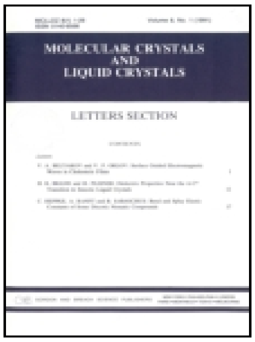

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Pectin-based Polymer Electrolytes with Ir(III) Complexes

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Pectin-based membranes with different salts such as $LiClO_4$, KCl, $LiClO_4$-Ir(III) and KCl-Ir(III) contents were prepared and characterized. The most conductive sample of Pectin@KCl exhibits the ionic conductivity of 1.45×10^{-3} $S.cm^{-1}$ and 6.31×10^{-3} $S.cm^{-1}$ at 25°C and 90°C, respectively. The X-ray diffraction (XRD) analysis reveals the predominantly amorphous nature of the samples and the atomic force microscopy (AFM) images show a roughness of 21.8 and 10.5 nm for the samples of Pectin@KCl and Pectin@$LiClO_4$, respectively. The overall redox stability of 7.0 V suggests that this material has an acceptable stability window for an application in solid state electrochemical devices.

Keywords Pectin; Iridium III complexes; polymer electrolytes

Introduction

During the last two decades a remarkable international research effort has been dedicated to the development of solvent-free solid polymer electrolytes based on poly(ethylene oxide) (PEO) [1]. The most probable applications of these materials are in primary and secondary batteries [2], in electrochromic windows [3] and related applications [1].

The increasing consumer demand as well as environmental regulation, pointing to reduce the use of synthetic-oil-derived materials, has recently impulse the researches to explore natural materials. One of the most promising approaches to overcome environmental problems is the use of biodegradable polymers useful for various applications in medical, pharmaceutical, agriculture, drug release, and electrochemical devices [4–6].

Biopolymers, such as polysaccharides, proteins, and their composites, which can be obtained from natural resources and also agriculture by-products, have been intensively studied [7–9]. However, the use of renewable polymers depends on several features, like availability, optical quality, barrier properties to water, O_2, and CO_2, but principally on their mechanical properties and structure resistance to water.

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Among natural polymers, pectin, being secondary product of fruit juice, sunflower oil, and sugar manufacture, is very good candidate for eco-friendly biodegradable materials [10]. Pectin is a complex mixtures of polysaccharides composed of a galacturonic acid backbone, i.e., homogalacturonan or so-called smooth regions of which variable proportions can be methyl-esterified [11]. Pectin was also already successful tested as polymer electrolyte where the ionic conductivity of 4.7×10^{-4} S.cm^{-2} was obtained [12]. Following the research on polymer electrolytes based on pectin the present work is focused on the preparation of ionic conducting membranes containing either $LiClO_4$, KCl or KCl-Ir(III) complex with different contents. Obtained polymer electrolytes were then characterized by conductivity measurements, cyclic voltammetry at a gold microelectrode, thermal analysis (DSC and TGA), X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM).

Experimental

Commercial pectin (0.6g, BRS-Z from CP Kelco Limeira S.A.) was dispersed in 20 mL of Milli-Q water and heated under magnetic stirring for a few minutes and up to 70°C for a complete dissolution [12]. To this solution was added glycerol (Himedia, 99.5%) as plasticizer and either $LiClO_4$, KCl or KCl-Ir(III) complex. The samples were denominated, Pectin@$LiClO_4$, Pectin@KCl, Pectin@Ir, Pectin@$LiClO_4$-Ir and Pectin@KCl-Ir. After complete dissolution the samples were poured on Petri plates and let to dry up at room temperature to form transparent membranes. For final drying, the films were transferred to an oven at 50°C and the samples were aged for 2 days.

