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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 diethylphtalate (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.

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 CO_2 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 successful 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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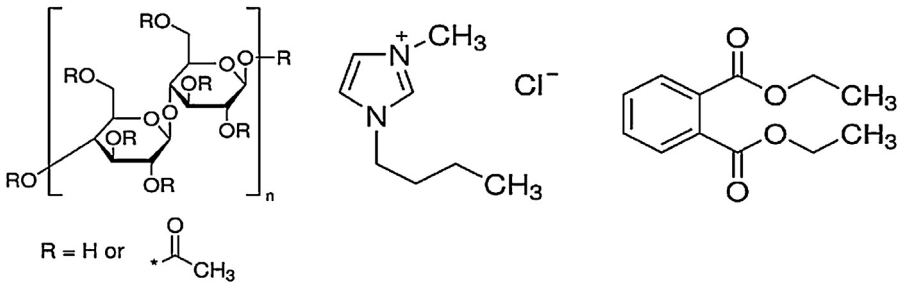

Fig. 1. Formulas of CA, BMIMCl and DEP

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 ϒ-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 ϒ-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-structuration 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, Mw = 30,000 g/mol, 39.8 wt.% of acetyl content), 1-butyl-3-methylimidazolium chloride (BMIMCl, purity ≥95%) and diethyl phthalate (DEP, purity ~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

Table 1
Properties of plasticizers and cellulose acetate at 25 °C.

Chemical	Density (g/cm³)	Mw (g/mol)	Solubility parameter ($MPa^{1/2}$)				
			δ_d	δ_p	δ_h	δ_{ES}[c]	δ_t[d]
BMIMCl	1.08	147.70	19.10[a]	20.70[a]	20.70[a]	29.27	34.95
DEP	1.12	222.24	17.60[a]	9.60[a]	4.50[a]	10.60	20.55
CA	1.30	198.00	15.55[b]	16.30[b]	12.95[b]	20.82	25.98

δ_d, dispersive parameter; δ_p, polar parameter; δ_h, hydrogen parameter; δ_{ES}, electrostatic parameter; δ_t, total solubility parameter.
[a] Hansen (2012).
[b] Xing et al. (2011).
[c] The $\delta_{ES} = (\delta_p^2 + \delta_h^2)^{0.5}$.
[d] The $\delta_t = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{0.5}$.

and disk plates with respectively the following characteristics: 30 mm × 10 mm × 2 mm and 25 mm × 2 mm.

The samples were then stored in a climatic and temperature test chamber (Froilabo – Firlabo) under a controlled relative humidity: 40% RH, 30 °C.

Films of neat CA (without plasticizers) were prepared by solvent casting method. The films were cast by being drawn on Petri dishes 10% solutions (w/w) of CA in acetone solvent. After removal of the solvent, the thickness of the films was approximately 130 μm.

All the characterizations of samples were made after water uptake equilibrium in the samples. No more variations were observed after 3 days.

2.3. Characterization

2.3.1. X-ray diffraction (XRD)

The crystalline structure of cellulose acetate powder treated with different plasticizers was studied using an XRD analyzer (BrukerAdvance D8) with respectively excitation voltage and current 43 kV and 35 mA (Cu Kα radiation). Wide-angle X-ray intensities were recorded from 5° to 50° in 2θ with a scanning rate of 3 °C/min.

The degree of crystallinity of samples was quantitatively estimated as the ratio of crystalline area to the total area under the diffraction peaks. Data analyses were performed using Fytik software.

2.3.2. Dynamic mechanical thermal analysis (DMTA)

The sample bars (30 mm × 10 mm × 2 mm) were conditioned at 40% RH and 30 °C for 3 days until no significant additional change of weight was observed.

The experiment was carried out with a DMTA Rheometrics scientific strain control at a frequency of 1 Hz with deformation amplitude of 0.1% to insure experimentation in the linear viscoelasticity region. The heating rate was 3 °C/min from −100 °C to 100 °C.

2.3.3. Rheology analysis

The measurements were performed using a Rheometric Scientific ARES with parallel plate geometry (25 mm). Tests were carried out in the dynamic frequency mode at 170 °C. Strain sweeps were performed to ensure that all data were acquired within linear viscoelastic conditions. The strain amplitude was kept constant at 0.1%.

2.3.4. Climatic tensile properties

The mechanical properties of the different samples which were pressed into films at 150 °C with an average thickness of 100 μm were determined by a laboratory tensile machine with a 2 daN cell and in climatic controlled conditions (40%RH-30 °C).

The advantage of this climatic tensile machine is to characterize the mechanical properties in a controlled temperature and humidity environment.

