two decomposition processes in each of the films studied; the first process was due to dehydration and depolymerization phenomena in the films. The temperatures recorded were 59.0 °C, 58.9 °C, and 89.9 °C for potato starch, cassava starch, and corn starch films. The second process evidenced the thermal decomposition at different temperatures, 267.7 °C in potato starch films, 280.6 °C in corn starch films, and 287.1 °C in cassava starch films. **Conclusions:** It could be concluded that the botanical origin of the starch used in the synthesis of solid biopolymer electrolyte films affects its behavior and electrochemical and thermal stability.

Keywords: Stability, Cyclic voltammetry, Corn, Cassava, Potato.

RESUMEN

Antecedentes: Los electrolitos de biopolímer sólido son un tipo de material con alto potencial tecnológico utilizado en el desarrollo de celdas solares, baterías, celdas de combustible, entre otros, debido a su naturaleza biodegradable y bajo impacto ambiental. Objetivo: Este estudio tuvo como objetivo evaluar el efecto del origen botánico del almidón utilizado para preparar películas sólidas de electrolitos biopoliméricos sobre sus propiedades electroquímicas y térmicas y establecer las variaciones en las temperaturas de descomposición térmica y los potenciales redox en función del origen botánico del almidón utilizado. Métodos: Se elaboraron películas de electrolito de biopolímero sólido mediante procesos de síntesis termoquímica utilizando almidón de maíz, almidón de vuca, almidón de papa, glicerol, polietilenglicol y glutaraldehído como plastificantes y sal de perclorato de litio. Las soluciones de síntesis se llevaron a un horno a 70 °C durante 48 horas. Las películas se caracterizaron electroquímicamente mediante voltamperometría cíclica utilizando una celda electroquímica seca y térmicamente mediante calorimetría de barrido diferencial y análisis termogravimétrico. Resultados y Discusión: Los resultados mostraron que el comportamiento electroquímico de las películas es similar en términos de procesos redox registrados. Sin embargo, los valores potenciales de oxidación y reducción son diferentes, al igual que la estabilidad e intensidad de los procesos. Por otro lado, el análisis térmico permitió establecer dos procesos de descomposición en cada una de las películas estudiadas; el primer proceso se debió a fenómenos de deshidratación y despolimerización en las películas. Las temperaturas registradas fueron 59.0 °C, 58.9 °C y 89.9 °C para las películas de almidón de papa, almidón de yuca y almidón de maíz, respectivamente. El segundo proceso evidenció la descomposición térmica que tuvo lugar a diferentes temperaturas, 267.7 °C en películas de almidón de papa, 280.6 °C en películas de almidón de maíz y 287.1 °C en películas de almidón de yuca. Conclusiones: Se pudo concluir que el origen botánico del almidón utilizado en la síntesis de películas de electrolítos de biopolímero sólido afecta su comportamiento y estabilidad electroquímica y térmica.

Palabras clave: Estabilidad, Voltamperometría cíclica, Maíz, Yuca, Papa.

1. INTRODUCTION:

In recent decades, conducting polymers have attracted the attention of many research groups due to their great technological potential (Le et al., 2017; Isikli and Ryan, 2020; Shirakawa, 2001; Ngai et al., 2016). These polymeric materials, because they are organic conductors, combine properties of traditional polymers such as resistance to corrosion, organic and inorganic solvents, flexibility, and metals such as high electrical conductivity and magnetic properties, which makes them attractive for applications in organic electronics. This is why they have been tested for use in chemical and physical sensors, electromagnetic shielding, intelligent windows, artificial nerves, actuators, corrosion protection, among others (Shi et al., 2021; Salgado et al., 2021; Nuñez et al., 2016)

