Short communication

Development of a biodegradable polymer electrolyte for rechargeable batteries

Carla Polo Fonseca [a], Derval S. Rosa [b], Flávia Gaboardi [b], Silmara Neves [a],*

[a] *Laboratório de Caracterização e Aplicação de Materiais, Programa de Pós-Graduação Strictu Sensu em Engenharia e Ciência dos Materiais, Universidade São Francisco, 13251-900 Itatiba, SP, Brazil*
[b] *Laboratório de Polímeros Biodegradáveis e Soluções Ambientais, Programa de Pós-Graduação Strictu Sensu em Engenharia e Ciência dos Materiais, Universidade São Francisco, 13251-900 Itatiba, SP, Brazil*

Abstract

The possibility of producing a biodegradable polymer electrolyte based on poly-ε-caprolactone (PCL) with different concentrations of $LiClO_4$ has been investigated. The maximum ionic conductivity obtained at room temperature was $1.2 \times 10^{-6}\,S\,cm^{-1}$ for PCL complexed with 10 wt.% $LiClO_4$. In this mixture, complete biodegradation occurred after 110 days and was attributed to the presence of ester groups in the polymer matrix. The large electrochemical stability window of approximately 5 V showed that the PCL/$LiClO_4$ electrolyte had important electrochemical properties that would make it useful in the production of rechargeable batteries with a lower environmental impact.
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1. Introduction

The battery industry represents one important sector, which is expected to continue growing with the increasing prevalence of laptop computers, telecommunications equipment, cordless tools, and other portable electronic devices [1,2]. Currently, batteries represent a large volume of toxic and hazardous materials in common use, and these materials must be managed throughout their life cycle to avoid harm to the environment and human health.

The most common secondary cells on the consumer market at the moment are nickel metal hydride, lithium-ion and lithium-polymer accumulators, whereas nickel–cadmium batteries are gradually being phased out [3]. Exceptions include reserve power sources for industry, hospitals, airports, and similar uses, where nickel–cadmium batteries are still needed. Current commercial Li-ion batteries use liquid electrolytes, which are highly flammable, so that metal casing

has to be used to prevent possible leakage. This problem does not exist for solid polymer electrolytes for which a laminated foil housing is safe [4].

In principle, polymer electrolyte batteries are formed by laminating a lithium metal (or composite carbon) anode, a lithium-ion conducting membrane (polymer electrolyte), and a composite cathode in a sandwich structure [5,6]. Intensive work is being done on developing various materials, and the use of environmentally "conscious" materials, or "ecomaterials", during manufacturing can help to reduce the environmental impact of many products throughout all phases of the product life cycle. However, little attention has been paid to polymer electrolytes [7,8] that, in large amounts, are also hazardous to the environment.

In this paper, we provide the first report of an ionic system based on a biodegradable polymer, poly-ε-caprolactone (PCL), with different concentrations of $LiClO_4$. PCL is one of the most promising synthetic biodegradable polymers because of its marked degradation in aqueous medium and in contact with microorganisms [9,10]. We demonstrate the possibility of developing a biodegradable polymer electrolyte

* Corresponding author. Tel.: +55 11 4534 8065; fax: +55 11 4524 1933.
E-mail address: silmara.neves@saofrancisco.edu.br (S. Neves).

(BPE) that can initiate the degradation of batteries, thereby decreasing the environmental impact of these devices.

2. Experimental details

2.1. Polymer electrolyte preparation

The biodegradable electrolyte was prepared by dissolving PCL and $LiClO_4$ in tetrahydrofuran (THF). The solvent was evaporated and dried at high vacuum for 72 h. The salt concentrations were 2.0, 6.0, 10.0 and 12 wt.% of $LiClO_4$.

2.2. Thermal and electrochemical characterization

The thermal behavior of the electrolyte was analyzed using a differential scanning calorimeter (NETZSCH DSC 204). The samples were heated to 100 °C, cooled to −100 °C and then heated to 150 °C. The thermograms were recorded at a rate of 10 °C min^{-1} in a nitrogen atmosphere. All DSC experiments were done in duplicate and the thermograms shown refer to the final heating.

The electrochemical experiments were done using an AUTOLAB-PGSTAT30 FRA. The ionic conductivity of the electrolyte was determined by electrochemical impedance spectroscopy in the frequency range from 0.1 to 10^5 Hz with an ac amplitude of 10 mV. The samples were sandwiched between two polished stainless steel disks with an area of 1.0 cm^2 that acted as ion-blocking electrodes. The electrochemical stability window was determined by cyclic voltammetry using a SS | electrolyte | Li cell in which Li was used as the counter and reference electrodes. All electrochemical experiments were done in a dry box under an argon atmosphere.

