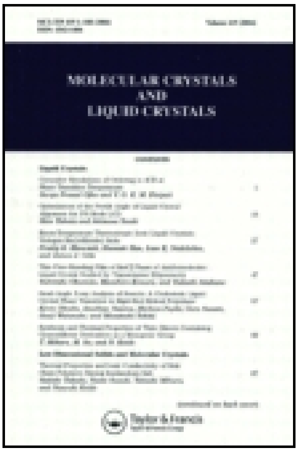

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Starch Based Solid Polymeric Electrolytes

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New solid polymeric electrolytes were obtained from amylopectin rich starch plasticized with glycerol and containing lithium perchlorate salt. The transparent film samples were characterized by X-ray diffraction and thermal analysis (DSC). The ionic conductivity measurements were obtained by impedance complex spectroscopy as a function of temperature three different salt contents. The conductivity of $5.05 \cdot 10^{-5}$ S/cm at room temperature were obtained for the samples of starch plasticized with 30% of glycerol and containing [O]/[Li] = 8. These results show that starch is very good material to be used for preparation of new solid polymeric electrolytes.

Keywords: starch, solid polymeric electrolytes, plasticization

INTRODUCTION

Advances in display technology, batteries and electrochromical devices have stimulate the study of solid polymeric electrolytes. These kinds of materials with lithium salts dissolved in a polymer matrix have been widely studied ever since the pioneering works of Wright *et al.* [1] and Armand *et al.* [2]. These polymeric materials represent a promising alternative for the substitution of liquid electrolytes and inorganic crystals used in batteries, sensors and electrochromic devices [3,4]. The most of described systems are based on polyether chains, most commonly poly(ethylene oxide) (PEO) that can be modified in order to decrease its crystallization tendency and glass transition temperature (Tg). The low Tg it is important parameter for preparation of solid polymeric electrolytes because better chain mobility and lithium ion conductivity. One of recent examples of PEO modification is the electrolyte based on poly(amide 6-b-ethylene oxide) that exhibit the conductivity in the range of 10^{-4} S/cm at 100°C [5,6]. Other ionic conducting systems based on low molecular weight poly(ethylene glycol) (PEG) with $LiClO_4$ and alpha Al_2O_3 have been developed[7].

Recently it was proposed by Gandini *et al.* [8,9] a new kind of solid polymeric electrolytes based on natural polymers. The most studied samples were the transparent films of hydroxyethylcellulose (HEC) grafted with poly(ethylene oxides) diisocyanates [10,11]. After addition of lithium salt ($LiClO_4$) to these networks it was possible to produce solid polymeric electrolytes with ionic conductivity values of about $2.08\cdot10^{-5}$ S/cm at 40°C and $8.8\cdot10^{-4}$ S/cm at 60°C [12].

Starch like cellulose is very interesting natural polymer because of their rich variety in nature and also that can be obtained from renewable sources. When cellulose is the major structural component of mature plants, starch is the major reserve material of many storage tissues. Starch is a mixture of the predominantly linear amylose and highly branched amylopectin [13] The interesting properties of starch is its solubility in some solvents and hot water giving with this film-forming and good mechanical properties. The chemical structure of starch is very similar to the cellulose and it can be also modified by chemical or physical process like grafting reactions with isocyanates or plasticization with water or glycerol [13]. Addition of plasticizer to starch reduce its crystallinity and glass transition temperature, very important parameter to obtain solid polymeric electrolytes.

In this work there are presented the results of new solid polymeric electrolytes based on amylopectin rich starch plasticized with 30% of glycerol and containing different quantities of $LiClO_4$.

EXPERIMENTAL

The samples of amylopectin rich starch (Amidex 4001 Corn products Brasil Ingredientes Industriais Ltda.) were dispersed in water (2% w/v) and heated during 2 hours at 100ºC. After, the solution was cold down to room temperature and then was added glycerol (Synth) with 30% of starch mass. It was added also lithium perchlorate ($LiClO_4$) giving the concentrations of [O]/[Li] = 8, 10 and 12 when calculated for all starch and glycerol oxygens. The viscous solution was dispersed in Teflon plaque and dried during 48 h at 40ºC. The resulting transparent film samples were stored in dry box [14].

The obtained materials were characterized by differential scanning calorimetry (DSC) with SHIMADZU DSC-50 equipment, to determine their glass transition temperature. These analyses were performed in duplicate in the temperature range from –100 to 200°C in a nitrogen atmosphere (20 ml/min). The first run was recorded at a heating rate of 20°C/min and the second, used for the Tg determination, at a heating rate of 10°C/min.

X-ray diffraction measurements have been performed on film samples with different [O]/[Li] reason with a URD-6, Carl Zeiss Jena instrument with the CuK_α radiation.

Conductivity measurements were done using an Eco Chemie-Autolab PGSTAT 30 with FRA2 module in vacuum atmosphere. Frequency range was from 10^6 to 10 Hz with amplitude of 5 mV.

RESULTS AND DISCUSSION

The amylopectin rich starch is a semi-crystalline polymer what is confirmed by X-ray diffraction measurements showed on Figure 1. After addition of 30% of glycerol (plasticization process) and different lithium salt ($LiClO_4$) quantities of [O]/[Li] = 8, 10 and 12 this structure was modified. The absence of crystalline peaks in the diffractograms confirm total salt dissolution and amorphous structure of the samples (Figure 1).