The conducting polymers can be divided into two large groups; intrinsic conducting

polymers (ICPs), which are capable of conducting electric current through their structure of conjugated bonds (alternating double and single bonds), which can transmit a charge generated in the polymer chain through oxidation or reduction processes (Le et al., 2017; Shirakawa, 2001; Bredas and etreet, 1985). On the other hand, solid polymeric electrolytes (SPEs) are capable of conducting the electric current and making artificial muscles, flexible batteries, fuel cells, among others. Due to the displacement of ions (i.e., electrolytes) through the polymer matrix, in this case, the polymer chains have fixed electrical charges that allow them to interact with species ionic mobiles to maintain their electroneutrality (Isikli and Ryan, 2020; Ngai et al., 2016; Owens, 2000). These polymers are mostlv of petrochemical origin and therefore generate contamination from the production of the raw material they produce to their final disposal. Therefore, work has been done to generate conducting polymers from natural sources that can

be used as solid electrolytes to store charge for batteries, fuel cells, transistors, organic actuators and diodes (Nuñez *et al.*, 2016; Acosta *et al.*, 2015).

Polymeric materials obtained from renewable sources have attracted the attention and interest of the scientific community and the industrial sectors in recent years. "Biopolymers or bioplastics" unlike other traditional materials synthesized from petrochemical sources, have an interesting set of advantages among which are. generate a lower environmental impact, need low energy consumption for their production, their resource status renewable, the potential to add value to products and waste from industries and its particular biodegradability. Its applications are numerous and varied; they can be found as constituents of packaging, medical materials, reinforced plastics, edible films, among others (Reddy et al., 2015; Zhang et al., 2021; Vijavendra and Shamala, 2013; Jorgensen et al., 2020; Salikova et al., 2020).

The explosion of technological developments based on electronic systems has generated great concern due to that electronic devices are a source of contamination due to its relatively short shelf life. Electronic devices contain polymers, heavy metals, and other polluting materials. For this reason, work has been done to develop biomaterials capable of conducting electric current. In this way, the elaboration of biopolymers capable of conducting electric current has been reported. These biopolymers have been called Solid Biopolymer Electrolytes (SBPEs) and have been used in the development of light-emitting diodes (LEDs), artificial muscles, sensors, batteries, fuel cells, among others (Ma and Sahai, 2013; Singh et al., 2016; Rosnah et al., 2020; Nuñez et al., 2016; Monisha et al., 2016).

Recent research has established that polysaccharides such as starch found in plants can be used to produce biopolymers. This polysaccharide can be modified through a plasticization and doping process to obtain films with high ionic conductivity (Arrieta et al., 2011; Singh et al., 2014). Electrolytes based on plasticized cassava starch and lithium salt contents have been proposed as solid biopolymer electrolytes and tested in applications such as electrochemical artificial muscles and accumulators (Nuñez et al., 2016; Arrieta et al., 2011; Acosta et al., 2015). The starch synthesized in plants is made up of two types of polymers: amylopectin and amylose. The ratio of amylose to amylopectin varies, depending on the source of

the starch (botanical origin). This generates differences in the morphology, size, crystallinity and molecular macrostructure of the polymer chains in the grains, affecting the properties of the solid biopolymer electrolytes generated from starches.

The aim of this study was to determine the effect generated by the botanical origin of the starch used to produce films of solid biopolymer electrolyte on its thermal and electrochemical properties studied through cyclic voltammetry, thermogravimetry and differential scanning calorimetry.

2. MATERIALS AND METHODS:

In this work, the synthesis of solid biopolymer electrolytes of starch from different botanical sources, specifically corn, cassava, and potato are presented and an evaluation of the effect of the origin of starch on the electrochemical and thermal properties in the biopolymeric materials was made.

2.1. Materials and Reagents

The following reagents were used in this work: $(HOCH_2CH(OH)CH_2OH),$ glycerol glycol polvethylene (H (OCH₂CH₂)nOH). glutaraldehyde (OHC(CH₂)₃CHO) and lithium perchlorate (LiClO₄). These reagents were purchased from Sigma-Aldrich. Potato starch and corn starch $((C_6H_{10}O_5)n)$ were purchased from Merck. Cassava starch was extracted in the laboratory by the traditional method that includes, washed of the material, peeled with a manual peeler, disintegrated by blending with an industrial blender at 24,000 r.p.m., sieved with a 200 µm sieve and dried in an oven at 50 °C for 24 H. The purity of the extracted cassava starch was verified by FTIR-ATR spectroscopy analysis. The spectra were recorded from 650 - 4000 cm⁻¹ at a resolution of 4 cm⁻¹ by 100 scans. The IR spectra of the starches were recorded, normalized and corrected with the air background. Additionally, the official method of AOAC (Association of Official Analytical Chemists) was used. All solutions were prepared using milli Q grade ultrapure water.

