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Effects of relative humidity and ionic liquids on the water content and glass transition of plasticized starch

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ABSTRACT

The purpose of the present work was to investigate the relationship between the glass transition temperature of the materials produced by the melting method and the water content, as well as the nature and concentration of the plasticizer used. Native starch was successfully treated with ionic liquid to obtain thermoplastic starch (TPS). Ionic liquids have shown a better plasticization, and low absorption of water compared to glycerol, which means a better interaction of starch with ionic liquids.

The water binding properties of TPS were studied by commenting the water absorption for the plasticized starch at different % RH and with different ratios of plasticizers. An amount of 22.5 wt% AMIMCl is the maximum that can act as a plasticizer. Above this composition, an increase in the wt% water and wt% AMIMCl induces a phase separation. This value corresponds to a chemical interpretation, which corresponds to a ratio of 1:3 AMIMCl/anhydro-glucose. A schematic representation of the different binding between starch, plasticizer and water has been proposed.

1. Introduction

The thermoplastic starch is obtained by destructurization of the semi-crystalline structure of native starch (Averous, 2004; Liu, Xie, Yu, Chen, & Li, 2009). Several low molar mass plasticizers were used such as glycerol, glucose, fructose or urea to obtain biodegradable and modifiable TPS (Lourdin, Bizot, & Colonna, 1997; Wilpiszewska & Spychaj, 2006). However, several shortcomings remain: water sensitivity, quantity of plasticizer (phase separation) and recrystallization during aging (retrogradation) which can cause brittleness and limit their application (Averous & Boquillon, 2004; Dean, Do, Petinakis, & Yu, 2008; Sarazin, Li, Orts, & Favis, 2008).

Ionic liquids (ILs) are organic salts with melting points below 100 °C. They consist in most cases of a large organic cation and an organic or inorganic anion. ILs have aroused growing interest in several areas (Seoud, Koschella, Fidale, Dorn, & Heinze, 2007; Tan & MacFarlane, 2010), due to their unique properties including non-flammability, negligible vapor pressure, ionic conduction and electrochemical stability. ILs have become attractive due to their recyclability, regardless of their rather high price (Kubisa, 2004; Singh & Sekhon, 2005). The physicochemical properties of ionic liquids can be finely tuned by the appropriate selection of the cation and/or anion (Dupont, Souza, & Suarez, 2002). ILs are considered a new green chemistry route for their use as a process solvent replacement and a biomass treatment (Gathergood, Garcia, & Scammells, 2004; Rogers & Seddon, 2003). In addition to being environmentally compatible and used as substitutes for organic solvents, ionic liquids have advantages in terms of optimizing the characteristics of products through a careful choice of the combination of the anion and cation, increasing the reaction rate with a better selectivity and achieving higher yields (Holbery & Seddon, 1999).

Important research efforts were made in the use of ILs in chemical processing biomass (Lehmann & Volkert, 2009; Wang & Xie, 2010). It was proved that hydrophilic ILs, especially imidazolium-based such as 1-butyl-3-methyl-imidazolium chloride BMIMCl and 1-allyl-3-methylimidazolium chloride AMIMCl, can act as solvents and dissolve various carbohydrate polymers (starch, chitin, cellulose and lignin) (Biswas, Shogren, Stevenson, Willett, & Bhowmik, 2006; Swatloski, Spear, Holbrey, & Rogers, 2002; Xie, Shao, & Liu, 2009). The IL interacts with the hydroxyl group of carbohydrates and breaks the hydrogen bonding network (Stevenson, Biswas, Jane, & Inglett, 2007). Most of the published works focus mainly in the dissolution and the homogenous modification of cellulose and lignin or direct wood dissolution (Fort et al., 2007; Laus et al., 2005). The interaction of ionic liquids with starch was much less studied (Qin, Lu, Sun, & Rogers, 2010). In most studies, plasticization is conducted in an aqueous medium and the composition is obtained by casting (Wang, Zhang, Liu, & Han, 2010).

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Leroy, Jacquet, Coativy, Reguerre, and Lourdin (2012), performed the compatibilization of starch–zein melt-processed blends using an ionic liquid as plasticizer in a micro-compounder. The characterization of the materials indicates that compared to glycerol, the use of BMIMCl leads to lower hygroscopicity, a more efficient plasticization of both starch and zein phases and a compatibilization of starch/zein blends.

Sankri et al. (2010) showed the possibility to use BMIMCl as plasticizers of starch by melt processing. The TPS obtained is less hydrophilic than glycerol-plasticized TPS, and shows better plasticization effect.

Wang, Zhang, et al. (2010) used AMIMCl as a corn starch plasticizer to prepare solid biopolymer electrolytes. They obtained films by casting from aqueous solutions. A higher level electrical conductivity value was obtained in the presence of AMIMCl. They also studied, via FTIR, the hydrogen bonding interaction between starch and the ionic liquid. They showed that the addition of LiCL in cast films increases the interaction between AMIMCl and starch, as well as the electrical conductivity and the water uptake.

Another aspect is the analysis of water binding in the thermoplastic starch (TPS). Water acts as plasticizer and interacts differently depending on the quantity present in the system. The first step is the absorption of water bound via H-bonds to starch (—OH) (Fringant et al., 1996). The second step consists of the formation of water multilayers finally condensed into a liquid phase.

Godbillot, Dole, Joly, Rogé, and Mathlouthi (2006) used the determination of water vapor absorption isotherms for the plasticized starch (casting films) at 20 °C with different ratios of glycerol to understand the interactions between water, glycerol and starch. They showed that the effect of plasticizers on water vapor absorption of films depends on glycerol content and on relative humidity (RH) value.

Another study (Ayadi & Dole, 2011) used a stoichiometric interpretation to characterize the water sorption of thermoplastic starch and the influence of cellulose introduction in the formulation to establish the relation between phase diagrams of starch/water/glycerol/cellulose systems.

The saturation of starch with glycerol is a function of the water activity. Godbillot et al. (2006) showed that the maximum quantity of glycerol bound to the starch is 23%. The author has proposed a chemical interpretation of this value, which corresponds to a ratio of 1:2 glycerol/AGU. The saturation point depends on several factors including the origin of the starch used, the type of water conditioning and the plasticizer used (Yu, Wang, Wu, & Zhu, 2008).

The goal of this study is to investigate the influence of the kind and concentration of ionic liquid and phase diagrams of water sorption isotherms and understand the interactions between starch, ionic liquid and water and their influence on the intrinsic property of thermoplastic starch (TPS) (W% water retention, structures and thermo-mechanical characteristics).

