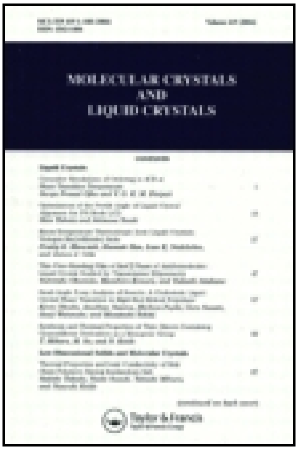

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Ionic Conductivity Thermogravimetry Measurements of Starch-Based Polymeric Electrolytes

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Ionic Conductivity Thermogravimetry Measurements of Starch-Based Polymeric Electrolytes

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Natural polymers are a very interesting matrix to obtain solid polymeric electrolytes (SPE). The principal advantage comes from their particularly interesting biodegradation properties due to the natural origin and also very low cost and good physical and chemical properties. These polymers contain heteroatoms in their structure and for this reason can interact with protons or lithium ions leading to the ionic conduction. Among different natural polymers, starch-based SPEs show good opto-electrochemical characteristics and can be applied to electrochemical devices. This work presents the results of starch and starch derivatives-based electrolytes, which were characterized by impedance spectroscopy and thermal analysis. The ionic conductivity results obtained for these SPEs varied from 10^{-6} *S/cm to* 10^{-4} *S/cm at room temperature, depending on the sample, and increased following Arrhenius model. The samples showed good stability up to 200°C evidenced by thermal analysis (TGA). Good conductivity results combined with transparency and good adhesion to the electrodes have shown that starch-based SPEs are very promising materials to be used as solid electrolytes in electrochromic devices.*

Keywords: ionic conductivity; polymer electrolyte; starch

1. INTRODUCTION

The research on polymeric electrolytes (SPE) has been known for over 20 years, and started with pioneering works of P. Wright (1975) [1] and M. Armand (1979) [2], who showed that poly(ethylene oxide) (PEO) could dissolve lithium salts and promote ionic conductivity.

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This property of PEO has opened new possibilities substituting liquid electrolytes and inorganic crystals used in electrochemical devices. However due to the PEO crystallization tendency, new and different systems, which are mostly based on polyether chains, as PEO, have been proposed.

Some polysaccharides and their derivatives possess great capacity for being processed in the film form with good mechanical and steel adhesion properties. Besides there are easily obtained from renewable and biodegradable sources and have low prices [3]. Among different polysaccharides, starch has gained attention; it is composed of a mixture of linear amylose (α(1,4) linked anhydroglucose) and branched amylopectin (α(1, 6) linked anhydroglucose) polysaccharide chains (Fig. 1).

A method to change the physico-chemical properties of the native starch and improve its functional characteristics is by performing starch modification through chemical reactions, such as etherification, esterification (Fig. 1), cross-linking and grafting or physical modification by plasticization. Derivatization reactions involve the introduction of functional groups into the starch molecule, resulting in the alteration of its gelatinization, pasting and retrogradation behavior. As an example acetylated starch is obtained by introducing hydroxypropyl groups into the starch chains, which results in the disruption of the inter- and intra-molecular hydrogen bonds, thereby weakening the semi crystalline structure of starch and leading to an increase in the motional freedom of starch chains in amorphous regions [4].

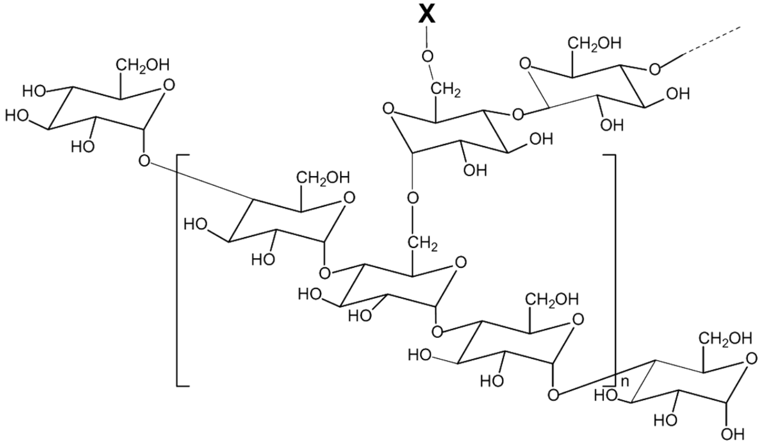


FIGURE 1 Representative formula of amylopectin-rich starch (X = H) and its derivatives (X = $-CH_2CH(OH)CH_2N^+(CH_3)_3$$-CH(OH)CH_3$, $-C(O)CH_3$).

