

Structural, Morphological, Ionic Conductivity, and Thermal Properties of Pectin Based Polymer Electrolytes

J. P. Mendes^a, J. M. S. S. Esperança^b, M. J. Medeiros^a, A. Pawlicka^b, M. M. Silva^{a*}

^aDepartamento / Centro de Química, Universidade do Minho, Gualtar, 4710-057 Braga, Portugal

^bInstituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa, Av. da República, 2780-157 Oeiras, Portugal

^cIQSC-Universidade de São Paulo, Av. Trabalhador São carlense 400, 13566-590 São Carlos-SP, Brazil

Corresponding author: *nini@quimica.uminho.pt

+351 253 60 40 58

Abstract

New polymer electrolytes (PEs), potentially interesting for solid-state electrochemical devices applications, were synthesized by a solvent casting method using pectin and ionic liquid (IL) N,N,N-trimethyl-N-(2-hydroxyethyl)ammonium bis(trifluoromethylsulfonyl)imide ($[N_{1112(OH)}][NTf_2]$). The resulting electrolytes besides being moderately homogenous and thermally stable below 155 °C, they also exhibited good mechanical properties. The SPE membranes were analyzed by differential scanning calorimetry (DSC), X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), and complex impedance spectroscopy.

Keywords: Pectin; Polymer electrolyte; Ionic liquid; Solid-state electrochemical devices

1. Introduction

Solid Polymer Electrolytes (SPEs) are macromolecular systems capable of transporting charged species such as ions or protons [1]. The SPEs have been widely studied, as they are a promising alternative to replace inorganic electrolytes and liquid crystals used in batteries, sensors, and other electrochemical devices [2-4]. Many authors have investigated blends systems and composites [5-7] with PEO, but also ionic conducting materials based on natural polymers, such as cellulose derivatives [8], starch [9], chitosan [10], gellan-gum [4] and natural rubber [11]. The interest in natural polymers is large due to the depletion of sources of finite raw materials, which is the case of oil and natural gas as well as the contribution to the reduction in the emission of industrial gases. Furthermore, the use of biopolymers reduces the environmental impact because they are biodegradable and take a part of organic carbon cycle, providing nutrients to the soil through the decomposition process. Studies of the use of biopolymers also take into account their low production cost due to a great variety and low prices of raw materials they are made.

Among different natural polymers, pectin, which is polysaccharide first isolated and described in 1825 by Heneri Bracannot, is a great candidate due to its abundance [12]. In terms of structure, pectin is a linear heteropolysaccharide contained in the primary cell walls of terrestrial plants [13]. The composition and structure of pectin are still not completely understood although pectin was discovered over 200 years ago [14]. Pectin is a polysaccharide that acts as a cementing material in the cell walls of all plant tissues. The white portions of skin of lemons and oranges contains approximately 30% of

pectin. Pectin is a methylated ester of polygalacturonic acid, which consists of chains of 300 to 1000 galacturonic acid units linked by 1 α →4 bonds. The degree of esterification affects the gelling properties of pectin. The structure shows three methyl ester forms (-COOCH₃) for every two carboxyl groups (-COOH), hence it has a 60 % degree of esterification. The substituted residues at C-4 with neutral and acidic oligosaccharide side chain are composed of arbinose, galactose, fructose, and glucuronic acid [15].

Polymer electrolytes based on natural polymers have attracted a lot of attention due to their mechanical, optical, and electrical properties [16, 17]. There are reports on natural polymers-based ionic conducting systems with lithium salts [18], acids [19], and ionic liquids (ILs) too [20,21] among others. Ionic liquids (ILs) are molten salts composed of organic cations and inorganic or organic anions, and by definition are salts with a melting point below 100 °C [22]. They also have high conductivity, non-volatility, non-flammability, wide electrochemical window, recyclability, and high thermal and electrochemical stability properties, which make them attractive candidates as electrolytes for electrochemical devices such as advanced batteries, electrochromic devices, and fuel cells [23-25]. Moreover, ILs depending on their chemical structure show a wide liquid range, densities between 0.85 and 1.6 g cm⁻³, miscibility with substances within a broad range of polarities, ability to dissolve both organic and inorganic substances, thermal stability and high viscosity at room temperature ranging from 10 to 10⁵ cP [26].