2. Experimental

2.1. Materials

Maize starch was purchased from Roquette Frères (Lestrem, France) (containing 40% of amylose). The initial moisture content was 9.4%. Glycerol (Aldrich) and ionic liquid, 1-butyl-3-methylimidazolium chloride BMIMCl (Aldrich), 1-ethyl-3-methylimidazolium acetate EMIMAC (Intershim, France) and 1-allyl-3-methylimidazolium chloride AMIMCl (synthesized in the lab) were used as plasticizer without further purification.

The synthesis procedure of AMIMCl was performed according to the method of Ren (2003). In a reactor, 1-methylimidazolium was added to allyl chloride with a 1:1.2 molar ratio under argon gas atmosphere. The mixture was stirred with reflux at 70 °C for about 6 h. After removing the residual allyl chloride in a rotavap, the resulting liquid was washed for a long time, with an excess amount of ether to eliminate the residual 1-methylimidazole. The final step was the drying in vacuum drier at 80 °C for 72 h to eliminate the residual ether.

The physical–chemical properties (density = 1.19, refractive index (RI) = 1.54 and pH = 8.80), FTIR and H NMR spectra of the AMIMCl were obtained by using respectively a spectrometer (Nicolet Nexus 470) and a Bruker DRX250 spectrometer operating at 250 MHz also showing in the end the characteristics of AMIMCl.

Formulas of AMIMCl, EMIMAC and BMIMCl are presented in Fig. 1.

The notations ST (starch), BM (BMIMCl), EM (EMIMAC), AM (AMIMCl), GL (glycerol) and the proportion by weight of the plasticizer (w/w, %) were adopted to distinguish the different formulations. For example: ST-AM-20 means a sample prepared with dispersed AMIMCl 20% (w/w) in starch.

2.2. Thermoplastic starch processing

Thermoplasticization of starch by the various plasticizers was carried out in the micro-compounder allowing the preparation of batches of samples of a few grams (<7 g). The Minilab micro-compounder (Thermo Haake) is a device with a conical screw system with a recirculation channel. The advantage of this device is that it can be used as a mixer and simulates the execution of a co-rotating extruder with small quantities of materials.

Starch (9.4%, w/w, initial water) and plasticizers (glycerol or IL) were premixed manually. Various compositions were investigated, three were retained: 20, 30 and 40% (w/w) of plasticizers (additional formulations were prepared for water sorption isotherms

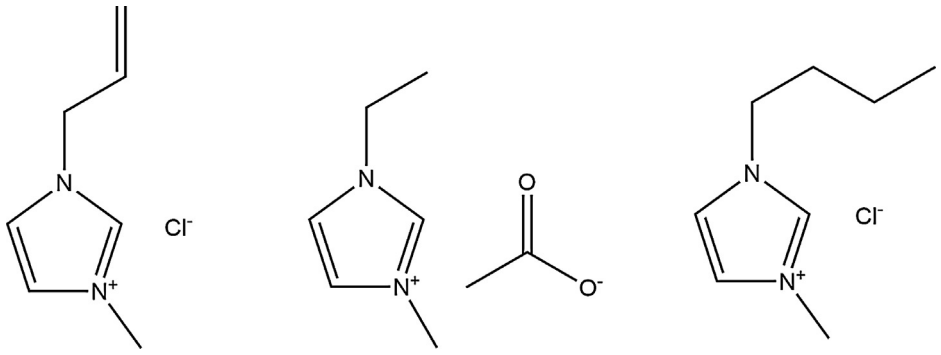


Fig. 1. Formulas of AMIMCl, EMIMAC and BMIMCl.

experiment). The premixed formulations were introduced into the micro-compounder at 150 °C with a rotation speed set at 150 rpm. The introduction of products into the micro-compounder was done in several steps: this filling operation took about 1min30. The mixture (closed loop) was thermo-mechanically processed for 3 min for all samples, then the thermoplastic starch was extruded through the exit die. Behavior in the melt was followed by recording the torque signal in the recirculation channel of the device.

After melt mixing, the samples were heat-pressed at 140–150 °C for 5 min at 200 bars. The samples obtained had the following characteristics: 30 mm × 10 mm × 2 mm for dumbbells. Before characterization, all samples were stored in climatic and temperature test chamber (Froilabo – Firlabo) under a controlled relative humidity of 35%, 60% and 80% RH at 30 °C.

The water absorption of the samples was measured until stable. Two experiments were conducted. In the first one, samples were conditioned under fixed conditions. No more variations were observed after 3 days. The second study aimed to establish the different kinetic curves of different samples so that all samples would have the same amount of water absorbed.

2.3. Characterization

2.3.1. Water absorption

These experiments were conducted on samples obtained from various extruded products. Before measurement of water absorption, all samples were dried at 70 °C until a constant mass was obtained.

The samples were conditioned under controlled humidity in climatic and temperature test chamber (Froilabo – Firlabo) (30 °C – 35% RH, 60% RH and 80% RH). The amount of water absorbed by the various samples was determined by weighing them regularly until a constant mass was reached. The water uptake (W.U.) was determined by the following relation (Eq. (1)):

$$\text{W.U.}(\%) = \frac{M_t - M_0}{M_0} * 100 \quad (1)$$

where M_t is the weight at t time and M_0 is the initial weight.

2.3.2. X-ray diffraction (XRD)

The crystal structures of the starch powder treated with different plasticizers were studied using an XRD analyzer (Bruker Advance D8) set at 43 kV and 35 mA. Wide-angle X-ray intensities were collected for 2θ, ranging from 4.5° to 50°. Traces were obtained using a Cu Kα radiation detector with a scanning rate of 3 °C/min.

The degree of crystallinity of samples was quantitatively estimated following the equation of Wang, Gao, Jia, and Xiao (2006), as the ratio of crystalline area to the total area under the diffraction peaks.

2.3.3. Differential scanning calorimetry (DSC)

Differential scanning calorimetry was performed with a TA-Q10 calorimeter calibrated with indium to characterize the glass transition of TPS. A hermetic empty pan was used as a reference. Samples cut from the plates which were previously conditioned under controlled relative humidity were weighed (10 mg) and put in sealed capsules. Measurements were carried out from −100 °C to 100 °C, at a heating rate of 10 °C/min. The glass transition temperatures were determined from the reheating thermograms as the mid-point of the transition.

