



Plasticizing effect of ionic liquid on cellulose acetate obtained by melt processing



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ABSTRACT

Cellulose acetate (CA) plasticized by 1-butyl-3-methylimidazolium chloride (BMIMCl) and with diethylphthalate (DEP) was obtained by melt processing at 150 °C. The effect and the interaction of ionic liquid with the cellulose acetate and their influence on structural, thermo-mechanical, rheological and tensile properties of CA materials were investigated.

Ionic liquid (BMIMCl) has shown a good plasticization and more efficient destruction of the crystalline structure of cellulose acetate than the DEP plasticized CA. BMIMCl interacts intensively with CA molecules due to the pronounced van der Waals interactions, hydrogen bonding and electrostatic nature of ionic liquid. The tensile test and the low Young's modulus for plasticized CA suggest a strong reduction of the interaction between the CA chains due to the presence of the ionic liquid.

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1. Introduction

The synthetic polymer industry in modern society offers many benefits but the decrease of natural resources, increasing oil prices and early growth of CO₂ emissions related to the complexity of environmental problems generated a need to move toward green material solutions that fit into a sustainable development policy and low environmental impact.

Cellulose acetate (CA) is one of the most important cellulose derivatives with a wide interest in several applications such as membrane separation, films, coatings, textile and cigarette filters (Ach, 1993). The characteristics that make CA a promising substrate are its renewable source, non-toxicity, low cost and biodegradability (Avérous, Fringant, & Moro, 2001; Buchanan, Gardner, & Komarek, 1993; Jiang & Hinrichsen, 1997; Wu, Wang, Li, Li, & Wang, 2009).

However, cellulose acetate presents several shortcomings: high viscosity, elevated glass transition temperature, high crystallinity and a melt processing temperature which is very close to its decomposition temperature, which makes its functionalization and

process difficult for many applications (Miyashita, Suzuki, & Nishio, 2002; Zugenmaier, 2004).

To find an answer to these issues, cellulose acetate should be blended with another suitable polymer (Han, Zhang, Shao, Kong, & Lv, 2013; Miyashita, Suzuki, & Nishio, 2002; Pizzoli, Scandola, & Ceccorulli, 1994) or plasticized with an appropriate plasticizer so as to be used in thermoplastic processing applications (Lee & Shiraishi, 2001; Yoshioka, Hagiwara, & Shiraishi, 1999).

The main plasticizers used in cellulose-acetate plastics are phthalate plasticizers but several other compounds such as triethyl citrate, glycerol derivatives and phosphate have also been successfully used (Fridman & Sorokina, 2006; Mohanty, Wibowo, Misra, & Drzal, 2003; Quintana et al., 2013; Schilling et al., 2010).

Many authors have shown that the type and the concentration of plasticizers can play a key role on the thermal and mechanical properties of cellulose acetate (Fridman & Sorokina, 2006; Zepnik, Kabasci, Kopitzky, Radusch, & Wodke, 2013).

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 (Ning, Xingxiang, Haihui, & Benqiao, 2009).

Recently, it was proved that room-temperature ionic liquids, especially imidazolium-based, can interact with cellulose, its derivatives and many other bio-polymers (Bendaoud & Chalamet,

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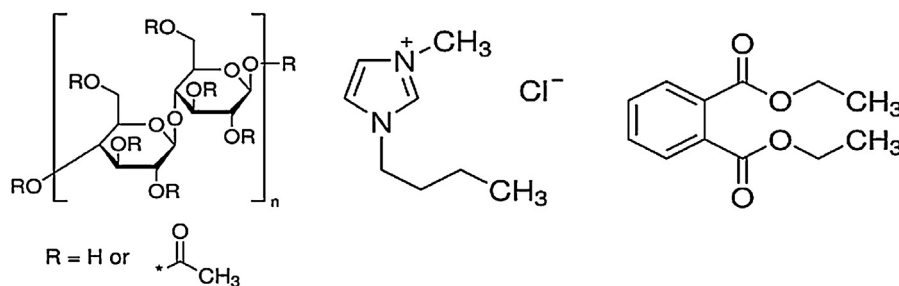


Fig. 1. Formulas of CA, BMIMCl and DEP

2013; Cao et al., 2009; El Seoud, Koschella, Fidale, Dorn, & Heinze, 2007; Mateyawa et al., 2013; Rogers & Seddon, 2003).

The interaction between the ionic liquid and cellulose acetate and the use of an ionic liquid as a safe and novel plasticizer of cellulose acetate involved in the formulation of polymer electrolyte have recently been reported (Jhong, Wong, Wan, Wang, & Wei, 2009; Ramesh, Shanti, & Morris, 2012, 2013a, 2013b).

