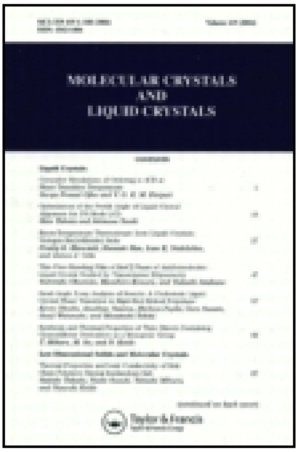

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Gellan Gum-LiI Gel Polymer Electrolytes

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Gellan Gum-LiI Gel Polymer Electrolytes

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Gellan-based polymer electrolytes (PEs), doped with lithium iodide (LiI), were prepared and their electrical properties were characterized. The samples are thermally stable up to 234°C and exhibit ionic conductivity of 3.8×10^{-4} S/cm at room temperature for the sample doped with 40 wt% of LiI. Addition of 10 wt% of glycerol promotes an increase of the ionic conductivity to 1.5×10^{-3} S/cm, which remains stable up to 100°C. The activation energies of 2.4 to 12.4 kJ/mol were derived from the Arrhenius model. The repeated ionic conductivity measurements as a function of temperature show that these membranes can be reversibly used between the room temperature and 100°C.

Keywords Gellan gum; ionic conducting membranes; polymer electrolyte

Introduction

Natural polymers are particularly interesting when compared with synthetic ones, due to their richness in nature, very low cost and principally the biodegradation properties. For these reasons different polymer electrolytes (SPE) have been obtained from cellulose derivatives [1], starch [2], chitosan [3] and pectin [4] among others. However, the main problem of these polymers is a low thermal stability when compared with the synthetic ones. To overcome this problem the crosslinking reactions are performed and the plasticization process is applied.

Gellan gum is an anionic polysaccharide produced by the fermentation of pure culture of *Sphingomonas elodea* [5–6]. It is a multifunctional gelling agent that can be used either alone or in combination with other products to obtain a wide variety of interesting textures, including the thermo-reversible membranes. Due to the compatibility and no danger for human body this macromolecule is intensively investigated in the development of new ophtalmic lenses with drug-delivery properties [7]. An important property of gellan gum gels is their high thermal stability, up to 120°C, and the thermal reversibility. Also aiming to

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modify the gellan gels stability, the calcium, magnesium and potassium ions can be added, similarly to sodium alginate [8].

Concerning the polymer electrolytes, which are systems of salts dissolved in polymer matrix, the suitable salts are made up of mono- or divalent cations, the most commonly Li^+ and Na^+ and anions that are soft bases as e.g., $ClO_4{}^-$, $CF_3SO_3{}^-$, $I_2{}^-$, SCN^- [9]. Lithium iodide (LiI) is an interesting salt due to its use in electrolytes for high temperature or long life operating batteries [10].

The present work reports the results of ionic conductivities and thermal stability measured for pure gellan gum as well as gellan plasticized with glycerol and containing LiI salt. The studied polymer electrolytes exhibit high and thermal reversible ionic conductivities between the room temperature and 100°C.

Experimental

The gellan gum-based samples were prepared dispersing 1.5 g of gellan gum (Kelco Brazil, HA) in 100 mL of distilled water under magnetic stirring at room temperature. Next, different amount of lithium iodide (LiI) (10–50 wt%) and glycerol (10–50 wt%) were added and stirred at room temperature for 24 hours. The final solution was poured into a Petri plate and dried at 40°C for 48 h, resulting in transparent and freestanding membranes, which were stored in a desiccator to avoid air humidity.

The ionic conductivity measurements were performed placing the film samples between two stainless steel electrodes with diameter of 1 cm, under spring pressure. The impedance of the films was measured in air using the HIOKI 3531 Z LCR Hi-tester impedance spectroscopy.

The FTIR measurements were recorded with the Thermo Scientific spectrophotometer, between 4000 and 600 cm^{-1}.

The thermal stability was studied by the thermo gravimetric analysis (TGA) using a TA Instruments TGA-Q500. The DSC measurements were done with TA Instruments DSC-Q200.

Results and Discussions

To analyze the influence of LiI quantity in sample on the ionic conductivity properties, the impedance measurements were performed. Figure 1 shows the ionic conductivity of the samples with different amount of lithium salt. With 0 wt% of salt, the ionic conductivity (σ) of gellan-based membranes is 10^{-8} S/cm and it increases with the increasing concentration of LiI to reach a maximum of 3.8×10^{-4} S/cm and 1.4×10^{-3} S/cm for 40 and 50 wt% of LiI, respectively. The increase of conductivity is certainly related to the increase in the number of mobile charge carriers [11]. As no decrease in the ionic conductivity with addition of LiI salt is observed, most likely no formation of ionic aggregates takes place, which is common for the systems with salts with bigger than iodide anion. The ionic association at high concentrations of salt is a determining factor for ionic transport [12].