The present work has been motivated to obtain electrolytes with essentially amorphous character, high or moderate ionic conductivity, and suitable mechanical properties that can be used cheap electrochemical devices. Therefore, the present work presents a study of pectin with [N_{1 1 2(OH)}][NTf₂]-based polymeric electrolytes, which were characterized by means of differential scanning calorimetry (DSC), X-ray

diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), and complex impedance spectroscopy.

2. Materials and methods

2.1 Materials

Commercial pectin (BRS-Z from CP Kelco Limeira S.A.), acetic acid (Sigma-Aldrich), and glycerol (Himedia, 99.5 %) were used as received. High-purity distilled water was used in all experiments (Millipore).

Eco-friendly ionic liquid, $[N_{1112(OH)}][NTf_2]$, was synthesized with a purity higher than 99 % following the procedure described in a previous paper [27]. Its chemical structure, composed by cation and anion is shown in Figure 1.

In order to reduce water and volatile compounds to negligible values, the IL was dried under low pressure of 10^{-1} Pa and vigorously stirred at moderate temperature of ca. 47 °C for at least a day. Coulometric Karl-Fischer titrations (Metrohm 831 KF Coulometer) revealed levels of water, always below 300 ppm. This value is a conservative estimate that takes into account the uncertainty associated with IL handling.



Figure 1. Chemical structure of cation (a) and anion (b) of the IL $[N_{1112(OH)}][NTf_2]$.

2.2 Polymer electrolyte preparation

PEs based on pectin, guest species $[N_{1112(OH)}][NTf_2]$, and/or glycerol were prepared by a solvent casting technique. 0.30 g of pectin was dissolved in 10 mL of 1% acetic

acid solution and stirred overnight at room temperature, until a homogeneous and viscous solution was formed. Then, 0.20-0.90 g of the IL and 0.15 g of glycerol as plasticizer, were added to this solution. The resulting solutions were cast onto Petri dishes and left to dry for 8 h at 25 °C, overnight at 40 °C, for 4 h at 60 °C, and finally cooled down to 25 °C [28].

Based on a terminology adopted previously [29], the samples were designated by the notations Pectin_n[N₁ 1 1 2(OH)] [NTf₂] where n is the ratio between the mass of polymer and added IL.

2.3 Characterization techniques

Thermal behaviour of the membranes was evaluated by differential scanning calorimetry (DSC). For the DSC experiment, section of samples was sealed, inside a glove box filled with dry argon, in 40 µL aluminum can with perforated lids. The analysis was carried out using a Mettler DSC 821 in – 60 to 200 °C temperature range, at a heating rate of 5 °C min⁻¹, and under argon flux atmosphere.

Scanning electron microscopy (SEM) images were obtained at 20 kV with a Hitachi S-3400N type II microscope equipped with a Bruker x-flash 5010. The micrographs were taken at a magnitude of 5.00 kx.

Atomic force microscopy (AFM) topographic images were obtained with a Nanosurf EasyScan 2 AFM (Nanosurf AG, Liestal, CH), working in the non-contact mode, equipped with a silicon (Si) probe with a resonance frequency of 190 KHz, and a force constant of 48 N.m⁻¹. The surface roughness was calculated as root mean square (RMS) height or RMS surface roughness (Sq).

An Autolab PGSTAT-12 (Eco Chemie) was used to obtain bulk ionic conductivities of the samples from room temperature to 100 °C using a complex plane impedance technique. Measurements were done on a cell with GE/polymer electrolyte/GE (GE

stands for 10 mm diameter ion-blocking gold electrodes; Goodfellow, > 99.95%) composition, which was secured in a suitable constant volume support. The frequency range was of 65 kHz to 500 mHz.

