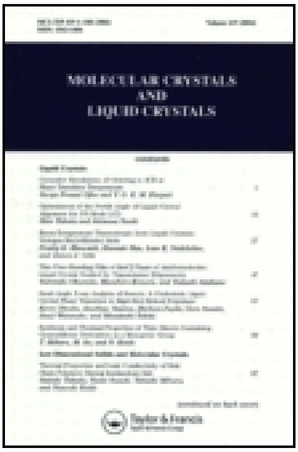

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Sodium Alginate-Based Ionic Conducting Membranes

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Sodium Alginate-Based Ionic Conducting Membranes

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The present study investigates gel polymer electrolytes (GPEs) based on sodium alginate plasticized with glycerol containing either CH_3COOH or $LiClO_4$. The membranes showed ionic conductivity results of 3.1×10^{-4} S/cm for the samples with $LiClO_4$ and 8.7×10^{-5} S/cm for the samples with CH_3COOH at room temperature. The samples also showed thermal stability up to 160°C, transparency of up to 90%, surface uniformity and adhesion to glass and steel. Moreover, Dynamic Mechanical Analysis revealed two relaxations for both samples and the Ea values were between 18 and 36 kJ/mol. All the results obtained indicate that alginate-based GPEs can be used as electrolytes in electrochemical devices.

Keywords Acetic acid; gel polymer electrolyte; lithium perchlorate; sodium alginate

Introduction

The ionic conductivity of polymers has been investigated since the P.V. Wright's [1] work on the poly(ethylene oxide) (PEO) salt dissolution properties, which initiated the solid polymer electrolyte (SPE) research area. In order to obtain high ionic conductivity values combined with thermal stability and transparency, different PEO-based systems have been investigated over the past 40 years. However, recently new polymers, such as poly(methyl metacrylate) (PMMA), poly(vinyl alcohol) (PVA) and other of natural origin have also been studied for use as polymer and gel electrolytes in eletrochromic devices. The motivation for the use of natural macromolecules is to propose alternatives to conventional PEO-based matrices, which are obtained from finite petroleum sources and present environmental problems with plastic waste. The use of natural polymers as substitutes for synthetic products is also less expensive and environmentally friendly; inded the former have convenient biodegradation properties [2]. Among various gel electrolytes based on natural macromolecules, gelatin [3,4], chitosan [5,6], cellulose derivatives [7,8] and pectin [9] can be mentioned.

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As described above the SPEs are solid solutions of inorganic salts, mainly lithium salts dissociated by a polymer matrix containing heteroatoms. In the case of PEO, the oxygen atoms promote a complexation of lithium ions, which leads to charge separation and after potential application the ionic displacement [1]. This charge mobility can occur by either Grotthuss mechanism, i.e., ion hopping between complexation sites, or vehicle mechanism, i.e., dislocation due to the polymeric chain movement or translational dynamics of larger species [10]. However, most PEO-based systems present problems due to the presence of a crystalline phase and its mealting when subjected to temperatures higher than 60°C [11]. The use of plasticizers may reduce the crystallinity of the polymeric systems by increasing the distance between the polymer chains and thus augmentation its amorphous phase; thus leading to improved displacement of ionic charge [12].

Here we present results for a new membranes based on sodium alginate. This heteropolysaccharide is obtained from brown marine *algae phaeophyceae* and is composed of two uronic acids, β-D-mannuronic (M) and α-L-guluronic (G), linked by glycosidic $(1 \rightarrow 4)$ bonds. These acids form three types of polymeric segments, G-, M- and MG-blocks [13], as shown in Fig. 1. M-blocks consist of D-mannuronic acid units, G-block is constitued by a L-guluronic unit and MG-blocks consist of a combination of M and G residues (Fig. 1). The interesting property of alginate is its capacity to form insoluble gels when complexed with Ca^{2+} ions [14–16], or when crosslinked in acidic solutions either (i) by hydrogen bonding of $-COOH$ and $-OH$ groups [13,17] or (ii) due to the reaction with glutaraldehyde [18,19].

We also report results for the preparation and characterization of sodium alginate-based GPE containing either acetic acid or lithium perchlorate. We expect to contribute to the study of the substitution of ionic conductors based on synthetic polymers by natural macromolecules. The main motivation for this alternative to use natural polymers is their low cost, biodegradability and abundance.