Rudaz and Budtova (2013) show that the understanding of the rheological properties are predominant in studying the molecular organization of the polymer in the solvent (cellulose acetate/IL solutions) and in understanding the role of ionic liquids on the cellulose acetate processing.

Another aspect is the study of the molecular structure transition. The relaxation transitions observed in biopolymers, and especially in cellulose acetate, with a correlation between NMR, dielectric and DMTA results can be divided into four main groups, in order of decreasing temperature (Keely, Zhang, & McBrierty, 1995; McBrierty, Keely, Coyle, Xu, & Vij, 1996; Számel, Klébert, Sajó, & Pukánszky, 2008; Zugenmaier, 2004).

The transition associated to the highest temperature, α relaxation (at 472 K), is assigned to glass transition of the main chains of the polymer.

The identification of the other relaxations is more difficult and contradictory due to the number of smaller structural units which can associate to these relaxations. These situations are more complicated with plasticization or chemical modification of CA.

The relaxation β^* (at 323–373 K) is associated to hydrated CA and it is related to the loss of water associated with different groups or the interaction of single repeat units (Yarsley, Adamson, Flavell, & Perkins, 1964). The peak is very weak and its identification is difficult.

The β relaxation (at 235 K) is complex to associate because it is involved in a superposition of different contributions: relaxation of the side groups (polar acetate group) on the one hand and/or local main chain (single monomeric units) on the other hand (Vidéki, Klébert, & Pukánszky, 2007).

The γ -relaxation (at 185 K) corresponds to a small peak which can be related to the mobility of the weakly bound water (Zugenmaier, 2004), glass transition of the plasticizers and movement of hydroxyl or hydroxymethyl groups (Backman & Lindberg, 2001).

Both water and plasticizers act as plasticizers (McBrierty, Keely, Coyle, Xu, & Vij, 1996), leading to the reduction of the glass transition temperature (T_g) and suppression of the γ -relaxation (Keely, Zhang, & McBrierty, 1995).

The most commonly used technique today for the processing of cellulose acetate with ILs is performed by solution casting methods (Jhong, Wong, Wan, Wang, & Wei, 2009; Ramesh, Shanti, & Morris, 2012, 2013a) and we did not find any literature reporting on the process of cellulose acetate with ILs by extrusion.

In this study, a co-rotating twin-screw extruder was used to do the plasticization of cellulose acetate with imidazolium ionic liquid, 1-butyl-3-methylimidazolium chloride, and conventional

phthalate-based plasticizers which can suppress the high degree of crystallinity of CA.

Therefore, the objectives of this study are (1) to replace phthalate plasticizers with an eco-friendly plasticizer, (2) to perform the de-structuring and plasticization of the cellulose acetate (CA) with ionic liquid and (3) to study the interaction of ionic liquid with the cellulose acetate and their influence on thermo-mechanical, structural, rheological and mechanical properties of CA materials.

2. Experimental

2.1. Materials

Cellulose acetate (CA, $M_w = 30,000$ g/mol, 39.8 wt.% of acetyl content), 1-butyl-3-methylimidazolium chloride (BMIMCl, purity $\geq 95\%$) and diethyl phthalate (DEP, purity $\sim 99.5\%$) were obtained from Aldrich.

Formulas of CA, BMIMCl and DEP are presented in Fig. 1.

2.2. Melting process

2.2.1. Micro-compounder

Blends of CA and plasticizers (BMIMCl and DEP) were prepared by melt processing methods. This process was performed in the micro-compounder allowing the preparation of small batches of samples (<7 g).

The Minilab micro-compounder (Thermo Haake) is a device with a conical screw system with a recirculation channel. This device can be used as a mixer and allows the simulation of a co-rotating extruder execution with small quantities of materials.

2.2.2. Materials processing and storage

Cellulose acetate and plasticizers were first premixed manually and then introduced into the micro-compounder at 150°C with a rotation speed set at 150 rpm. Various compositions were prepared: 20, 30 and 40% (w/w) of plasticizers. In fact, based on our preliminary testing, it is not possible to process CA with less than 20 wt% of plasticizers. For formulations with plasticizers exceeding 40 wt%, the mechanical properties of materials become very low.

The notations CA (cellulose acetate), BM (BMIMCl), DEP (diethyl phthalate) and the proportion by weight of the plasticizer (w/w, %) were adopted to distinguish between the different formulations. For example, CA-BM-20 blends were obtained by mixing BMIMCl 20% (w/w) with cellulose acetate.

The introduction of products into the micro-compounder took about 1 min and the mixture (closed loop) was thermo-mechanically processed for 4 min for all samples. Then the formulation was extruded through the exit die. The melt behavior was characterized by recording the torque signal in the recirculation channel of the device.

After melt processing, the samples were heat-pressed at 150°C and 200 bars for 10 min and were thermo-molded into dumbbells

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