3. Results and discussion

Aiming to analyze thermal properties of pectin-based electrolytes measurements of DSC were performed, and the obtained results are shown in Figure 2. As one can see in this figure, no glass transition temperature was detected within the temperature between -60 and 200°C. Moreover, it can be also stated that the pectin-based electrolyte has predominantly semi-crystalline morphology in the temperature range studied. Besides that, all analyzed samples reveal a presence of one endothermic peak between -5 and 0 °C, which can be explained by solid-state phase transition of ionic liquid. Another endothermic peak is observed between 15 and 20 °C, which possibly might correspond to a melting temperature of ionic liquid, T_m [30]. Additionally, at 0 °C, there is observed one more endothermic peak for Pectin_{0.37} [N_{1 1 1 2(OH)}][NTf₂] sample, which is attributed to melting of free water. Pectin_{0.43} [N_{1 1 1 2(OH)}][NTf₂] produced also small endothermic peak at 110 °C, which may correspond to a crystalline complex.

More detailed analysis of Figure 2 reveals that Pectin_{0.37} [N_{1 1 1 2(OH)}][NTf₂] sample has a lowest degradation temperature onset at ~ 155 °C when compared with other samples. This indicates that none of the SPEs components are volatile up to ~155 °C. Consequently, this temperature can be considered as samples' stability limit, which is far enough for a material to be applied as an electrolyte/separator component in electrochemical devices.

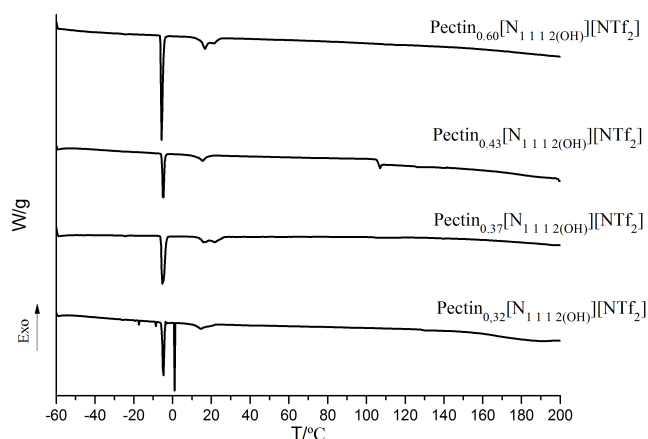


Figure 2. DSC thermograms of PEs based on pectin and $[N_{1112(OH)}][NTf_2]$.

Structural analysis of $Pectin_n[N_{1112(OH)}][NTf_2]$ -based electrolytes were done by XRD measurements at room temperature, and the results are shown in Figure 3. As already observed in other natural macromolecules-based samples, these diffractograms exhibit a broad and Gaussian in shape peak with maximum centered at ca. 21° . This result is very similar to the results obtained by Lutz et al [31] for apple pectin and for pectin-based electrolyte reported by Andrade et al [18]. Moreover, a close inspection of the XDR diffractograms reveals that the profile of this band (ca. 21°) changes slightly depending on the sample. The diffraction peaks observed at $\sim 32^\circ$ in the XRD pattern of the $Pectin_{0.43}[N_{1112(OH)}][NTf_2]$ electrolyte are probably associated with formation of a crystalline phase results of interaction of pectin with $[N_{1112(OH)}][NTf_2]$, as pointed out by corresponding DSC curve (Figure 2).

These results confirm a predominantly amorphous structure of the PEs studied here, similarly, to other biopolymers-based systems [20,32,33].

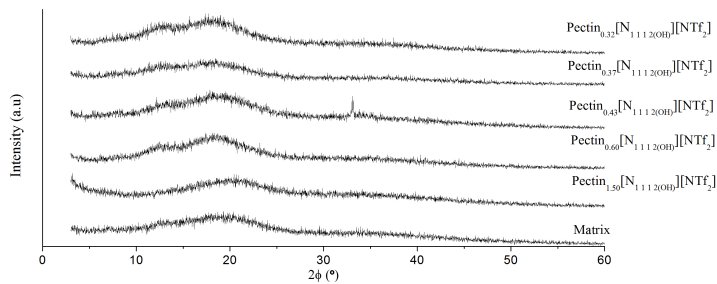


Figure 3. XRD patterns of selected samples.