Five conditioned tensile specimens were tested at 10 mm/min. The stress–strain curves allow the determination of the elastic modulus (MPa), the elongation at break (%) and the rupture stress (MPa).

3. Results and discussion

3.1. Cellulose acetate processing

The solubility parameters and the density of the plasticizers and polymer at 25 °C were summarized in Table 1.

The results show that the total solubility parameter, δ_t, related to BMIMCl, is more away from the value of cellulose acetate than between CA and DEP, a commonly plasticizer of cellulose acetate, which suggest a better interaction of DEP.

However, the greatly electrostatic interactions and hydrogen bonding developed between BMIMCl and CA make up an efficiency plasticization (Xing, Peng, & Chung, 2011).

Further, ionic liquid comparatively to DEP has smaller size and higher polarity of [$BMIM^+$] and above a critical temperature, ion pair dissociation mechanism can happen (Wu, Zhang, Zhang, He, Ren, & Guo, 2004; Zhang, Wu, Zhang, & He, 2005). The dissociation of BMIMCl, increase the diffusion rate of ions and intensive interaction with CA can occur.

Cellulose acetate and plasticizers blends were processed by twin-screw extrusion at 150 °C. Fig. 2 shows a typical curve of the evolution of the torque vs mixing time, indicating that a mixing time of 240 s was sufficient for the de-structuration and melting process. Longer periods can lead to the degradation of the materials.

The different peaks observed on the torque curve correspond to the successive introductions of the powder premix in the machine.

Table 2 shows the visual observation and the evolution of torque according to the formulation of plasticized CA with ionic liquid and DEP.

The processed samples above 20 wt.% DEP were clear, transparent, and homogeneous while the plasticized CA with BMIMCl were also transparent, homogeneous with faint yellow/brown color (Fig. 3 and Table 2).

Moreover, for all formulations, the torque signal evolution decreased with the concentration of the plasticizers and this is

Table 2
Composition, torque signal and visual appearance of the CA plasticized samples.

Sample identification	Torque (Nm)	Visual and handling characteristics of pressed samples
CA-DEP-20	3.8 ± 0.1	Transparent, clear and fragile
CA-DEP-30	1.1 ± 0.1	Transparent, clear and flexible
CA-DEP-40	0.4 ± 0.1	Transparent, clear and flexible
CA-BM-20	2.6 ± 0.1	Transparent, colored and fragile
CA-BM-30	1.3 ± 0.1	Transparent, colored and flexible
CA-BM-40	0.5 ± 0.1	Transparent, colored and flexible

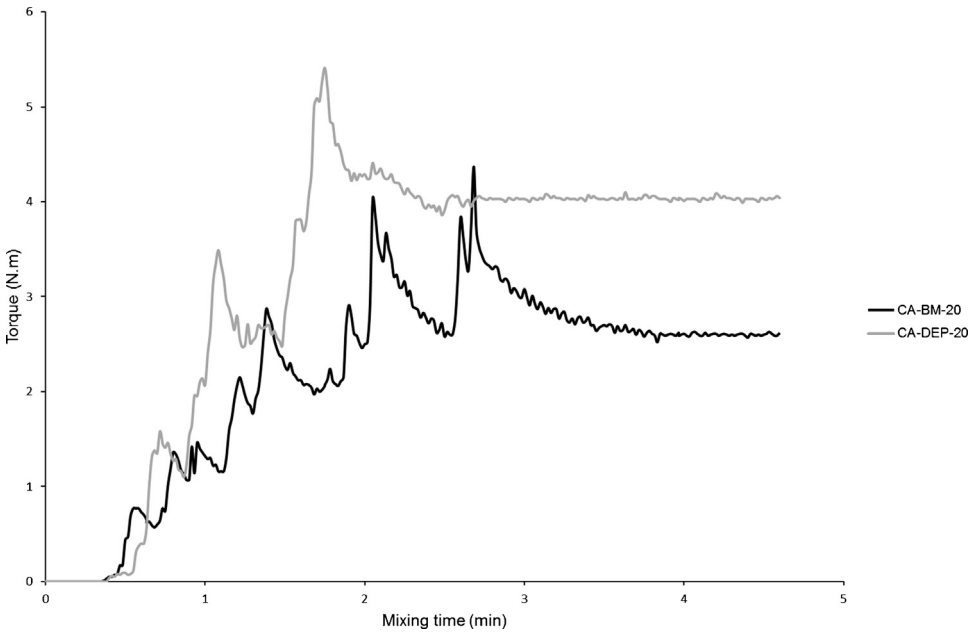

Fig. 2. Curves of the torque obtained for plasticized CA.

linked to the decrease in the viscosity due to the lubricant and plasticizer effect.