A sample of dry film was subjected to Differential Scanning Calorimetry (DSC) analysis under a flowing argon atmosphere between −60 and 200°C and at a heating rate of 5°C.min^{-1} using a Mettler DSC 821 e. The sample was transferred to a 40 μL aluminum can with perforated lids within a dry argon-filled glove-box. Samples for thermogravimetric (TGA) studies were prepared in a similar manner, transferred to open crucibles and analyzed using a TA Instruments TGA Q50 thermobalance operating between 25 and 750°C and at a heating rate of 10°C.min^{-1}.

The evaluation of the electrochemical stability window of the electrolyte composition was carried out under an argon atmosphere using a two-electrode cell configuration. The preparation of a 25 μm diameter gold microelectrode surface, by polishing it with a moist cloth and 0.05 μm alumina powder (Buehler), was completed outside the dry box. The cell was assembled by locating a clean lithium disk counter electrode (Aldrich, 99.9%; 19 mm diameter and 0.75 mm thick) on a stainless steel current collector and centering a sample of electrolyte on the electrode surface. To achieve a reproducible microelectrode/electrolyte interfacial contact 2 μL of THF was placed on the microelectrode surface, fixed on the electrolyte surface and supported firmly by means of a clamp. Voltammograms were recorded with Autolab PGSTAT-12 (Eco Chemie) at a scan rate of 100 mV.s^{-1}; at room temperature and within a Faraday cage.

The total ionic conductivity of the samples was determined by locating an electrolyte disk between two 10 mm diameter ion-blocking gold electrodes (Goodfellow, $>$ 99.95%) to form a symmetrical cell. The electrode/polymer electrolyte/electrode assembly was secured in a suitable constant volume support and installed in a Büchi TO51 tube oven with a type K thermocouple placed close to the electrolyte disk to measure the sample temperature. Bulk conductivities of the electrolyte samples were obtained during heating cycles using the

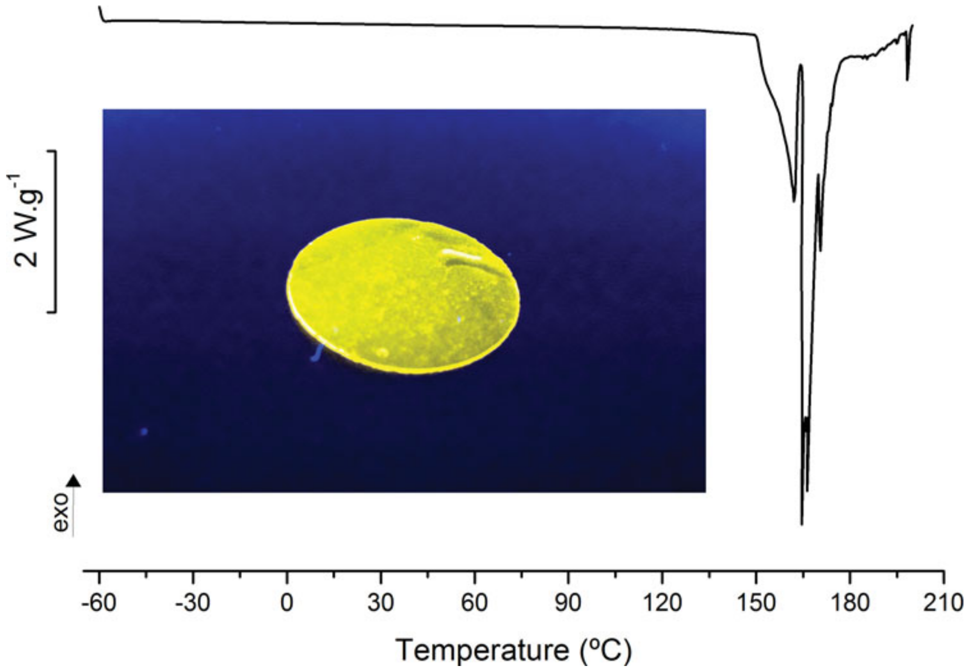

Figure 1. DSC curve of the Pectin@KCl-Ir sample. Inset: physical appearance in UV chamber.

complex plane impedance technique with Autolab PGSTAT-12 or Eco Chemie equipment between 25 and 100°C and at approximately 7°C intervals.