Figure 4 shows a morphology of pristine pectin and pectin with different contents of $[N_{1112(OH)}][NTf_2]$. The pectin host exhibits a non-porous, homogeneous texture (Fig. 4 a), which changes to spherulitic microstructure upon IL addition (Figure 4b-d). More defined spherulite contours are observed in Figure 4b and d. This large number of spherulites within the samples with ILs is due to the fact that ILs acts as nucleation centres for polymer crystallization, leading to a larger number of smaller spherulites [34]. Similar results were obtained in other ILs containing polymer-based samples [35]. However, the texture of pectin-based samples resemble that based on DNA-IL [20], but it contrasts deeply with that reported for agar-based materials containing ILs [32]. This last exhibited good homogeneity with no phase separation. In present case, all membranes studied here have a heterogeneous morphology with phase separation, and its degree depends on IL content.

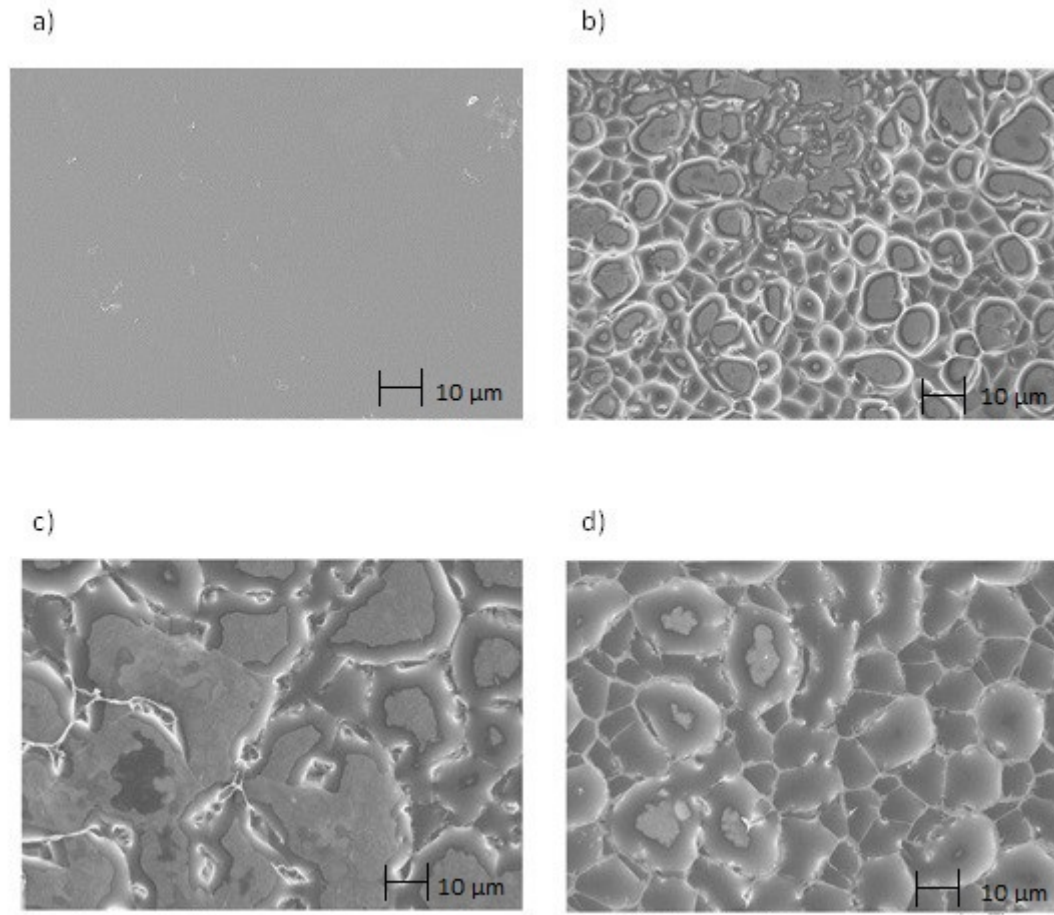


Figure 4. SEM images of pectin (a), Pectin_{0.60}[N_{1 1 1 2(OH)}][NTf₂] (b), Pectin_{0.43}[N_{1 1 1 2(OH)}][NTf₂] (c), and Pectin_{0.37}[N_{1 1 1 2(OH)}][NTf₂] (d) at magnification of 5.000x.