For each sample, 3 batches were prepared in order to ensure the reproducibility of the mixing conditions.

3.2. X-ray diffraction

The crystallinity of the polymer influences the chemical and physical properties of cellulose acetate.

Powder X-ray diffraction was used to study the effect of the plasticizing process in the modification on the crystalline structure of transformed CA.

The degree of crystallinity can be quantified by the relation:

$$\%X_c = \frac{A_c}{A_c + A_a} \times 100$$

where A_c and A_a are the areas under the crystalline peaks and the amorphous peaks, respectively.

Fig. 4 shows the X-ray diffraction patterns of initial CA and plasticized CA with the different plasticizers conditioned for 2 weeks (CA-BM-20-2w means cellulose acetate prepared with BMIMCl 20% conditioned for 2 weeks).

Fig. 3. Visual observations of pressed plasticized samples: (a) CA-DEP-30 and (b) CA-BM-30 processed by melt processing.

Initial cellulose acetate (CA) presents a crystalline pattern structure with strong reflection (2θ) located at 8.5°, 10.5°, 13.5°, 17.5° and 23.5°(Ramesh, Shanti, & Morris, 2013a). The crystalline structures of CA processed with the DEP plasticizer present a diffraction pattern centered at 8.5° and 23.5°. The crystallinity of these samples decreases comparatively to the initial cellulose acetate but these decreases are barely dependent on the compositions of the DEP.

However, the intensity of the diffraction peaks was reduced with the increase in the concentration (after 20%) of ionic liquid, which suggests that most of the crystalline structure of the CA was converted into the amorphous shape, especially for the formulation of CA-BM-40.

Furthermore, Table 3 shows that the intensity of the diffraction peaks was reduced when the concentration of the plasticizers increased.

The decrease in crystallinity of CA shows the destructuration induced by the presence of ionic liquid, which weakens the bonds connecting between the oxygen (–O) and acetate (–Ac) atoms in –OAc functional groups. These allow the increase of the accessibility and electronegativity of oxygen atoms in order to develop doping polymer electrolytes and for other applications.

Table 3
The % of remained crystallinity of the different formulations conditioned for (a) 2 weeks and (b) 3 months.

Sample	Crystallinity (%)
(a)	
CA	40
CA-DEP-20-2w	11.9
CA-DEP-30-2w	9.7
CA-DEP-40-2w	7
CA-BM-20-2w	9
CA-BM-30-2w	2
CA-BM-40-2w	Amorphous
(b)	
CA	40
CA-DEP-20-3M	13.5
CA-DEP-30-3M	10
CA-DEP-40-3M	6.8
CA-BM-20-3M	9
CA-BM-30-3M	3
CA-BM-40-3M	Amorphous

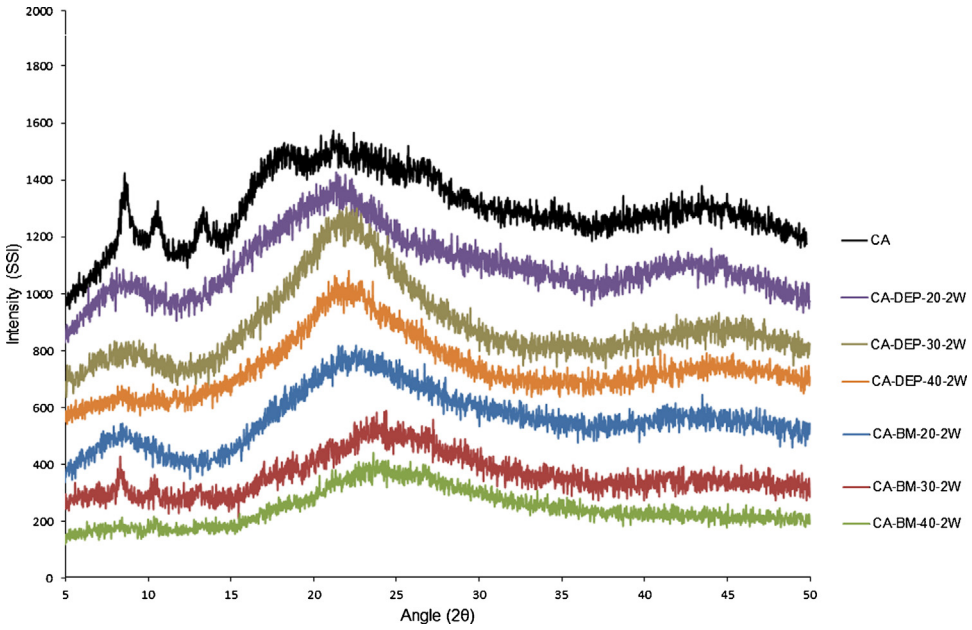

Fig. 4. X-ray diffraction patterns of native CA and CA plasticized with DEP and BMIMCl conditioned for 2 weeks.