An other possibility is to obtain starch-based plastics by plasticization process [5].

The plasticization of polymer electrolytes by low molecular weight components is a well established phenomenon whereby the addition of these components enhances the ionic conductivity of the resulting electrolyte. While the mechanism of this effect remains unclear, the interaction of these mobile ions with the specific sites along the polymer chain and the plasticizer are considered to be important determining factors. In particular the role the plasticizer plays in separating the charge from the polymer backbone is believed to be a crucial function in the determination the ionic conductivity of a polymeric electrolyte [6].

Water and glycerol are widely used as plasticizers for starch and act as agents of polymeric network formation through the polymer-polymer and polymer-plasticizer interactions. These interactions are van der Waals forces and strong hydrogen bonds, which leads to the increase on the toughness and strength of the starch plasiticized with glycerol materials [5].

This article presents the characterization results of transparent films of solid polymeric electrolytes based on corn and cassava starches plasticized with glycerol and containing different quantities of $LiClO_4$. The aim of this work was to verify the influence of the kind of starch on the conductivity values and thermal stability of these new ionic conducting materials.

These easy to prepare ionic conducting films tested in electrochromic windows showed very good performances, which are described in recent publications [7,8].

2. EXPERIMENTAL

2.1. Sample Preparation

The samples of corn amylopectin rich starch (Amidex 4001 Corn products Brasil Ingredientes Industriais Ltda.) and the samples of cassava starch and its oxidized, acetylated, etherified and cationic (AVEBE Ltda.) derivatives (Fig. 1) were dispersed in water (2–4% w/v) and heated for 2 hours at 100°C. The solution was cooled up to room temperature and glycerol (Synth) was then added with a percentage of 30% of starch mass. Lithium perchlorate ($LiClO_4$, Aldrich) was also added giving the concentrations of $[O]/[Li] = 4–40$ when calculated for all starch and glycerol oxygens. The viscous solution was dispersed on a Teflon plate and dried for 48 h at 40°C. The resulting transparent film samples were stored in a dry box [9].

2.2. Thermogravimetry

The materials obtained in the film form were characterized by thermogravimetry (TGA) with SHIMADZU TGA-50 equipment, to determine their mass loss as a function of temperature. These analyses were performed in the temperature range from 25 to 800°C in a nitrogen atmosphere (50 ml/min) at a heating rate of 10°C/min.

2.3. Impedance

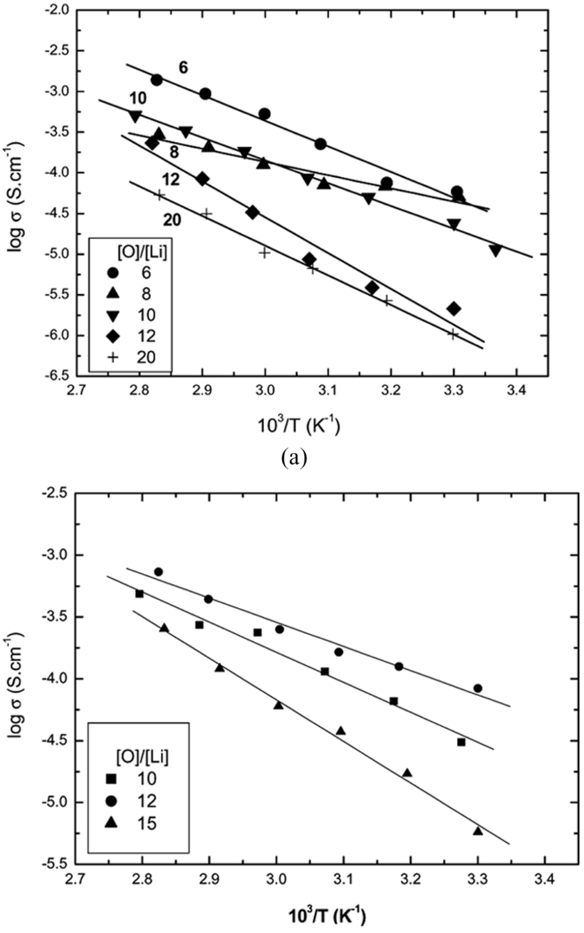
Impedance spectroscopy measurements were used to determine the ionic conductivity and frequency behavior of the electrolyte. A 2 cm round and 0.5 mm thick piece of the electrolyte was pressed against two steel electrodes. The measurements were taken with an Autolab 30 instrument equipped with an FRA2 module, applying a voltage of 5 mV rms amplitude in the frequency range $f = 10^6$ Hz to 10^1 Hz.

