

# The superior properties of polyelectrolyte-based hydrogels made in presence of ionic liquids

K. B. Rufato<sup>a</sup>, C. S Nunes<sup>a</sup>, L. C. Bonkovoski<sup>a</sup>, A. F. Rubira<sup>a</sup> and E. C. Muniz<sup>a,b</sup>

<sup>a</sup>Chemistry Department, State University of Maringa, Maringa, Brazil <sup>b</sup>Federal University of Technology - Parana - UTFPR, PPGCEM, Londrina, Brazil

Polyelectrolyte complex (PEC) is a type of hydrogel in which the polymers are physically crosslinked and classified as physical hydrogel. For some applications, for instance in medical applications, PEC are preferred instead the chemical hydrogels. In chemical hydrogels the crosslinking are made through covalent bonds. So, there is the need for using crosslinking agent for preparing chemical hydrogels which often leads to the decrease of biocompatibility. In our lab we have prepared PECs using different pathways and using several pairs of cationic and anionic polymers. In this contribution, we will discuss about the new methodology we have adopted for preparing PEC: using ionic liquids (IL) as solvent for both polycation and polyanion or using aqueous solution of such polymers in presence of ionic liquids instead of using only water. In this presentation, three different PECs systems will be presented and discussed: i) PEC constituted of chitosan/alginate prepared in presence of 1- Methylimidazolium hydrogen sulfate [Hmim][HSO<sub>4</sub>]; ii) Chitosan/chondroitin sulfate hydrogels prepared in [Hmim][HSO<sub>4</sub>]; and iii) PEC of poly[(2-dimethylamino) ethyl methacrylate] and chondroitin sulfate (PDMAEMA/CS) prepared in presence of ionic liquids of the 1-alkyl-3-methylimidazolium tetrafluoroborate.

i) PEC of chitosan/alginate prepared in presence of 1- Methylimidazolium

The system chitosan/alginate prepared in IL presented exceptional capability for adsorbing plumb: the maximum adsorption capacity ( $q_e$ ) was 607 mg g<sup>-1</sup> as compared to hydrogel made in water (in absence of IL) that is 60.3 mg g<sup>-1</sup>. Also, in this methodology the IL used for preparation of PEC can be recovered (because the PEC is washed Just after the PEC preparation) and reused for new PEC preparation. So, this methodology can be considered as a green process. Also, the [Hmim][HSO<sub>4</sub>] displays an excellent potential to conceive PECs with outstanding performances to be used in the development of eco-friendly and sustainable adsorbate- based materials made from natural sources. A manuscript containing these results is in final writing process [1].

ii) PEC of Chitosan/chondroitin sulfate hydrogels prepared in [Hmim][HSO<sub>4</sub>]

The PEC of Chitosan/chondroitin sulfate (50/50) and (30/70) prepared in aqueous solution of Hmim][HSO<sub>4</sub>] presented higher swelling capability as compared to analogous PEC prepared in aqueous medium in absence of IL. Beyond this, the PECs prepared in presence of IL presented higher

cellular viability (VERO cells and HT-29 cells) as compared to analogous PEC prepared in aqueous medium in absence of IL or compared to parent polymers. The results of this project were recently published by our research group [2].

iii) PEC of (PDMAEMA/CS) prepared in presence of ionic liquids of the 1-alkyl-3-methylimidazolium tetrafluoroborate

In this project the target is to evaluate the effect of ILs of different 1-alkyl-3-methylimidazolium tetrafluoroborate (with different alkyl chain lengths: butyl, octyl and dodecyl) on PDMAEMA/CS complexation. PDMAEMA is a cationic polymer that presented sensibility to pH and temperature (due to its LCST phase diagram in aqueous media). It is also mentioned in literature that PDMAEMA has bactericide effects. We observed that the morphologies of PECs are different of the PEC obtained in absence of IL and are dependent of the type of IL used for PEC preparation. PECB (alkyl = butyl) and PECO (alkyl = octyl) presented smaller average pore size as compared to PECD (alkyl = dodecyl). SEM micrographs showed that the presence of the ionic liquid, used during the PDMAEMA/SC complexation, causes a structural organization with well distributed pores. The pore diameter, measured through the micrographs of the complexes, was dependent on the ionic liquid used. Images obtained by TEM demonstrated that the PECD particles are spherical with a heterogeneous morphology, formed by a PDMAEMA core, an outer layer of SC and hydrophobic cation sites [Dmim]. A manuscript containing these results is in final writing process [3].

The results in this presentation show that the new methodology for PEC preparation (using ILS as solvent or IL in aqueous media) represents an open window for obtaining PECs hydrogels with different and interesting properties.

[1] Rufato, K.B. et al. PEC of chitosan/alginate prepared in presence of 1-Methylimidazolium as adsorbent of Pb. To be submitted.

[2] Nunes, C. S., Rufato, K. B., Souza, P. R., de Almeida, E. A. M. S., da Silva, M. J. V., Scariot, D. B., Muniz, E. C. Chitosan/chondroitin sulfate hydrogels prepared in [Hmim] [HSO<sub>4</sub>] ionic liquid. *Carbohydrate Polymers*, 170, 99-106. 2017.

[3] Bonkovoski, L.C. et al. PEC of (PDMAEMA/CS) prepared in presence of ionic liquids of the 1-alkyl-3-methylimidazolium tetrafluoroborate. To be submitted