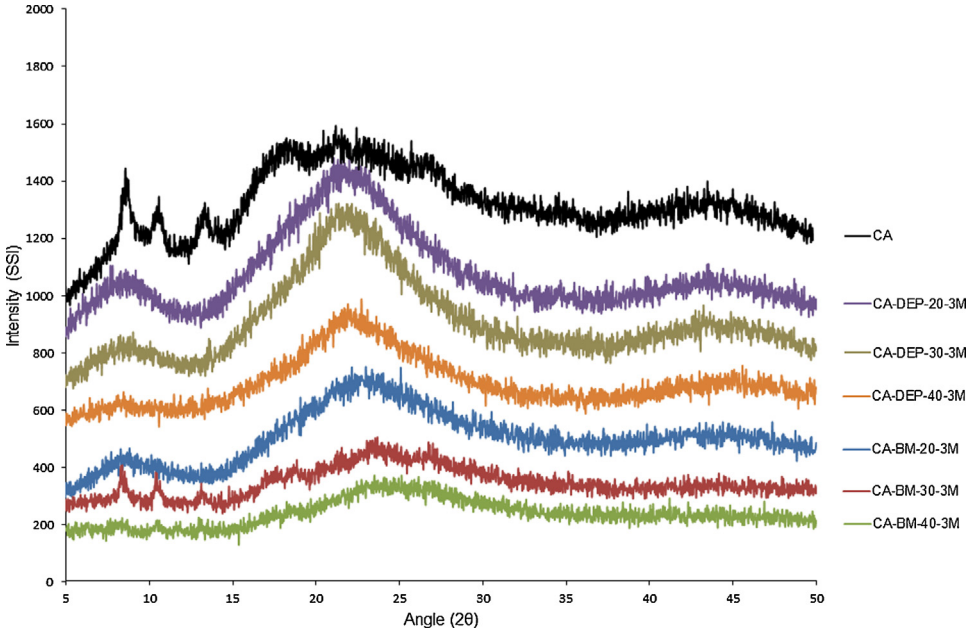

Fig. 5. X-ray diffraction patterns of native CA and CA plasticized with DEP and BMIMCl conditioned for 3 months.

Table 3 shows that the effect of time has no significant influence on the evolution of the crystalline structure of CA samples, especially CA plasticized with ionic liquid (Fig. 5).

3.3. Dynamic mechanical thermal analysis (DMTA)

The different samples prepared were conditioned at 40%RH-30 °C, until the equilibrium was reached. Dynamic mechanical analysis (storage modulus (G') and tan δ) results of CA-DEP-40 and CA-BM-40 are represented in Fig. 6. Temperatures corresponding to the maxima of the mechanical relaxations of neat CA films and plasticized CA are reported in Table 4.

Un-plasticized cellulose acetate films exhibit a relaxation at 201 °C associated to α relaxation (T_α) (Scandola & Ceccorulli, 1985). The curves of tan δ for all the plasticized samples showed two transition peaks; the upper transition (α relaxation (T_α)) will associate to the glass transition of the main chain (cellulose acetate) while the lower transition (β relaxation (T_β)) can be partly linked to the

Table 4
Relaxation temperature measured by DMTA for un-plasticized and plasticized samples.

Sample	T_β (°C)	T_α (°C)
CA	–	201
CA-DEP-20	−38	123
CA-DEP-30	−42	94
CA-DEP-40	−49	75
CA-BM-20	−40	120
CA-BM-30	−50	84
CA-BM-40	−70	78