Experimental

The membranes based on sodium alginate were prepared dispersing 0.6 g of glycerol in 10 mL of water and heating the solution under magnetic stirring at 80°C. Next, 0.6 g of sodium alginate (Sigma-Aldrich; medium and high viscosity), and 30 mL of water were added and heated at 160°C. The solution was cooled down to room temperature. Different

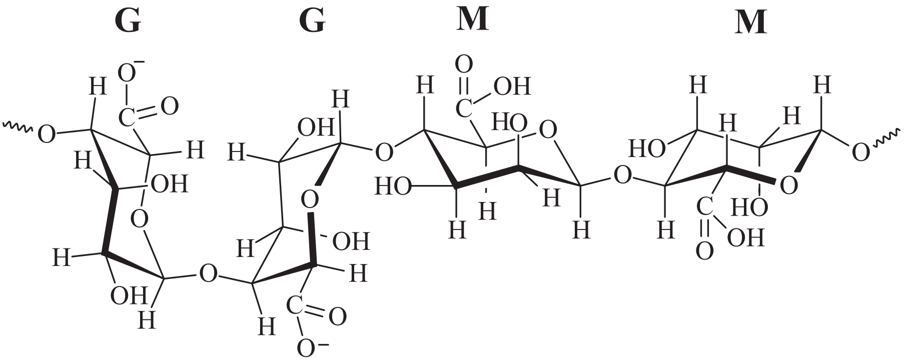

Figure 1. Alginate molecular structure fragment consisting on G-, GM- and M-blocks.

Table 1. Composition of samples of alginate-based GPEs with acetic acid

Sodium alginate		CH_3COOH		Glycerol	
g	wt.%	mL	wt.%	g	wt.%
0.6	50.0	0.1	0.008	0.6	50.0
0.6	50.0	0.3	0.023	0.6	50.0
0.6	50.0	0.4	0.033	0.6	50.0
0.6	50.0	0.5	0.042	0.6	50.0
0.6	50.0	1.0	0.083	0.6	50.0

amounts of either acetic acid or lithium perchlorate were added, as pointed in Tables 1 and 2. The final solution was poured into a Petri plate and dried at 40°C for 24 h, resulting in transparent and freestanding membranes of the thickness of 15 to 24 μm, which were stored in a dessicator to avoid air humidity.

The ionic conductivity measurements were performed placing 2 cm round and 15–24 μm thick membranes between two mirror-polished stainless steel electrodes fixed in a Teflon electrochemical cell. The conductivity values were obtained in vacuum by electrochemical impedance spectroscopy using a SOLARTRON SI 1260 Impedance/Gain Phase Analyser coupled to a computer in the 10^6 to 10 Hz frequency range with amplitude of 5 mV. All measurements were taken in triplicate.

The diffraction patterns of the membranes were obtained with Rigaku Rotaflex, model RU200B, power of 50 kV/100 mA, $CuK_\alpha = 1.540$ Å, in an angle range (2θ) of 5 to 40°, at room temperature.

The UV-Vis measurements were taken with an Agilent Instruments spectrophotometer between 190 and 800 nm.

The surface was analysed using scanning electronic microscopy (SEM), LEO model 440.

The thermal stability was studied using thermogravimetric analysis (TGA) in the temperature range of 25 to 800°C using a SHIMADZU TGA-50. The second order transition

Table 2. Composition of samples of alginate-based GPEs with $LiClO_4$

Sodium alginate		$LiClO_4$		Glycerol	
g	wt.%	g	wt.%	g	wt.%
0.6	44.7	0.142	10.6	0.6	44.7
0.6	43.8	0.170	12.4	0.6	43.8
0.6	42.5	0.213	15.0	0.6	42.5
0.6	40.9	0.268	18.2	0.6	40.9
0.6	40.4	0.284	19.2	0.6	40.4
0.6	36.9	0.426	26.2	0.6	36.9
0.6	34.6	0.532	30.8	0.6	34.6

temperature was determined using Dynamical Mechanical Analysis (DMA) in the temperature range of −90 to 150°C utilizing a TA Instruments DMA model 2980 with deformation rate of 0.1%, heating rate of 2°C and in N_2 atmosphere.