AFM experiments were carried on pectin based **membranes** in order to **evaluate** their surface topography, and the results of this analysis is shown in Figure 5. As already observed by SEM analysis, the films with different quantities of IL exhibit a more irregular topography than the pectin matrix. The membranes surface roughness was evaluated in terms of root mean square (RMS) height or RMS surface roughness (Sq) and the results are shown in Table 1.

Table 1. Roughness mean square (RMS) values for pectin and pectin-ILs PEs.

| Sample | Average Roughness (nm) |
|--|------------------------|
| Pectin | 20.3 |
| Pectin _{1.50} [N ₁₁₁₂ (OH)][NTf ₂] | 259.0 |
| Pectin _{0.43} [N ₁₁₁₂ (OH)][NTf ₂] | 376.3 |
| Pectin _{0.37} [N ₁₁₁₂ (OH)][NTf ₂] | 427.7 |
| Pectin _{0.32} [N ₁₁₁₂ (OH)][NTf ₂] | 573.2 |

According to these results, lowest Sq = 20.3 nm was registered for pectin membrane. All other samples containing ionic liquids exhibit Sq of more than 259.0, and this value increases up to 573.2 with IL content increase. This suggests that addition of IL increased the surface roughness of the pectin-based membranes. Moreover, these results might be potentially explained by the existence of undissolved polymer fragments in the samples or just phase separation. Comparing the obtained Sq values for each composition, it is possible to state that similar results were achieved with found by other authors [36,37].

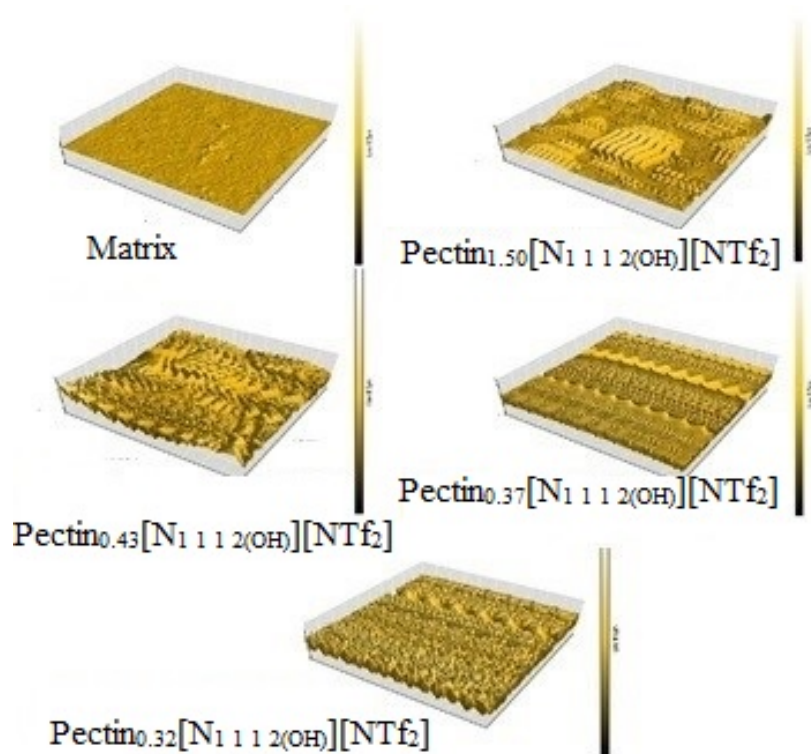


Figure 5. AFM images of pectin (a), Pectin_{1.50}[N_{1 1 1 2(OH)}][NTf₂] (b), Pectin_{0.43}[N_{1 1 1 2(OH)}][NTf₂] (c), Pectin_{0.37}[N_{1 1 1 2(OH)}][NTf₂] (d), and Pectin_{0.32}[N_{1 1 1 2(OH)}][NTf₂] (e).