Furthermore, BMIMCl–water mixtures were prepared (pure BMIMCl, 80 and 90% of BMIMCl). Every formulation (10 mg) is put in sealed capsules and measurements were carried out from −120 °C to 20 °C, at a heating rate of 10 °C/min.

2.3.4. Dynamic mechanical thermal analysis (DMTA)

The dumbbell samples (30 mm × 10 mm × 2 mm) were conditioned at 35% RH, 30 °C for 3 days until no significant additional change of weight was observed. These tests were conducted with a DMTA Rheometrics scientific strain control at 1 Hz with a deformation amplitude of 0.8%. This value is in the range of linear viscoelasticity. The heating rate was 3 °C/min from −100 °C to 100 °C.

3. Results and discussion

3.1. Starch plasticization by extrusion processing

Table 1 presents the evolution of torque depending on the formulation and concentration of the plasticizer used. The torque decreases as the plasticizers concentrations increase and it is linked to the gradual decrease in the viscosity of the formulation due to the lubricants and plasticizers effect (Wang, Yu, et al., 2010; Xie, Halley, & Avérous, 2012), especially that of the ionic liquids (Leroy et al., 2012).

In the experiments conditions, all the formulations of starch–plasticizers above 20 wt% were effective in the destruction and plasticization of starch. Moreover, visual observation for these plasticized TPS with ionic liquids, contrary to glycerol (Table 1) showed that the extruded and pressed samples (dumbbells) obtained by hot pressing were clear, homogenous and transparent. At 20 wt% of plasticizers (ILs or glycerol), the appearance of the premix was in the form of powder not impregnated, unlike at the other formulations.

Table 1
Composition, appearance and torque signal of all extruded samples of the plasticized TPS.

Sample identification	Characteristic of pre-mix	Visual and handling characteristics of pressed samples	Torque (Nm)
ST-BM-20	Un –premixed –in powder form	Transparent and fragile	2.62
ST-BM-30	Homogenous mass	Intermediate	0.51
ST-BM-40	Homogenous mass	Transparent and flexible	<0.10
ST-EM-20	Un –premixed –in powder form	Transparent and fragile	2.75
ST-EM-30	Homogenous mass	Intermediate	0.89
ST-EM-40	Homogenous mass	Transparent and flexible	<0.10
ST-AM-20	Un –premixed –in powder form	Transparent and fragile	1.88
ST-AM-30	Homogenous mass	Intermediate	0.66
ST-AM-40	Homogenous mass	Transparent and flexible	<0.10
ST-GL-20	Un –premixed –in powder form	Not transparent	2.40
ST-GL-30	Un –premixed –in powder form	Not transparent	1.30
ST-GL-40	Un –premixed –in powder form	Not transparent	0.43

Table 2
The % of remained crystallinity of the different formulations.

Sample	Crystallinity (%)
Starch	12.5
ST-BM-20	4.5
ST-BM-30	2
ST-BM-40	Amorphous
ST-EM-20	5
ST-EM-30	Amorphous
ST-EM-40	Amorphous
ST-AM-20	2.7
ST-AM-30	Amorphous
ST-AM-40	Amorphous
ST-GL-20	7
ST-GL-30	6.9
ST-GL-40	4.8

For each sample, 2 batches were prepared in order to ensure the reproducibility of the mixing conditions.

3.2. X-ray diffraction of TPS

To study the effect of ILs process in the modification on the crystalline structure of starch, native and transformed starches were examined by powder X-ray diffraction. X-ray diffraction patterns of native starch and plasticized starch with the different plasticizers, conditioned for 1 week, are displayed in Fig. 2.

Native corn starch (Fig. 2) exhibited a typical A-type pattern structure. In the XRD pattern of native corn starch, a strong reflection (2θ) was found at about 15° and 23°, and a doublet at nearly 2θ of 17° and 18° (Kuo & Lai, 2007; Puchongkavarin, Bergthaller, Shobsngob, & Varavinit, 2003). However, the intensity of the diffraction peaks was reduced significantly with the increase in the concentration (after 20%) of ionic liquid, which suggests that most of the crystalline structure of the starch was converted into the amorphous shape.

The X-ray diffractograms for formulations at 20% of ionic liquid and glycerol plasticized starch show VH-type (7.5°, 13°, 19.5°, and 22.5°) crystallinity corresponding to the complexation of amylose with residual lipid and plasticizers.

Table 2 regroups the % of crystallinity of the different samples. It decreases with the increase in the concentration of the plasticizer. The loss in crystallinity of native starch could be attributed to the fact that IL weakened the inter- and intra-molecular hydrogen bonds. However, and according to Table 2, the effect of AMIMCl was more notable than other plasticizers on the destruction of the crystalline structure of starch.

The destruction of the semi-crystalline starch structure allowing the reagent to have a better access to the starch hydroxyl groups for homogeneous chemical modification process and the retrogradation for the sample process with ILs were not observed.

3.3. Water absorption

A water vapor sorption isotherm leads to control the level of hydration of the plasticized polysaccharide samples. The water contents of the samples equilibrated at 35, 60 and 80% RH at 30 °C are studied. ST-AM and ST-BM formulations have the lowest trend in terms of water absorption, which means limited disposition for water.

A graphic representation of the water absorption by starch samples which takes into account the ratio of plasticizer is reported in Fig. 3.

At low and constant RH (for example: ST-AM, 35% RH, 30 °C), an increase in the plasticizer ratio was found to display a two-step behavior: below a certain value of plasticizer, there is a decrease in water absorption as a function of plasticizer concentration, and above this value, water absorption increases (Godbillot et al., 2006; Lourdin et al., 1997; Shogren, Swanson, & Thompson, 1992).

The explanation for these two regions involves specific binding of the plasticizer in the first step and phase separation in the second step. The concentration (critical concentration) between the two steps corresponds to the saturation of starch-binding sites, which is a combination of H-bonding of starch with plasticizers on the one hand and with water on the other.

An increase in the % RH (from 35% to 60% RH), for the formulation ST-AM for example, decreases the critical concentration, which means that a smaller amount of plasticizer contributes to the saturation of the primary sites of the starch. This decrease in the critical concentration is explained by containing a higher amount of water. And at 80% RH, the critical concentration is exceeded.

Many studies reported by different authors (Godbillot et al., 2006; Myllärinen, Partanen, Seppala, & Forssell, 2002) mention the presence of a minimum of plasticizer content in the plasticized starch sample. It is reported at around 20% for glycerol samples, but this value depends on the % RH, plasticizers and starch origin.

