Chemical Engineering Journal 241 (2014) 122–130

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Supercritical fluid processing of natural based polymers doped with ionic liquids

M. Martins [a,b], Rita Craveiro [c], Alexandre Paiva [c], Ana Rita C. Duarte [a,b,*], Rui L. Reis [a,b]

[a] 3B's Research Group – Biomaterials, Biodegradable and Biomimetic, University of Minho, Headquarters of the European Institute of Excellence on Tissue Engineering and Regenerative Medicine, Avepark 4806-909 Taipas, Guimarães, Portugal
[b] ICVS/3B's PT Government Associated Laboratory, Braga, Guimarães, Portugal
[c] REQUIMTE/CQFB, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

HIGHLIGHTS

- Modification and processing of natural based materials following a green chemistry approach.
- Natural based polymeric foams doped with ionic liquids as hybrid materials with advanced properties.
- Characterization of the role of ionic liquids in supercritical fluid foaming process.
- Preparation of new supports for catalysis, chromatography, micro extraction.

ARTICLE INFO

Article history:
Received 12 June 2013
Received in revised form 11 October 2013
Accepted 28 November 2013
Available online 4 December 2013

Keywords:
Ionic liquids
Supercritical fluid foaming
Polymer processing
Starch
Poly (lactic acid)
Carbon dioxide

ABSTRACT

Some approaches have been developed in our group to investigate the role of novel ionic liquids as process and property modifiers of natural-based polymers. In our previous work, we proposed the use of ionic liquids as plasticizing agents for the creation of porous structures from a semi-crystalline natural-based polymer. The current work intended to complement the previous studies, evaluating the ability of ionic liquid (IL) to plasticize polymers such as blends of starch-poly-lactic acid (SPLA) and its effect on supercritical fluid foaming process (SCF) and providing more insights on the mechanisms involved. For this purpose, blends of starch with poly (lactic) acid, with different ratios of starch and poly-lactic acid of 50:50 and 30:70 were modified and processed using 1-butyl-3-methylimidazolium chloride ([bmim]Cl). Supercritical fluid foaming was studied at different soaking times (1, 3 and 6 h) using carbon dioxide at 20.0 MPa and 40 °C. The blends were characterized by different techniques, such as infra-red spectroscopy, differential scanning calorimetry and compression and tensile mechanical analysis. The morphology of the foamed structures was analyzed by scanning electron microscopy and micro-computed tomography. The results suggest that after 3 h of soaking time an equilibrium state of carbon dioxide into the bulk samples is attained, yielding structures with 6% and 15% of porosity, for SPLA70 and SPLA50 respectively. The solubility of carbon dioxide within the matrices was studied for the same conditions and the results demonstrate a higher sorption degree in the samples doped with ionic liquid. Sorption and desorption diffusion coefficients of supercritical CO_2 in the SPLA matrix were determined for the raw polymer and for the SPLA doped with [bmim]Cl. It was found that the lower desorption diffusion coefficients are related with the higher porosity obtained by the foaming process.

1. Introduction

In recent years, there has been a marked increasing interest in biodegradable polymers due to their obvious environment-friendly properties when compared to conventional petroleum derived polymeric materials [1,2]. Starch is a natural polymer which possesses many unique properties and is one of the most promising biodegradable polymers, readily available from different sources, such as maize, corn or potato. The flexibility of starch based materials can be improved by some approaches, for example blending this polymer with others. Blends of starch with synthetic polyesters have been reported in the literature for different applications that go from food industry and agriculture to biomedical field [3]. Poly-lactic acid is one of the polymers which can be blended

* Corresponding author at: 3B's Research Group- Biomaterials, Biodegradable and Biomimetic, University of Minho, Headquarters of the European Institute of Excellence on Tissue Engineering and Regenerative Medicine, Avepark, 4806-909 Taipas, Guimarães, Portugal. Tel.: +351 253 510 900; fax: +351 253 510 909.
E-mail address: aduarte@dep.uminho.pt (A.R.C. Duarte).

1385-8947/$ - see front matter © 2013 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.cej.2013.11.080

