



Effect of a supercritical fluid on starch-based polymer processed with ionic liquid



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ARTICLE INFO

Article history:

Received 30 September 2014

Received in revised form 22 December 2014

Accepted 22 December 2014

Available online 30 December 2014

Keywords:

Starch

Natural-based polymers

Ionic liquid

Extrusion

Polymer processing

Supercritical carbon dioxide

ABSTRACT

Recently, ionic liquids have been proposed as a promising plasticizing agents of starch. In this work, starch was treated with ionic liquid to obtain thermoplastic starch (TPS). The effects of supercritical carbon dioxide (ScCO_2) on the processing of starch with 1-butyl-3-methylimidazolium chloride (BMIMCl) were also studied. For this purpose, the effects of different operating parameters such as temperature, pressure and processing time on the structural and thermal properties of TPS were evaluated.

The results suggest that carbon dioxide leads to a low change of crystalline structure and this change is primarily influenced by temperature processing. Furthermore, the use of supercritical CO_2 with different pressures and temperatures induces a decrease of the glass transition compared to formulations without it. This result can be interpreted as the plasticizing effect of CO_2 and the preferred interaction between CO_2 and starch plasticized with ionic liquid compared to glycerol–starch samples.

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1. Introduction

Recently, biodegradable polymers obtained from renewable resources have constituted a viable and important alternative to petroleum-derived polymers due to their ecologically-friendly properties [1–3]. Indeed, polysaccharide materials are largely considered as good candidates to replace synthetic polymers and their applications [4–6].

Among them, starch is a promising resource which has largely been used for its unique qualities, such as abundance, low price and renewability [7]. However, starch, like all other natural-based polymers, is water sensitive, with high crystallinity and a melt processing temperature close

to its decomposition temperature which makes its processing difficult for most applications [8,9].

To overcome this limitation and to improve the properties and the processing of starch, it should be blended with another polymer [9–11] or plasticized with a suitable plasticizer so as to be used in thermoplastic processing applications [12–14].

Ionic liquids (ILs) are organic salts which consist in most cases of a combination of a large organic cation and an organic or inorganic anion. ILs present interesting properties such as negligible vapor pressure, non-flammability, ionic conduction as well as thermal and electrochemical stability [15]. ILs present some drawbacks [16], nevertheless the infinity of combinations of anions and cations to make an ILs will lead us to find greener, cheaper and biodegradable forms with fine-tuned physical and chemical properties.

Many studies show that ILs can be used in biomass chemical processing [17,18]. In fact, hydrophilic ILs such as 1-butyl-3-methyl-imidazolium chloride (BMIMCl) and

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1-allyl-3-methylimidazolium chloride (AMIMCl) can act as plasticizers and interact with various carbohydrate polymers (starch, chitin, cellulose and lignin) [19–22].

The processing of starch with ILs was showed in our previous study [19] and these ionic liquids allow us to produce thermoplastic starch (TPS) with efficient plasticization. We have also investigated the effects of the concentration of ionic liquids and phase diagrams of water sorption isotherms on the intrinsic properties of starch thermoplastics.

The investigation of new processing techniques is one of the major topics in thermoplastic applications. In fact, the combination of supercritical fluid technology with ILs in the process of natural-based materials as a green approach represents an important alternative to conventional processing techniques [23–26]. One of the most commonly used fluids is carbon dioxide (CO_2), which is non-toxic, low price and requires low temperature and pressure to reach the supercritical condition ($T_c = 31^\circ\text{C}$ and $P_c = 73\text{ bar}$) [24].

Martins et al. [27] studied the foaming process of supercritical carbon dioxide in the presence of ionic liquid as plasticizer of starch-poly-lactic acid (SPLA) blends. They showed that the foaming effect was linked to the crystallinity and had an impact on the diffusion coefficient on the solute (CO_2) in the polymer which influenced the porosity observed in the materials.