In Fig. 4, a phase diagram is associated to the curve evolution of the amount of water depending on the concentration of plasticizer and moisture conditioning. The pattern of interaction may be the following: during the first step, adsorption of the plasticizer and water occurs in the primary sites of the starch; the second step is the formation of multilayers; this step will be followed by a phase separation.

Fig. 4 and Scheme 1 also show the characteristic point necessary to understand the binding between starch, plasticizer and water for the formulation ST-AM (Godbillot et al., 2006).

Point A corresponds to a monomolecular layer of starch with water. Water content at this point is 13.55 wt%. The calculated molar ratio is equal to 1.22 (mol H_2O/mol anhydro-glucose).

Point B corresponds to a complete saturation of the starch site (3-OH) with a water uptake of 17.51 wt% which corresponds to a stoichiometric ratio of 1.58 (mol H_2O/mol anhydro-glucose).

Point C corresponds to a graphical extrapolation at zero water content of the line crossing the minima of hydration curve at the different % RH studied. Water content at this point is 22.5 wt%, which is equivalent to a calculated molar ratio equal of 0.3 (mol AMIMCl/mol anhydro-glucose).

Point D corresponds in this case to the minimum hydration of starch plasticized with 15 wt% AMIMCl at 35% RH. This situation corresponds to the double bonding of AMIMCl and water to starch. This minimum point represents the primary starch site which was occupied by AMIMCl reducing the proportion of absorbed water molecules.

Point E is located on the AMIMCl saturation line. It corresponds to 10 wt% AMIMCl and 80% RH, equivalent to a molar ratio equal 0.12: a molecule of AMIMCl binds to 8 glucoses. At this point, 2 molecules of water bind to a glucose. This situation implies a part of AMIMCl and water binds to the primary hydroxyls of starch and the excess of water implies multi-layer binding. We suppose that AMIMCl are preferred to bind with starch.

Point F corresponds to 30 wt% AMIMCl and 40 wt% water content. At this level, water can be associated by H-bonds either to starch or to AMIMCl (free or multilayered).

Point G corresponds to 30 wt% AMIMCl and 0 wt% water. In this situation, part of AMIMCl binds to the primary hydroxyls of starch and the excess are multi-layer binding.

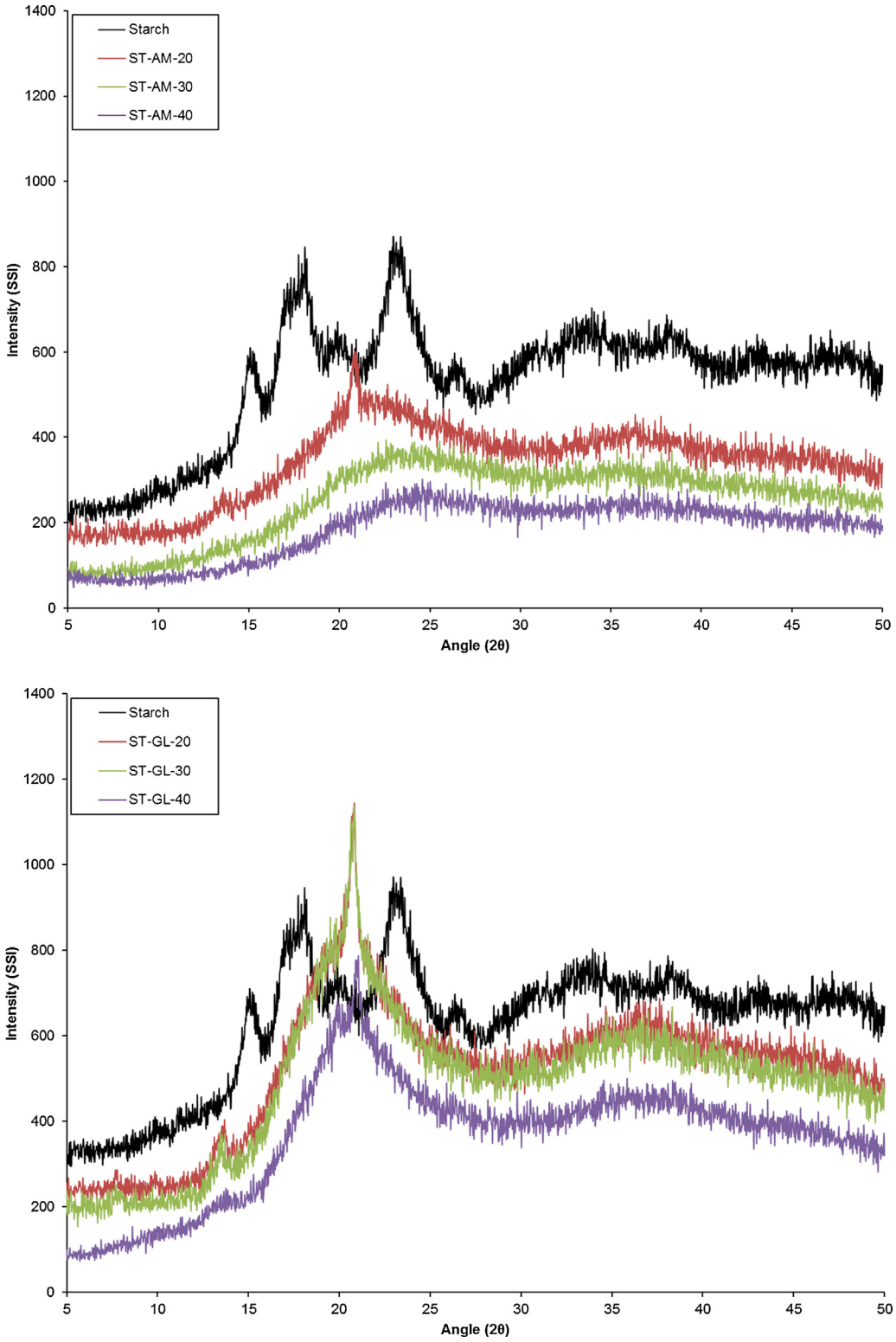


Fig. 2. XRD profile of native starch and starch plasticized with AMIMCL and glycerol.

3.4. Dynamic mechanical thermal analysis (DMTA)

Two moisture conditioning experiments were conducted on the different samples prepared. The first was a conditioning at 35% RH – 30 °C until the equilibrium was reached.