X-ray diffraction (XRD) measurements were performed at room temperature with a PANalytical X′Pert Pro equipped with a X′Celerator detector using monochromatic CuK$_\alpha$ radiation ($\lambda = 1.541$ Å) over the 2θ range between 10 and 60°.

Scanning Electron Microscopy (SEM) pictures were obtained with LEO model 440.

The Atomic Force Microscopy (AFM) images were obtained with Nanosurf easyScan 2 AFM System (Nanosurf AG, Switzerland). In all AFM analysis, the noncontact mode, were employed by using silicon AFM probes with a force constant of 48 N/m and the resonance frequency was 190 kHz.

Results and Discussion

Figure 1 shows a DSC curve obtained between −60 and 200°C for the Pectin@KCl-Ir sample. The absence of any thermal event between −60 and 150°C confirms that the pectin based electrolyte have predominantly amorphous morphology in the temperature range studied. These thermal analyses are very similar in behavior when compared with other natural macromolecules-based electrolytes [13–15]. As can be observed on Figs. 1 and 2 the results of DSC and TGA analysis are consistent with a minimum thermal stability of about 150°C for all the samples, a value considered acceptable for most applications under normal operating conditions. Figure 1 also reveals on inset picture a physical appearance of the sample in UV chamber where one can observe very smooth surface without any cracks but with some small white spots.

The onset temperature of thermal decomposition was estimated by thermogravimetric analysis using extrapolation of the baseline and tangent of the curve of thermal events to

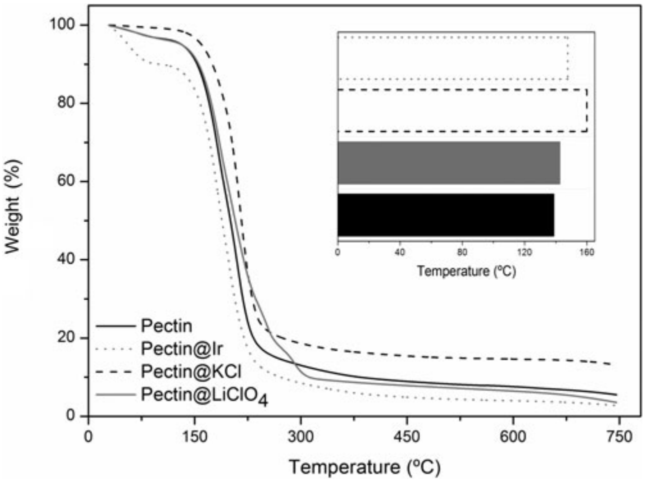

Figure 2. TGA curves of the pectin-based electrolytes. Inset: Onset temperature of thermal decomposition.

identify the beginning of the sample weight loss (Fig. 2). The values of the initial weight loss of the samples are shown in the inset of Fig. 2. These results confirm that weight loss associated with thermal degradation of samples occurred at temperatures above 140°C for all compositions, including the host matrix without salt.

The TGA measurements showed in Fig. 2 evidence a 5–15% loss of mass from ambient temperature to ≈120°C of pure pectin and pectin-based samples, which can be attributed to free water loss. At this point it should be stated that glycerol and lithium perchlorate are hydrophilic substances and their presence promotes an increase of the water absorption capacity of the film [16]. Moreover, all studied samples present a characteristic two or three-step thermal degradation, typical of pectin [17–19].

In the case of pure Pectin and Pectin@$LiClO_4$ samples, the first weight loss of 5% of the initial mass occurs at ≈75°C and corresponds to the water loss. Then, for pure Pectin, it is followed by the second weight loss of about 80% between 140 and 300°C. This weight loss is due to the pyrolitic decomposition, result of a primary and secondary decarboxylation involving the acid side group and a carbon in the anhydroglucose ring. The observed third weight loss between 500 and 750°C corresponds to the oxidation reactions [17–19]. The remaining residue is 5%.