Craveiro et al. [28] also studied a blend of starch and poly- ϵ -caprolactone (PCL) doped with different concentrations of 1-butyl-3-methylimidazolium acetate (BMIMAc) and 1-butyl-3-methylimidazolium chloride (BMIMCl). The result of this study showed that the blend of starch and poly- ϵ -caprolactone (PCL) doped with 30% of BMIMCl was a good conductive material.

Duarte et al. [29] used ionic liquids as promoting foaming agents. In fact, BMIMAc promote the supercritical gas foaming of a polymeric blend of starch and poly- ϵ -caprolactone in order to make porous materials.

Many studies in the literature report the interaction of ILs and supercritical carbon dioxide (ScCO_2) systems [30–34]. They show that in the majority of cases ScCO_2 is soluble in ILs, but ILs are not soluble in ScCO_2 [32] and the solubility of ScCO_2 in the IL rich-phase is advantageous because it reduces the viscosity of the IL and enhances the mass transfer process [33].

Blanchard et al. [32] showed also that the solubility of CO_2 in [BMIM][PF₆] systems which are extensively studied in the literature [35] increases not only as pressure increases but also with the decrease of temperature [36].

Other authors [34,37,38] showed that the solubility of CO_2 in ionic liquids depended strongly on the choice of anion and also on the length of the cation alkyl chain. On the other hand, Wu et al. [39] showed that to increase the solubility of ILs in CO_2 -rich phase, the CO_2 phase should contain sufficiently polar organic compounds in sufficient concentrations.

Ionic liquids (ILs) hold great potential as plasticizers for numerous bio-polymers. This work investigates the effects of supercritical carbon dioxide on the processing of plasticized thermoplastic starch with ionic liquid prepared by two methods: the first one is a mixture of starch and

plasticizers in a batch reactor and the second method is using a micro-compounder. The effects of the processing pressure, temperature and the duration of processing time of supercritical carbon dioxide (ScCO_2), which is an environmentally-friendly component, on the properties of plasticized starch were studied.

2. Experimental

2.1. Materials

Maize starch (containing 40% of amylose) was purchased from Roquette Frères (Lestrem, France). The initial moisture content was 9.4 wt%. Glycerol (Aldrich), ionic liquid, 1-butyl-3-methylimidazolium chloride BMIMCl (Aldrich) and carbon dioxide (CO_2) (Air Liquide) were used without further purification.

2.2. Processing

2.2.1. Samples preparation

The samples used in this work were based on a blend of corn starch and plasticizers (glycerol and BMIMCl). Two compositions were prepared: starch with 20 wt% of BMIMCl (ST-BM-20) and starch with 20 wt% of glycerol (ST-GL-20).

Two methods of preparation of the blends were used: the first one is a mixture of starch and plasticizers in a batch reactor and the second method is using a micro-compounder.

2.2.1.1. Batch autoclave. Blend formulations of starch and plasticizers are directly introduced into the batch reactor (Parr instrument) which serves as a mixing and treatment device (rotation speed set at 100 rpm).

2.2.1.2. Extrusion process. In this case, blends of starch and plasticizers (glycerol and BMIMCl) are first prepared in the micro-compounder (Thermo Haake) which allows the preparation of small quantities of batch of thermoplastic starch (TPS). This device can be used as a mixer and allows the simulation of a co-rotating extruder.

The samples were first premixed manually and then introduced into the micro-compounder at 150°C with a rotation speed set at 150 rpm. The mixture was thermo-mechanically processed for 3 min for all samples (closed loop) and then extruded through the exit die.

After melt mixing, the samples were heat-pressed at 150°C and 200 bars for 5 min and were thermo-molded by compression molding into disk plates with the following characteristics: $25\text{ mm} \times 2\text{ mm}$.

2.2.2. Supercritical fluid treatment

The different samples previously prepared (batch samples and disk plates) were loaded in the pressure reactor (Parr instrument) and submitted to supercritical fluid at different pressures (from 10 MPa up to 15 MPa), temperatures (from 100°C up to 120°C) and for different soaking times (from 1 up to 4 h).

First, the samples were introduced in the high-pressure CO_2 reactor and then heated to the desired temperature

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