The ionic conductivity behaviour of the Pectin [N_{1 1 1 2(OH)}][NTf₂] PE membranes can be related to the free volume theory. An increase of the ionic conductivity with temperature is interpreted as a ion hopping mechanism between coordinating sites together with local structural relaxations and segmental motions of the polymer salt complexes [38]. This, in turn, favours an inter-chain hopping and intra-chain ion movements, resulting in an increase of the electrolyte conductivity. The highest conductivity registered was $1.43 \times 10^{-6} \text{ S.cm}^{-1}$ at room temperature ($T = 25^\circ\text{C}$), for Pectin_{0.43}[N_{1 1 1 2(OH)}][NTf₂] composition. At 90°C , this electrolyte exhibited a conductivity of about $6.03 \times 10^{-5} \text{ S.cm}^{-1}$. This value is smaller than those reported for other natural macromolecules [20],

but it can be explained by the SEM image (Figure 4c), where it is observed a better dissolution of the ionic liquid compared to other materials.

4. Conclusion

A novel family of polymer electrolytes based on pectin and ionic liquids was synthesized and characterized in this work in terms of their thermal behavior, structure, morphology nature, and electrochemical properties. Results revealed that the PEs' surface roughness and ionic conductivity values increased with the IL content. The highest ionic conductivity values of 1.43×10^{-6} and 6.03×10^{-5} S cm⁻¹ at 25 and 90 °C, respectively were obtained for the Pectin_{0.43}[N_{1 1 1 2(OH)}][NTf₂] sample.

The PEs has predominantly amorphous structure and have a heterogeneous morphology with phase separation, and its degree depends on IL content.

The fulfillment of the most relevant characteristics desired in a PE justifies further studies as for example, the application and consequent characterization of these materials in ECDs prototypes.

Acknowledgements

This work was supported by FEDER through the COMPETE Program and by Fundação para a Ciência e a Tecnologia (FCT) in the framework of the Strategic Projects PEST-C/QUI/UI0686/2013, grants FCT Investigator contract (J.M.S.S.E.). The authors are also indebted to CNPq (grant 201820/2014-5), FAPESP, and CAPES for the financial support given to this research. M.M. Silva acknowledges CNPq (PVE grant 406617/2013-9) for the mobility grant provided by these institutions. The authors are also acknowledges to Dra. Ivana for AFM data.

