Advance Journal of Food Science and Technology 15(SPL): 28-32, 2018
DOI:10.19026/ajfst.15.5869
ISSN: 2042-4868; e-ISSN: 2042-4876

Submitted: September 9, 2017 Accepted: October 31, 2017 Published: July 10, 2018

Research Article

Impedanciometric Study of Conducting Polymer Composite Films from Cassava Starch/ Poly (3,4-Ethylenedioxythiophene)

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Abstract: The aim of this study was to study, by electrochemical impedance spectroscopy, the electrochemical properties of a new conductive polymer composite made from cassava starch and poly (3, 4-ethylenedioxythiophene) (PEDOT). The results show that the polymer composite shows excellent conductivity with resistance values in the order of kΩ and capacitance values in the order of mF as a result of possible interactions of polymer chains of cassava starch and PEDOT. The results allow to establish a high potentiality of the starch/PEDOT polymer composite for applications as batteries, charge accumulators or electrochemical actuators.

Keywords: Cassava, electroactivity, electrochemical impedance spectroscopy, PEDOT, starch

INTRODUCTION

The materials have marked the history and development of civilizations. This fact has not changed over time and at the present, the new materials address the trends of technological development. Thus, in particular, the polymers have contributed enormously on different aspects of society, for example, the development of new products in different industries and economic sectors, but they have also negatively impacted the environment. In this sense, two lines of work are currently an important focus for the development of numerous researches. The first is the development of polymeric materials with new properties and the second is the important effort to synthesize new biodegradable and environmentally friendly polymeric materials.

In this sense, polypyrrole (PPy), polyaniline (PANI), poly(3-methylthiophene) (P3MT) andpoly (3,4-ethylenedioxythiophene) (PEDOT) are some of the most studied conductive polymers due to their properties, as such adequate electrical conductivity, rich electivity, stability and easy processability (Awuzie, 2017; Skotheim and Reynolds, 2007; Verheyen *et al*., 2017). In particular, the PEDOT has been studied and used in the development of electronic devices due to its electrochromic and electrochemical properties. However, this polymer has some restrictions related with its mechanical properties and in consequence, their industrial applications are seen to be limited.

By the above, PEDOT has been combined with different polymers and other materials such as poly (Styrene Sulfonate) (PSS), poly[dithio-2, 5- (1,3,4-thiadiazole)] (PDMcT), carbon nanotubes (SWNT), 2, 5-dimercapto-1,3,4-thiadiazole (DmCT) among other (Lenz *et al*., 2011; Kiya *et al*., 2007; Thanh Tung *et al*., 2011; Rodríguez-Calero *et al*., 2015). Additionally, the PEDOT has been combined with some natural polymers and materials such as chitosan, cellulose, dextrin and hyaluronic acid (Bhagwat *et al*., 2016; Zhou *et al*., 2017; Jeon *et al*., 2005).

On the other hand, the use of natural polymers (biopolymers) has acquired great importance in recent years, because these are friendly to the environment, have a relatively easy availability in comparison with synthetic polymers, a generalized biodegradability and a relatively low cost. The above has made that biopolymers become the object of numerous research and industrial developments.

In this context, starch is one of the most abundant polymers widely used in different industries. Recently, starch has been combined with conducting polymers in order to develop new materials and expand their technological possibilities. In addition, starch films

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capable of conducting the electric current have been developed (Arrieta *et al*., 2011). However, though the corn starch is one of the most used starch type, the starch extracted from tubers, e.g., cassava, has recently called the interest to develop new materials. At the present, there are very few reports of the application of cassava starch in the manufacture of conductive materials (Arrieta *et al*., 2011; Arrieta and Palencia, 2016).

The aim of this study was to elucidate the conduction mechanism and electrical properties of a composite conductive polymer synthesized from plasticized cassava starch and PEDOT by electrochemical impedance spectroscopy technique.