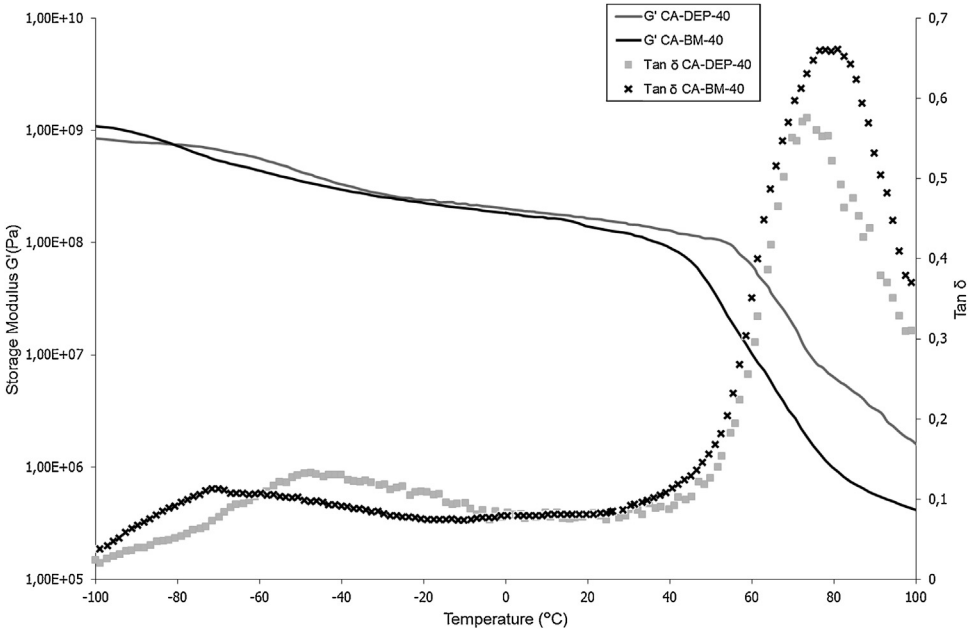

Fig. 6. Dynamic mechanical behavior of cellulose acetate plasticized with DEP and BMIMCl.

plasticizers (water and plasticizers) associated with CA functional groups (Seymour, Weinhold, & Haynes, 1979; Számel, Klébert, Sajó, & Pukánszky, 2008). The two relaxations appeared, respectively, between 75 and 123 °C and between −70 and −38 °C.

These values obtained for a given polymer depend on several factors, including the degree of substitution, water and plasticizer content, and conditions of the measurement.

In Table 4, we can see that the plasticization with DEP and ionic liquids comparatively to un-plasticized CA films leads to the decrease of the upper transition (α relaxation (T_α)) associated to the glass transition temperature of CA. In fact, further addition of the plasticizers leads to the decrease of the glass transition of CA due to an increase of chain flexibility (Scandola & Ceccorulli, 1985).

In addition to decreasing the glass transition temperature (T_g) of the main CA chain, ionic liquids (BMIMCl) are capable of decreasing the position of the β relaxation, from temperature −40° to −70°, when concentrations of ionic liquid increase respectively from 20 to 40 wt.%.

This can be explained by the breaking down of large segments of the main chain to smaller and individual glucose ring units, which decrease the β relaxation (Vidéki, Klébert, & Pukánszky, 2007). The ability of ionic liquid on the destruction of the crystalline structure of cellulose acetate (Section 3.2), allows them to play an important role in this decrease and the motion responsible for the β relaxation. This relaxation involves a superposition with T_α of BMIMCl (T_α = −54 °C) (Bendaoud & Chalamet, 2013).

The β-transition temperatures of CA plasticized by DEP are relatively less shifted by the increase of DEP concentration compared to the effect of ionic liquids, as shown in this study (Crofton & Pethrick, 1982).

This can be partly explained by the remained crystalline (Section 3.2) structure of CA-DEP formulation and therefore weak interaction with the cellulose acetate groups responsible for the β relaxation.

Further, these relaxation temperatures are higher than the T_α of the DEP pure component (T_α = −63 °C) (Scandola & Ceccorulli, 1985). Possible explanations of the retained constant and higher relaxation temperature comparatively to the T_α of the DEP are the presence of a DEP-rich phase and saturation with CA.

3.4. Rheology measurement and tensile behavior

3.4.1. Rubbery plateau modulus

The plateau modulus with the different formulations is shown in Table 5.

The rubbery plateau region can decrease significantly with the decrease in crystallinity and with the decreased entanglement and physical cross-linking.

It is noted (in Table 5) that the plateau modulus decreases with the increasing concentration of the plasticizer. This can be explained by the effect of the plasticizer, which creates a free volume and increases the weight (Me) between entanglements.

The CA-BM formulation, compared to CA-DEP, has a lower rubbery plateau modulus, due to the greater efficiency of the ionic liquid in the destruction of the crystalline region and molar volume of BMIMCl.

3.4.2. Tensile behavior

The mechanical tensile tests were presented in Fig. 7 and conducted on the plasticized CA samples which were pressed into films with an average thickness of 100 μm. Comparisons with neat CA films were conducted.

