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Abstract:

Maize starch was plasticized by glycerol, choline chloride ([Chol][Cl]) and ionic liquids (Choline acetate ([Chol][Ace]), 1-Ethyl-3-methylimidazolium Chloride ([EMIM][Cl]) and 1-Ethyl-3-methylimidazolium acetate ([EMIM][Ace]). Melt rheology at 120°C was assessed with a twin-screw micro-compounder used for processing small quantities (8-10g), and with a capillary rheometer with pre-shearing (Rheoplast). Qualitative agreement was found between shear viscosities obtained by both rheometry devices, showing the interest of the micro-compounder for screening of plasticizers' influence. The lower shear viscosity values were obtained in presence of [EMIM][Ace] whereas [Chol][Cl] led to the largest ones. Rather than processing induced macromolecular degradation, the glass transition temperature depressing effect of the plasticizers was found to better explain viscosity differences. This underlines the strong influence of the nature of the plasticizers on starch melt rheology. Finally, results from extensional viscosity shows the specific influence of [EMIM][Ace], suggesting that this plasticizer could be particularly relevant for thermoplastic starch processing.

1) Introduction

Starch is an abundant, edible, cheap and carbon neutral biopolymer produced worldwide from several different major crops. It is used for a variety of food and non-food applications including bioplastics (Gozzo & Glittenberg, 2009). Native starch granules can be converted into a thermoplastic material by using conventional thermomechanical processing techniques. This requires the presence of small amounts of plasticizers, water and glycerol being the most commonly used. The resulting so called "thermoplastic starch" (TPS) can be shaped into films, foams or bulk parts by compression molding, extrusion or injection molding (H. S. Liu, Xie, Yu, Chen, & Li, 2009). Biodegradable polymer blends and composites can also be produced by melt mixing of TPS with other bioplastics or natural fibers (Averous, 2004). The variations of the viscosity of molten starch with strain and strain rate affect all mixing and shaping processes. Besides flow conditions and deformation modes, the viscous behavior is known to depend on starch botanical origin, plasticizers type and content, and also on processing temperature and particularly previous thermomechanical treatment which affects starch macromolecular structure (Xie, Halley, & Averous, 2012). A minimum specific mechanical energy (SME) input of about 100-200 J g^{-1} is typically required for a complete destructuring of the native semi-crystalline structure of starch granules under shear (Barron, Bouchet, Della Valle, Gallant, & Planchot, 2001). However, the temperature and SME levels during processing also result in a more or less pronounced degradation of starch macromolecules which strongly affects the viscous behavior (DellaValle, Boche, Colonna, & Vergnes, 1995; Vergnes, Villemaire, Colonna, & Tayeb, 1987). This difficulty is addressed by specific rheometry techniques for measurements under controlled SME conditions: in line (Vergnes, Dellavalle, & Tayeb, 1993); (Horvat, Emin, Hochstein, Willenbacher, & Schuchmann, 2013) or off line with the Rheoplast (Vergnes & Villemaire, 1987). Rheoplast is a reference capillary rheometer with pre-shearing which also allows evaluating extensional viscosity (Della Valle, Vergnes, & Lourdin, 2007), an

important property for shaping processes. Concomitantly, models predicting the shear viscosity as a function of temperature, SME, moisture and glycerol content have been developed and validated for starches of different botanical origin (Martin, Averous, & Della Valle, 2003; Vergnes & Villemaire, 1987). In parallel, a few studies have been focused on the viscous behavior of TPS in presence of other plasticizers: small molecules such as formamide (Ning, Yu, Ma, & Han, 2009), citric acid (Wang, Yu, Chang, & Ma, 2007), triethylene glycol, urea and glycerol monostearate (Willett, Jasberg, & Swanson, 1995). A strong influence of plasticizer's structure on starch melt viscosity has been observed (Xie et al., 2012).

Room Temperature Ionic Liquids (RTILs) are a new family of starch plasticizers allowing melt processing (Sankri et al., 2010; Xie et al., 2014; Zdanowicz & Spychaj, 2011). RTILs can be tailored by modifying the chemical structure of the cation and anion moieties, opening perspectives for the design of specific plasticizers for starch. However, new RTILs are usually synthetized in small quantities, which makes it difficult to evaluate their potential for starch plasticization. Screening approaches have been proposed using film casting for quantities below 1 gram to determine the impact of RTILs on the glass transition temperature (T_g) of TPS, and on film mechanical properties (Colomines, Decaen, Lourdin, & Leroy, 2016). For larger quantities (≈ 10 grams), such properties may be determined on films processed by compression molding (Decaen et al., 2017; Xie et al., 2014; Zdanowicz & Spychaj, 2011) as well as by twin screw micro-compounding (Decaen et al., 2017; Sankri et al., 2010). Such batch process presents the advantage of mimicking twin screw extrusion, with the possibility to quantify SME (Cousin, Berto, Budtova, Kurek, & Navard, 2017; Leroy, Decaen, et al., 2012; Leroy, Jacquet, Coativy, Reguerre, & Lourdin, 2012) and thus to determine its impact on starch macromolecular structure (Decaen et al., 2017). Although the micro-compounder has not been specifically designed for rheological measurements under controlled SME conditions, it has also been shown to be able to evaluate the shear viscosity of non-Newtonian fluids (Yousfi et al., 2014).

Hence, it would be interesting to apply it to assess the potential of RTILs for TPS processing at small scale (≈ 10 grams).

The aim of the present work is to investigate the effect of different RTIL plasticizers on the viscous behavior of TPS. In this purpose, shear viscosity has been measured at 120 °C with the micro-compounder and with Rheoplast. In complement, Rheoplast allowed estimating the extensional viscosity. The structural changes of RTIL plasticized starches during measurements with both techniques are assessed for their glass transition and macromolecular degradation.

2) Experimental

2.1) Materials

A polystyrene LACQRENE® 6631 was kindly supplied by Arkema. Regular corn starch was purchased from Tate & Lyle (Meritena 100). It has an amylose content of 27%, a weight-average molar mass $\bar{M}_w \approx (198 \pm 10) \times 10^6$ g.mol^{-1} and a dispersity $\bar{M}_w/\bar{M}_n = (2.1 \pm 0.1)$. The macromolecular characterization techniques are described in detail below. Note that in the present article, a great attention will be paid to the influence of melt processing on the degradation of this pristine macromolecular structure, affecting molar masses and rheology.

Glycerol was purchased from Sigma-Aldrich. Potassium acetate and choline chloride ([Chol][Cl]) were purchased from Sigma-Aldrich. This salt, although not being a RTIL, is an efficient plasticizer of starch (Abbott, 2009; Decaen et al., 2017; Zdanowicz & Spychaj, 2011). The RTIL used are: i) Choline acetate ([Chol][Ace]), synthesized by ion exchange as described in detail in a previous paper (Colomines et al., 2016); ii) 1-Ethyl-3-methylimidazolium Chloride ([EMIM][Cl] ; and iii) 1-Ethyl-3-methylimidazolium acetate ([EMIM][Ace]) both purchased from Solvionic (Toulouse, France).