MATERIALS AND METHODS

The analytical-grade reagents were obtained from Sigma-Aldrich. The water employed in all experiments was milli-Q quality. The starch was extracted from the *Manihot esculenta Crantz* variety by the traditional method of washing, peeling, grating, sieving, decanting, drying and spraying. The purity of the starch was determined by mass difference, taking into account the content of proteins, fats, ash and raw fiber using the application of the official methods of AOAC (1995).

The synthesis of the starch/PEDOTpolymer composite was carried out by thermochemical method (Arrieta *et al*., 2011; Arrieta and Palencia, 2016). For that, initially 3.0 g of starch were dissolved in 100 mL of water at pH 9.0 and heated to 70°C. Later, 1.5 g of polyethyleneglycol, 2.0 g of glycerol, 1.0 g of lithium perchlorate and 3.0 g of 3, 4-ethylenedioxythiophene monomer were added to starch solution. The mixture was heated to 75°C for 15 min and kept under constant stirring. Then, the mixture was deposited in Teflon containers and dried in an oven at 70°C for 48 h. Plasticized starch polymer films were also prepared following the process of preparing for starch/PEDOT polymer films described above, without the addition of the 3, 4-ethylenedioxythiophene monomer. In addition, unplasticized and without-PEDOT starch films were prepared using the procedure described above. On the other hand, PEDOT films were synthesized to make comparison studies with polymer composite films. The synthesis was carried out by chronoamperometric electrode position of PEDOT on a steel electrode. For this, an electrochemical cell of three electrodes was arranged; saturated calomel reference electrode, auxiliary platinum electrode and steel working electrode. The synthesis solution was made with 0.2 M of 3, 4-ethylenedioxythiophene and 0.1 M of lithium perchlorate, a polymerization potential of 1.1 V was applied for 500 s. The generated film was detached from the steel substrate by ultrasonic application for 5 s.

The thickness of the films was measured with a digital micrometer to ensure uniform thickness in all working films. The electrochemical characterization was carried out by Electrochemical Impedance Spectroscopy (EIS) using a potentiostat/galvanostat FRA 2263 PARSTAT (Princeton Applied Research) controlled by Power Suite software. Electrochemical impedance measurements were performed on 1 cm^2 polymer samples at room temperature over a frequency range of 1 Hz to 0.1 MHz and 10 mV (rms).

The potentials were measured in relation to the Open Circuit Potential (OCP), which had a value of 0.15 V. The measurement cell consisted of a cell for solid samples consisting of two 2×2 cm stainless steel sheets, fixed on acrylic plates that are closed by a system of nuts (Arrieta and Palencia, 2016). To perform the measurements, the films were cut into 1×1 cm samples and placed between the steel sheets of the sample holder.

RESULTS AND DISCUSSION

During the preparation of the polymeric films, it was seen that the starch/PEDOT polymer composite films showed an amber coloration which was changed to darker coloration at the time (5 days approximately). This color transition can be explained by a slow PEDOT polymerization by the absence of oxidizing substances and a slow diffusion. Since polymerization was thermally activated and reaction medium cannot be considered as homogenous medium by the presence of polymer chains of starch, a higher difficulty and a slow diffusion of PEDOT-associated reactive species is expected. Thus, the PEDOT polymer chains interact with the starch polymer chains through hydrogen bonds formed by the remaining hydroxyl groups on the starch molecules and the alkoxy and alkylthio groups on the PEDOT molecules. Figure 1 shows the possible hydrogen bonds between the PEDOT polymer chains and starch chains in the polymer composite.