These samples were conditioned in a constant relative humidity 30°-45%RH and the mechanical properties were conducted in a climatic tensile machine.

With DEP and BMIMCl plasticized CA, comparatively to neat CA films, the increase of the concentration of plasticizers induces a decrease of the values of the stress. This decrease can be explained

Table 5
Variations of rubbery plateau modulus with the different formulations.

Sample	Rubbery plateau modulus (Pa)
CA-DEP-20	478,000
CA-DEP-30	353,000
CA-DEP-40	54,000
CA-BM-20	250,000
CA-BM-30	43,100
CA-BM-40	40,100

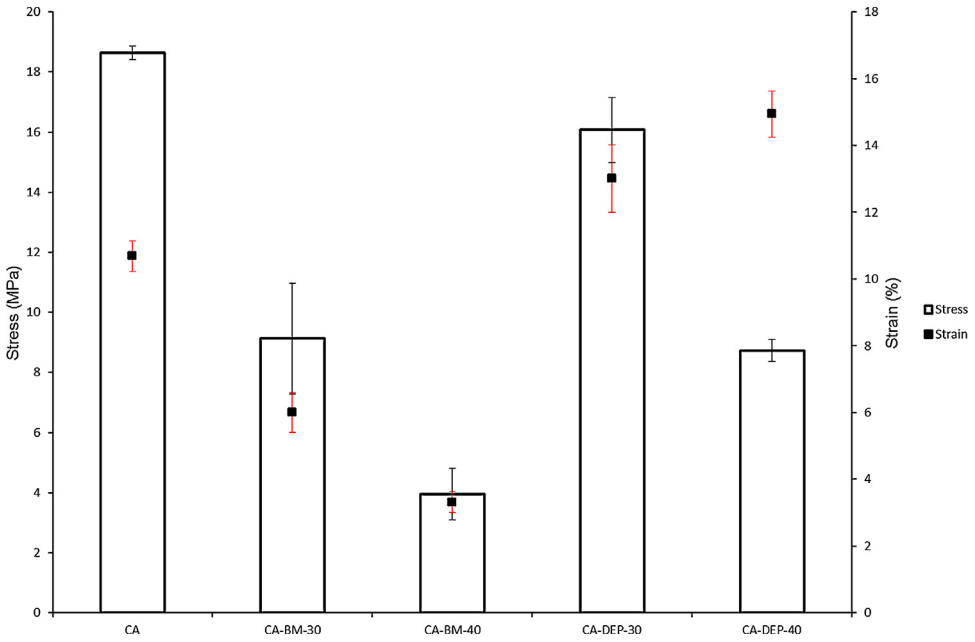

Fig. 7. Mechanical tensile test of un-plasticized and plasticized CA samples.

by the plasticizers effect, which creates a free volume (Quintana et al., 2013).

Contrary to the DEP formulation, the elongation at break decreases from 6 ± 0.6% to 3.3 ± 0.3% when the concentration of ionic liquid increases from 30% to 40%. This situation can be explained by the effect of BMIMCl in weakening and breaking the interactions of the molecules of cellulose acetate.

The Young's modulus of CA-DEP-40 presents a higher value, comparatively to CA-BM-40, respectively, 238 ± 29 MPa and 162 ± 20 MPa. This suggests that the interaction between the CA chains become weaker in the presence of BMIMCl.

4. Conclusion

The plasticization of cellulose acetate by an environment-friendly ionic liquid plasticizer, 1-butyl-3-methylimidazolium chloride (BMIMCl) was shown to be an efficient plasticizer of cellulose acetate, allowing the production of processable materials at 150 °C by melt processing. Visual observations for these pressed cellulose acetate materials were transparent and homogenous.

Due to the electrostatic nature of BMIMCl, it interacts intensively with CA molecules. XRD results clearly showed that the crystalline structure of cellulose acetate was widely and effectively damaged when using ionic liquid comparatively to DEP.

Two relaxation transitions were detected by DMTA with cellulose acetate plasticized by BMIMCl and DEP: an α-relaxation temperature which corresponds to the glass transition of the main chain and a lower β relaxation, which can depend on plasticizers flexibility and concentration.

Dynamic mechanical analysis showed also that BMIMCl acted as an efficient depressor of glass transition temperature of CA with values close to those obtained by DEP (relaxation temperatures measured by DMTA were respectively 84 °C and 95 °C for 30% of plasticizers). For the β relaxation, BMIMCl showed capability to lower this relaxation contrary to DEP.

Mechanical tensile tests and rheology analyses showed a strong reduction of the interactions between cellulose acetate chains due to the presence of the ionic liquid.