The four different ionic plasticizers ([Chol][Cl] ; [Chol][Ace] ; [EMIM][Cl] and [EMIM][Ace]) and glycerol were premixed with the starch powder containing 12% of water using a kneading

112 machine. The dry basis plasticizer content was fixed to 23%. These premixed powders, were
113 stored 24h at 4 °C before melt processing and rheological characterization.

114 2.2) Processing and rheological characterization with the micro-compounder

115 A micro-compounder (Haake Minilab, Thermo Scientific GmbH, Karlsruhe, Germany) was
116 used for small scale evaluation of shear viscosity. This batch device, with a working volume
117 V=7 cm^3, makes it possible to simulate extrusion for a typical quantity of 8-10 g of TPS. It
118 consists of a conical twin screw system (L_{screw} = 12 cm) with a slit shaped back flow channel
119 (64 x 10 x 1.5 mm^3). The material can be recirculated during the desired residence time before
120 being extruded through the exit die.

121 *2.2.1) Rheometry*

122 Two pressure sensors located in the recirculation channel allow estimating the shear stress. The
123 shear rate is determined on the assumption that the flow rate in the recirculation channel, Q
124 [$m^3.s^{-1}$], is proportional to the screw speed N (rpm):

125 $$Q = C.N \qquad (1)$$

126 Where: C is a calibration constant which depends on the screw type (co-rotating or counter
127 rotating) and can vary slightly (± 20%) with the polymer type (Yousfi et al., 2014). In our case,
128 it was obtained by calibration with a polystyrene (LACQRENE® 6631) of known rheological
129 behavior, as explained below.

130 Since the backflow channel's thickness (h= 1.5 mm) is small in comparison to its width (w =
131 10 mm), the shear stress τ_w at the wall of the channel can be evaluated as follows (Son, 2007):

132 $$\tau_w = \frac{h \times \Delta P}{2 \times \Delta L} \times \left(\frac{1}{\frac{h}{w} + 1} \right) \approx \frac{h \times \Delta P}{2 \times \Delta L} \quad (2)$$

133 Where ΔL = 64 mm is the distance between the pressure sensors.

The apparent shear rate is given by (Son, 2007):

$$\dot{\gamma}_{app} = \frac{6 \times Q}{w \times h^2} \qquad (3)$$

A power law is assumed for the shear rate dependence of TPS shear viscosity η:

$$\eta = K \times \dot{\gamma}^{n-1} \qquad (4)$$

The pseudo plasticity index *n* is obtained from the slope of the plot of (log τ) *vs. (log* $\dot{\gamma}_{app}$*).* This allows applying the modified Rabinowitsch correction taking into account the dimensions of the slit backflow channel (Son, 2007):

$$\dot{\gamma}_w = \dot{\gamma}_{app} \times \frac{2}{3}\left(\frac{b^*}{f^*} + \frac{a^*}{f^*} \times \frac{1}{n}\right) \qquad (5)$$

Where: a^*= 0.3781, b^*= 0.8745 and f^* = 0.8351 for (h/w)=0.15.

Finally the viscosity is given by:

$$\eta = \frac{\tau_w}{\dot{\gamma}_w} \qquad (6)$$

2.2.2) Calibration with a commercial polystyrene

To determine the value of parameter C in equation (1), a commercial polystyrene (LACQRENE® 6631) was used. This polymer was chosen because around 180 °C – 200 °C, it has a viscosity range close to that of TPS at 120 °C, while not being sensitive to SME. The viscosity of LACQRENE® 6631 follows a Cross/Carreau law:

$$\eta = \frac{\eta_0}{1 + \left(\frac{\eta_0 \cdot \dot{\gamma}}{\tau^*}\right)^{1-n}} \qquad (7)$$

According to the MOLDFLOW™ database the parameters are given by:

$$\eta_0 = D_1 e^{\left[\frac{-A_1(T-T^*)}{A_2+(T-T^*)}\right]} \qquad (8)$$

$$T^* = D_2 + D_3 . P \qquad (9)$$

$$A_2 = \tilde{A}_2 + D_3.P \qquad (10)$$

Where : D_3=0 ($Pa.K^{-1}$) ; $\tilde{A}_2$=51.6 (K) ; D_2 = 373.15 (K) ; A_1=23.629; D_1=$2.75.10^{10}$ (Pa.s) ; τ^*=18549 (Pa) et n=0.3195.

Therefore, the theoretical flow curve can be calculated using equations 7-10, and the constant C in equation (1) is derived by matching experimental measurements from the micro-compounder, treated through equations 3-6, with this theoretical flow curve.

Calibration measurements were conducted at 180 °C and 200 °C with LACQRENE® 6631. The material was introduced in the micro-compounder at 100 rpm. After complete filling, the rheological characterization step was started: the screw speed N was decreased step by step down to 5 rpm. Each step was maintained during approximately 20 s allowing the pressure drop (ΔP) between the two pressure sensors in the back flow channel to stabilize. The recorded values (N, ΔP) were used for viscosity calculations and adjustment of the constant C.

2.2.3) Processing and rheological characterization experiments with TPS

The starch/plasticizer premixed powders were introduced at 120 °C with a screw speed of 100 rpm in co-rotating mode with recirculation and melt-processed during 150 seconds before the rheological characterization was started: measurements were first conducted by decreasing the screw speed N by steps of 10 rpm from 100 to 10 and then at 5 rpm. Then, a second series of measurements was performed starting at 5 rpm and increasing to 25, 50, 75 and 100 rpm. Each step was maintained during approximately 30 s. The total duration of one experiment was typically 700 s. The average pressure drop (ΔP) between the two pressure sensors in the back flow channel was calculated for each screw speed (N). The (N, ΔP) values were used for the evaluation of shear viscosity, using the constant C obtained with LACQRENE® 6631. In order to evaluate the influence of processing on the calculated viscosity, two sets of (N, ΔP) values

were considered: those obtained for decreasing N (100; 90 …10, 5) and those for increasing N (5, 25, 50, 75, 100).

During such measurements, an increase of SME, cumulated by the recirculating TPS, takes place. An average SME value was thus evaluated by performing a second series of experiment at 120 °C with a constant screw speed of 100 rpm, for a total residence time of 300 s and without rheological measurement. The engine torque signal was recorded allowing the calculation of the Specific Mechanical Energy (SME) (J g^{-1}) input:

$$\mathrm{SME} = \int_0^t \frac{T.2\pi.N.dt}{M.60} \qquad (11)$$

Where: T is the torque [N m], N is the screw speed [min^{-1}], t, the residence time [s], and M, the mass of TPS in the micro-compounder [g].

2.3) Rheoplast processing and rheological characterization.