2.2. Synthesis of Solid Biopolymer Electrolyte Films of Starch

The synthesis of the films was carried out by means of a thermochemical process that consisted of using 3g of starch which was dispersed in 100 mL of water with a pH of 9.0 for 15 min, with constant agitation (1500 r.p.m.). The starch dispersion was heated to 75°C and once the starch was completely dissolved, it was allowed to cool to room temperature to add the plasticizers glycerol (1g), polyethylene glycol (1g) and glutaraldehyde (2g), and 1.5 g of lithium perchlorate were also added. The mixture was heated to 75°C with constant stirring of 1500 r.p.m. The mixtures were deposited in Teflon petri dishes and taken to an oven at 70°C for 48 hours. This procedure was applied without variations for each one of the starches studied. Each of the films were made in triplicate. Once processed, the samples could be detached from the petri dishes without breaks or cracks and allowed to cool to room temperature.

2.3. Electrochemical characterization of Solid Biopolymeric Electrolyte Films

Characterizations were carried out on each of the samples. In the electrochemical characterization, sample sections of 1 x 1 cm were taken. The samples were placed in a dry electrochemical cell, which consisted of two stainless steel sheets supported on acrylic sheets. Figure 1 shows an image of the dry cell used. The samples were sandwiched in the cell and the characterization was performed cyclic by voltammetry using a sweep speed of 100 mV s⁻¹ and a sweep range of -2.0 V to 2.0 V. The voltage measurements were carried out with the open circuit potential (OCP) as reference which had a value of 0.10 V. The voltammograms were analyzed using PowerSuite Software V 2.60.

2.4. Thermal characterization of Solid Biopolymeric Electrolyte Films

Thermal characterization was carried out using differential thermogravimetric analysis (DTG), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), which were performed with a simultaneous thermal analyzer (STA-625/DSC/TGA) of Rheometric Scientific. All measurements were carried out in triplicate and the averages were used to calculate the thermal parameters. The thermograms were analyzed using the Advantage / Universal Analysis (UA) Software V 5.5.24.

The TG analyzes and DTG were carried out in an argon atmosphere with a constant gas flow of 100 L min⁻¹. The experiments were carried out using 5 mg samples, which were deposited in aluminum crucibles and empty crucibles were used as a reference. The samples were heated from 30 to 800 °C at heating rate of 10 °C min⁻¹.

For DSC analysis. 5 mg of starch samples were placed in hermetically sealed aluminum capsules and hydrated with 3 parts of distilled water (75%). The samples were kept at 30 °C for 30 min and subsequently heated to 800 °C at a heating rate of 10 °C min⁻¹. An Argon purge was performed at a flow rate of 100 L min⁻¹. The calibration of the equipment was performed prior to the measurements using an empty aluminum capsule. The enthalpy expressed as J g⁻¹ of starch, were determined by integrating the area under the peaks of the thermal processes. The parameters onset temperature (To), peak temperature (Tp), conclusion temperature (Tc) and enthalpy of the process (H), of the observed thermal processes were determined from the DSC curves.

3. RESULTS AND DISCUSSION:

Figure 2 presents images of solid biopolymeric electrolyte films from corn starch (Figure 2a), potato starch (Figure 2b) and cassava starch (Figure 2c). In all cases, the films showed a transparent white color and had a stable consistency to handling. It can be seen that it does not present cracks or breaks since it could be removed from the mold without difficulty.

It has been reported that the use of plasticizing agents allows obtaining starch films with good mechanical properties to be obtained because these compounds form hydrogen bonds between the polymeric starch chains, giving the films flexibility, wetting and mechanical resistance (Arrieta *et al.*, 2011).