Results and Discussion

The thermogravimetric measurements were performed in order to establish the maximum temperature at which the polymer-based sample maintained its physico-chemical properties and could be still functional. Analyzing the thermograms (Fig. 2a and b) it is possible to observe that all the samples lose from 10 to 20% in weight up to 170°C, which can be due to their residual water. The alginate powder loses 20% of weight up to 170°C. In the temperature range of 170 to 280°C, the samples lose approximately 60% of their weight due to degradation processes. The weight loss slowly continues as the temperature is increased to 700°C, at which most of the samples lose another 10% in weight. The remaining residue was 10% in mass of the starting material. As in other polysaccharides-based ionic conducting membranes, the degradation process is accelerated and catalysed probably by $LiClO_4$ and acetic acid [20]. From these measurements it is possible to observe a higher weight loss up to 170°C in the samples with high lithium salt concentration, when compared with the sample with acetic acid, in which the weight loss is only 10%. This difference may be due to the hygroscopic properties of $LiClO_4$ and consequent higher amount of absorbed water.

Figure 3 shows typical X-ray diffraction patterns obtained for the sodium alginate-based electrolytes with different amounts of $LiClO_4$ (Fig. 3a) and acetic acid (Fig. 3b). It also shows the diffractogram pattern of sodium alginate powder, in which a semi-crystalline structure, typical for polysaccharide is observed. Moreover, alginate powder presents two X-ray peaks: one at 14° and another at 21.5°. In all other difractograms no crystalline peaks are observed and only a broad weak peak is seen at $2\theta = 22°$. Also the absence of any $LiClO_4$ crystalline peaks indicates the complete dissolution of the salt in the polymer matrix. However, in the sample with acetic acid and probably due to more crystalline structure, it seems that the peaks at 22° are sharper when compared with the sample with $LiClO_4$, suggesting greater structural ordering produced by the presence of hydrogen

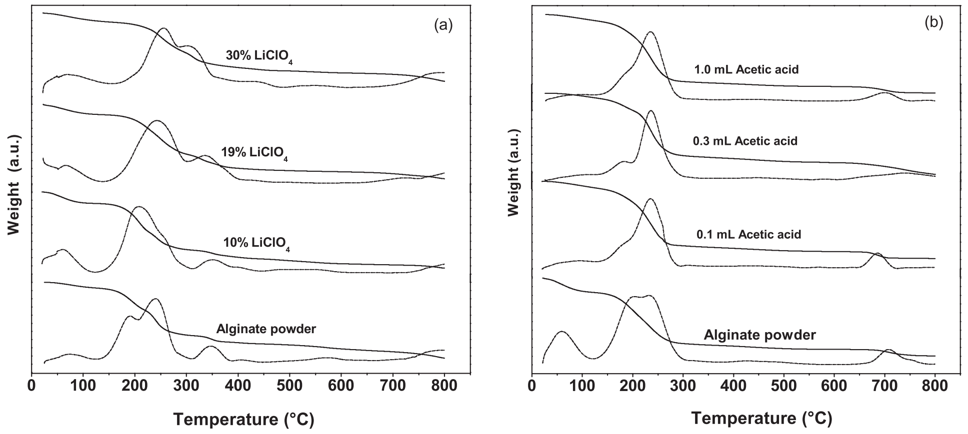

Figure 2. TGA (—) and DTGA (- - -) results of sodium alginate and sodium alginate-based electrolytes containing different quantities of $LiClO_4$ (a) and acetic acid (b).

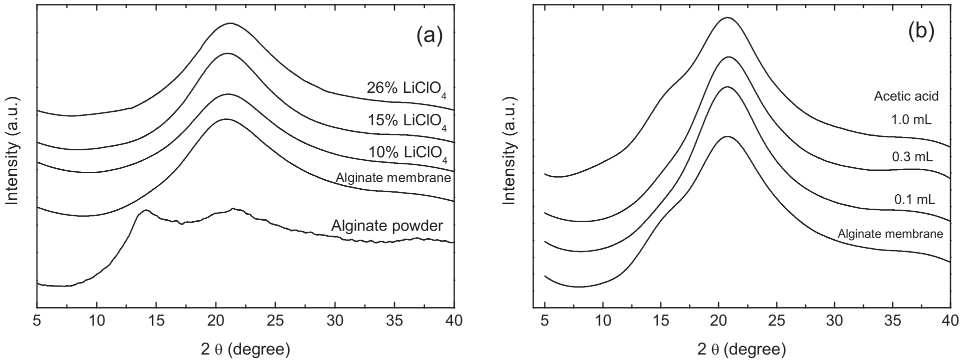

Figure 3. X-ray diffractograms of sodium alginate and sodium alginate GPEs with different quantities of $LiClO_4$ (a) and acetic acid (b).

bonds [13]. Moreover, similarly to previous studies, the electrolytes can be considered X-ray predominantly amorphous with a weak partially crystalline structure [21].