The total quantity of starch/plasticizer premixed powder required for rheological measurements with Rheoplast is typically 150-300g (compared to 8-10g for the micro-compounder). This specific capillary rheometer has been used to determine the shear viscosity of molten maize starch, whilst simulating extrusion treatment under controlled thermomechanical conditions (Vergnes & Villemaire, 1987). In this purpose, the powdery material is introduced by batches of 15 g in the machine: the piston used to push the material and inject it through the capillary die can also rotate at a constant set speed, like in a Couette geometry, prior to moving down. Hence, it allows imposing to the material a well-defined shear during a given time, and then a fixed amount of SME. In the present case, inner piston rotation speed was 100 rpm. Barrel temperature was adjusted through two heating elements at 110 °C in the Couette geometry and 115 °C in the injection reservoir, for all TPS formulations. Sample temperature, measured before the capillary die was 120 °C (+/-2 °C). This temperature value was selected to avoid any thermal degradation, possible in the case of Choline based IL. Four

cylindrical dies of diameter 2 mm and various *L/D* ratio values (0.05, 4, 8 and 16) were used. The conical entrance angle was 90°. Once pressure *P* values have been measured for different values of apparent shear rate $\dot{\gamma}_a$ in the interval [0.64, 166 s^{-1}], starch/plasticizer premixed powder was added in the hopper and the operation was repeated until obtaining three pressure profiles $P(\dot{\gamma}_a)$ within an interval of +/-10 %. From these pressure profiles, Bagley end corrections were performed in order to derive the wall shear stress τ_w. The true wall shear rate $\dot{\gamma}_w$ was then determined after performing Rabinowitsch corrections, according to conventional capillary rheometry treatment, as indicated by Della Valle et al. (Della Valle et al., 2007). Elongational viscosity was derived from entrance pressure drop according to the analysis proposed by (Cogswell, 1972).

2.4) Characterization of TPS samples

The samples collected for each Rheoplast experiment and for the second series of processing experiments with micro-compounder were characterized in order to determine the glass transition temperature and the macromolecular degradation associated to the measured melt viscosity.

2.4.1) Glass transition temperature

Differential scanning calorimetry (DSC) was used to determine the glass transition temperature T_g of the extruded samples with a DSC Q100 apparatus (TA Instruments, New Castle, DE, USA). Stainless steel sealed pans prevented any water loss during tests. A scan was then performed from −60 to 100 °C at 10 °C min^{-1}. T_g was defined as the midpoint of the heat capacity jump on thermograms.

2.4.2) Macromolecular characterizations

High-Performance Size-Exclusion Chromatography coupled with Multi-Angle Laser Light Scattering and Differential Refractive Index detection (HPSEC-MALLS) was used to

225 determine the macromolecular characteristics of the samples. Collected plasticized starch
226 samples (and native starch used as a reference) were first solubilized in dimethylsulfoxide,
227 precipitated with ethanol and dried. They were then solubilized in filtered Millipore water (0.1
228 µm, Durapore GV membrane from Millipore) at a concentration of 0.5 g L^{-1} by microwave
229 heating under pressure, as described in previous works (Rolland-Sabate, Amani, Dufour,
230 Guilois, & Colonna, 2003; Sciarini et al., 2015). After filtration through 5 µm Durapore ™
231 membranes (Waters, Bedford, MA, USA), 100 µL of each solution was injected into the
232 HPSEC-MALLS system. Sample recoveries were calculated from the ratio of the initial mass
233 and the mass after filtration (Rolland-Sabate et al., 2003). The HPSEC-MALLS- equipment
234 and the method used were the same as that described previously (Sciarini et al., 2015). The SEC
235 column was a Shodex® KW-802.5 (8 mm ID×30 cm) together with a KW-G guard column (6
236 mm ID×5 cm) both from Showa Denko K.K. (Tokyo, Japan), maintained at 30 °C. The two on-
237 line detectors were a Dawn® Heleos® MALLS system fitted with a K5 flow cell and a GaAs
238 laser, (λ = 658 nm), supplied by Wyatt Technology Corporation (WTC, Santa Barbara, CA,
239 USA,) and an RID-10A refractometer from Shimadzu (Kyoto, Japan). Sample recovery rates
240 were calculated from the ratio of the mass eluted from the column (integration of the
241 refractometric signal) and the injected mass (Rolland-Sabate et al., 2003).

242 The weight-average and the number average molar masses ($\overline{M}_w$, $\overline{M}_n$) and the dispersity ($\overline{M}_w / \overline{M}_n$)
243 were established using ASTRA® software from WTC (version 6.1 for PC), as
244 previously described (Rolland-Sabate, Mendez-Montealvo, Colonna, & Planchot, 2008). A
245 value of 0.146 mL g^{-1} was used as the refractive index increment (dn/dc) for glucans and the
246 normalization of photodiodes was achieved using a low molar mass pullulan standard (P20).

247

3) Results and discussion

3.1) Specific Mechanical Energy and induced macromolecular degradation

The SME values determined during rheological testing with the Rheoplast and Micro-compounder are given in **Table 1**. Also reported in Table 1 are the values of T_g measured on plasticized starch samples, and their macromolecular characteristics determined from HPSEC-MALLS chromatograms (**Fig. 1**). It is noteworthy that solubilization rate through the HPSEC-MALLS system is between 91 and 100%, except for the plasticized starch obtained by Rheoplast with glycerol (80%), and elution recovery rate is between 86 and 100%. These high recovery rate values show that the macromolecular characterizations by HPSEC-MALLS are representative of the processed TPS samples.

The SME values obtained with the micro-compounder are generally higher than with the Rheoplast (except for [EMIM][Cl]) but all average values fall in the 100-500 J g^{-1} range which is generally expected to allow an efficient starch granule destructuring, without too strong molar mass degradation (Vergnes et al., 1987). Indeed the macromolecular characteristics confirm a moderate degradation of starch macromolecules, stronger in the case of micro-compounder due to higher SME. As reported in **Table 1,** TPS samples processed with Rheoplast present $\overline{M}_w$ values ranging from 4.33 x 10^7 to 1.25 x 10^8 g mol^{-1}; while samples processed with micro-compounder have lower $\overline{M}_w$ values ranging from 5.0 x 10^6 to 1.69 x 10^7 g mol^{-1}. Compared to native starch ($\overline{M}_w$ = 1.98 x 10^8 g mol^{-1}), the decrease of molar mass seems large, nevertheless all $\overline{M}_w$ values remain higher than 10^6 $gmol^{-1}$. This is particularly important since for $\overline{M}_w$ values lower than 10^6 g mol^{-1}, the glass transition temperature (T_g) of TPS can become dependent of molar mass, as observed in previous studies in the case of hydrolyzed pea starch (Lafargue, Pontoire, Buleon, Doublier, & Lourdin, 2007). It is also noteworthy that for maize starch, the entanglement molecular weight is close to 10^5 $gmol^{-1}$ (Carriere, 1998). So, despite

macromolecular degradation, macromolecular masses weights remain much higher than this critical value.