The influence of glycerol on the ionic conductivity of gellan-based membranes is depicted in Fig. 2. One can observe that addition of 10 wt% of glycerol promotes an increase of the ionic conductivity values to 1.7×10^{-3} S/cm for the sample containing 40 wt% of LiI. Higher amount of glycerol does not promote other significant increase of ionic conductivity values indicating that even without glycerol the gellan matrix provide good environment for ionic mobility. Although the plasticization process promotes only

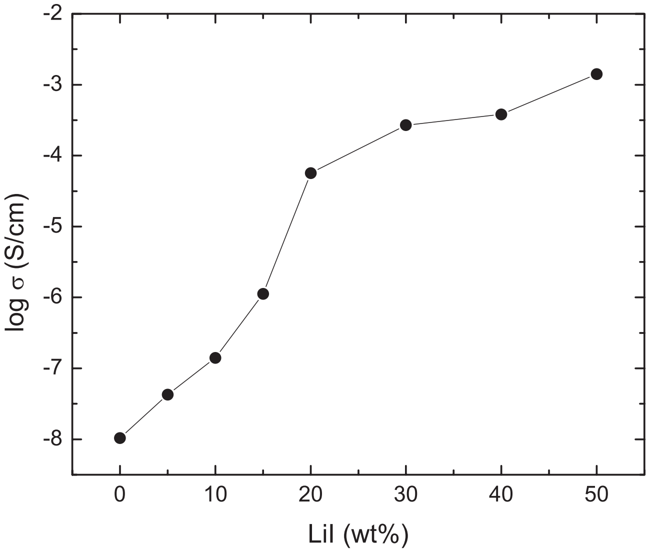

Figure 1. Log of ionic conductivity as function of the LiI content (wt%) for gellan-based PEs.

a slight increase of the ionic conductivity it should be noted that in analogy with other plasticized samples the addition of glycerol leads to samples with better adhesion to the glass and steel surfaces than in the case of samples without glycerol [13].

To verify the thermal stability of the membranes the ionic conductivity was measured as function of temperature (Fig. 3). From this figure one can see that the ionic conductivity of the sample with 40 wt% of LiI increases linearly with temperature for both non- and plasticized with 10 wt% of glycerol samples. The logarithm of the ionic conductivity

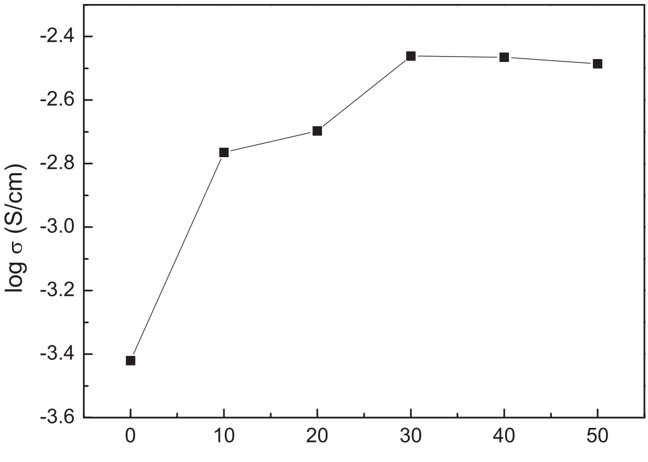

Figure 2. Log of ionic conductivity as a function of the glycerol of gellan-based PEs containing 40 wt% of LiI.

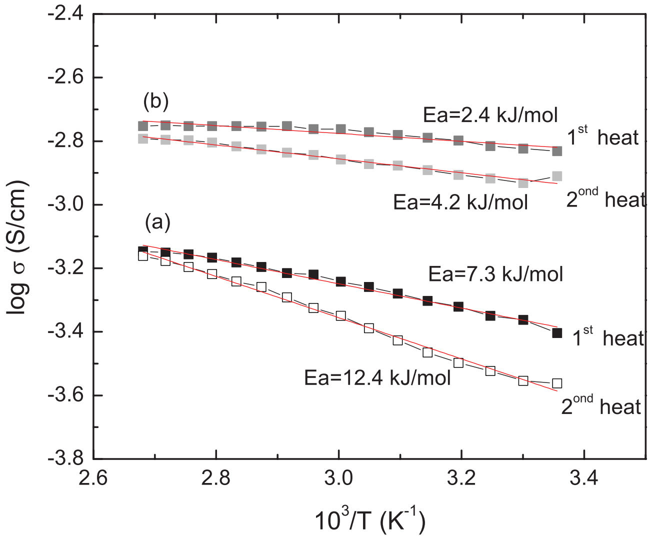

Figure 3. Log of ionic conductivity as function of temperature for the gellan-based samples with 40 wt% of LiI (a) and with 40 wt% of LiI and 10 wt% of glycerol (b); in the first and second heating run of the same sample.