As polymer electrolytes are developed aiming at the substitution of liquid substances in several electrochemical devices, as, for instance electrochromic windows, they should be transparent. It has already been observed in our previous studies that gel electrolytes based on natural polymers and obtained in the selfstanding membrane forms present transparency of 90% in the visible range of electromagnetic spectrum [21]. In the present work also high optical transmittance properties of ionic conducting membranes were observed (Fig. 4a and b). All membranes, startig at 220 nm, show an increase from zero of transmittance to a maximum of 60–90% at 800 nm and depending on the sample. In the case of $LiClO_4$ containing samples it is possible to observe a decrease in the transmittance with the increase in the lithium salt concentration (Fig. 4a), as already observed in the samples based on amylopectin-rich starch [22]. The highest value was 80% at 600 nm for the sample with 12 wt.% of $LiClO_4$. The small difference in the transmittance values of the samples with 10 and 12 wt.% of $LiClO_4$ is probably due to the thickness of the membrane. The low transparency of two other samples, i.e., with 20 and 25 wt.% of salt is probably due to the formation of ionic aggregates. The samples containing acetic acid, independently of the

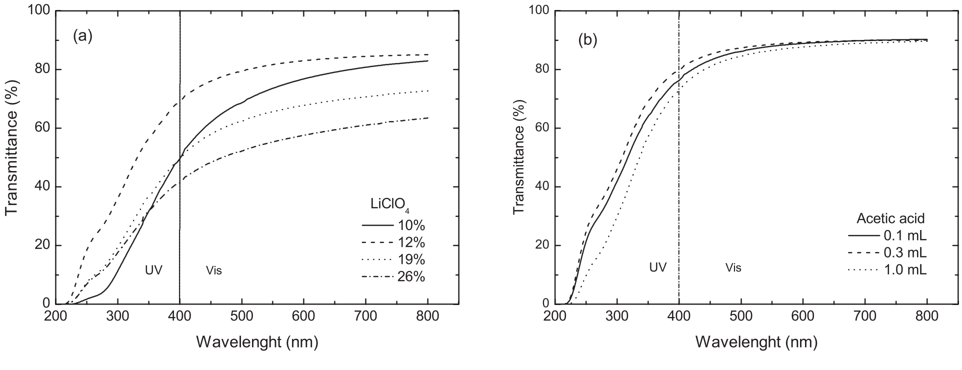

Figure 4. Transmittance spectra of sodium alginate GPEs with different quantities of $LiClO_4$ (a) and acetic acid (b).