Fig. 5 shows the temperature dependence of storage modulus (G') and tan δ of ST-GL-30 and ST-AM-30. The relaxation temperatures can be taken at the maximum of the respective tan δ peaks.

The ST-GL-30 shows two transition peaks at around 18 °C and −57 °C due to the α relaxation (T_α) of starch and the β relaxation (T_β) of glycerol respectively (Curvelo, Carvalho, & Agnelli, 2001; Mathew & Dufresne, 2002).

For samples plasticized with AMIMCL, the result shows that the α relaxation is significantly more shifted at lower temperatures. Results of Table 3 show that for a given formulation, the increase in the concentration of IL makes the glass transition temperature

(T_g) of the two phases decrease. The position of the β-relaxation depends on both the nature of plasticizer and water content.

The second experiment was carried out at a constant water content (10 ± 0.05 wt% water). Table 4 summarizes all these results. This experiment shows as expected (Hulleman, Janssen, & Feil, 1998) that water is a plasticizer which, by weakening the interaction of the molecules of starch, improves the movement of chains of starch (Lourdin et al., 1997). For ST-AM-20, for example, the increase of the water content from 7.9 to 10 wt% shifts

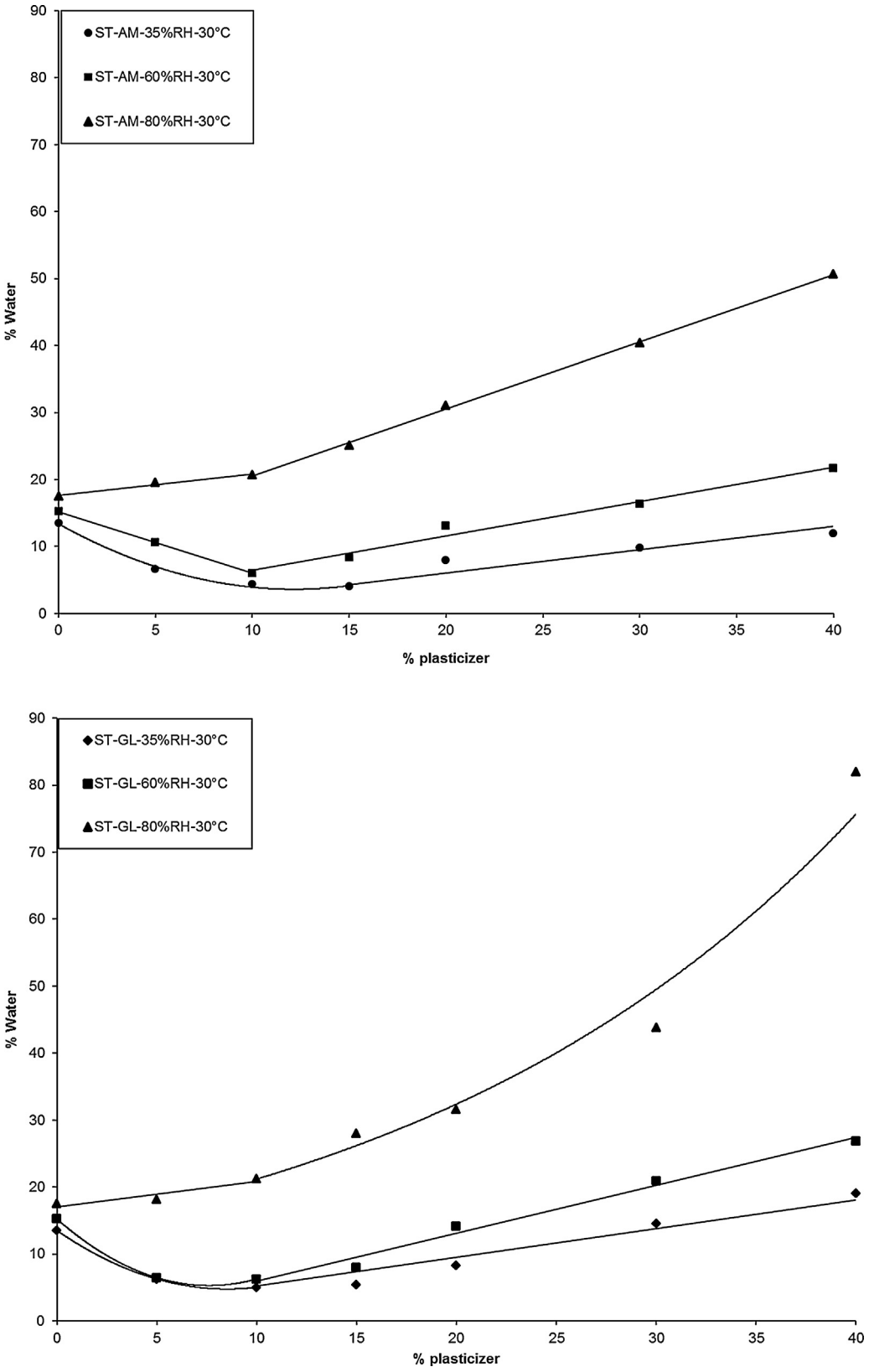
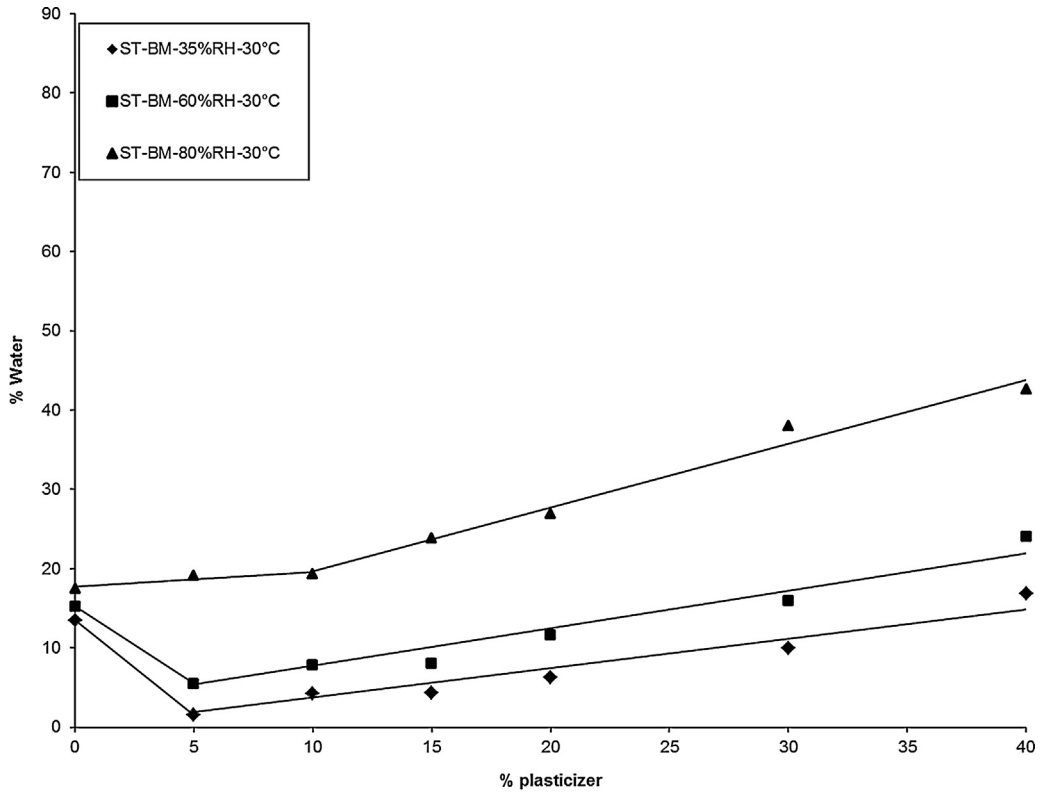