3. RESULTS AND DISCUSSION

3.1. Starch

The chemical formula of starch and its derivatives can be represented as showed in Figure 1, where $X = -H$ (amylopectin rich starch), $-CH_2CH(OH)CH_2N^+(CH_3)_3$ (cationic), $-CH(OH)CH_3$ (eterified), $-C(O)CH_3$ (acetylated). In oxidized starch the hydroxyl groups are transformed into carbonyl groups.

The conductivity results as a function of temperature for the samples of amylopectin-rich corn starch and cassava starch plasticized with glycerol and containing different concentrations of lithium salt are shown in Figure 2. As can be observed, the best conductivity results for corn starch-based SPEs (Fig. 2a) of $6.12 \cdot 10^{-5}$ S/cm at 30°C and $1.41 \cdot 10^{-3}$ S/cm at 80°C were obtained with the samples containing a large quantity of the lithium salt of $[O]/[Li] = 6$ exactly on the frontier of dissolution of the salt in this system, as observed by X-ray measurements (not showed here). Cassava starch SPEs (Fig. 2b) show the comparable ionic conductivity results, but for a smaller lithium salt concentration, i.e., $[O]/[Li] = 12$, where the values of $8.38 \cdot 10^{-5}$ S/cm at 30°C and $7.43 \cdot 10^{-4}$ S/cm at 80°C were obtained. This small difference can be due to the compositions of both starches, when the native starches differ in the amylose:amylopectin ratio. The corn starch was rich in crystalline amylopectin, (waxy starch), leading to a more compact and organized structure as cassava starch, which is composed of both amylose and amylopectin [5]. Moreover the



(a)

(b)

FIGURE 2 Ionic conductivity measurements as a function of temperature for corn starch (a) and cassava starch-based SPEs (b) with 30% of glycerol and containing different $LiClO_4$ concentrations.

network formation by plasticization with glycerol seems to create more favorable ways to lithium ions and water movement, which leads to good ionic conductivity values.

All the samples also showed linear increase in the conductivity values with temperature, which characterizes the ionic conduction mechanism as Arrhenius, i.e. the hopping of conducting species, in this case lithium ions between complexation sites [10].

The thermal analysis (TGA) results of the starch SPE-based samples can be observed in Figure 3. Figure 3a shows an increase of degradation temperature with lithium salt contents and Figure 3b shows that there was an amylopectin pure starch loss of about 11% of water in the temperature range between 25 and 120°C. The SPE samples show a smaller water loss in the same temperature range, which can be due to the smaller hydroxyl group contents [11]. However, the larger the quantity of the salt, i.e., [O]/[Li] < 6.5, the larger the water loss when