increases linearly in function of the inverse of temperature suggesting that the charge carriers displacement might be described by a Grotthuss-type model [14]. The conductivity values increase from 3.8×10^{-4} S/cm at 25°C to 7×10^{-4} S/cm at 100°C for the sample without glycerol and from 1.5×10^{-3} S/cm at room to 1.8×10^{-3} S/cm at 100°C for the sample plasticized with 10 wt% of glycerol, respectively. Also from this figures one observes a good reversibility of the ionic conductivity in function of temperature. Only a small decrease in the ionic conductivity is observed at room temperature and the same values at 100°C during the second heating cycle.

By using the Arrhenius formula and a log (σ) versus 10^3/T plot, a fairly good agreement with the Grotthuss model is observed. From this plot, depending on the studied sample, one gets for the activation energy (Ea) the values between 2.4 and 12.4 kJ/mol.

The infrared spectra obtained for the samples of pure gellan membrane, gellan with LiI and gellan plasticized with 10 wt% of glycerol and containing 40 wt% of LiI are shown in Fig. 4. All spectra show a very large band at 3316 cm^{-1} (pure gellan) and at 3348 cm^{-1} (gellan without and with glycerol) corresponding to –OH vibration of hydroxyl groups of both glycerol and polysaccharide molecules. The bands located in the range of 2891 to 2934 cm^{-1} correspond to the CH_3 and CH_2 stretching vibration groups. In the 700 to 2000 cm^{-1} wave number range there are no differences between pure gellan and gellan-based electrolyte FTIR spectra. The band at 1600 cm^{-1} is attributed to glycosidig bond [15], and that at 1409 cm^{-1} to the C-H bending. The characteristic bands at 1026 cm^{-1} corresponds to the acetates stretching vibration of different ligands. The band at 1719 cm^{-1} is probably due to $C = O$ acetate stretching. The unique difference is a new band at 922 cm^{-1}, probably due to the interaction of iodide with glycerol, and a decrease of the band intensity at 888 cm^{-1}, although Sudhamania et al [15] registered a band at 925 cm^{-1} for pure gellan. No other shift of the FTIR spectra bands after lithium salt and/or glycerol addition to the gellan membranes indicates that there is no strong interaction of

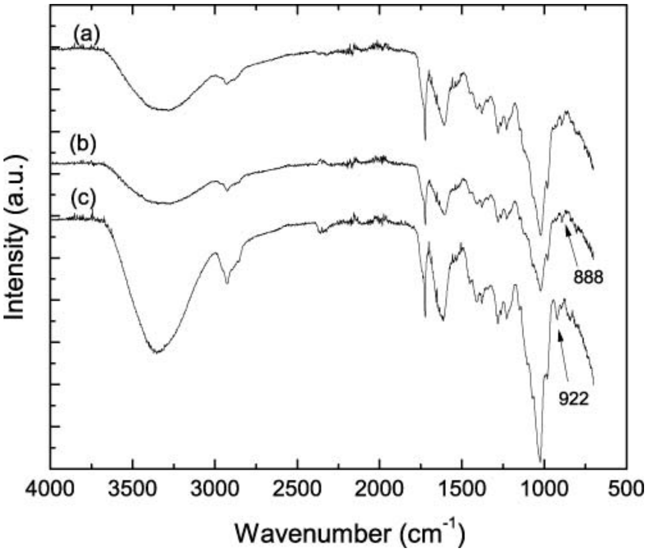

Figure 4. FTIR spectra of the pure gellan (a), gellan-based samples with 40 wt% of LiI (b) and with 40 wt% of LiI and 10 wt% of glycerol (c).

the salt and polymer backbone, which could indicate a free movement of dissociated salt in gellan based polymer matrix.

Aiming to verify the thermal stability of the gellan-based electrolytes, the thermogravimetric analysis (TGA) and DSC measurements were performed. Fig. 5 shows the TGA results for membranes of pure gellan (a), gellan containing 40 wt% of LiI (b) and gellan plasticized with glycerol (10 wt%) and containing also LiI (40 wt%) (c). All samples