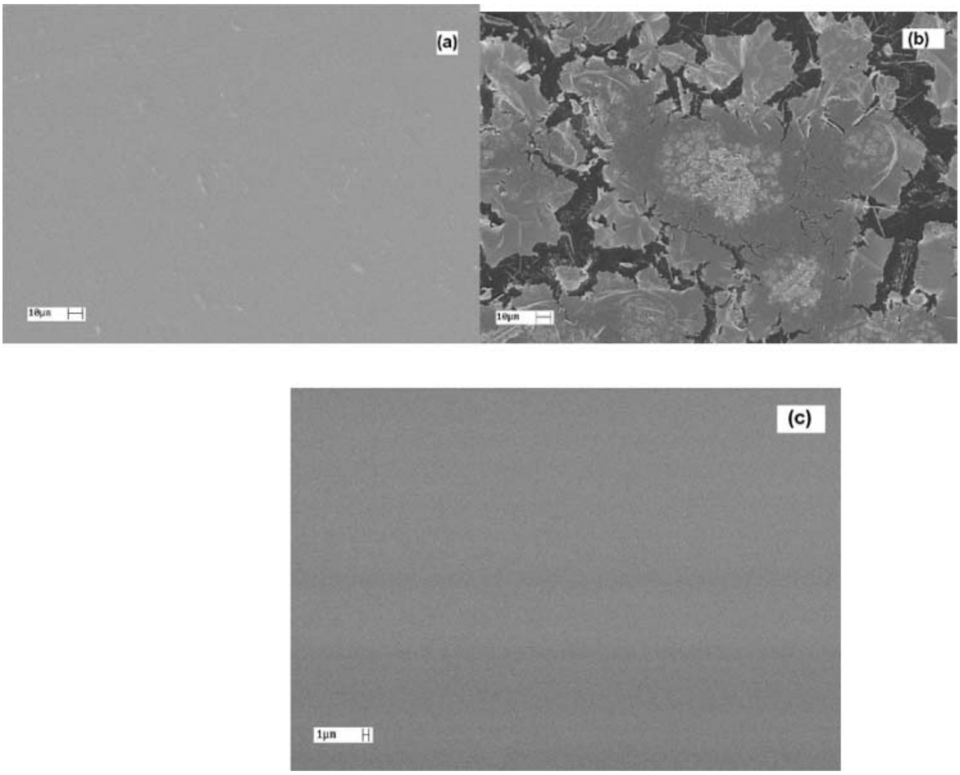

Figure 5. SEM pictures of sodium alginate-based GPEs with 12 wt.% of $LiClO_4$ (1000×) (a), 22 wt.% of $LiClO_4$ (1000×) (b) and with 0.3 mL of acetic acid (4000×) (c).

quantity, showed transmittance of 90% at 550 nm, which is a slightly different result, when compared with agar-acetic acid-based membranes [23].

SEM pictures of sodium alginate-based electrolytes with 12 wt.% of $LiClO_4$ and 0.3 mL of acetic acid reveal unique homogeneous phase (Fig. 5a and c). The SEM micrograph of the sample with 22 wt.% of lithium salt (Fig. 5b) shows cracks and lack of homogeneity, which can be due to the high salt concentration, resulting probably in a syneresis process, i.e., expulsion of liquid from the gel matrix [24]. The samples with acetic acid or with less than 22 wt.% of lithium salt, as other natural polymer-based electrolytes samples, were translucent and showed adhesion properties to glass and steel.

The ionic conductivity (σ) of the sodium alginate-based electrolyte at room temperature is presented as a function of the $LiClO_4$ salt and acetic acid concentration in Fig. 6. The ionic conductivity was calculated using the relation $\sigma = l/R_bA$, where l is the thickness of the electrolyte sample, A is the area of contact between the electrolyte and electrode (1.54 cm^2), and R_b is the measured resistance. This value was determined by the intercept of the fitted semicircle with the real axis of the Z'' vs Z' Nyquist plot (not showed here). The ionic conductivity of sodium alginate-based membranes is 10^{-6} S/cm and increases with the amount of $LiClO_4$ to reach a maximum of 3.2×10^{-4} S/cm for 15 wt.% of $LiClO_4$ (Fig. 6a). GPE samples with acetic acid (Fig. 6b) also show an increase in the ionic conductivity values with the increase of the CH_3COOH content, reaching the maximum of 8.7×10^{-5} S/cm for 0.3 mL of CH_3COOH. The increase of conductivity is certainly related to the increase in the number of mobile charge carriers. For high quantity of both $LiClO_4$ salt and

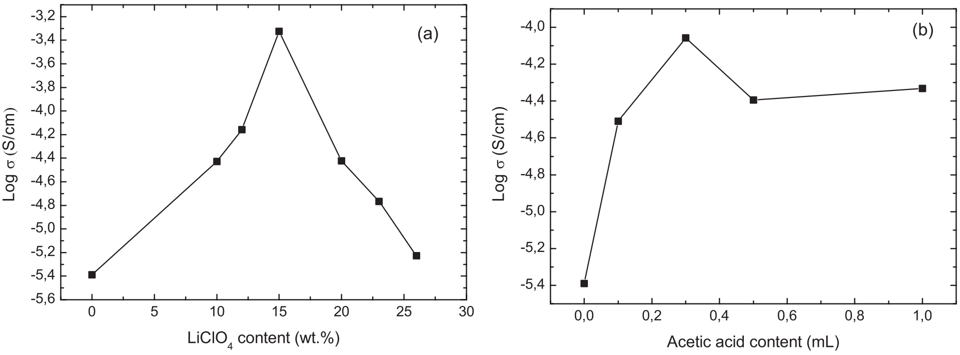

Figure 6. Ionic conductivity as a function of the $LiClO_4$ (a) and acetic acid (b) content of sodium alginate-based electrolytes measured at room temperature.