The charges generated by the alkoxylation (Cardoso *et al*., 2007) of the polymer chains of starch

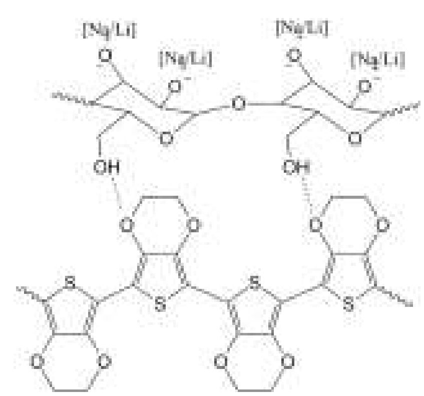

Fig. 1: Schematic representation of the interaction by hydrogen bonds between the polymer chains of PEDOT and cassava starch

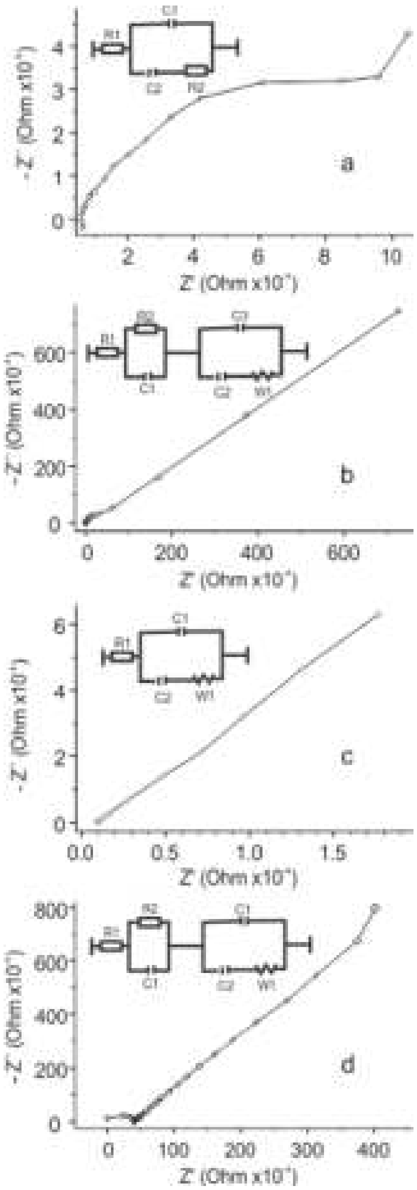

Fig. 2: Electrochemical impedance spectra Nyquist of a) unplasticized and without-PEDOT starch polymer; b) without-PEDOT plasticized starch polymer; c) PEDOT and d) polymer composite starch/PEDOT

allow that polymer conducts electricity, whereas the delocalization of charges on the PEDOT chains are responsible of electrical conduction in this polymer. Thus, both polymers contribute to the electrical conduction in the polymer composite. The conduction process was studied through electrochemical impedance spectroscopy. The impedanciometric response for the different synthesized films by Nyquist (Cole-Cole) plots is shown in the Fig. 2.

The Nyquist plot of unplasticized starch films without PEDOT is shown in the Fig. 2a, a semicircle with an intercept on the axis of the abscissa (real Z) is observed, which determines the value of the film resistance (R1) with 76.4 kΩ. The kinetics of the movement of charges in the pure starch biopolymer films are given by a resistance of the electron passage of the electrode to the films (R2) and a capacitance (C1) formed by a double layer of diffusion of the ions, the capacitive phenomenon evidenced at low frequencies is negligible. The equivalent circuit for this case is given by R1[C1R2]. The resistance values of the plasticized starch polymer films without PEDOT (Fig. 2b) and with PEDOT (Fig. 2c) were much lower, with values of 74.8 Ω and 0.105 kΩ, respectively. This high conductivity is due to the presence of the lithium per chlorate ions present in the polymers. In addition, the charges of the polymer composite chains and in the particular case of those containing PEDOT, is also determined by the electro conductivity of the charges moving in the PEDOT due to its architecture of conjugated bonds (single and double alternates) that allow the displacement of charges in the polymer chain.