For Pectin@$LiClO_4$, the weight loss behavior as a function of temperature is quite different. The sample degradation starts at 145°C and occurs in two stages, which can be due to the interactions of lithium salt and glycerol with the polysaccharide chain. The 80% weight loss ends at ≈ 400°C and practically there is no more change up to 750°C. The ≈ 8% remaining residues are probably due to the lithium carbonate formation as in the case of LiCMC and NaCMC and their grafted products [20].

In the Pectin@KCl-Ir, the first weight loss of 10% occurs at ≈ 75°C, corresponds to the water loss and is followed by the second weight loss between 150 and 400°C (Fig. 2). After that, there are no more changes in the TGA curves up to 750°C. The remaining residue is 5%. For the Pectin@KCl the loss of water doesn't appear and this is the most stable sample. The sample degradation starts at 160°C, occurs in one stage and ends at 300°C with 85% of weight loss. It can be also noted that at 750°C the residues of 15% are higher than for other

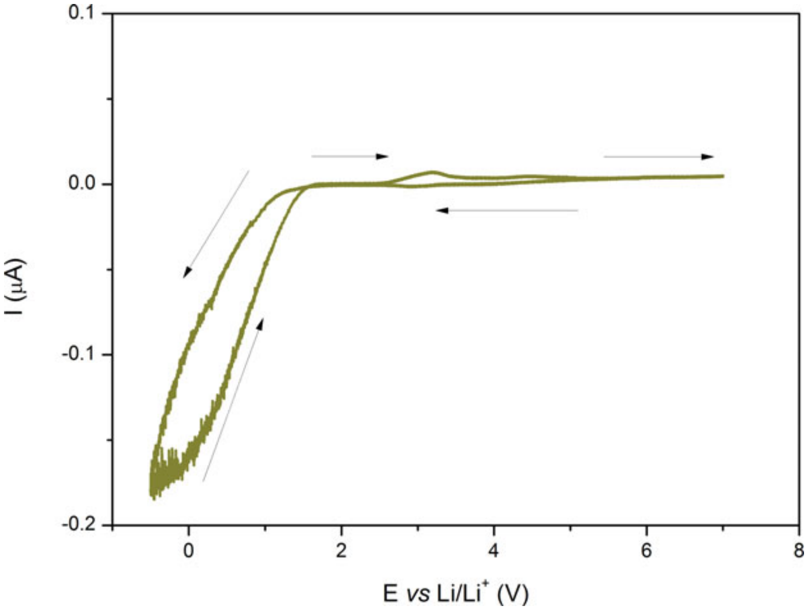

Figure 3. Cyclic voltammogram of the Pectin@KCl-Ir at room temperature with a 25 μm gold microelectrode as working electrode. The initial sweep direction is anodic and the sweep rate is 100 mV.s^{-1}.

samples. It means that the sample probably contains some impurities that were removed from the sample with the Ir complex addition.

For displays applications, it is necessary to investigate the electrochemical-operating window within the operating voltage of the devices. The electrochemical window was determined by cyclic voltammetry over the potential range of -1.0 to 7.0 V. Figure 3 reveals the voltammogram of the Pectin@KCl-Ir solid polymer electrolyte membrane, where 7.0 V of electrochemical stability can be observed. The cathodic current onset observed at about 0.0V may also correspond to the electrochemical deposition of lithium [21]. Moreover, the presence of a small peak at 1.0 V is also observed. Previously, the peaks in this region have been ascribed to reduction of low level of water present in polymer electrolytes or oxygen impurities. Analogous behavior has been observed for other systems based on PEO and lithium salt [22].

The temperature dependence of the ionic conductivity calculated from equation 1 for all solid polymer electrolytes is shown in Fig. 4. From this figure one can observe that the addition of KCl or $LiClO_4$ salt increases the ionic conductivity of the membranes in comparison to the matrix polymer in the entire temperature range under consideration.