References

- [1] F.M. Gray, Transport properties: effects of dynamic disorder, in: *Solid Polymer Electrolytes: Fundamentals and Technological Applications*, 252, VCH Publishers Inc., New York, USA, 1991.
- [2] R.E. Sousa, M. Kundu, A. Gören, M. Silva, L. Liu, C.M. Costa, S. Lanceros-Mendez, Poly (vinylidene fluoride-co-chlorotrifluoroethylene)(PVDF-CTFE) lithium-ion battery separator membranes prepared by phase inversion, *RSC Advances* 5 (2015) 90428.
- [3] A. Gören, C. Costa, M.M. Silva, S. Lanceros-Méndez, State of the art and open questions on cathode preparation based on carbon coated lithium iron phosphate, *Composites Part B: Engineering* 83 (2015) 333.
- [4] M.J. Neto, F. Sentanin, J.M.S.S. Esperança, M.J. Medeiros, A. Pawlicka, V. de Zea Bermudez, M.M. Silva, Gellan gum—Ionic liquid membranes for electrochromic device application, *Solid State Ionics* 274 (2015) 64.
- [5] R.A. Zoppi, C. Fonseca, M.A. DePaoli, S.P. Nunes, Solid electrolytes based on poly(amide 6-b-ethylene oxide), *Solid State Ionics* 91 (1996) 123.
- [6] R. Borkowska, A. Reda, A. Zalewska, W. Wieczorek, Composite polyether electrolytes with Lewis acid type additives, *Electrochim. Acta* 46 (2001) 1737.
- [7] Z. Florjanczyk, E. Zygadlo-Monikowska, W. Wieczorek, A. Ryszawy, A. Tomaszewska, K. Fredman, D. Golodnitsky, E. Peled, B. Scrosati, Polymer-in-salt electrolytes based on acrylonitrile/butyl acrylate copolymers and lithium salts, *J. Phys. Chem. B* 108 (2004) 14907.
- [8] C.E. Tambelli, J.P. Donoso, A.M. Regiani, A. Pawlicka, A. Gandini, J.F. LeNest, Nuclear magnetic resonance and conductivity study of HEC/polyether-based polymer electrolytes, *Electrochim. Acta* 46 (2001) 1665.
- [9] D.C. Dragunski, A. Pawlicka, Starch based solid polymeric electrolytes, *Mol. Cryst. Liq. Cryst.* 374 (2002) 561.
- [10] R. Alves, J.P. Donoso, C.J. Magon, I.D.A. Silva, A. Pawlicka, M.M. Silva, Solid polymer electrolytes based on chitosan and europium triflate, *J. Non-Cryst. Solids* 432, Part B (2016) 307.
- [11] M.D. Glasse, R. Idris, R.J. Latham, R.G. Linford, W.S. Schindwein, Polymer electrolytes based on modified natural rubber, *Solid State Ionics* 147 (2002) 289.
- [12] *Natural-based polymers for biomedical applications*, editor-in-chief: Rui L. Reis, Woodhead Publishing Limited Cambridge England (2008).
- [13] A.I. Suvorova, I.S. Tyukova, E.A. Smirnova, A.L. Peshekhonova, Viscosity of blends of pectins of various origins with ethylene-vinyl acetate copolymers, *Russ. J. Appl. Chem.* 76 (2003) 1988.
- [14] C. Krishnamurti, K. Giri, Preparation, purification and composition of pectins from Indian fruits and vegetables, *Proceedings: Plant Sciences* 29 (1949) 155.
- [15] B.L. Ridley, M.A. O'Neill, D. Mohnen, Pectins: structure, biosynthesis, and oligogalacturonide-related signaling, *Phytochemistry* 57 (2001) 929.
- [16] R. Alves, Leandro P. Ravaro, A. Pawlicka, M. M. Silva, Andrea S. S. de Camargo, “Eco-friendly luminescent hybrid materials based on Eu³⁺ and Li⁺ co-doped chitosan”, *Journal of the Brazilian Chemical Society*, 26 (2015) 2590-2597.
- [17] R. Leones, M. Fernandes, R. A. S. Ferreira, I. Cesarino, J. F. Lima, L.D. Carlos, V. de Zea Bermudez, C. J. Magon, J. P. Donoso, M. M. Silva, A. Pawlicka, “Luminescent DNA-and Agar- based membranes”, *Journal of Nanoscience and Nanotechnology*, 14 (9) (2014) 6685-6692.