with starch and is the product that at the present time has one of the highest potentials due to its availability in the market and its low price [4]. Furthermore, its biodegradation does not present any toxicological concerns. Blends of starch and PLA, when compared to starch, present a more hydrophobic character, lower water permeability and improved mechanical properties [5]. Processing natural-based materials still presents, however, major challenges in polymer science. The combination of supercritical technology with ionic liquids has been suggested as a green approach to overcome the drawbacks of conventional polymer processing techniques [6]. Carbon dioxide is the most commonly used fluid due to its non-toxic properties and to the low operation temperature involved in supercritical processes (Tc = 31 °C and Pc = 73 bar) [7]. Ionic liquids (ILs), on the other hand, are organic molten salts, that typically have extremely low volatility and high functionality. ILs are powerful solvents widely used due to their chemical and thermal stability, and high ionic conductivity properties. Although ILs are usually considered as green solvents, there are some drawbacks regarding its use. Besides having a certain level of toxicity, heat and mass transfer problems as well as phase changes may occur in their synthesis. Furthermore, the effect of water content on ILs, can strongly affect their viscosity. Nonetheless, the variety of ionic liquid structures resulting from the numerous possible combinations of cations and anions, may lead in the future to the synthesis of greener and biodegradable solvents [8]. The dissolution of natural polymers in ionic liquids as well as the plasticizing effect of ionic liquids has been reported in different studies. In particular [bmim]Cl, which was the IL studied in this work has been reported to be a good solvent for cellulose [9], chitin and chitosan [10] and a plasticizing agent of starch [11]. Doping a natural-based polymer with an ionic liquid has been described in literature as strategy to enhance polymer foaming [12]. In the reported work a blend of starch and poly-ε-caprolactone was studied and the results suggest the plasticizing ability of the ionic liquid [13]. In the present work we evaluate the characteristics of SPLA dopped with an ionic liquid and the effect of the presence of the IL on supercritical carbon dioxide foaming of the polymer. One of the great advantages of working under supercritical media is the possibility of modifying the morphological and functional properties of polymers by swelling, furthermore, carbon dioxide at high pressure can be impregnated in the polymeric matrix due to the molecular forces that are established between the two species [14]. The supercritical fluid foaming relies on the ability of carbon dioxide to act as a temporary plasticizing agent, lowering the glass transition temperature (T_g) of semi-crystalline polymers [15,16]. The reduction of the T_g is a thermodynamic effect highly dependent on the interactions between polymer–carbon dioxide. Stronger interactions will enhance the T_g depression and polymer chain flexibility.

The behavior of different classes of polymers in supercritical carbon dioxide, particularly the manipulation of their physical properties and their selective control has become an area of interest in polymer synthesis and processing. The knowledge of the solubility and diffusion coefficients of carbon dioxide in the polymeric matrix is important for the determination of the best operating parameters and the understanding of the process. Different methods have been reported in the literature for the determination of these parameters and the most commonly used are the use of a quartz micro-balance [15] or a gravimetric or barometric method [16,17]. In situ spectroscopic techniques have also been reported to be a valuable tool for the quantification of the weight percentage of carbon dioxide dissolved in the polymeric matrix [18,19]. In this work, a gravimetric method was used to determine the sorption degree and diffusion coefficients of carbon dioxide in the raw SPLA samples and in the samples doped with ionic liquid.

2. Material and methods

2.1. Materials

The polymers used on this study were based on a blend of corn starch and poly (lactic acid) with different compositions of poly (lactic acid) 50 wt% (SPLA50) and 70 wt% (SPLA70). These polymers were obtained from Novamont. The ionic liquid used was 1-butyl-3-methylimidazolium chloride ([bmim]Cl) obtained from Sigma Aldrich. Carbon dioxide (99.998 mol%) was supplied by Air liquide. All materials were used without any additional purification.

2.2. Sample preparation

SPLA samples blended with IL were prepared by compression moulding using a Moore Hydraulic Press (UK) at 80 °C and 6 MPa for 15 min. Disc shape like samples of SPLA 50 and SPLA 70, with 10 wt% [bmim]Cl were prepared using steel rings (12 × 2 mm) as mould. Table 1 summarizes the materials prepared.

2.3. Supercritical fluid foaming

The porous matrixes were prepared by supercritical fluid foaming (SCF) at 20.0 MPa and 40 °C for different soaking times (1, 3 and 6 h). The samples were loaded in the high pressure vessel, heated to the desired temperature by using an electric thin band heater (OGDEN) connected to a temperature controller. Carbon dioxide was pumped into the vessel using a high pressure piston pump (P-200A Thar Technologies) until the operation pressure was attained and the pressure inside the vessel was measured with a pressure transducer. The system was closed in order to promote the foaming of the matrixes. Afterwards, the system was slowly depressurized.

3. Characterization

3.1. Differential scanning calorimetry (DSC)

The DSC experiments were performed using DSC Q100 V9.8 Build 296 apparatus. The samples were placed in aluminum pans and heated at a rate of 10 °C/min from 20 to 220 °C, cooled to 20 °C and heated at 5 °C/min until 200 °C. Standard calibrations were performed using indium leads.

3.2. Compressive and tensile mechanical analysis

Compressive and tensile mechanical analysis of the materials produced were measured using an INSTRON 5540 (Instron Int. Ltd., High Wycombe, UK) universal testing machine with a load cell of 1 kN.

Compression testing was carried out at a crosshead of 2 mm min^{-1}, until a maximum reduction in sample weight of 60%. The compressive modulus is defined as the initial linear modulus on the stress/strain curves. In tensile mode, the dimensions of the specimens used were 60 mm of length, 1 mm width and 3 mm

Table 1
Summary of the matrices prepared.

Polymer	Ionic liquid	IL concentration (wt%)	Reference
SPLA 50	–	–	SPLA50
SPLA 70	–	–	SPLA70
SPLA 50	[bmim]Cl	10	SPLA50 10Cl
SPLA 70	[bmim]Cl	10	SPLA70 10Cl