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References

Ach, A. (1993). Biodegradable plastics based on cellulose acetate. *Journal of Macromolecular Science, Part A*, *30*, 733–740.
Avérous, L., Fringant, C., & Moro, L. (2001). Plasticized starch–cellulose interactions in polysaccharide composites. *Polymer*, *42*, 6565–6572.
Backman, A. C., & Lindberg, K. A. H. (2001). Differences in wood material responses for radial and tangential direction as measured by dynamic mechanical thermal analysis. *Journal of Materials Science*, *36*, 3777–3783.
Bendaoud, A., & Chalamet, Y. (2013). Effects of relative humidity and ionic liquids on the water content and glass transition of plasticized starch. *Carbohydrate Polymers*, *97*, 665–675.
Buchanan, C. M., Gardner, R. M., & Komarek, R. J. (1993). Aerobic biodegradation of cellulose acetate. *Journal of Applied Polymer Science*, *47*, 1709–1719.
Cao, Y., Wu, J., Zhang, J., Li, H., Zhang, Y., & He, J. (2009). Room temperature ionic liquids (RTILs): A new and versatile platform for cellulose processing and derivatization. *Chemical Engineering Journal*, *147*, 13–21.
Crofton, D. J., & Pethrick, R. A. (1982). Dielectric studies of cellulose and its derivatives: 2. Effects of pressure and temperature on relaxation behaviour. *Polymer*, *23*, 1609–1614.
El Seoud, O. A., Koschella, A., Fidale, L. C., Dorn, S., & Heinze, T. (2007). Applications of ionic liquids in carbohydrate chemistry: A window of opportunities. *Biomacromolecules*, *8*, 2629–2647.
Fridman, O. A., & Sorokina, A. V. (2006). Criteria of efficiency of cellulose acetate plasticization. *Polymer Science Series B*, *48*, 233–236.
Han, B., Zhang, D., Shao, Z., Kong, L., & Lv, S. (2013). Preparation and characterization of cellulose acetate/carboxymethyl cellulose acetate blend ultrafiltration membranes. *Desalination*, *311*, 80–89.
Hansen, C. M. (2012). *Hansen solubility parameters: A user's handbook* (2nd ed.). Broken Sound Pkwy NW Boca Raton, FL 33487, USA: Taylor & Francis.
Jhong, H.-R., Wong, D. S.-H., Wan, C.-C., Wang, Y.-Y., & Wei, T.-C. (2009). A novel deep eutectic solvent-based ionic liquid used as electrolyte for dye-sensitized solar cells. *Electrochemistry Communications*, *11*, 209–211.
Jiang, L., & Hinrichsen, G. (1997). Biological degradation of cellulose acetate films: Effect of plasticizer. *Angewandte Makromolekulare Chemie*, *253*, 193–200.
Keely, C. M., Zhang, X., & McBrierty, V. J. (1995). Hydration and plasticization effects in cellulose acetate: A solid-state NMR study. *Journal of Molecular Structure*, *355*, 33–46.
Lee, S.-H., & Shiraishi, N. (2001). Plasticization of cellulose diacetate by reaction with maleic anhydride, glycerol, and citrate esters during melt processing. *Journal of Applied Polymer Science*, *81*, 243–250.

Mateyawa, S., Xie, D. F., Truss, R. W., Halley, P. J., Nicholson, T. M., Shamshina, J. L., et al. (2013). Effect of the ionic liquid 1-ethyl-3-methylimidazolium acetate on the phase transition of starch: Dissolution or gelatinization? *Carbohydrate Polymers*, *94*, 520–530.

McBrierty, V. J., Keely, C. M., Coyle, F. M., Xu, H., & Vij, J. K. (1996). Hydration and plasticization effects in cellulose acetate: Molecular motion and relaxation. *Faraday Discussions*, *103*, 255.

Miyashita, Y., Suzuki, T., & Nishio, Y. (2002). Miscibility of cellulose acetate with vinyl polymers. *Cellulose*, *9*, 215–223.

Mohanty, A. K., Wibowo, A., Misra, M., & Drzal, L. T. (2003). Development of renewable resource-based cellulose acetate bioplastic: Effect of process engineering on the performance of cellulosic plastics. *Polymer Engineering and Science*, *43*, 1151–1161.

Ning, W., Xingxiang, Z., Haihui, L., & Benqiao, H. (2009). 1-Allyl-3-methylimidazolium chloride plasticized-corn starch as solid biopolymer electrolytes. *Carbohydrate Polymers*, *76*, 482–484.