The voltammetric response obtained from the electrochemical characterization applied to the films, was recorded during 50 consecutive cycles so that, in addition to evaluating their redox activity, their stability could also be evaluated. Figure 3 shows the voltammograms recorded in the solid biopolymeric electrolyte films elaborated with the starch from corn (Figure 3a), starch from potato (Figure 3b) and starch from cassava (Figure 3c). It can be observed that although there is a similar trend regarding the number of redox processes, the current intensities and the position of the oxidation/reduction peaks are different from each other.

In general terms, the voltammetric signals are formed by three well-defined redox processes, which are indicated in Figure 3 such as PI, PII and PIII. The processes registered with the solid biopolymer electrolytes of starch from corn, present more intense and better-defined peaks, in

Periódico Tchê Química. ISSN 2179-0302. (2021); vol.18 (n°38) Downloaded from www.periodico.tchequimica.com that same order the cassava starch films have well defined but less intense peaks than those observed in the corn starch films.

On the other hand, the signal obtained with potato starch films shows less defined and less intense peaks. Although if the stability of the signals is compared, the recordings carried out with the potato starch films after 50 consecutive cycles showed less loss of intensity, so they are more stable. Otherwise, the signals recorded with the cassava starch film showed a moderate and less marked stability than that registered with the films made from corn starch.

Regarding the potentials registered in the oxidation/reduction processes in the three types of starch films, it was observed that the position (i.e. potentials) varies between them. The oxidation potentials (EO) of potato starch films are more positive than those observed in the voltammetric curves of cassava starch films. These, in turn, are more positive than the potentials observed in corn starch films. The reduction potentials (ER) also present different values for each one of the films studied. However, a trend as marked as in the case of oxidation potentials is not observed. Table 1 shows the oxidation and reduction potentials of the films and the medium peak potentials (Ep/2) for each case.

The Ep/2 presented in Table 1 show that the redox processes of starch potato films are more positive than the Ep/2 values of cassava starch and corn starch films, which have values close to each other. These differences in electrochemical behavior may be caused by the different amylose/amylopeptin ratio of starches and the amount of charges formed during the thermochemical synthesis process. Due to that during the process of solid biopolymeric electrolyte synthesis of starch, the glucose chains, in their hydroxyl groups (OH) experiment the alkilinization reaction and are converted to alkoxide groups (RO-), which generates charges on the polymeric chains of the starch and allows the ionic interactions in the matrix that confer the ability to conduct electric current through ion movement (Arrieta et al., 2019; Chin et al., 2014).

This characterization allowed determining the thermal stability of the conductive films synthesized from starch from different plant sources. The curves recorded in the thermogravimetric analysis are presented in figure 4 and correspond to the characterization curves by differential thermogravimetric analysis (Figure 4a) and thermogravimetric analysis (Figure 4b). In all of them, two thermal decomposition processes

occurred, which in the case of the DTG is evidenced in the peaks of the graphs and in the TGA they are evidenced in the abrupt falls of the weights (%).

The first process occurs at 59.0 °C, 58.9 °C, and 89.9 °C for potato starch, cassava starch, and corn starch films, respectively. This first process may be due to dehydration of the films, so the dehydration of the potato and cassava starch films are similar. In contrast, the dehydration of the corn starch films occurs at much higher temperatures and with weight loss higher. This difference may be due to the different amylase/amylopeptin ratios of each of the starch molecules in these plant species, affecting the amount of plasticizer and water molecules that the polymers can contain. The solid biopolymer electrolyte films of potato starch and cassava starch showed a weight loss of about 16.1% during the first thermal process. In comparison, the films made of corn starch presented a weight loss of approximately 22.8%.