Fig. 3. Water uptake of plasticized starch conditioned at 35, 60 and at 80% RH, 30 °C.



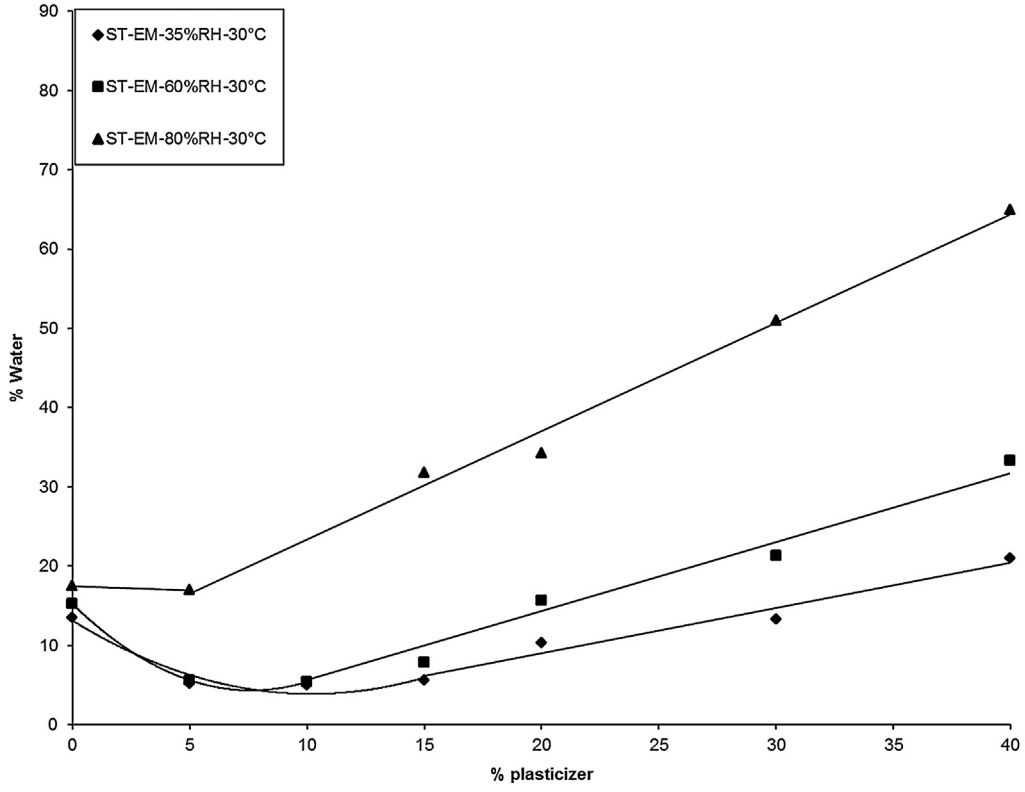


Fig. 3. (*Continued*).

the temperatures of the two relaxations toward lower temperatures (−37 °C to −58 °C and 16 °C to 5 °C). We can report regarding the ST-GL and ST-AM formulation that the β relaxation (plasticizer-rich phase) was sensitive to the amount of water.

3.5. Differential scanning calorimetry

The glass transitions of samples plasticized with ionic liquids and glycerol were measured after conditioning in a relative humidity of 35% RH – 30 °C and water equilibration.