Pizzoli, M., Scandola, M., & Ceccorulli, G. (1994). Crystallization kinetics and morphology of poly(3-hydroxybutyrate)/cellulose ester blends. *Macromolecules*, *27*, 4755–4761.

Quintana, R., Persenaire, O., Lemmouchi, Y., Sampson, J., Martin, S., Bonnaud, L., et al. (2013). Enhancement of cellulose acetate degradation under accelerated weathering by plasticization with eco-friendly plasticizers. *Polymer Degradation and Stability*, *98*, 1556–1562.

Ramesh, S., Shanti, R., & Morris, E. (2012). Plasticizing effect of 1-allyl-3-methylimidazolium chloride in cellulose acetate based polymer electrolytes. *Carbohydrate Polymers*, *87*, 2624–2629.

Ramesh, S., Shanti, R., & Morris, E. (2013a). Characterization of conducting cellulose acetate based polymer electrolytes doped with "green" ionic mixture. *Carbohydrate Polymers*, *91*, 14–21.

Ramesh, S., Shanti, R., & Morris, E. (2013b). Employment of [Amim] Cl in the effort to upgrade the properties of cellulose acetate based polymer electrolytes. *Cellulose*, *20*, 1377–1389.

Rogers, R. D., & Seddon, K. R. (2003). Chemistry. Ionic liquids—Solvents of the future? *Science*, *302*, 792–793.

Rudaz, C., & Budtova, T. (2013). Rheological and hydrodynamic properties of cellulose acetate/ionic liquid solutions. *Carbohydrate Polymers*, *92*, 1966–1971.

Scandola, M., & Ceccorulli, G. (1985). Viscoelastic properties of cellulose derivatives. 2. Effect of diethylphthalate on the dynamic mechanical relaxations of cellulose acetate. *Polymer*, *26*, 1958–1962.

Schilling, M., Bouchard, M., Khanjian, H., Learner, T., Phenix, A., & Rivenc, R. (2010). Application of chemical and thermal analysis methods for studying cellulose ester plastics. *Accounts of Chemical Research*, *43*, 888–896.

Seymour, R. W., Weinhold, S., & Haynes, S. K. (1979). Mechanical and dielectric relaxation in cellulose esters. *Journal of Macromolecular Science, Part B*, *16*, 337–353.

Számel, G., Klébert, S., Sajó, I., & Pukánszky, B. (2008). Thermal analysis of cellulose acetate modified with caprolactone. *Journal of Thermal Analysis and Calorimetry*, *91*, 715–722.

Vidéki, B., Klébert, S., & Pukánszky, B. (2007). External and internal plasticization of cellulose acetate with caprolactone: Structure and properties. *Journal of Polymer Science, Part B: Polymer Physics*, *45*, 873–883.

Wu, J., Zhang, J., Zhang, H., He, J., Ren, Q., & Guo, M. (2004). Homogeneous acetylation of cellulose in a new ionic liquid. *Biomacromolecules*, *5*, 266–268.

Wu, R. L., Wang, X. L., Li, F., Li, H. Z., & Wang, Y. Z. (2009). Green composite films prepared from cellulose, starch and lignin in room-temperature ionic liquid. *Bioresource Technology*, *100*, 2569–2574.

Xing, D. Y., Peng, N., & Chung, T.-S. (2011). Investigation of unique interactions between cellulose acetate and ionic liquid [EMIM]SCN, and their influences on hollow fiber ultrafiltration membranes. *Journal of Membrane Science*, *380*, 87–97.

Yarsley, V. E., Adamson, P. S., Flavell, W., & Perkins, N. G. (1964). *Cellulosic plastics: Cellulose acetate, cellulose ethers, regenerated cellulose, cellulose nitrate*. London: Iliffe for the Institute.

Yoshioka, M., Hagiwara, N., & Shiraishi, N. (1999). Thermoplasticization of cellulose acetates by grafting of cyclic esters. *Cellulose*, *6*, 193–212.

Zepnik, S., Kabasci, S., Kopitzky, R., Radusch, H.-J., & Wodke, T. (2013). Extensional flow properties of externally plasticized cellulose acetate: Influence of plasticizer content. *Polymers*, *5*, 873–889.

Zhang, H., Wu, J., Zhang, J., & He, J. (2005). 1-Allyl-3-methylimidazolium chloride room temperature ionic liquid: A new and powerful nonderivatizing solvent for cellulose. *Macromolecules*, *38*, 8272–8277.

Zugenmaier, P. (2004). 4. Characteristics of cellulose acetates—4.1. Characterization and physical properties of cellulose acetates. *Macromolecular Symposium*, *208*, 81–166.