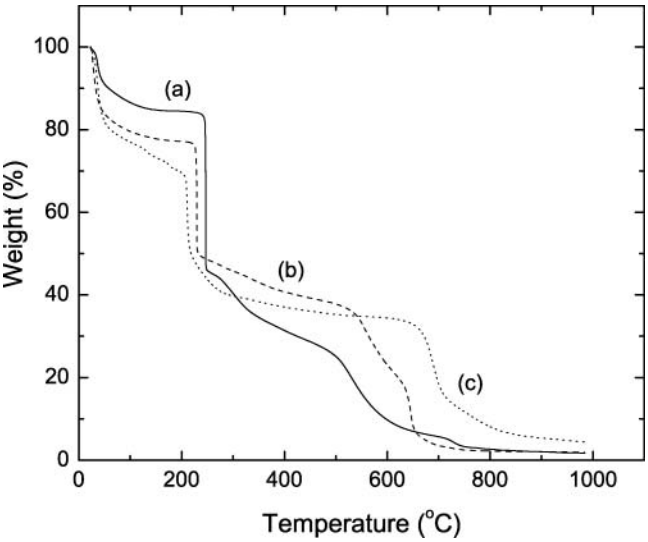

Figure 5. TGA analysis of the pure gellan (a), gellan-based samples with 40 wt% of LiI (b) and with 40 wt% of LiI and 10 wt% of glycerol (c).

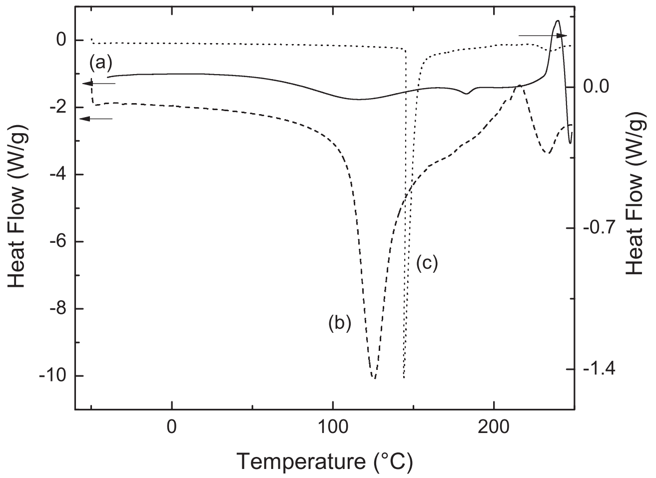

Figure 6. DSC curve of pure gellan (a), gellan-based samples with 40 wt% of LiI (b) and with 40 wt% of LiI and 10 wt% of glycerol (c) (3th run after heating to 100°C).

show a weight loss of 15–35% in the temperature range from room to about 220°C, which can be interpreted as due to the water loss. The water retention was found to be higher in the plasticized sample and containing salt than in the pure gellan. It is certainly due to the hydrophilic properties of glycerol and salt [4]. The addition of salt does not alter the degradation temperature too, which starts at 234°C for all samples. Also, in the case of all membranes the first step of degradation promotes a weight loss of 40% and the next starts a gradual weight loss of 44% up to 800°C. The remaining residue is of 2–3% of initial weight of the sample. As in the previous studies on natural polymer-based electrolytes, during the stage of degradation, the sample suffers the endothermic reactions of oxidation and hydrolysis followed by polysaccharide pyrolysis exothermic reactions [16]. The degradation can be also due to the water, which influence the depolymerization process in high temperatures [17]. The remaining residue is around 12%.

The DSC curves in the temperature range from −40 to 220°C are shown in Fig. 6. These measurements reveal a very sharp peak centered at 125°C, which accordingly to other studies can be attributed to a melting of crystalline portion of the gellan gum [15]. Another endothermic peak at 232°C is due to the initial degradation process, confirming the TGA results shown in Fig. 5.

Conclusions

Pure gellan-based polymer electrolytes, doped with LiI and plasticized with glycerol were obtained and characterized. The FTIR measurements revealed an increase of intensity and small shift of –OH bands as well as appearance of a weak band at 922 cm^{-1} indicating an interaction of polysaccharide with glycerol and of glycerol with salt. As no other significant shifts were observed, consequently no strong interaction between gellan gum and LiI can be concluded.

The thermal analysis (TGA) shows the beginning of thermal degradation process at 234°C for all samples. The DSC analysis reveals a sharp endothermic peak centered at 125°C, which is due to the melting of the crystalline phase of gellan. Another peak observed at 232°C is due to the thermal degradation process, as observed in TGA.

The ionic conductivity measurements show that the salt concentration influences the ionic conductivity of electrolyte increasing it from 10^{-8} S/cm (pure gellan) to 3.8×10^{-4} S/cm for gellan doped with 40 wt% of LiI. Addition of 10 wt% of glycerol promotes another increase of the ionic conductivity, up to 1.5×10^{-3} S/cm for the sample with 40 wt% of LiI. The ionic conductivity remains stable when heating the sample up to 100°C and does not change significantly during the second heating cycling. The activation energy varies between 2.4 and 12.4 kJ/mol for the studied samples, as calculated using the Arrhenius model. All these results indicate that gellan-based PEs are very promising candidates to be used as electrolytes in electrochemical devices.

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