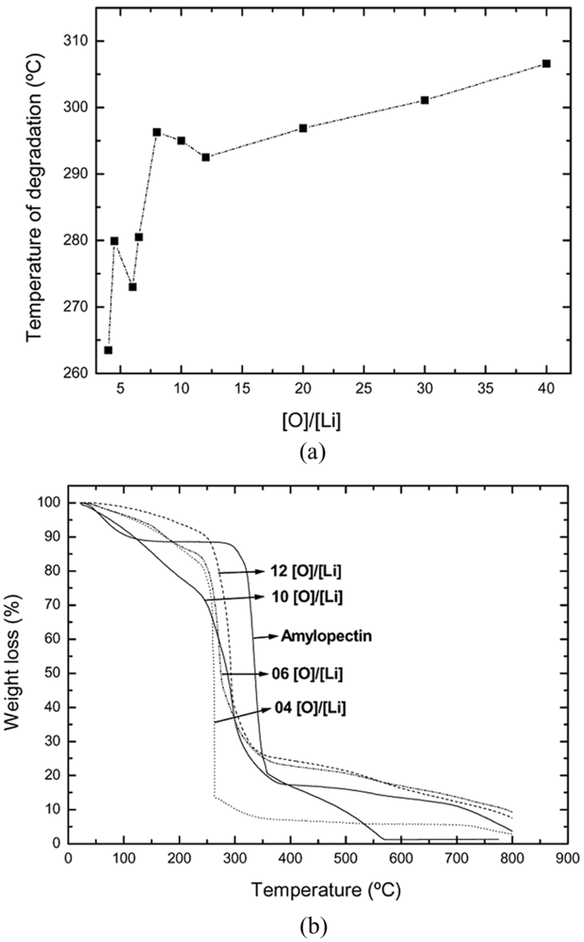


FIGURE 3 Temperature of degradation (a) and weight loss (b) of SPEs amylopectin-based films plasticized with 30% of glycerol and different $LiClO_4$ concentrations.

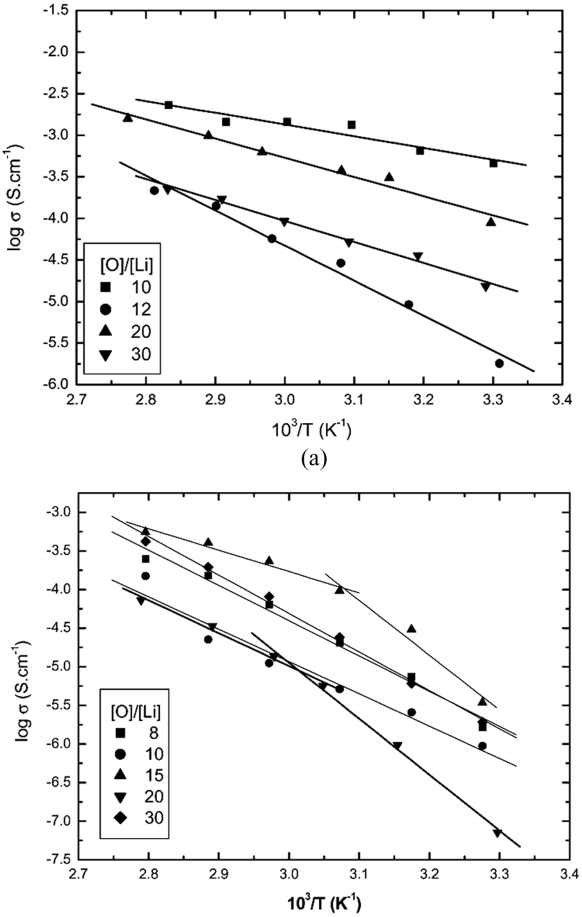
compared with the samples containing smaller quantities of the salt. This is due to the hygroscopic properties of both salt and plasticizer. Above 260°C all the samples show a very accentuated mass loss of about 70%, which is attributed to the thermal degradation of the samples. This change has already been cited in the literature as endothermic hydrolysis and oxidation process followed by exothermic reactions, which start at 340°C and corresponds to final pyrolisis [12]. The other 6% probably corresponds to the carbon formation [13] and lithium oxidation products. Only amylopectin rich-starch showed complete degradation, due to the CO, CO_2 and H_2O formation [13].

3.2. Starch Derivatives

Figure 4 shows the ionic conductivity measurements for different gel electrolytes obtained using acetylated (Fig. 4a) and etherified (Fig. 4b) starch derivatives with different $LiClO_4$ concentrations. It is possible to observe that ionic conductivity values at room temperature vary independent by of the salt concentration, showing a different behavior when compared with the samples containing amylopectin-rich starch (Fig. 2a). However, Figure 4a shows that the samples based on acetylated starch showed better ionic conductivity values when compared with the etherified starch-based SPEs plasticized with 30% of glycerol and containing a lithium salt concentration of [O]/[Li] = 8 and the samples showed in Figure 2. The obtained values are $4.54 \cdot 10^{-4}$ S/cm at room temperature and $2.4 \cdot 10^{-3}$ S/cm at 80°C for the sample with [O]/[Li] = 10 and $8.71 \cdot 10^{-5}$ S/cm at room temperature and $1.55 \cdot 10^{-3}$ S/cm at 87°C for the sample with [O]/[Li] = 20.