2.3. Biodegradation tests

The biodegradation tests were done in soil compost containing 23% loamy silt, 23% organic matter (cow manure), 23% sand and 31% distilled water (all w/w). Calcium hydroxide was added to obtain a soil compost of pH 11. PCL/$LiClO_4$ films were weighed and buried in the soil compost, in triplicate. The biodegradability was monitored by calculating the weight loss after periods in soil compost. The buried samples were retrieved, washed with distilled water and dried in the open air before being weighed. The films were buried again in their respective trays after weighing.

3. Results and discussion

The films formed by casting PCL, $LiClO_4$ and tetrahydrofuran (THF) solution were auto-supported, flexible and apparently homogeneous. The thermal behavior of pure biodegradable PCL and of PCL containing 2, 6, 10 and 12 wt.% $LiClO_4$ is shown in Fig. 1.
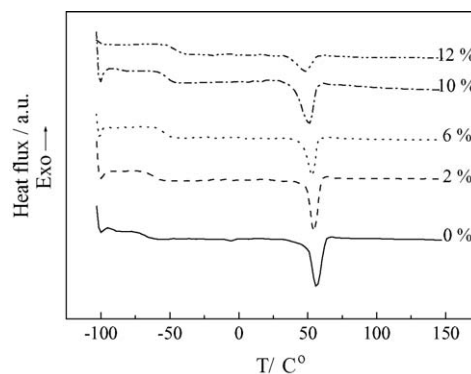

Fig. 1. Differential scanning calorimetry curves for poly-ε-caprolactone samples containing 2, 6, 10 and 12 wt.% $LiClO_4$.

PCL showed a phase transition at −65 °C that was attributed to the glass transition temperature (T_g). PCL had a melting process between 40 and 66 °C, with a $T_m = 55.7$ °C that reflected the presence of a crystalline phase. The decrease in T_m from 56.5 to 48.3 °C in the presence of salt provided evidence of ion complexation that to decrease the degree of crystallinity and consequently increase the amorphous phase [11–13]. This fact was very important because ionic conductivity occurred in the amorphous phase.

A polymer with a low T_g is a suitable candidate for combination with salts to form polymeric electrolytes. Below the T_g, physical properties such as viscosity, diffusion and conduction become less sensitive to temperature, whereas above the T_g, the segmental motion of the polymeric chain increases. In the case of PCL, Fig. 2, an increase in salt concentration produced a corresponding increase in the T_g value that led to a decrease in the segmental motion of the chain polymeric and, consequently, to a decrease in the ionic conduction. The latter parameter was measured by electrochemical impedance spectroscopy (Fig. 3).

Fig. 3a shows impedance plots of PCL with different concentrations of $LiClO_4$, at room temperature. At low salt concentration, a semi-circle related to the impedance of the polymer electrolyte (Z) was observed. The bulk resistance was determined from impedance spectra in which the arc
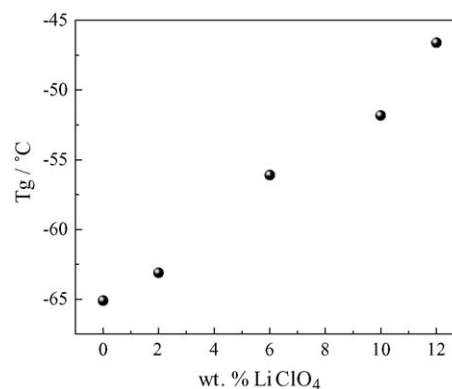

Fig. 2. Variation in the T_g as a function of the salt concentration.
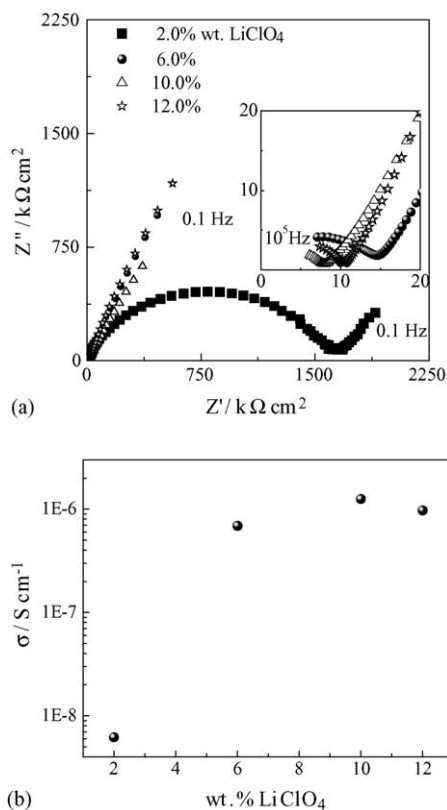
(a)

(b)

Fig. 3. ac impedance spectrum (a) and ionic conductivity (b) of a stainless steel (SS)/PCL/SS system with different salt concentrations, at room temperature.

intercepted the real part in the lower frequency region. With increasing salt concentration, this semi-circle tended to disappear and moved to lower resistance value, thereby increasing the ionic conductivity that was calculated accord to Fonseca et al. [14].