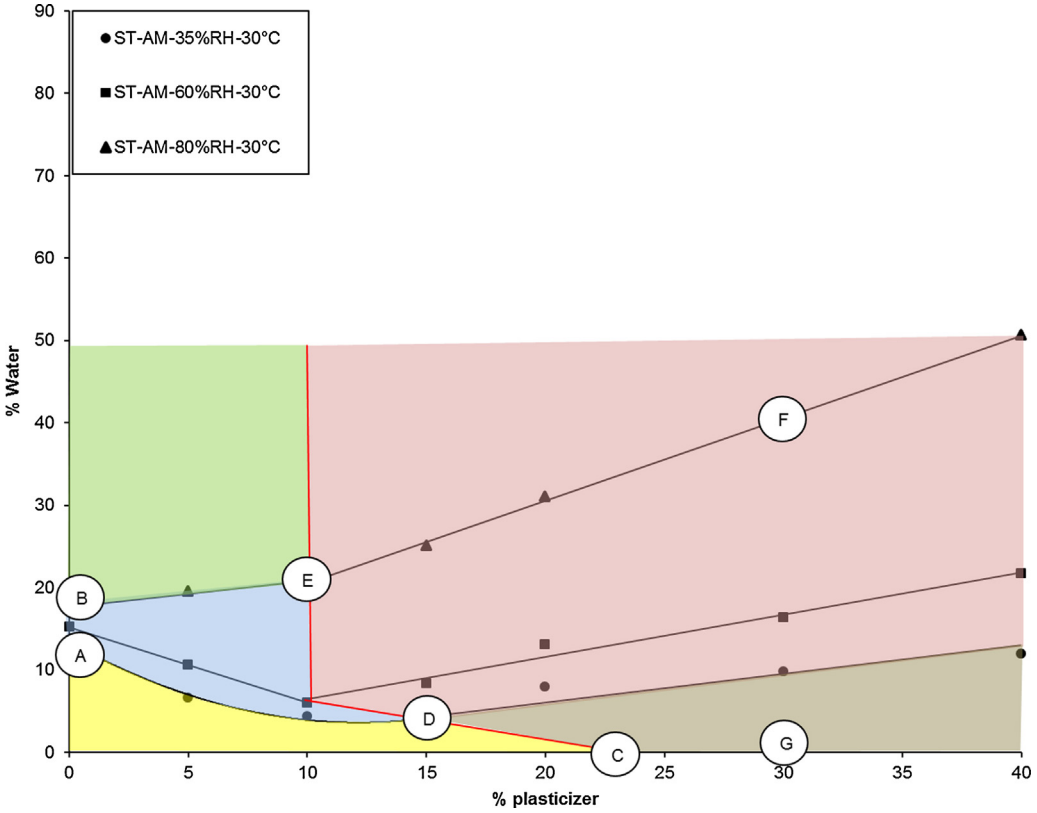
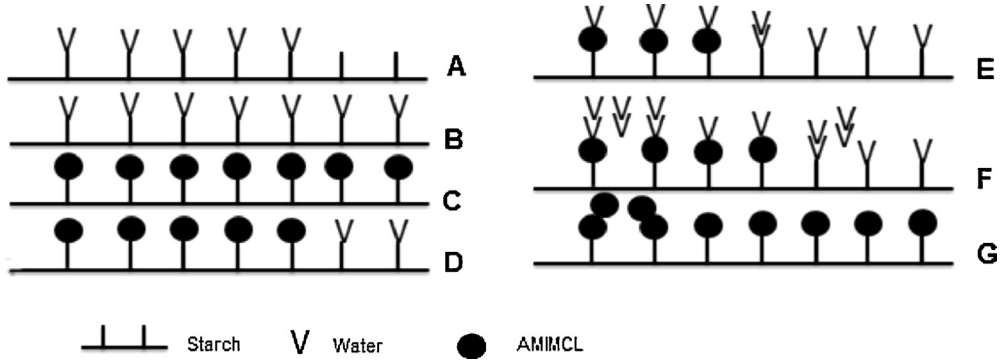


Fig. 4. Phase diagram and characteristic points of ST-AM according to the concentration of plasticizer and the amount of water.



Scheme 1. The schematic interaction between starch, AMIMCL and water. These different cases are associated to characteristic points in Fig. 4.

Table 3
Relaxation temperature measured by DMTA respectively with their water content.

Sample	T_β (tan δ) plasticizer rich phase	T_α (tan δ) starch rich phase	Water content (%)
ST-AM-20	−37	16	7.9
ST-AM-30	−50	−14	9.8
ST-GL-20	−54	55	8.3
ST-GL-30	−57	18	14.5
35% RH – 30 °C			

Table 4
Relaxation temperature measured by DMTA respectively for all formulation studied with 10 ± 0.05 wt% of water.

Sample	T_β (tan δ) plasticizer rich phase	T_α (tan δ) starch rich phase
ST-AM-20	−58	5
ST-AM-30	−55	−20
ST-GL-20	−63	23
ST-GL-30	−65	5

Table 5(a) regroups the T_g of the different mixtures studied. The heat flow shows one broad step, but this does not prevent associating these values to the different phases (Section 3.4) according to the formulation.

The upper transition is due to a rich starch phase corresponding to T_g of TPS, whereas the lower transition is due to a poor starch phase, as reported by many writers for starch–glycerol–water systems (Forssell, Mikkilä, Moates, & Parker, 1997).

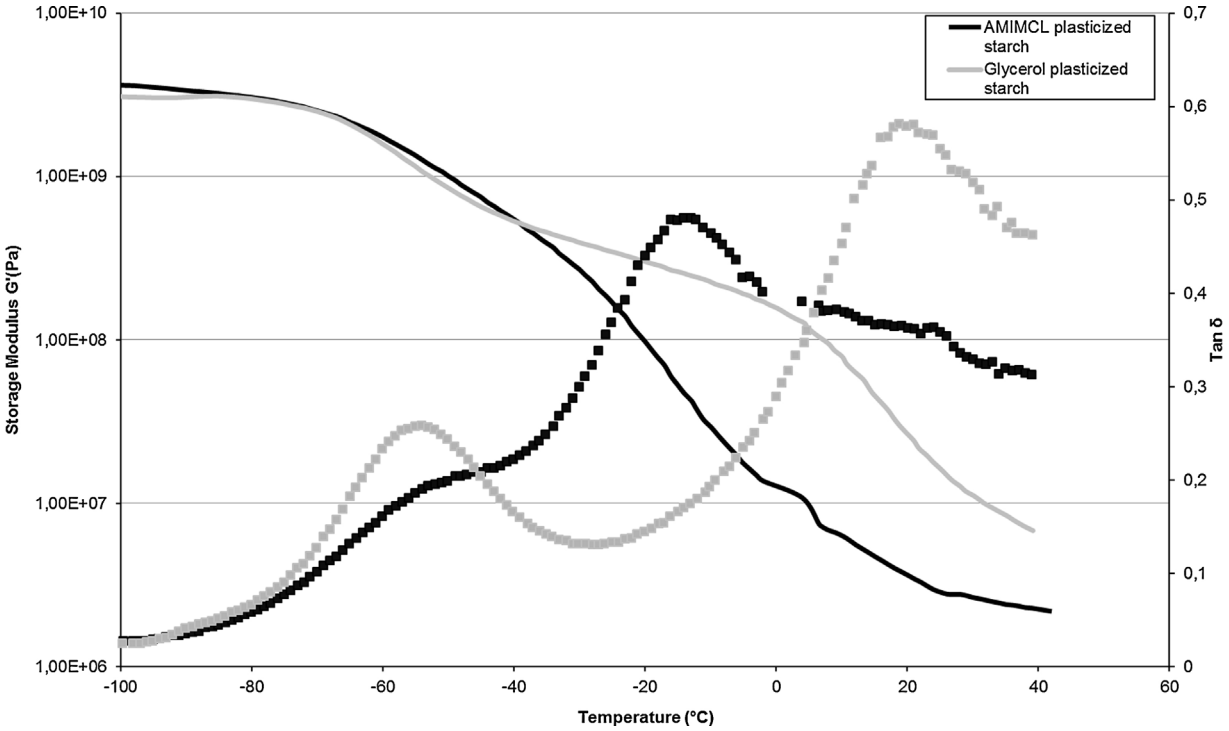


Fig. 5. Dynamic mechanical behavior of AMIMCL and glycerol plasticized starch.