Plasticizer of starch	HPSEC MALLS			Processing	DSC	
	$\overline{M}_w$ (10^6 g mol^{-1})	$\overline{M}_n$ (10^6 g mol^{-1})	$\overline{M}_w / \overline{M}_n$	EMS (J g^{-1})	T_g (°C)	Water (%)
Micro-compounder						
Glycerol	16.1	4.6	3.5	443 ±50	12	13
[Chol][Cl]	11.0	6.6	1.7	322 ±50	15	15
[Chol][Ace]	5.0	2.9	1.8	362 ±50	5	16
[EMIM][Cl]	10.8	5.8	1.9	114 ±50	-6	12
[EMIM][Ace]	16.9	11.6	1.5	199 ±50	0	16
Rheoplast						
Glycerol	43.3	9.6	4.5	140 ±50	not measured	
[Chol][Cl]	97.2	13.3	7.3	140 ±50		
[Chol][Ace]	104.0	14.6	7.1	130 ±50		
[EMIM][Cl]	125.0	19.4	6.5	250 ±50		
[EMIM][Ace]	57.5	10.5	5.5	170 ±50		
Native starch*	198.0	93.0	2.1	_		

**without process. Standard deviations were about 5% for molar masses*

Table 1: SME values and Macromolecular characteristics: Weight-average and number-average molar masses ($\overline{M}_w$, $\overline{M}_n$), dispersity ($\overline{M}_w / \overline{M}_n$) obtained by integrating the HPSEC-MALLS signals for the whole population of macromolecules present in the sample, for corn starch samples processed with different plasticizers and for native corn starch.

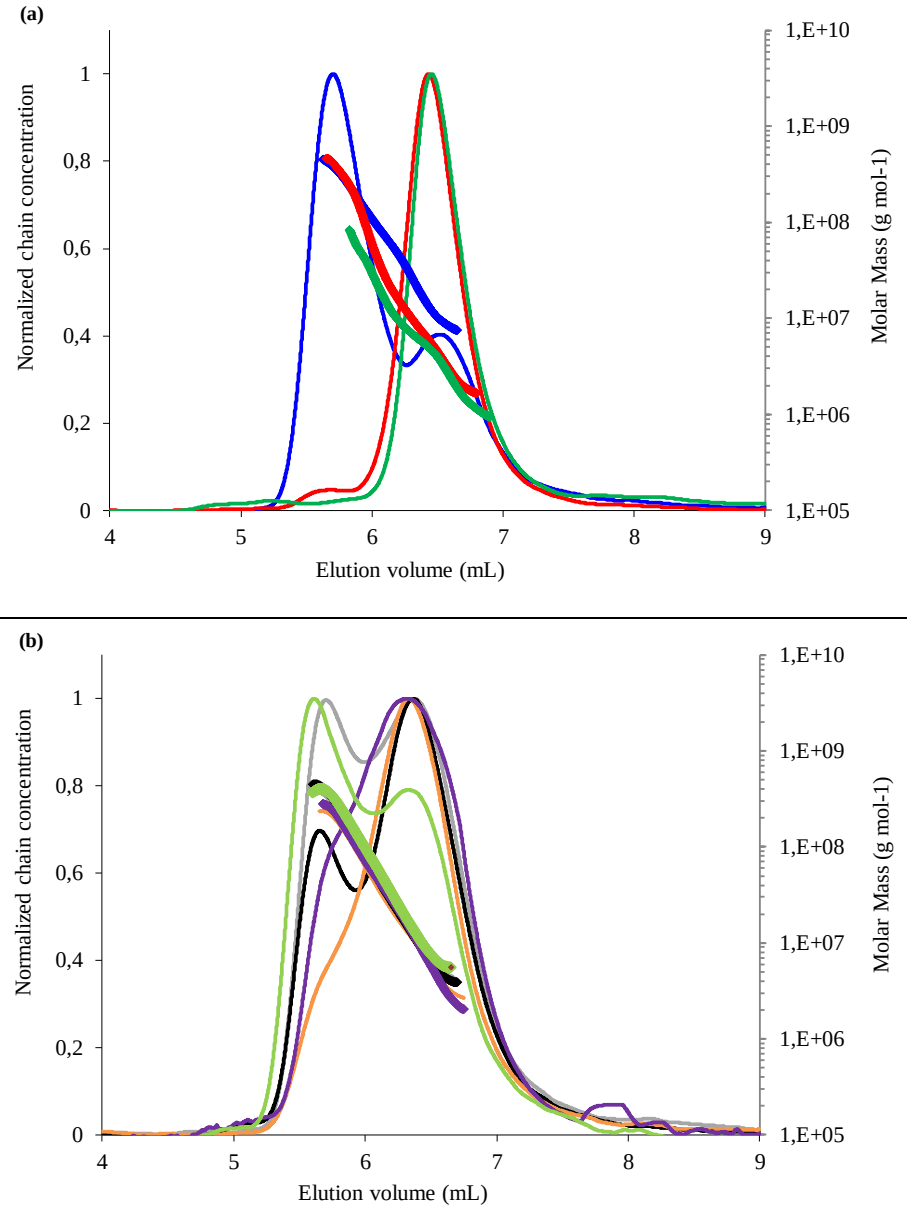


Figure 1: Chromatograms of native and processed corn starches: Normalized chain concentration obtained from the DRI answer (thin lines) and molar masses (thick lines) versus elution volume. (a) Native corn starch (blue) and TPS processed with the micro-compounder, plasticized with glycerol (red) and [Chol][Ace] (green), (b) TPS processed with Rheoplast, plasticized: with glycerol (orange), [Chol][Cl] (black), [Chol][Ace] (grey), [EMIM][Cl] (green) and [EMIM][Ace] (purple).

281

T_g values measured for the samples processed with the micro-compounder are reported in **Table 1**: no correlation can be drawn neither with $\overline{M}_w$ values, nor with water content values, thus indicating that the the nature of the plasticizer affects T_g value. As in previous work on TPS films obtained by casting from water solutions (Colomines et al., 2016), imidazolium ionic liquids lead to larger T_g depression than glycerol and cholinium ionic liquids (**Table 1**).

However, a closer look at chromatograms (**Fig. 1**) indicates that the macromolecular structure of TPS and dispersity are strongly affected by both processing/SME and plasticizer nature. If we consider first native starch as a reference, the chromatogram shows a main peak at 5.7 mL corresponding to the amylopectin population and a peak at 6.45 mL corresponding to the amylose population (**Fig. 1a**).

The chromatograms of plasticized starches exhibit peaks shifted to higher elution volumes, showing a decrease of amylopectin macromolecular size. This decrease has already been observed for extruded starches (W. C. Liu, Halley, & Gilbert, 2010; Logie, Della Valle, Rolland-Sabate, Descamps, & Soulestin, 2018; van den Einde, Akkermans, van der Goot, & Boom, 2004; van den Einde, Bolsius, et al., 2004) and starches processed with ionic liquids (Decaen et al., 2017; Sankri et al., 2010; Sciarini et al., 2015). It results from the amylopectin degradation into dextrins and has been attributed to the larger sensitivity of this macromolecule to shear, compared with the one of amylose. However, a significant difference can be observed depending on the processing conditions:

- For TPS samples processed with the micro-compounder: while the initial amylopectin peak (between 5.5 and 6 mL) is still present after processing with glycerol, it completely disappears after processing with the ionic liquids as illustrated in the case of [Chol][Ace] (**Fig. 1a)**. The curves obtained with the other ionic liquids are not shown for the sake of clarity but in all cases, a single peak is obtained, between 6 and 7 mL, resulting in a low

dispersity for starches processed with ionic liquids ($\overline{M}_w / \overline{M}_n$ = 1.5 - 1.9) compared to native and glycerol plasticized starches (4.7 and 3.5 respectively, **Table 1**).