- [18] J.R. Andrade, E. Raphael, A. Pawlicka, Plasticized pectin-based gel electrolytes, *Electrochim. Acta* 54 (2009) 6479.
- [19] A. Al-Kahlout, D. Vieira, C.O. Avellaneda, E.R. Leite, M.A. Aegerter, A. Pawlicka, Gelatin-based protonic electrolyte for electrochromic windows, *Ionics* 16 (2010) 13.
- [20] R. Leones, J.M.S.S. Esperança, A. Pawlicka, V. de Zea Bermudez, M.M. Silva, Polymer electrolyte based on DNA and N,N,N-trimethyl-N-(2-hydroxyethyl)ammonium bis(trifluoromethylsulfonyl)imide, *J. Electroanal. Chem.* 748 (2015) 70.
- [21] R. Leones, F. Sentanin, S.C. Nunes, J.M.S.S. Esperança, A. Pawlicka, V.d.Z. Bermudez, M.M. Silva, Effect of the ionic-liquid-alkyl-chain anion length on polymer electrolytes properties, *Electrochim. Acta* 184 (2015) 171.
- [22] O.A. El Seoud, A. Koschella, L.C. Fidale, S. Dorn, T. Heinze, Applications of ionic liquids in carbohydrate chemistry: a window of opportunities, *Biomacromolecules* 8 (2007) 2629.
- [23] H. Ohno, *Electrochemical aspects of ionic liquids*, Wiley, USA, 2005.
- [24] M. Petkovic, K.R. Seddon, L.P.N. Rebelo, C.S. Pereira, Ionic liquids: a pathway to environmental acceptability, *Chem. Soc. Rev.* 40 (2011) 1383.
- [25] M. Li, L. Yang, S. Fang, S. Dong, Novel polymeric ionic liquid membranes as solid polymer electrolytes with high ionic conductivity at moderate temperature, *J. Membrane Sci.* 366 (2011) 245.
- [26] M. Dash, F. Chiellini, R.M. Ottenbrite, E. Chiellini, Chitosan-A versatile semi-synthetic polymer in biomedical applications, *Prog. Polym. Sci.* 36 (2011) 981.
- [27] A.J. Costa, M.R. Soromenho, K. Shimizu, I.M. Marrucho, J.M. Esperança, J.N.C. Lopes, L.P.N. Rebelo, Density, Thermal Expansion and Viscosity of Cholinium-Derived Ionic Liquids, *ChemPhysChem* 13 (2012) 1902.
- [28] R. Leones, F. Sentanin, J.M.S.S. Esperança, A. Pawlicka, V. de Zea Bermudez, M.M. Silva, Chitosan and Ionic Liquid Based Solid Polymer Electrolytes: The Anion Alkyl Chain Length Effect, *ECS Transactions* 61 (2014) 51.
- [29] M.J. Neto, R. Leones, F. Sentanin, J.M.S.S. Esperança, M.J. Medeirosa, A. Pawlicka, M.M. Silva, Electrochemical Applications of Electrolytes Based on Ionic Liquids, *ECS Transactions* 45 (2013) 235.
- [30] H. Ohno, *Electrochemical aspects of ionic liquids*, John Wiley & Sons, 2011.
- [31] R. Lutz, A. Aserin, L. Wicker, N. Garti, Structure and physical properties of pectins with block-wise distribution of carboxylic acid groups, *Food Hydrocoll.* 23 (2009) 786.
- [32] R. Leones, F. Sentanin, L.C. Rodrigues, I.M. Marrucho, J.M.S.S. Esperança, A. Pawlicka, M.M. Silva, Investigation of polymer electrolytes based on agar and ionic liquids, *Express Polym. Lett.* 6 (2012) 1007.
- [33] R. Leones, F. Sentanin, L.C. Rodrigues, R.A.S. Ferreira, I.M. Marrucho, J.M.S.S. Esperança, A. Pawlicka, L.D. Carlos, M.M. Silva, Novel polymer electrolytes based on gelatin and ionic liquids, *Optical Mat.* 36 (2012) 187.
- [34] C. Xing, M. Zhao, L. Zhao, J. You, X. Cao, Y. Li, Ionic liquid modified poly(vinylidene fluoride): crystalline structures, miscibility, and physical properties, *Polymer Chemistry* 4 (2013) 5726.
- [35] R. Mejri, J. Dias, A. Lopes, S.B. Hentati, M.M. Silva, G. Botelho, A.M. de Ferro, J. Esperança, A. Maceiras, J. Laza, Effect of ionic liquid anion and cation on the physico-chemical properties of poly(vinylidene fluoride)/ionic liquid blends, *Europ. Polym. J.* 71 (2015) 304.

- [36] P.K. Singh, B. Bhattacharya, R.K. Nagarale, K.W. Kim, H.W. Rhee, Synthesis, characterization and application of biopolymer-ionic liquid composite membranes, *Synth. Met.* 160 (2010) 139.
- [37] S.C. Barros, A.A. da Silva, D.B. Costa, I. Cesarino, C.M. Costa, S. Lanceros-Méndez, A. Pawlicka, M.M. Silva, Thermo-sensitive chitosan–cellulose derivative hydrogels: swelling behaviour and morphologic studies, *Cellulose* 21 (2014) 4531.
- [38] D. Baril, C. Michot, M. Armand, Electrochemistry of liquids vs. solids: Polymer electrolytes, *Solid State Ionics* 94 (1997) 35.

Figures captions

Table's captions