The ionic conductivity (σ) was calculated for each heating cycle according to:

$$\sigma = \frac{d}{R_b A} \tag{1}$$

Where, R_b is the bulk resistance, d is the thickness and A is the area of the sample. R_b is obtained from the intercept of the imaginary impedance (minimum value of Z'') with the slanted line in the real impedance (Z') through the Randles circuit [23].

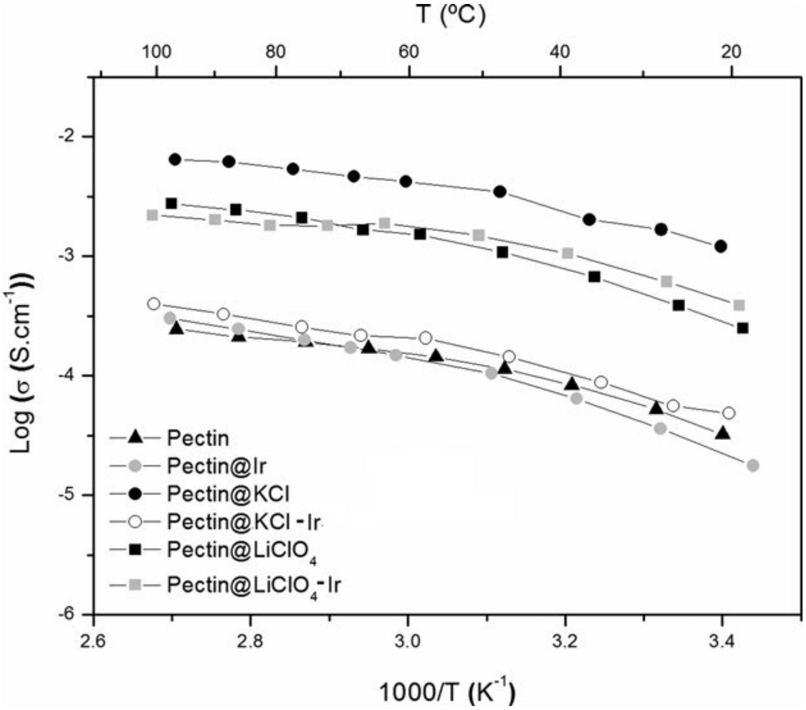

Figure 4. Ionic conductivity as a function of temperature of pectin-based electrolytes.

The sample that displays the highest conductivity of 1.45 × 10^{-3} S.cm^{-1} and 6.31 × 10^{-3} S.cm^{-1} at 25°C and 90°C, respectively is the Pectin@KCl, however after addition of the Ir complex, the conductivity decreases and is similar to the pure matrix, i.e., 5.42 × 10^{-5} S.cm^{-1} at 25°C and 3.42 × 10^{-4} S.cm^{-1} at 90°C. Analyzing this phenomenon it can be stated that although the number of charge carriers increases with the increase of iridium complex amount, a high concentration of salt leads to the decrease of free volume, as well as available coordination sites. Additionally, the influence of the complex size should also be taken into account. Aiming to understand obtained results sample of Pectin@LiClO$_4$-Ir was prepared and analyzed. It was observed that this sample displays higher conductivity than Pectin@KCl-Ir, probably because smaller quantity of water as evidenced by TGA results (Fig. 2). Hygroscopic and amorphous pectin absorbs water and undergoes plasticization to acquire more rubber state that improves molecular mobility [24].

The XRD patterns of the pectin-based electrolytes, represented in Fig. 5, reveal that these samples are entirely amorphous. These diffractograms exhibit a broad and Gaussian in shape peak, centered at ca. 21°. This result is very similar to the results obtained by Lutz et al. [25] for apple pectin and also by Andrade et al [12]. The sample with the complex of Ir exhibits sharp crystalline peaks at ca. 2.5, 5.0 and 10.0°, revealing an ordered structure.