- For samples plasticized on Rheoplast, the initial amylopectin peak is still present in the chromatograms, yet in different proportions depending on the plasticizer (**Fig. 1b**). In all cases, Rheoplast processing with ionic liquids results in a high dispersity (6.5 to 7.3) compared to native starch and glycerol plasticized starch (4.5, **Table 1**). The latter exhibits the highest amylopectin degradation (the lowest amount of residual amylopectin, the lowest average molar mass). Conversely, the least amylopectin degradation is observed for [EMIM][Cl].

These results show that besides processing conditions and SME, the nature of the plasticizer influences macromolecular degradation.

3.2) Shear viscosity

Fig. 2 shows the calibration curves obtained by the micro-compounder for the polystyrene reference and the shear viscosity curves obtained TPS plasticized with glycerol (considered as a reference plasticizer) with the micro-compounder and Rheoplast. The adjusted value of C = 6.10^{-10} m^3 s^{-1} rpm^{-1} (equation 2) allows fitting of the experimental points to the Cross-Carreau reference model describing polystyrene viscosity (**Fig. 2a**) for both temperatures (180 °C and 200 °C). As expected, the TPS plasticized with glycerol displays the classical viscous behavior (**Fig. 2b**) described by the power law (equation 4). The shear viscosity values calculated from micro-compounder measurements cover a smaller range of shear rate than the one covered by the Rheoplast. As shown in **Table 2,** the viscosity values at 10 s^{-1} are rather close: 10.9 kPa s for Rheoplast and 7.5 kPa s for micro-compounder operated at decreasing screw speed. The pseudo plasticity index values are the same (m=0.28), while the values of consistency index K are 57 kPa s^{n-1} with Rheoplast and 39 kPa s^{n-1} with micro-compounder. The lower values

obtained with the latter may be explained by the significantly higher SME and thus, stronger induced macromolecular degradation, as discussed previously (**Table 1**), and in agreement with the results of Martin et al. (Martin et al., 2003). Looking more precisely at the results obtained with the micro-compounder, viscosity measurements with decreasing N (screw speed) lead to lower values than those obtained when increasing N. This result was observed for all other plasticizers, and it suggests that viscosity increases during measurement, as explained in the experimental section (2.2.3). It may be explained by water loss during measurement, the influence of which balances the strong sensitivity of consistency to SME (Martin et al., 2003).

Fig. 3 shows the shear viscosity curves obtained with micro-compounder and Rheoplast. For clarity's sake, they are presented according to ionic plasticizers: Acetate salts (**Fig. 3a**) and Chloride salts (**Fig. 3b).** In both cases, the imidazolium ionic liquids lead to the lower viscosity values. Besides, all viscosity values at 10 s^{-1} are lower than for glycerol plasticized starch (**Table 2**) except for [Chol][Cl] in micro-compounder measurements. Actually, for this plasticizer, it was not possible to obtain stable pressure data during the decreasing screw speed steps. Therefore, the viscosity values were obtained for the increasing screw speed test. In this case, the high viscosity obtained may be explained by water loss, and the possible crystallization at low water content of [Chol][Cl], which is not a RTIL and has a dry melting point at 302 °C.

Whatever the variations, the consistency values of the TPS obtained for the other plasticizers, with both Rheoplast and micro-compounder, rank in the same following order:

$$K_{[Chol][Cl]} > K_{Glycerol} > K_{[Chol][Ace]} > K_{[EMIM][Cl]} > K_{[EMIM][Ace]}.$$

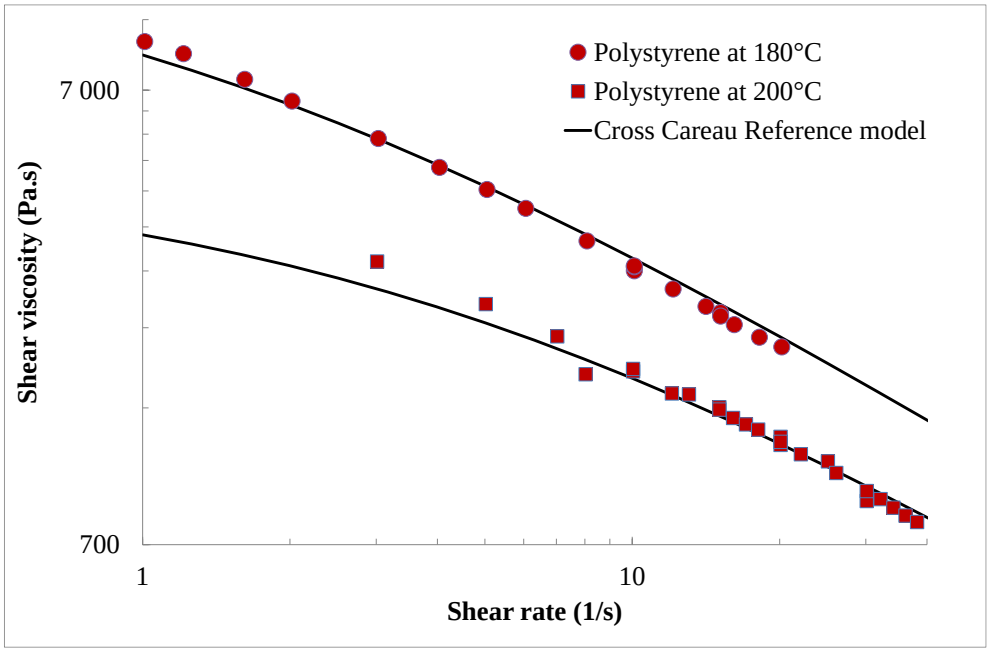
This agreement between the results found with the two different equipment suggest that the micro-compounder has potential as a rheometrical tool, for testing TPS when only small quantites of material are available. The values of pseudo-plasticity index *n* slightly differ from one equipment to another, in the case of imidazolium ionic liquids. This difference is likely due to the slight uncertainty in the measurements with the micro-compounder, because of the

narrow range of shear rate values used to determine n from the slope of the curve (log τ) *vs.* (*log* $\dot{\gamma}_{app}$), rather than to a real influence of this plasticizer on starch rheological behavior in these thermomechanical conditions.