acetic acid in the electrolyte, a decrease in the ionic conductivity is observed, probably due to the formation of ionic aggregates, as already observed for other polysaccharide-based electrolytes [23]. In the case of samples with acetic acid a decrease of ionic conductivity with acetic concentration increase can be explained also in therms of protonation of carboxylate groups and hydrogen bond formation [13,25]. The ionic association at high concentrations of salt is a determining factor of the ionic transport [26]. The decrease is also different for the two types of electrolytes, here compared. The ionic conductivity of the samples with $LiClO_4$ after reaching the maximum decreases steadily with the increase in the salt content and the ionic conductivity of the samples with acetic acid decreases up to 3.7×10^{-5} S/cm for the samples with 0.5 mL, remaining almost at the same value for the sample with 1.0 mL of CH_3COOH. This difference can be related to the interraction of lithium salt with the polymeric backbone, as well as with the aggregates formation, resulting in an increased viscosity and the second order transition temperature of the polymer matrix [27]. Indeed, this is observed in the present study and may be confirmed in Table 3.

The evolution of the ionic conductivity as a function of temperature in the 25 to 80°C range and for the samples with different salt and acetic acid concentrations is shown in Fig. 7. For the electrolyte with 15 wt.% of $LiClO_4$ (Fig. 7a), one observes that the value of 3.2×10^{-4} S/cm at 26°C increases to 1.2×10^{-3} S/cm at 82°C. For the sample with 3 mL of

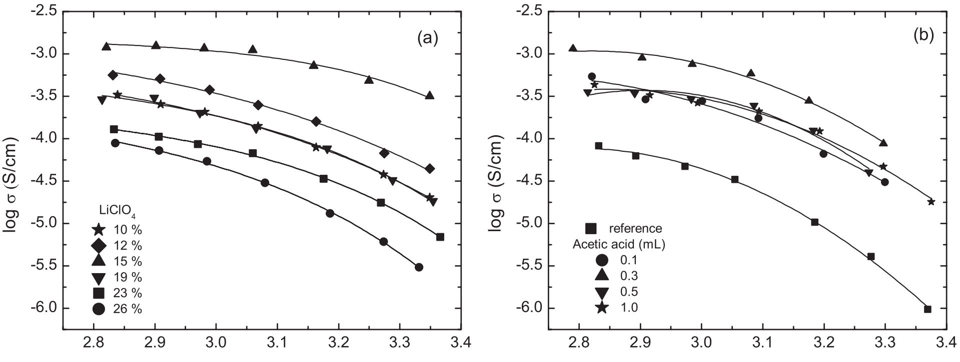

Figure 7. Ionic conductivity as a function of temperature of sodium alginate-based electrolytes with different $LiClO_4$ (a) and acetic acid (b) quantities.

Table 3. Glass transition temperature, energy of activation and ionic conductivity values for the sodium alginate-based GPEs with $LiClO_4$ and acetic acid

	$LiClO_4$ (wt.%)				CH_3COOH (mL)		
	12	15	19	26	0.3	0.4	0.5
Tg (°C)							
β	−49	−51	−50	−48	−42	−46	−44
α	3	10	5	11	33	11	31
Ea (kJ/mol)	34.8	18.4	29.2	26.5	36.1	33.6	36.0
σ (S/cm) at 30ºC	7.0×10^{-5}	4.7×10^{-4}	3.8×10^{-5}	5.9×10^{-6}	8.7×10^{-5}	4.0×10^{-5}	4.7×10^{-5}

acetic acid (Fig. 7b), the ionic conductivity value of 8.8×10^{-5} S/cm at 30°C increases to 1.1×10^{-3} S/cm at 85°C. As can be observed on this figure this increase in conductivity with temperature is non-linear, what has been usually interpreted as the ionic motion coupled to the segmental motion of the polymeric chains. However, other complex behaviors such as hopping mechanism between coordinating sites or local structural relaxations could be involved simultaneously with segmental motions of the polymer. As the temperature increases, the polymer chain acquires faster internal modes in which bond rotations produce segmental motion [28].

Due to the non-linear behavior of the ionic conductivity versus temperature, these results also follow a Vogel-Tamman-Fulcher (VTF) [11] thermally activated process model expressed by $\sigma = (A/T^{1/2}) \exp[-B/k(T-To)]$, where k is the Boltzmann constant, B is the pseudo activation energy and $To = Tg\text{-}50\ K$, where Tg is considered as the second order transition temperature.