Figures 6 a–d shows the SEM images of the pectin-based membranes without and with different salt contents. As can be seen on Fig. 6a Pectin host exhibits a non-porous homogeneous texture however with very small cracks probably due to the drying process. The addition of small amounts of lithium perchlorate to the sample composition promotes an increase of these cracks and consequently a change of morphology (Fig. 6b). The Pectin@KCl sample exhibits different morphology when compared with other samples,

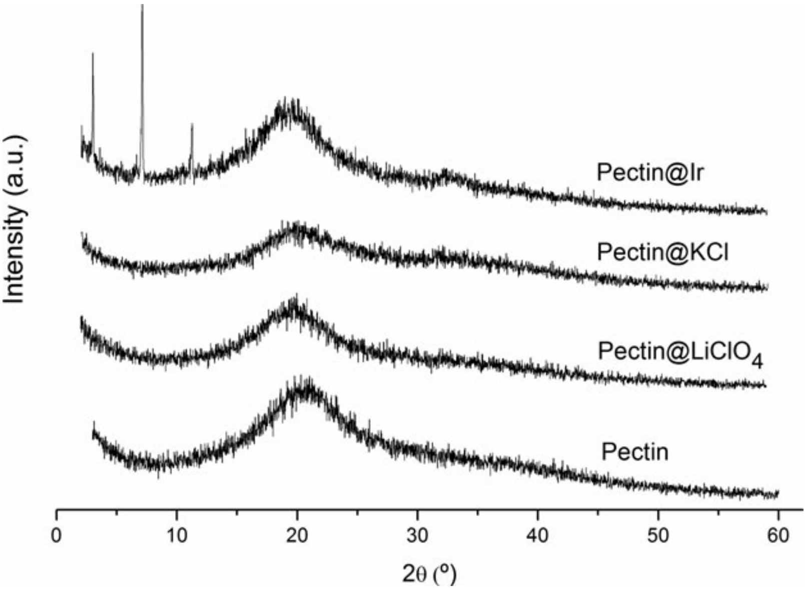

Figure 5. XRD patterns of the pectin-based electrolytes.