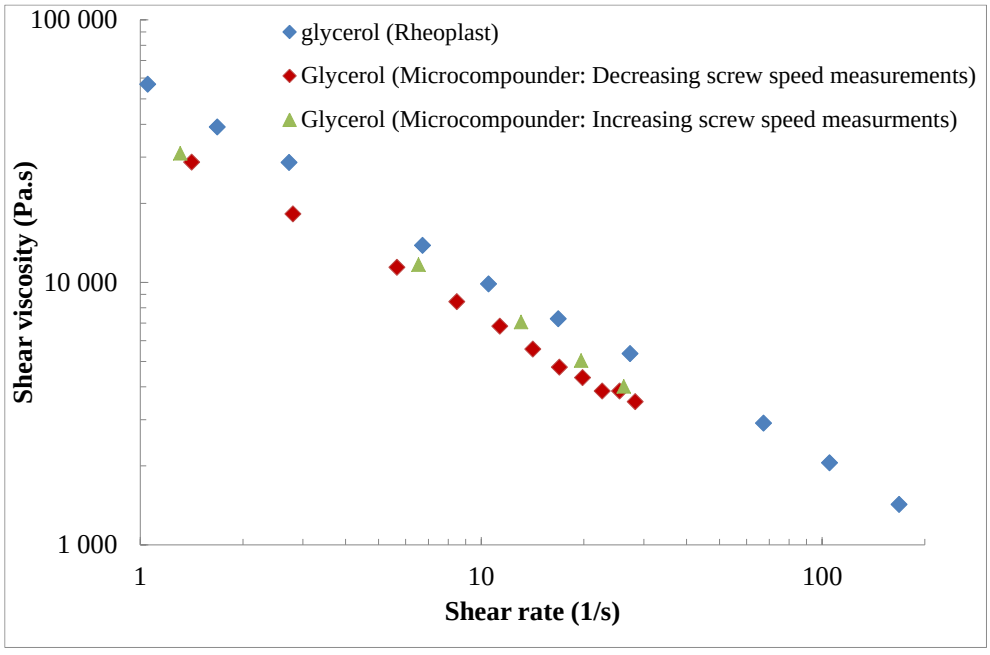
Plasticizer	Rheoplast			Micro-compounder		
	K (kPa s)	n	η at 10 s^{-1} (KPa s)	η at 10 s^{-1} (KPa s)	K (kPa s)	n
Glycerol	57	0.28	10.9	7.5	39	0.28
[Chol][Cl]	65	0.18	9.8	11.8	74	0.20
[Chol][Ace]	51	0.30	10.2	7.3	35	0.32
[EMIM][Cl]	44	0.21	7.1	4.0	19	0.33
[EMIM][Ace]	31	0.23	5.2	3.9	18	0.33

Table 2: Comparison of shear viscosity and power law values obtained with the Rheoplast and the Micro-compounder for the different TPS.

(**a**)



(**b**)



(a)

Figure 2: Reference shear viscosity curves: (**a**) Calibration of the Micro-compounder : Shear viscosity flow curves for polystyrene reference sample and Cross-Carreau model. (**b**) Shear viscosity flow curves for TPS plasticized by Glycerol with Rheoplast and Micro-compounder at 130°C (including measurements at decreasing screw speed and at increasing screw speed).

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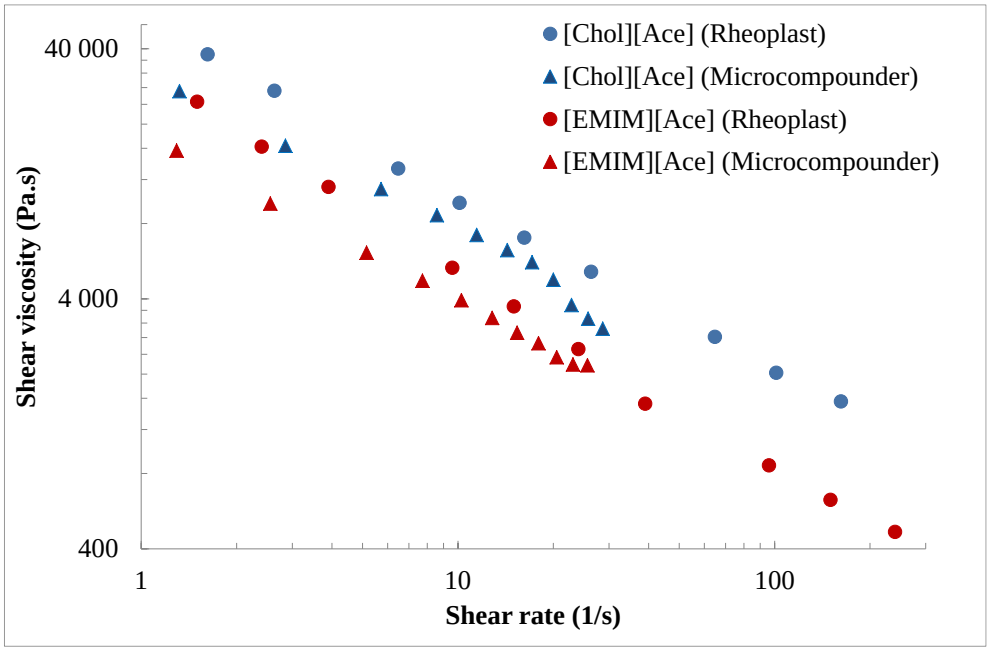
(a)



(b)

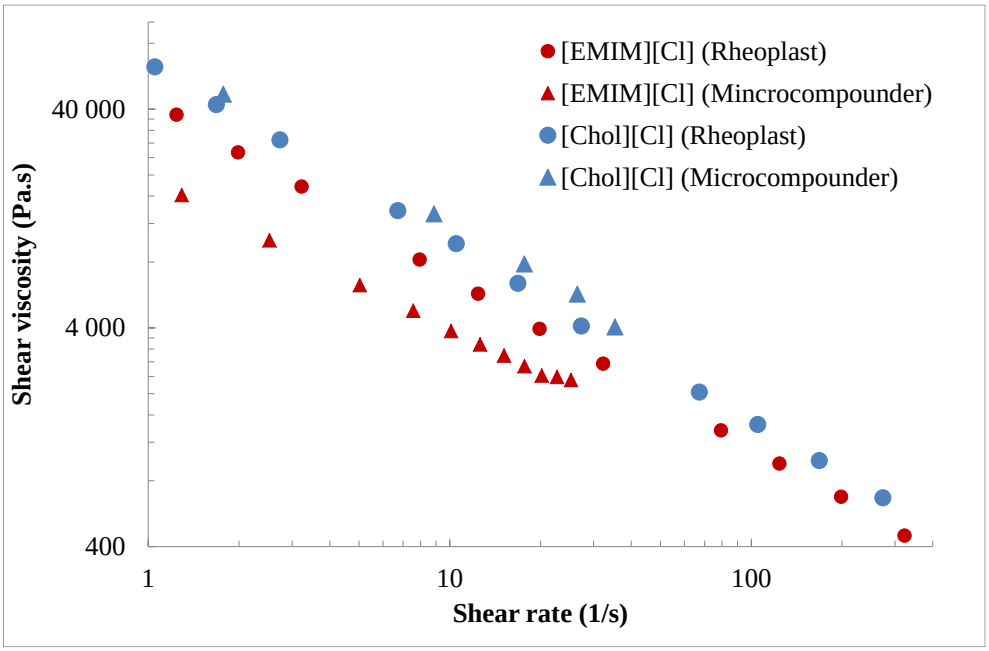


Figure 3: Shear viscosity curves for TPS containing ionic plasticizers obtained with Rheoplast and Micro-compounder: **a**) TPS plasticized by Acetate salts; (**b**) TPS plasticized by Chloride salts. All measurements with micro-compounder are performed at decreasing screw speed, except for [Chol][Cl] (measurement at increasing screw speed).