In the plasticized starch polymer films, the Nyquist graph (Fig. 2b) shows a sloped line with an angle of 45° which can be attributed to the impedance of polymeric electrolytes with non-homogeneous distribution of the salt in the polymer matrix or roughness of the films. The equivalent circuit given by R1[R2C1][C3(W1C2)], shows the resistance due to the movement of ions in the matrix of the polymer film (R1), a complex component with Warburg impedance that may be due to the transport of mass in the electro active species and the roughness of the films together with the capacitance (C1). On the other hand, the capacitance (C2) and the resistance R2, are due to the formation of the double layer and the resistance of the charge diffusion process in this region. The impedantiometric response of the PEDOT (Fig. 2c) is given by a line with an average slope corresponding to the equivalent circuit R1[C1(C2R2)]. Although the equivalent circuit is similar to that observed in pure starch films, the shape of the Nyquist curve is significantly different because in this case the second capacitance is not negligible, on the contrary is important because it is associated with the mass transport and the cumulative loads between the polymer and the counterions.

The presence of PEDOT in the starch polymer composite films modifies their impedanciometric behavior. In the Nyquist plot obtained from starch/PEDOT polymer composite films (Fig. 2d), a small semicircle and a straight line with a smooth deflection that marks an angle slightly higher than 45° are seen. The equivalent circuit corresponding to this behavior is R1 [R2C1] [C2 (W1C3)], the movement phenomena of ions and charges represented by capacitances and resistances, as well as, the Warburg impedance, are evidenced. The above can be due to that the phenomena associated with the plasticized starch polymer are dominant in the composite starch/PEDOT polymer. Thus, the presence of the semicircle is not

Table 1: Values of the components of the equivalent circuits obtained from the electrochemical impedance spectroscopy

	Electrical Component					
Polymer film	R1 (Ohm)	R2 (ohm)	C1 (F)	C2 (F)	C3 (F)	W1 (1/Ohm sqr)
a	7.64×10^{2}	4.38×10^{-1}	7.34×10^{-6}	6.90×10^{-7}		
b	7.48×10^{1}	4.38×10^{-5}	7.26×10^{-5}	9.14×10^{-4}	8.57×10^{-4}	7.12×10^{-4}
c	1.05×10^{2}		9.98×10^{-5}	3.31×10^{-5}		1.68×10^{-4}
d	5.68	1.00×10^{-4}	6.70×10^{-5}	4.81×10^{-4}	4.49×10^{-5}	3.06×10^{-4}

a) Unplasticized and without-PEDOT starch polymer, b) plasticized starch polymer without PEDOT, c) PEDOT and d) starch/PEDOT polymer composite

very noticeable and the graph is mainly dominated by a line similar to that observed in starch films plasticized without PEDOT. However, in this case a smaller inclination of its slope is observed (very close to 45°), probably due to the presence of Warburg impedance that possibly contributed by the PEDOT, which favors the movement of charges in the matrix material because of its ease to move charges through the polymer chain and also, it promotes the diffusion of the counter ions that stabilize these charges generating a semi-infinite diffusion.

A high conductivity of the polymers was evidenced, with resistance values in the order of kΩ. The values of the components of the equivalent circuits of the different films are summarized in Table 1. These values give a view of the excellent conductivity of the films. The low resistance and high capacitance values allow to see that the starch/PEDOT polymer composite has excellent electrical conductivity and the ability to store charge, which makes it potentially interesting for applications in batteries, accumulators or electrochemical actuators.

The results obtained when combining PEDOT and cassava starch in a polymer composite are in agreement with what has been reported in similar studies carried out by our research group with polypyrrole (Arrieta and Palencia, 2016). However, the conductivity values found with PEDOT were an order of magnitude higher. The values in the capacitances were also higher, in two orders of magnitude, which makes the polymer composite starch/PEDOT, a material with better potentialities in applications like charge storing and semiconductor material.

CONCLUSION

The results obtained show that it is possible to make an environmentally stable starch/PEDOT polymer composite capable of conducting the electric current.

Electrochemical impedance spectroscopy showed that the response of the polymer composite reflects the agreement of the plasticized starch and PEDOT responses. The polymer composite has a high conductivity and capacity to charge storing, which makes it a material of interest for possible technological applications of charge storage.

ACKNOWLEDGMENT

The authors acknowledge the financial support provided by the University of Sucre.

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