The transition temperatures of samples are shifted to lower temperatures when the ionic liquids or glycerol content increase. Indeed, there is a transition from an upper T_g to a lower T_g.

To determine the influence of plasticizer on the thermal transition determined by DSC, the samples ST-BM and ST-GL were conditioned in order to contain 10 ± 0.05 wt% of water. The results were presented in Table 5(b). These results show that in both cases the T_g is depressed by the addition of plasticizer.

Concerning the effect of water, the T_g of the formulation of ST-BM-20 decreases from 15 °C to −15 °C when the concentration of water increases from 6 to 10 wt% (Bizot et al., 1997).

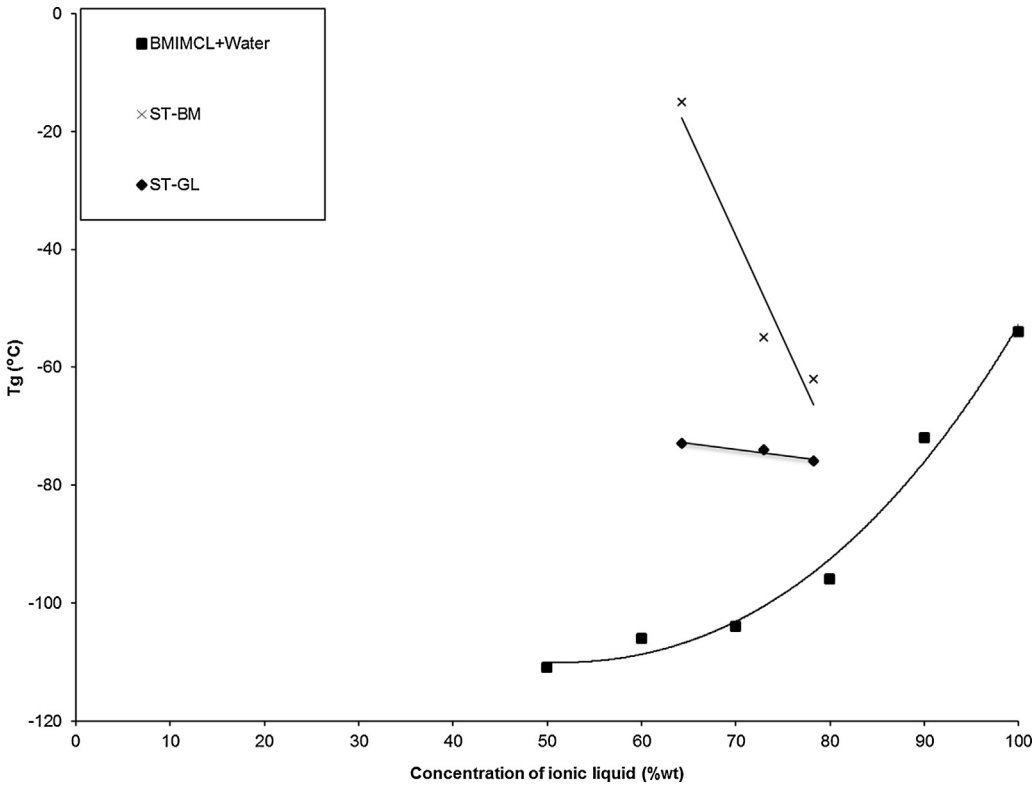


Fig. 6. Evolution of the T_g of ionic liquid–water mixture composition and starch samples with 10 ± 0.05% fixed moisture content.

Table 5
Glass transition temperature of starch plasticized with varying compositions of ionic liquid and glycerol conditioned at 35% RH, at 30 °C and at a constant water content (10 ± 0.05 wt% water).

Sample	T_g (°C)	Water content (w/w, %)
(a)		
ST-BM-20	15	6.3
ST-BM-30	−60	10
ST-BM-40	−87	16.8
ST-EM-20	20	10.4
ST-EM-30	−28	13.4
ST-EM-40	−59	21
ST-AM-20	23	7.9
ST-AM-30	−49	9.8
ST-AM-40	−62	11.9
ST-GL-20	−67	8.3
ST-GL-30	−77	14.5
ST-GL-40	−83	19

Sample	T_g (°C)
(**b**)	
ST-BM-20	−15
ST-BM-30	−55
ST-BM-40	−62
ST-GL-20	−73
ST-GL-30	−74
ST-GL-40	−76
10 ± 0.05 wt% of water	

Finally, the T_g of BMIMCl–water mixture was also plotted in Fig. 6. The T_g of 50, 60 and 70 wt% of BMIMCl in BMIMCl–water mixture are given in literature Takahiro, Miwa, Takuto, and Seiji (2011).

The slightly elevated glass transition of ST-BM and ST-GL formulation (Fig. 6) above the IL–water curve suggested that the polymeric starch materials enhanced the value. Unlike IL-based formulations, one sees that for conditions of fixed water content, the effect of glycerol concentration on the evolution of the glass transition of associated formulations has no effect. In IL-based formulations, interactions are conditioned by the concentration of ILs.

4. Conclusion

The formulation of ionic liquid above 20 wt% allows the production of TPS with efficient destruction and plasticization. Visual observations for these pressed TPS were clear and homogenous.

The interaction between starch–water–plasticizers was discussed by commenting the water absorption for the plasticized starch with different ratios. A phase diagram and a schematic representation are reported and contain some characteristic points which illustrate the interaction between the different components of the study.

AMIMCl and BMIMCl plasticized TPS obtained have the lowest trend in terms of water absorption, which means limited disposition for water compared to glycerol plasticized TPS taken as reference. Despite the low quantity of water uptake of AMIMCl plasticized TPS, AMIMCl acts as a more efficient depressor of glass transition temperature than glycerol (relaxation temperature measured by DMTA (35% RH, 30 °C) is respectively 16 °C and 55 °C for 20% of plasticizers). XRD results obviously showed that the crystalline structure of native starch was damaged with the process by ionic liquid. This process can enhance chemical reagent access to the hydroxyl groups of starch and increase reactivity. The phase diagram proposed in this paper is necessary for future interpretation of mechanical properties as a function of ionic liquid and water content.

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