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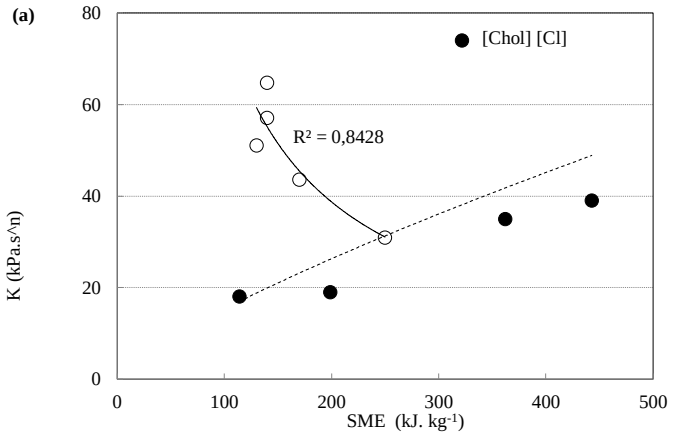
These results underline the need to examine more precisely the dependence of the viscosity with processing variables and structural features:

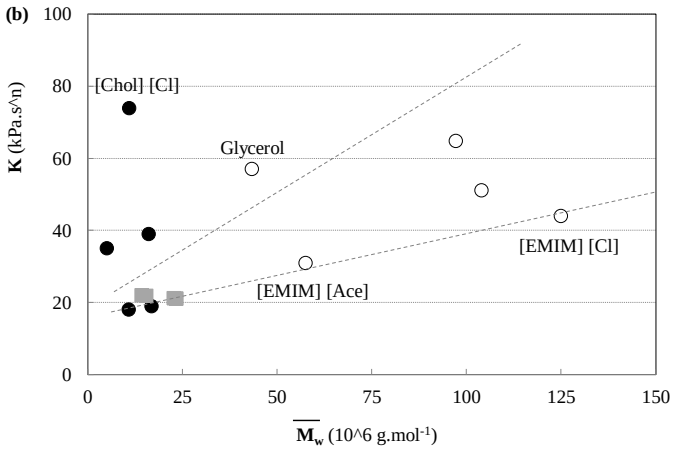
- Surprisingly, when considering data from Rheoplast and Micro-compounder together, no straightforward correlation appears between consistency values and SME (**Fig. 4a**). However, for results obtained with Rheoplast, despite uncertainty on SME measurement, it can be observed that K decreases with SME (**Fig. 4a**), in agreement with the usual trend found in literature (Xie et al., 2012). Conversely, an increasing trend is observed with SME in the case of the micro-compounder, once excluded the values obtained for [Chol][Cl] plasticized TPS, for the reasons discussed above. This apparent contradiction arising from the opposite variations of K with SME may be explained by considering how the thermomechanical treatment is applied to the product. In the Rheoplast, the product is mechanically treated before measurement, therefore, the more intense this treatment, the lower the viscosity of the plasticized starch melt. Conversely, in the micro-compounder, the mechanical energy input increases during measurements. Indeed, as explained in the experimental section, for the micro-compounder, the SME values reported in **Table 1** and plotted in **Figure 4a** are obtained for a series of experiments without rheological measurements and for a residence time of 300 s, while in the rheological measurement take place for residence times from 150 s to 700 s. Therefore the viscosity is partly measured before the effective SME reaches the value reported on **Fig. 4a**. Therefore, the more viscous the melt, the larger the SME measured on the micro-compounder. This opposite trend qualifies the potential of the micro-compounder as a rheometry tool for SME sensitive materials.

- The variations of consistency index K vs molar mass $\overline{M}_w$ display an overall increasing trend in the case of Rheoplast measurements (**Fig.4b**), obeying the rule of thumb "the larger the polymer, the more viscous". This trend is enhanced by the presence of

previous results obtained for maize starch, extruded in presence of water, for which K was computed using the viscosity model proposed by (Vergnes & Villemaire, 1987) for maize starch. However, significant dispersion is observed. Excluding again the values obtained for [Chol][Cl], two dotted lines can be drawn as guides for the eyes: One with higher slope for glycerol and Cholinium based RTILs, and one with lower slope for immidazolium based RTILs, suggesting that the later lead to lower viscosities than the former for similar starch macromolecular degradation.

- Indeed, the variations of consistency values vs glass transition temperature (**Fig. 4c**) show a good correlation for results from both micro-compounder and Rheoplast, with the rule of thumb "the more efficient the plasticizer, the lower the viscosity". As discussed previously, for $\overline{M}_w$ above 10^6 g mol^{-1} the glass transition depends only on the plasticizer (and water) present between polymer chains but is not expected to be influenced by molar mass (Lafargue et al., 2007). The observed correlation between K and T_g suggests that a similar trend applies for melt viscosity. Actually, the nature of the plasticizer has a stronger influence than macromolecular degradation on shear viscosity.





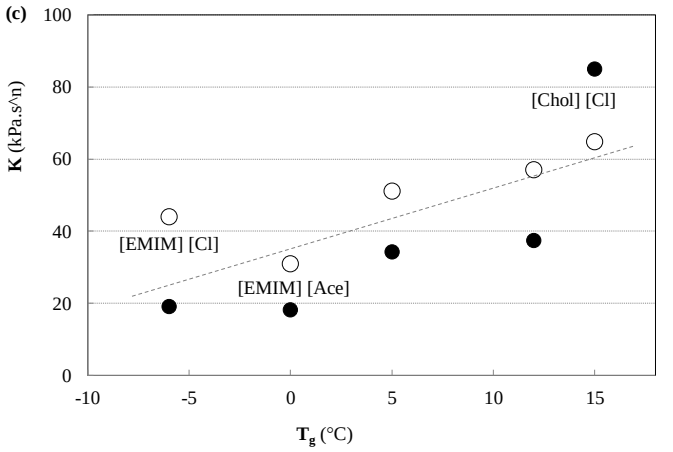


Figure 4: Variations of the consistency index (obtained with micro-compounder (●) and with Rheoplast (**O**)) with : (**a**) the SME (dotted line just show a trend whereas continuous line is the best fit for Rheoplast data) (**b**) the weight average molar mass $\overline{M}_w$ (additional point for starch extruded in presence of water (■) (data from Baud et al., (Baud, Colonna, Della Valle, & Roger, 2001) , viscosity is computed using model from Vergnes & Villemaire (Vergnes & Villemaire, 1987), dotted line illustrates a trend). and (**c**) the glass transition temperature.