SPE etherified starch-based samples (Fig. 4b) with [O]/[Li] = 15 and 20 show slopes of the Arrhenius plots close to 50°C, which can be due to the undissolved salt [14].

Figure 5 shows the Arrhenius plots of the ionic conductivity of cationic (Fig. 5a) and oxidized (Fig. 5b) starch-based SPE films with 30% of glycerol. The ionic conductivity values of the best samples with [O]/[Li] = 8 were 10^{-5} S/cm at 30°C and $5.75 \cdot 10^{-4}$ S/cm at 80°C for cationic starch and $1.78 \cdot 10^{-4}$ S/cm at 32°C and $1.48 \cdot 10^{-3}$ S/cm at 85°C, for oxidized starch. The latter is comparable with the value obtained for the samples based on acetylated starch (Fig. 4a). Comparing all the ionic conductivity measurements of the best samples, which are showed in Table 1, one can observe that, the ether substitution in these plasticized systems does not improve the ionic conductivity as expected when compared with PEO based systems, which are generally responsible for the ionic conduction. The samples containing ether substitution in the polysaccharide chains are poor ionic conductors,

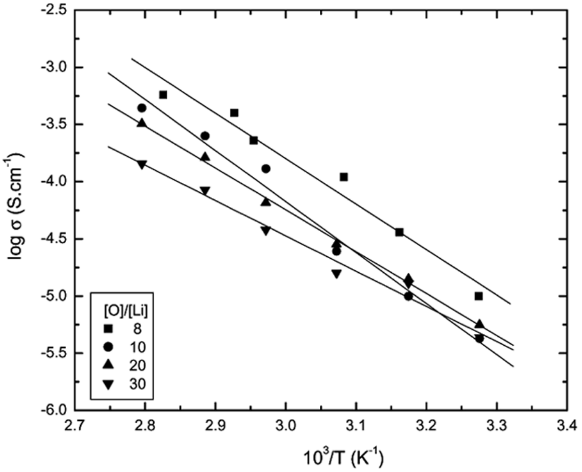


(a)

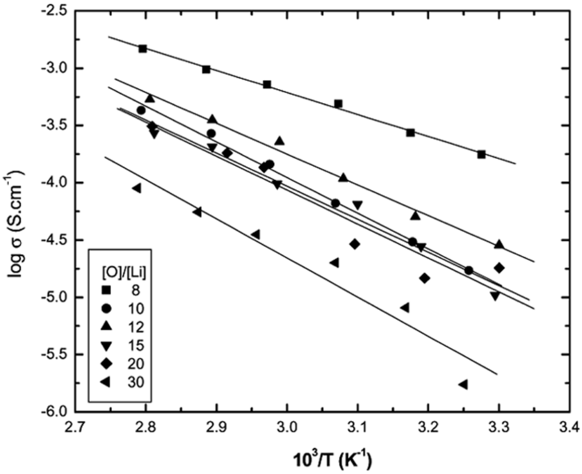
(b)

FIGURE 4 Arrhenius plots of the ionic conductivity of acetylated (a) and etherified (b) starch films with 30% of glycerol and different salt concentrations.

when compared with starch and its other derivatives. The low conductivity values of $1.07 \cdot 10^{-5}$ S/cm at 30°C were also observed in the samples of hydroxyl ethyl cellulose (HEC) plasticized with 48% of glycerol [15] and also in grafted systems [16]. The best results were obtained with oxidized and acethylated starch. This phenomenon can be due to the kind of groups in the polymeric chain as well as to the modification process, where the promoted reactions also lead to polymeric chain breaking. The introduction of acetyl groups into starch



(a)



(b)

FIGURE 5 Arrhenius plots of the ionic conductivity of cationic (a) and oxidized (b) starch films with 30% of glycerol.

molecules leads to a structural reorganization owing to steric hindrance, which results in the repulsion between starch molecules, facilitating an increase in water percolation within the amorphous regions capacity [4]. Also the acethylated and oxidized cassava starch-based SPEs have the carbonyl groups, which are electronegative and probably play some role in the complexation of the