On the other hand, the second process evidenced in the graphs is observed at temperature values of 267.7 °C in potato starch films, 280.6 °C in corn starch films, and 287.1 °C in cassava starch films. The percentage of weight lost was lower in the corn starch films (about 78.7%), while the potato and cassava starch films showed loss percentages of 79.9% and 80.1%, respectively. This second thermal decomposition process, it corresponds to the depolymerization of the polymeric starch chains and the elimination of the polyhydroxyl groups. When comparing the temperatures of the second process, it is observed that the potato starch films have lower thermal stability than those of corn at almost 13 °C. The thermal stability of the cassava starch films is greater than those of corn and potato at approximately 7 °C and 20 °C, respectively. These temperatures are lower than those reported for pure starch films around 315 °C (Wang et al., 2009; Noivoil and Yoksan, 2020). This may be due to plasticizing agents that act as cross-linkers, separating the polymeric chains in the starch matrix. The difference between the depolymerization temperatures of the starch films from different plant sources may be due, not only to the differences between the amylose/amylopeptin ratios of each, but also to the number of charges that form in the polymers during the process of thermochemical synthesis and that in addition to affecting the thermal properties, they also affect the electrochemical properties as evidenced in the electrochemical characterization.

The thermograms obtained from the DSC analysis are shown in Figure 5. All the samples presented curves with two thermal processes, which correspond to those obtained in the TG analyzes. The first process associated with the dehydration of the films was observed in a broad endothermic peak between approximately 35 and 100 °C. The water contained in the films interacts with the polymer chains and plasticizers, being evaporated at this temperature range, this process is typical in this type of biopolymer. Table 2 shows a summary of the transition temperatures (To, onset; Tp, peak; and Tc, conclusion) and enthalpy of the process (H) of the DSC thermosgrams obtained for the solid biopolymer electrolytes of corn, potato and cassava starch.

The behavior of the solid biopolymer electrolyte samples from cassava starch, corn starch and potato starch was very similar in this first thermal process. The *To* and *Tc* values were close to each other. However, the *Tp* and *H* present a small difference, with the lowest values $(Tp = 59.7 \,^{\circ}\text{C} \text{ and } H = 1.6 \,\text{J g}^{-1})$ being observed in the films made with cassava starch, followed by the films made with potato starch $(Tp = 60.1 \,^{\circ}\text{C} \text{ and } H = 1.8 \,\text{J g}^{-1})$ and finally those of corn starch $(Tp = 75.2 \,^{\circ}\text{C} \text{ and } H = 2.4 \,\text{J g}^{-1})$ These differences associated with the interaction of water with the polymer matrix and plasticizers may be due to the crystallinity levels of the starch molecules in each case.

The second endothermic peak could be seen between approximately 247 at 345 °C. Although the To were close to each other (next to 248 °C), the Tp, Tc and H present some variation in their values. The solid biopolymer electrolyte films from corn starch presented Tp, Tc and H values of 287.6 °C, 345.9 °C and 10.8 J g-1 respectively, the films made with potato starch presented Tp = 275.6 °C, Tc = 331.1 °C and H = 9.3 J g-1 and the cassava starch films registered a Tp = 286.8 °C, Tc = 322.2 °C and H = 7.2 J g-1. This second process showed differences in the behavior of solid biopolymer electrolytes made with cassava, corn, and potato starches. These differences may be mainly due to the particularities of the polymeric matrix of the starches used, generated by their botanical origin.

4. CONCLUSIONS:

Stable and consistent solid biopolymer electrolyte films could be made from the use of starch from different plant sources. The electrochemical characterization by cyclic voltammetry showed that, although the response

is similar in trend and number of processes, the botanical origin of the starch used affected the values registered for the oxidation and reduction potentials of the processes and also in the signal strengths and stability.

Besides, the characterization of the thermal stability allowed establishing that regardless of the botanical origin of the starch used to make the solid biopolymeric electrolyte films, there are two thermal processes, one consisting of dehydration and the other of depolymerization and decomposition of the starch polymer chains. The temperatures of the thermal processes and the enthalpies showed significant differences in the decomposition process of the polymeric chains of cassava, potato and corn starches. While the dehydration processes were more uniform in the films of the three types of starches studied

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6. REFERENCES:

- Acosta, M.F., Arrieta, A., Ávila, A., Martínez, A., Palacio, M., Nova, V. (2015). Development of Charge Electrochemical Accumulator of Conductive Polypyrrole/ Cassava Starch Biopolymers. ASME-Energy. 6A, 1-5.
- Arrieta, A., Gañán, P.F., Márquez, S.E., Zuluaga, R. (2011). Electrically conductive bioplastics from cassava starch. *Journal of the Brazilian Chemical Society*, 22(6), 1170–1176.
- Arrieta, A. Garcia, C., Combatt, E. (2019). Effect of elaboration ph on the electroactivity of cassava starch solid biopolymer electrolyte films. *Rasayan Journal of Chemistry*, 12(4), 1766 –1773.
- 4. Bredas J.L., Street, G.B. (1985). Polarons, bipolarons, and solitons in conducting polymers. *Accounts of Chemical Research*, 18(10), 309-315.
- 5. Chin, S.F., Azman, A., Pang, S.C. (2014). Size Controlled Synthesis of Starch Nanoparticles by a Microemulsion Method. *Journal of Nanomaterials*, 2014, 1-7.
- 6. Isikli, S., Ryan, K.M. (2020). Recent advances in solid-state polymer electrolytes and innovative ionic liquids based polymer electrolyte systems.

Current Opinion in Electrochemistry, 21, 188-191.

- Jorgensen, M.R., Räägel, H., Rollins, T. S. (2020). Advances in Biocompatibility: A Prerequisite for Biomedical Application of Biopolymers. Bernd Rehm, M. Fata Moradali Editors. *Biopolymers for Biomedical and Biotechnological Applications*, 1–17.
- Le, T.H., Kim, Y., Yoon, H. (2017). Electrical and Electrochemical Properties of Conducting Polymers. *Polymers*, 9(12), 1-32.
- 9. Ma, J., Sahai, Y. (2013). Chitosan biopolymer for fuel cell applications. *Carbohydrate Polymers*, 92(2), 955–975.
- Monisha, S., Selvasekarapandian, S., Mathavan, T., Milton Franklin Benial, A., Manoharan, S., Karthikeyan, S. (2016). Preparation and characterization of biopolymer electrolyte based on cellulose acetate for potential applications in energy storage devices. *Journal of Materials Science: Materials in Electronics*, 27(9), 9314–9324.
- 11. Ngai, K.S., Ramesh, S., Ramesh, K., Juan, J. (2016). A review of polymer electrolytes: fundamental, approaches and applications. *Ionics*, 22(8), 1259–1279.
- 12. Noivoil, N., Yoksan, R. (2020). Compatibility improvement of poly(lactic acid)/thermoplastic starch blown films using acetylated starch. *Journal of Applied Polymer Science*. 49675, 1-16.
- 13. Nuñez, Y.E., Arrieta, A.A., Segura, J.A., Bertel, S.D. (2016). Synthesis of an airworking trilayer artificial muscle using a conductive cassava starch biofilm (manihot esculenta, cranz) and polypyrrole (PPy). *Journal of Physics: Conference Series*, 687, 1-7.
- 14. Owens, B.B. (2000). Solid state electrolytes: overview of materials and applications during the last third of the Twentieth Century. *Journal of Power Sources*, 90(1), 2–8.
- 15. Reddy, N., Reddy, R., Jiang, Q. (2015). Crosslinking biopolymers for biomedical applications. *Trends in Biotechnology*, 33(6), 362–369.
- 16. Rosnah Mustapa, S., Min Aung, M., Rayung, M. (2020). Physico-Chemical, Thermal, and Electrochemical Analysis of

Solid Polymer Electrolyte from Vegetable Oil-Based Polyurethane. *Polymers (Basel)*, 13(1), 132-152.