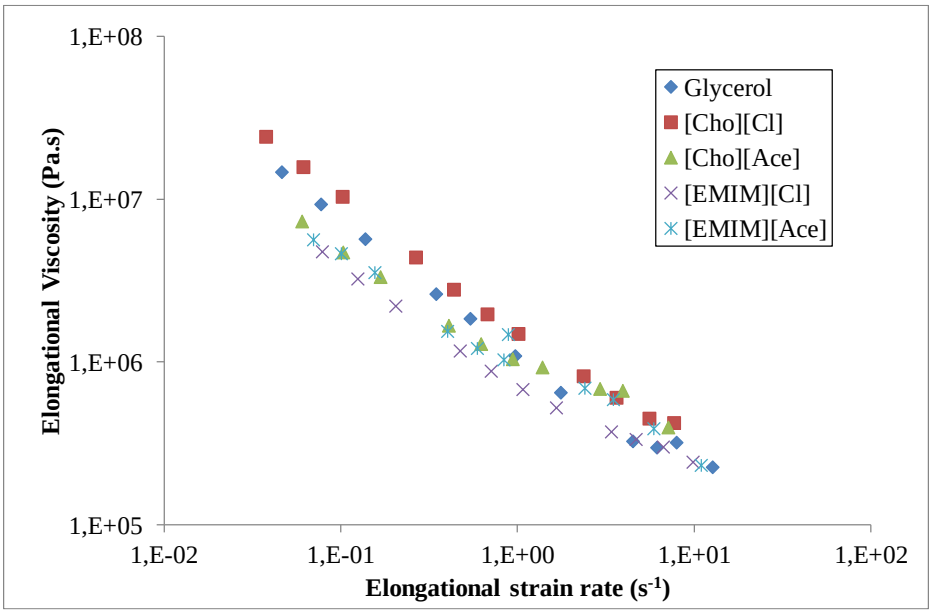
3.3) Extensional viscosity

In addition to shear viscosity, the Rheoplast allows estimating the extensional viscous behavior (**Fig.5**).

Fig. 5a shows the extensional viscosity flow curves obtained for each plasticized starch formulation. The decreasing viscosity order is roughly the same as the one previously observed for consistency values in **Table 2,** except for [EMIM][Ace] plasticized TPS. This plasticized starch had the lowest shear viscosity values, but its extensional viscosity displays values among the highest for extensional strain rate values larger than 1 s^{-1}. **Fig. 5b** shows the evolution of the Trouton number defined as the ratio between extensional and shear viscosities, for equal values of extensional strain and shear rates. All plasticized starches show Trouton numbers significantly higher than the typical value of 3 for a Newtonian fluid. Ionic liquid plasticizers also lead to higher values than for glycerol. Indeed, [EMIM][Ace] shows a unique behavior with Trouton numbers as high as 50 due to its low shear viscosity combined with a high extensional viscosity.

The comparison of extensional viscosity and Trouton number values also suggests that more melt strength could be expected from Ionic liquid plasticized starches, and overall with imidazolium acetate, which could perform better than glycerol TPS in processes, like film blowing or foam manufacturing, where material stretching prevails (Munstedt, Steffl, & Malmberg, 2005).

(a)



(b)

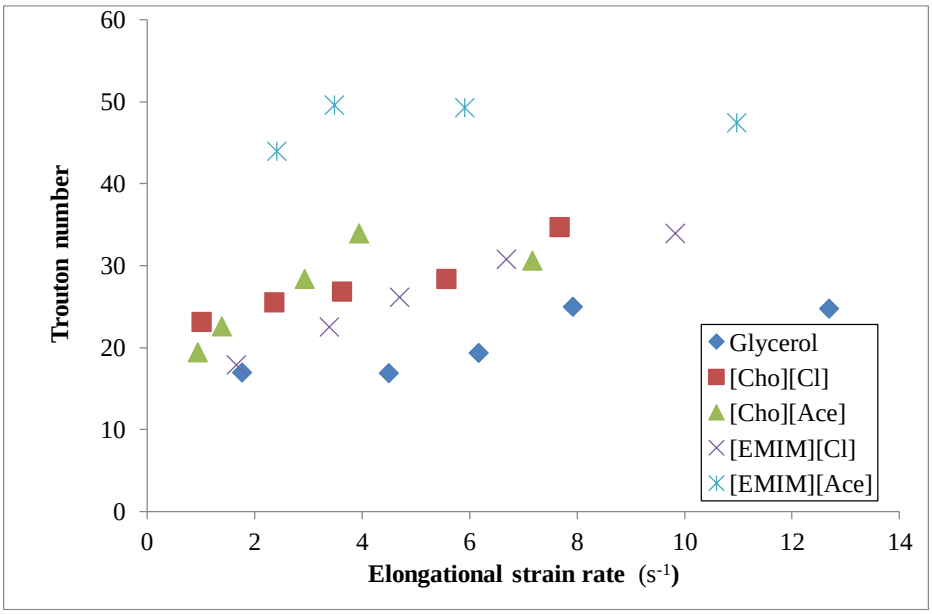


Figure 5: Extensional behavior of the plasticized starch: (**a**) extensional viscosity flow curves obtained with Rheoplast and (**b**) Trouton numbers.

4) Conclusion

In this work, maize starch was plasticized with different ionic plasticizers (Choline Chloride and three room temperature ionic liquids) and glycerol used as a reference plasticizer. Two different equipment allowing melt processing and rheological characterization have been used: a micro-compounder and a capillary rheometer with pre-shearing. The shear viscosity of plasticized starch was measured on both devices.

We have shown that, like for starches extruded in presence of water, significant macromolecular degradation is obtained. Although this phenomenon induces a decrease of shear viscosity, it does not account for all the variations of this rheological property. Indeed plasticizers have a significant and specific action, as shown by their depressing effect on T_g . Indeed, the melt consistency is found to better correlate to T_g than to the specific mechanical energy input or the molar mass decrease due to processing.

The consistency values of the thermoplastic starches obtained for the different plasticizers, with both Rheoplast and micro-compounder, rank in the same following order:

$$K_{[Chol][Cl]} > K_{Glycerol} > K_{[Chol][Ace]} > K_{[EMIM][Cl]} > K_{[EMIM][Ace]}.$$

This agreement found for the viscosity results between both equipment suggest that micro-compounder can be used to evaluate the plasticizing efficiency of ILs, all the more when small quantities are available. Conversely, Rheoplast has confirmed to be an efficient mean to process starchy material in similar but controlled conditions, like extrusion, whilst allowing an accurate determination of shear viscosity and assessing extensional viscosity, all meaningful properties for processing plasticized starches. Among all the tested ionic plasticizers 1-Ethyl-3-methylimidazolium acetate ([EMIM][Ace]) is particularly promising since it leads to the lowest shear viscosity, with limited macromolecular degradation and significantly higher Trouton number values than for the other plasticizers.

458 **Acknowledgments**

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461

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