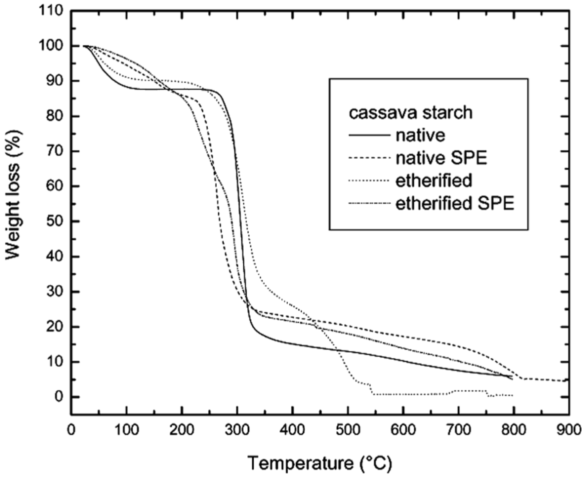
TABLE 1 Ionic Conductivity Results of the SPEs Based on Different Starch Samples Plasticized with 30% of Glycerol

Starch	σ (S/cm) at ~30°C	σ (S/cm) at ~80°C	[O]/[Li]
Corn	$6.12 \cdot 10^{-5}$	$1.41 \cdot 10^{-3}$	6
Cassava	$8.38 \cdot 10^{-5}$	$7.43 \cdot 10^{-4}$	12
Etherified cassava	$1.62 \cdot 10^{-6}$	$2.51 \cdot 10^{-4}$	8
Cationic cassava	$1.00 \cdot 10^{-5}$	$5.75 \cdot 10^{-4}$	8
Oxidized cassava	$1.78 \cdot 10^{-4}$	$1.48 \cdot 10^{-3}$	8
Acethylated cassava	$4.54 \cdot 10^{-4}$	$2.40 \cdot 10^{-3}$	10

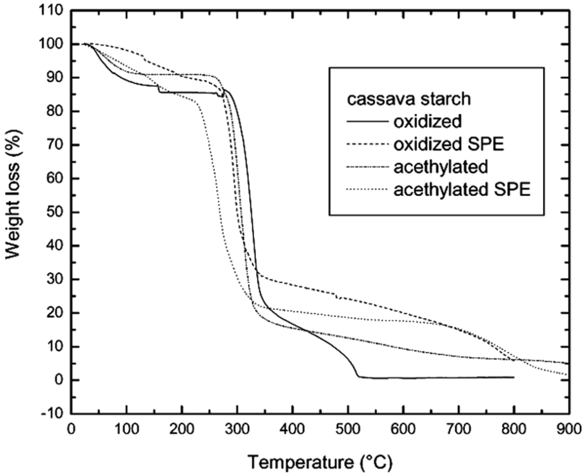
lithium ions and their dislocation from one site to another. On the other hand, the samples containing positive charge, which is the case of cationic cassava starch-based SPE samples, hinder this complexation and, consequently, the ionic movement. All these results also suggest that starch not only yields film forming properties, but also plays an important role in the conduction mechanism.

Figure 6 shows the weight loss of the samples of native and modified cassava-based SPEs, with 30% of glycerol and containing different lithium salt quantities. As can be seen in this figure the samples of native starch and oxidized starch lost 12 to 15% of the absorbed water in the temperature range between 25 and 120°C. As in the case of the samples based on corn starch, the cassava SPE samples show a smaller water loss, of about 5%, in the same temperature range and almost no water loss of the SPE samples based on oxidized cassava starch. The thermal degradation of cassava-based samples starts at 270°C for native starch [11], 250°C for modificated starches and 220°C for SPE samples, with a weight loss of about 70%. These temperatures are lower when compared with amylopectin-rich starch, which can be due to the chain extension and derivatization. The degradation is complete at 550°C only for two samples of etherified and oxidized starches, which can be explained in terms of the purity of the samples, where the dehydratation process [11] was complete. All the other samples showed 5–20% of degradation products up to 750°C of lithium salt and carbon formation [13]. All the samples showed good thermal stability up to 200°C, which is a very interesting property for this system to be applied to electrochemical devices.