- 17. Salado, M., Lanceros-Mendez, S., Lizundia, E. (2021). Free-standing intrinsically conducting polymer membranes based on cellulose and poly(vinylidene fluoride) for energy storage applications. *European polymer journal*, 144, 110240.
- 18. Salikova. N.S.. Bektemissova. A.U.. V.D., Begenova, Nazarova, B.E., Ostafeichuk, N.V. (2020). Preparation of mixed hydrogels based on biopolymers and the studv of their rheological properties. Periódico Tchê Química. 17(35), 23-40.
- 19. Saviour, A.U., Moses, M.S. (2019). Protective polymeric films for industrial substrates: A critical review on past and recent applications with conducting polymers and polymer composites/nanocomposites. Progress in materials science, 104, 380-450.
- 20. Shi, H., Dai, Z., Sheng, X., Xia, D., Sha, P., Yang, L., Luo, X. (2021). Conducting polymer hydrogels as a sustainable platform for advanced energy, biomedical and environmental applications. *Science of the total environment*, 786, 147430.
- 21. Shirakawa, H. (2001). The Discovery of Polyacetylene Film: The Dawning of an Era of Conducting Polymers (Nobel Lecture). *Angewandte Chemie International Edition*, 40(14), 2574-2580.
- Singh, R., Baghel, J., Shukla, S., Bhattacharya, B., Rhee, H.W., Singh, P.K. (2014). Detailed electrical measurements on sago starch biopolymer solid electrolyte. *Phase Transitions*, 87(12), 1237–1245.
- Singh, R., Polu, A.R., Bhattacharya, B., Rhee, H.W., Varlikli, C., Singh, P. K. (2016). Perspectives for solid biopolymer electrolytes in dye sensitized solar cell and battery application. *Renewable and Sustainable Energy Reviews*, 65, 1098– 1117.
- Vijayendra, S.V.N., Shamala, T.R. (2013). Film forming microbial biopolymers for commercial applications—A review. *Critical Reviews in Biotechnology*, 34(4), 338–357.

- Wang, N., Zhang, X., Liu, H., Wang, J., (2009). N, N dimethylacetamide/lithium chloride plasticized starch as solid biopolymer electrolytes. *Carbohydrate Polymers*, 77, 607–611.
- Zhang, S., Bilal, M., Zdarta, J., Cui, J., Kumar, A., Franco, M., Romanholo Ferreira, LF., Iqbal, HMN. (2021). Biopolymers and nanostructured materials to develop pectinases-based immobilized nano-biocatalytic systems for biotechnological applications. *Food Research International*, 140, 109979.

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Figure 1. The dry electrochemical cell used for the electrochemical characterization of solid biopolymeric electrolyte films



Figure 2. Image of a solid biopolymer electrolyte films of a) starch from corn b) starch from potato, and c) starch from cassava



Figure 3. Cyclic voltammetry recorded with solid biopolymer electrolyte films of starch from a) corn, b) potato, and c) cassava



Figure 4. Graphs of differential thermogravimetric (a) and thermogravimetric analysis (b) of solid biopolymer electrolyte films from potato starch, corn starch, and cassava starch



Figure 5. Differential scanning calorimetry thermograms of solid biopolymer electrolyte films from potato starch, corn starch, and cassava starch

Process		SBPE Films				
		Corn	Potato	Cassava		
	EO	-0.50 V	-0.63 V	-0.45 V		
PI	ER	-1.48 V	-1.39 V	-1.42 V		
	E _{p/2}	-0.99 V	-1.01 V	-0.93 V		
PII	EO	0.25 V	0.38 V	0.29 V		
	ER	-0.36 V	-0.40 V	-0.19 V		
	E _{p/2}	-0.05 V	-0.01 V	-0.05 V		
PIII	EO	1.15 V	1.49 V	1.21 V		
	ER	0.49 V	0.46 V	0.51 V		
	E _{p/2}	0.82 V	0.97 V	0.86 V		

Table 1. Values of oxidation/reduction potentials and medium peak potentials recorded in the solid biopolymeric electrolyte films from corn starch, potato starch, and cassava starch

Table 2. Values of onset temperature, peak temperature, conclusion temperature, and enthalpy of the process of solid biopolymer electrolytes from corn starch, potato starch, and cassava starch

SBPE Films	Peak 1			Peak 2				
	То	Тр	Тс	Н	То	Тр	Тс	Н
	(°C)	(°C)	(°C)	(J g⁻¹)	(°C)	(°C)	(°C)	(J g⁻¹)
Corn	35.0	75.2	98.7	2.4	247.8	287.6	345.9	10.8
Potato	34.7	60.1	97.9	1.8	247.6	275.6	331.1	9.3
Cassava	35.0	59.7	97.6	1.6	247.8	286.8	322.2	7.2