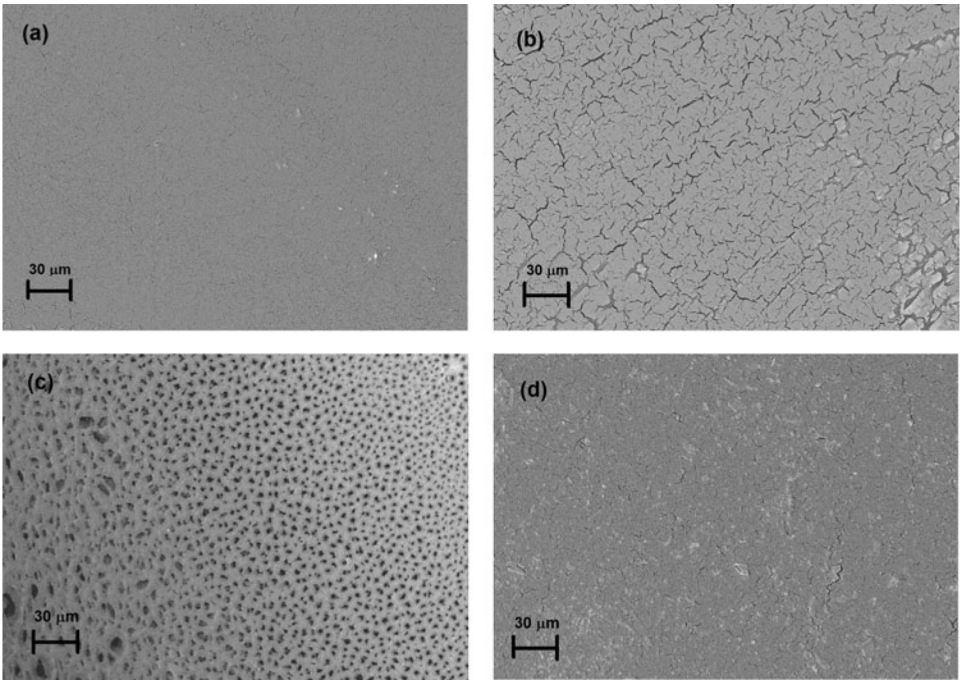

Figure 6. SEM micrographs of the pectin-based electrolytes: (a) Pectin; (b) Pectin@LiClO$_4$; (c) Pectin@KCl and (d) Pectin@KCl-Ir.

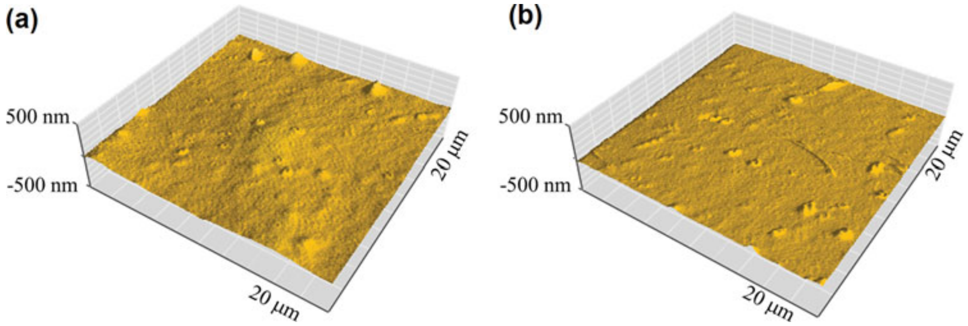

Figure 7. AFM images for Pectin@KCl (a) and Pectin@LiClO$_4$ (b) membranes.

where uniformly distributed dark spots with less than 5 μm of diameter are observed (Fig. 6c). This image can represent a porous microstructure as a result of the solvent evaporation. The surface image of the sample Pectin@KCl-Ir on Fig. 6d reveals small cracks and some light spots being very similar to the Pectin sample. Good surface homogeneity and the presence of the cracks was already observed in the pectin-based electrolytes described by Andrade et al. [12].

The morphological characteristics of pectin-based membranes without and with different salt contents were also examined by Atomic Force Microscopy (AFM). Figure 7 displays a typical AFM image of the Pectin@KCl (Fig. 7a) and Pectin@LiClO$_4$ (Fig. 7b). Based on Pectin@KCl and Pectin@LiClO$_4$ topographic analyses, the roughness mean square (RMS) are 21.8 and 10.5 nm, respectively. A decrease of the RMS of the Pectin@LiClO$_4$ is evidenced by smoother surface when compared with the image of the Pectin@KCl sample leading in 2.1-fold RMS decrease.

Conclusions

The results showed that the LiClO$_4$, KCl, and a complex of Ir(III), can be successfully incorporated into a natural macromolecule matrix as pectin. Six different kind of membranes were prepared and analyzed by DSC, TGA, X-ray, AFM, SEM, cyclic voltammetry and impedance spectroscopy. The samples were obtained in the form of transparent membranes and can be used as free-standing polymer electrolytes.

The results of DSC and TGA analyses give a minimum thermal stability of about 140°C for all samples, a value considered more than adequate for applications in displays under normal operating conditions. Also the encouraging results of the ionic conductivity of 1.45×10^{-3} S.cm^{-1} and 6.31×10^{-3} S.cm^{-1} at 25°C and 90°C, respectively; the overall redox stability of 7.0 V; predominantly amorphous structure; homogenous surface properties and a roughness of 10.5 to 21.8 nm reveal that pectin-based membranes are sufficient to justify further studies. Finally, the preliminary tests performed in this study, suggest that these materials may find application in light-emitting electrochemical cell (LEC) devices, but further optimization of the device assembly procedures is required.

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