The degradation temperature as a function of the lithium salt quantity of the SPE samples based on acethylated starch is shown in Figure 7a. One can observe that the decrease in the salt quantity promotes an increase in the degradation temperature from 260°C to 285°C for the samples with the salt quantity in the range from 6 to



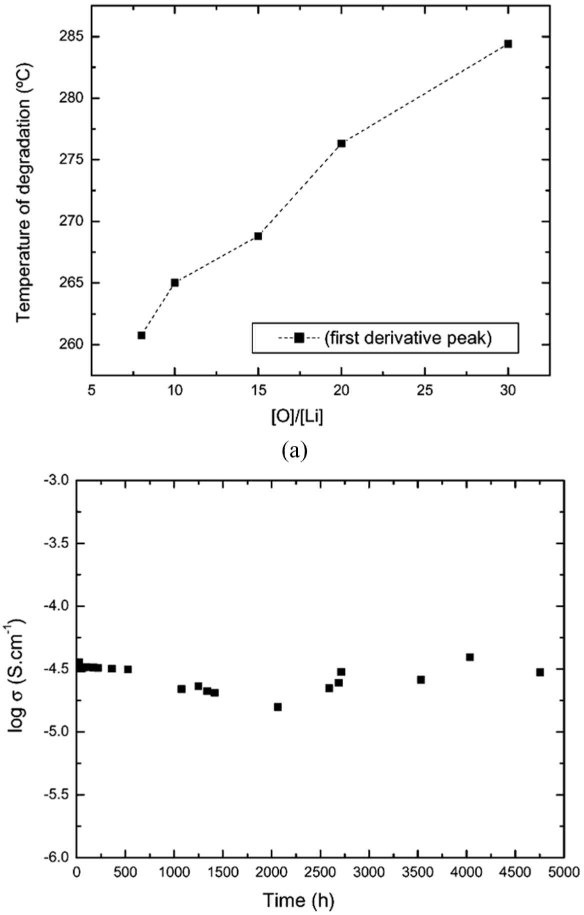
(a)



(b)

FIGURE 6 TGA results of cassava starch: native, modified and SPEs plasticized with 30% of glycerol; native and etherified (a) oxidized and acethylated (b).

30[O]/[Li]. This is probably due to the catalyst action of the lithium salt on the polymeric polysaccharide chain degradation. The stability of the SPE films were also verified, when stored in the closed recipient, i.e., without exposure to the ambient humidity. Figure 7b shows that the corn SPE-based samples demonstrated very good stability during the 6 months of measurements.



(a)

(b)

FIGURE 7 Temperature of degradation of acethylated starch-based SPEs plasticized with 30% of glycerol as a function of $LiClO_4$ contents (a) and ionic conductivity as a function of time of amylopectin-rich starch plasticized with 30% of glycerol and containing 10[O]/[Li].

4. CONCLUSIONS

Polymer electrolytes based on native and modified corn and cassava straches were prepared and analysed by thermal and ionic conductivity measurements. The ionic conductivity values of all analysed samples varied in the reange from 10^{-6} to 10^{-4} S/cm, where the best ionic conductivity values were obtained for the samples of oxidized and acethylated starches plasticized with 30% of glycerol and containing 8 and 10[O]/[Li] lithium salt concentration. The values were $1.78 \cdot 10^{-4}$ S/cm at 32°C and $1.48 \cdot 10^{-3}$ S/cm at 85°C for the oxidized starch-based SPEs and $4.54 \cdot 10^{-4}$ S/cm at room temperature and $2.4 \cdot 10^{-3}$ S/cm at 80°C for acethylated starch-based SPEs samples. The poor ionic conductivity values of $1.62 \cdot 10^{-6}$ S/cm at room temperature were obtained for the cationic starch-based SPEs.

The thermal analysis indicates that SPEs based on native and modified starches lost less water up to 120°C when compared with pure and modified starch samples. It also indicates that the samples of amylopectin-rich starch, acethylated and oxidized starches were completely degradated with liberation of CO, CO_2 and H_2O gases, when some of the samples, after heat treatment, still presented products of degradations, as carbon and lithium salt oxidation residues.

Good ionic conductivity values and thermal stability show that starch-based SPEs are very interesting to be applied to electrochemical devices.

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