To obtain the activation energy values, Dynamic Mechanical Analyses were performed (Fig. 8). DMA is a very interesting technique for polymer system analysis, as it sense any change in the molecular mobility in the sample as the temperature is raised or lowered. These changes depend on the properties of the sample, its composition and morphology. In the case of the multicomponent samples, the nature of the phase can also be evaluated. The DMA of the pristine sodium alginate membrane reveals a second order transition temperature value at 109°C [18] and also shows a second transition at 30°C, which can be due to the β transition ascribed to the motion of the side groups or short segments. The DMA measurements obtained for the sodium-alginate-based samples containing LiClO$_4$ (Fig. 8a) also showed two second order transition temperatures, the first one at around 5°C and the second one at around −50°C. From these measurements it can be stated that both α and β transistions decreased due to the sample composition, as a consequence of the plasticization process. In the samples with acetic acid (Fig. 8b), two second order transition temperatures are also observed, however the corresponding values are higher, i.e., around 20°C and −45°C. This increase in the second order transition can be due to the more rigid structure already observed in the X-ray difractogramms. The results showed in Fig. 8b for the samples containing acetic acid also show a third peak, which is large and centered at 110°C and can be atributed to the loss of water, corroborating the TGA measurements. Similar results were obtained for plasticized hydroxyethyl cellulose [20].

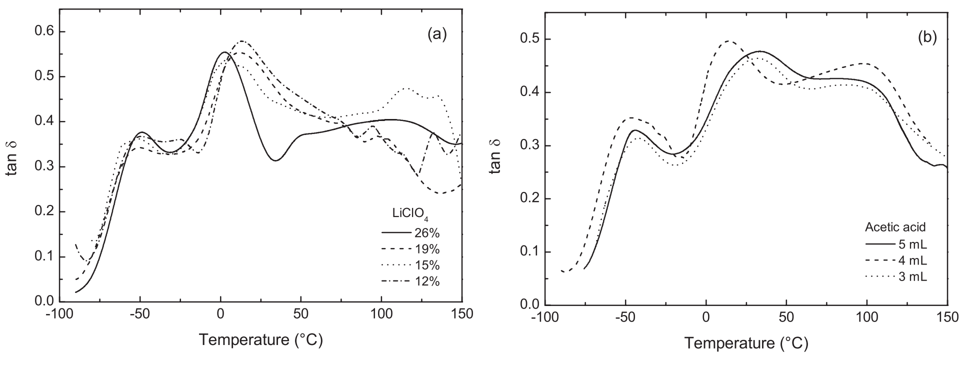

Figure 8. DMA analysis of sodium alginate-based electrolytes with different LiClO$_4$ (a) and acetic acid (b) quantities.

DMA results were also used to calculate the activation energy values of the samples. The comparision of the second order transition temperature, energy of activation and ionic conductivity results is shown in Table 3. The lowest pseudo activation energy value of 18.4 kJ/mol was for the samples with 15 wt.% of $LiClO_4$. The samples with acetic acid present activation energy values around 36 kJ/mol, similarly to polymer electrolytes based on agar with acetic acid [23] or other natural macromolecules [3,22] and all of them are quite low in comparison with sodium alginate without plasticizer which are ranging between 73 and 83 kJ/mol [29].

Conclusions

Sodium alginate-based gel polymer electrolytes with $LiClO_4$ and CH_3COOH were obtained and characterized in this study. The results revealed that the lithium salt concentration influences the ionic conductivity of electrolyte and the best value of 3.1×10^{-4} S/cm at room temperature was obtained for 15 wt.% of $LiClO_4$. The samples with acetic acid showed ionic conductivity values of 8.7×10^{-5} S/cm. It was also observed that the rise in temperature up to 80°C promotes an increase in the ionic conductivity of 1.2×10^{-3} S/cm for the samples with $LiClO_4$ and 1.1×10^{-3} S/cm for the sample with 3 mL of acetic acid. These results show a VTF behavior with activation energies of $Ea = 18.4$ and 36 kJ/mol, respectively. The samples in the self-standing membranes form were predominantly amorphous, showing transparency of 60 to 90% in the visible range of the electromagnetic spectrum. SEM visualisation revealed a very uniform surface for all samples containing acetic acid and samples with up to 20 wt.% of $LiClO_4$. The samples also showed thermal stability up to 170°C and second order transition temperature of -42 to -51°C. All the results obtained indicate that alginate-based GPEs are good candidates to be used as electrolytes in electrochemical devices.

Acknowledgements

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