Fig. 3b shows the ionic conductivity behavior of the electrolyte as a function of the salt concentration. A typical ionic conductivity curve with a maximum conductivity of $1.2 \times 10^{-6}\,\mathrm{S\,cm^{-1}}$ at 10 wt.% $LiClO_4$ was observed for experiments done at room temperature. This maximum ion conductivity value may be explained by the increase in the concentration of charge carrier when salt is added to the polymer until a maximum value is reached, after which the ionic conductivity decreases. The decrease in ionic conductivity with increasing salt concentration can be attributed to three interrelated phenomena: (i) an increase in the macromolecular rigidity of the amorphous phase because of the high salt concentration that acts as a reticulate agent in the polymeric matrix, (ii) a non-linear increase in the number of charge carriers as a function of salt concentration, favoring the appearance of ion pairs, and (iii) the appearance of a crystalline phase formed by the salt–polymer complex [14,15].

The electrochemical stability window provides essential information for assessing the success of any device, particularly energy storage devices. Fig. 4 shows the cyclic
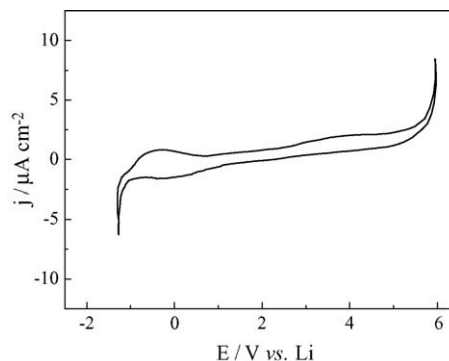

Fig. 4. Cyclic voltammogram for an SS | PCL + 10 wt.% $LiClO_4$ | Li system. The scan rate was $5\,\mathrm{mV\,s^{-1}}$.

voltammetry for an SS | PCL + 10 wt.% $LiClO_4$ | Li mixture at room temperature.

The salt-polymer complex showed an excellent electrochemical stability window of approximately 5 V that was cathodically limited by pseudo-reversible lithium deposition. The wide cathodic peak between 1 and 0 V was attributed to salt reduction. The anodic limit was related to anion oxidation followed by a possible polymeric degradation [16,17].

The biodegradation results obtained using simulated soil showed a larger loss of mass by the sample containing $LiClO_4$, with total degradation occurring in approximately 110 days (Fig. 5).

Although PCL is a biodegradable polymer [18], it did not present a significant weight loss up to 140 days in the used conditions. On the other hand, the sample containing $LiClO_4$ disappears after 110 days. The photomicrographs illustrate the alteration of the films morphology during the biodegradation process, what evidences a fragmentation of the samples containing lithium salt and consequently the weight loss. This behavior is related to the increase of the amorphous phase as a function of salt addition, which improves the biodegradation. This result agreed with the thermal analysis since the
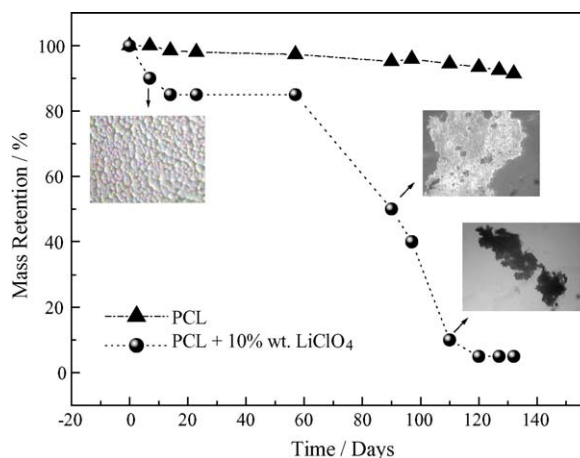

Fig. 5. Biodegradation of PCL and PCL containing 10 wt.% $LiClO_4$ in soil compost at pH 11. Inset: optical images of PCL + 10 wt.% $LiClO_4$ after 3, 90 and 110 days of biodegradation; magnification 40×.

addition of salt reduced the orientation of the polymer chains and, consequently, accelerated the biodegradation.

4. Conclusions

In summary, the main finding of this work was the possibility of producing a biodegradable polymer electrolyte. PCL/LiClO$_4$ films are auto-supported, flexible and apparently homogeneous. The maximum ionic conductivity obtained at room temperature was 1.2×10^{-6} S cm^{-1} for PCL complexed with 10 wt.% LiClO$_4$. In this mixture, complete biodegradation occurred after 110 days and was attributed to the presence of ester groups in the polymer matrix. These groups favored the hydrolysis and cleavage of the films in alkaline soil compostage. The large electrochemical stability window of approximately 5 V showed that the PCL/LiClO$_4$ electrolyte had one important electrochemical property that would make it useful in the production of rechargeable batteries with a lower environmental impact. However, the ionic conductivity determined at ambient temperature is still low. Then some modifications such as addition of a plasticizer agent and substitution of LiClO$_4$ by another more safe salt may confer to proposed system more suitability to practical use. The work continues to make these modifications.

Acknowledgements

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