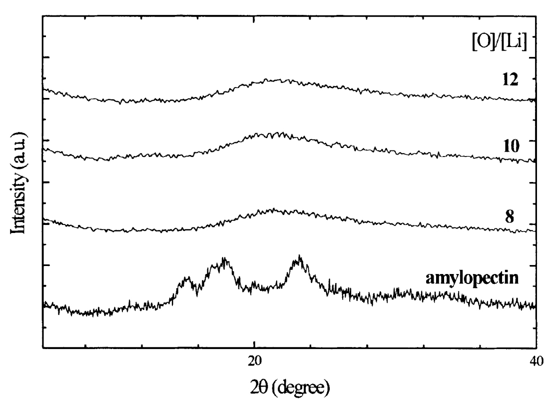

Figure 1. X-ray diffraction of amylopectin rich starch pure and plasticized with glycerol and containing $LiClO_4$.

The thermal analysis (DSC) of the samples reveal changes in the base line typical to the glass transition (Tg) change phase (Figure

2). The amylopectin rich starch show relatively high Tg of about 50°C (not showed here), already reported by other researchers [13] with ΔCp = -0.012 mW/mg. This very low calorific capacity is generally observed for this kind of natural polymers. After addition of the plasticizer and lithium salt there was observed a decrease in Tg value up to –12, -22 and –29°C for the sample with [O]/[Li] = 8, 12 and 10 respectively. The ΔCp =-0.013mW/mg for the samples with [O]/[Li] = 8, 12 was almost the same as for unmodified starch and for [O]/[Li] = 10 was –0.020mW/mg.

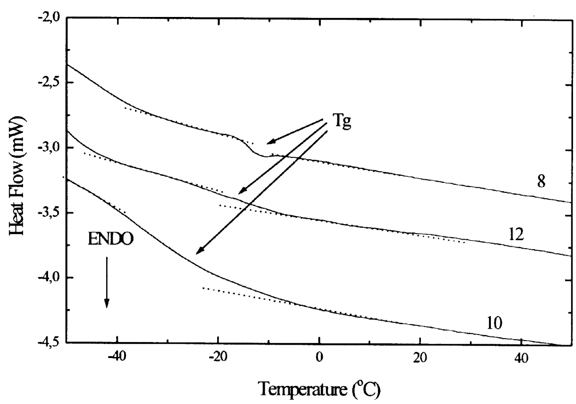

Figure 2. Thermal analysis (DSC) of amylopectin rich starch plasticized with glycerol (30%) and [O]/[Li] = 8, 10 and 12.

The conductivity results as a function of temperature for the samples with [O]/[Li] = 8, 10 and 12 are shown on Figure 3. The results for [O]/[Li] = 8 and 12 shows slops of the Arrhenius plots close to 50°C. In other systems containing plasticizant, like poly(ethylene oxide) (PEO) / poly(ethyleneglycol) (PG) / $LiCF_3SO_3$ this slope is attributed to the additive (PG) rather than PEO [15]. PEO in all these systems generally is responsible for ionic conduction. In our case there is not PEO and it is probably that starch give not only film forming properties but also play some role in the conduction mechanism. Figure 3 show also increase of conductivity values with temperature. For the sample with [O]/[Li] = 8 this change was from $5.05 \cdot 10^{-5}$ S/cm at 30°C to $7.15 \cdot 10^{-3}$ S/cm at 80°C and for the sample [O]/[Li] = 12 from $2.13 \cdot 10^{-6}$ S/cm to $2.32 \cdot 10^{-4}$ S/cm in the same temperature interval.

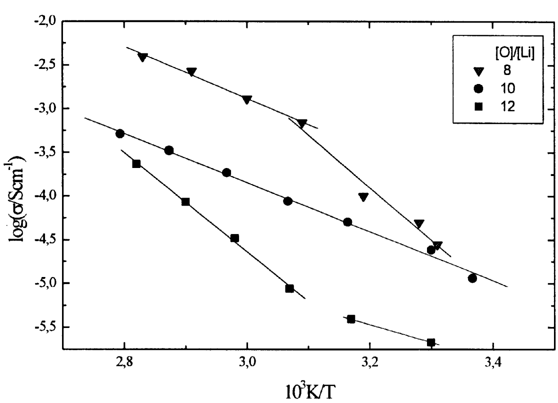

Figure 3. Log of conductivity measurements as a function of inverse of temperature for the samples of amylopectin plasticized with glycerol (30%) and containing [O]/[Li] = 8 (▼), 10 (•) and 12 (■).

CONCLUSIONS

The starch based new solid polymeric electrolytes were prepared by plasticization of amylopectin rich starch with glycerol (30%) and addition of three different $LiClO_4$ quantities. The transparent film samples showed low glass transition temperature in the range from –12°C to –29°C, important properties to the ionic conductivity. It was observed that the samples are amorphous and the lithium salt is totally dissolved in the polymer matrix. The measurements of conductivity dependence of temperature show the Arrhenius type dependence with the slopes at about 50°C in three samples with [O]/[Li] = 8 and 12. These results show also increase of two orders of magnitude in the conductivity values in the temperature interval from 30 to 80°C. The good results were obtained for the sample with [O]/[Li] = 8 that change its conductivity value from 10^{-5} S/cm at 30°C to 10^{-3} S/cm at 80°C. All these results show that starch is very good candidate to be used as solid polymeric electrolytes.

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