RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2016, **6**, 90331

Biofriendly ionic liquids for starch plasticization: a screening approach†

G. Colomines,*[a] P. Decaen,[bc] D. Lourdin[c] and E. Leroy[b]

Received 27th June 2016
Accepted 13th September 2016

DOI: 10.1039/c6ra16573g

www.rsc.org/advances

A series of cholinium cation-based bioionic liquids (BioILs) were synthetized with the aim of screening their performance as potential plasticizers of thermoplastic starch. To synthesize these BioILs, two easy and fast synthetic routes were selected: an ion exchange reaction, direct and economical, and a two-step acid–base reaction. Most of these BioILs allowed efficient plasticization of starch by film casting. The structure of the anion used significantly influences the thermo(hygro)mechanical and recrystallization behavior, making it possible to modulate the properties of the final material.

Introduction

Starch is one of the most abundant natural biopolymers found in various crops worldwide.[1] As a petroleum-based polymer, it can be melt-processed as a thermoplastic material using thermomechanical processes such as extrusion or injection-molding.[2] However, this requires the presence of smaller molecules known as plasticizers, which play a double role: first, by favoring the destructuring of native starch, a granular semi-crystalline structure,[3] and, second, by reducing intermolecular interactions between starch chains in the amorphous state. Water is the most efficient starch plasticizer. Typically, an increase in moisture content of 1 wt% results in a decrease of 10 K of the glass transition of the biopolymer.[4] Unfortunately, water is a highly volatile molecule. This results in a high sensitivity of the thermomechanical properties of starch materials to relative humidity (RH). In order to better control mechanical properties, various non-volatile plasticizers have been studied.[4–6] This results in a wide range of mechanical properties that depend on plasticizer type and content.[7] Since the 1990s, polyols (in particular, glycerol) have emerged as the most widely used compounds for starch plasticization. Nevertheless, they present some severe drawbacks, the main one being their influence on plasticized starch recrystallization during storage.[8] This phenomenon results in a relatively fast stiffening and embrittlement of plasticized starch objects.[8]

In recent years, ionic compounds such as Ionic Liquids (ILs)[9–11] or Deep Eutectic Solvents (DES)[12–15] have been investigated as new types of plasticizers for starch.[9,16] Due to their strong ability to form hydrogen bonds, these compounds are highly efficient both during the destructuration stage of native starch and as glass transition depressors in the final plasticized starch material.[9,17,18] In addition, it has been observed that the presence of ILs or DES can hinder starch recrystallization during storage,[13,16] resulting in more stable thermomechanical properties. Last but not least, it was shown that these new plasticizers convey plasticized starch conductivity properties due to their ionic nature. However, the range of conductivity obtained is greatly influenced by ionic liquid structure and water content.[9,11,19]

Nevertheless, most of these scientific results have been obtained for commercial ionic liquids based on imidazolium cations that are currently too expensive and non-biodegradable (and toxic in many cases; only EMIM acetate was shown to display relatively low toxicity),[20] impeding their use in large-scale applications.[21–27] On the contrary, cholinium cation-based systems offer a promising alternative for cheap, environmentally-friendly ionic plasticizers for starch. The use of cholinium chloride-based DESs has already been studied.[12,16,28,29] Depending on the hydrogen donor counterpart used (glycerol, urea, *etc.*), various efficient plasticizers can be designed.

However, an even higher versatility can be expected from the design of cholinium-based ILs using different anions. The objective of the present work is to propose a small-scale screening approach that would make it possible to select the most efficient combinations for starch plasticization. A series of cholinium ILs was synthesized using naturally-derived counter anions with structures similar to compounds formerly known as starch plasticizers. For example, since citric acid and sodium lactate are known as starch plasticizers,[4] we studied cholinium lactate and cholinium tricitrate. Other anion structures not previously reported as starch plasticizers (furoate, salicylate,

---

[a] *LUNAM Université, IUT de Nantes, CNRS, GEPEA, UMR 6144, OPERP, 2 Avenue du Professeur Jean ROUXEL, BP 539, 44475 Carquefou, France. E-mail: gael.colomines@univ-nantes.fr*

[b] *LUNAM Université, CNRS, GEPEA, UMR 6144, CRTT, 37, Boulevard de l'Université, 44606 St Nazaire Cedex, France*

[c] *INRA Nantes-Angers, Unité Biopolymères Interactions Assemblages (BIA-UR 1268), Rue de la Géraudière, BP 71627, 44316 Nantes Cedex 3, France*

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6ra16573g

etc.) were also selected for their low toxicity and/or biocompatibility (cholinium salicylate has been recognized since 1960 as a well-tolerated analgesic).[30] The synthesis route of these bio-friendly ionic liquids (BioILs) was kept as simple as possible, focusing on starch plasticization studied by the characterization of water-casted films.

Experimental

Raw materials

Regular corn starch (amylopectin/amylose ratio: 70/30) was purchased from Tate & Lyle (Meritena 100), with an initial moisture content of 12%. Potassium acetate, furoic acid, cholinium chloride ([Chol][Cl]), sodium saccharinate, anhydrous methanol and 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]) were purchased from Sigma-Aldrich; Hydranal® and Composite 5 from Fluka; citric acid, L-lactic acid and sodium salicylate from Panreac; potassium hydroxide from LabOnline; absolute ethanol from Alcogroup; silver nitrate from Labosi; sodium chloride standard from Thermo Scientific; and deuterium oxide from Euriso-top. They were all of analytical grade and were used without further purification.

Syntheses and characterization of ionic liquids

Synthesis by ion exchange. [Chol][Cl] (0.2 mol) and carboxylate compound (0.2 mol of carboxylate equivalent) were separately dissolved in absolute ethanol to obtain a 0.25 mol L^{-1} solution. Carboxylate solution was added to a stirred [Chol][Cl] solution. A white precipitate of sodium chloride (or potassium chloride) was formed and removed by filtration after the solution was stirred for 1 h at room temperature. Ethanol was evaporated under vacuum. The compound obtained was the ionic liquid. The sodium chloride (or potassium chloride) obtained was dried at 100 °C for 24 h and then heated at 750 °C to eliminate organic compounds and to estimate the reaction yield in another way. Cholinium acetate ([Chol][Ace]) and cholinium salicylate ([Chol][Sal]) were synthesized according to this method. Cholinium saccharinate ([Chol][Sac]) was synthesized according to the Nockemann method[31] but without further purification. The NMR spectra of [Chol][Ace],[32] [Chol][Sal][33] and [Chol][Sac][31] have already been described. Our spectra were made in D_2O and present some differences in chemical shift due to the nature of the deuterated solvent.

Synthesis using the acid–base method

On the one hand, cholinium hydroxide ([Chol][OH]) was prepared according to the ion exchange method. Potassium hydroxide (0.1 mol) and [Chol][Cl] (0.1 mol) were dissolved in 800 mL and in 200 mL absolute ethanol, respectively. Hydroxide solution was added to a stirred [Chol][Cl] solution. The white precipitate was removed by filtration after stirring for 1 h at room temperature.

On the other hand, carboxylic acid (0.1 mol of carboxylic acid equivalent) was dissolved in ethanol (50 mL).

The carboxylic solution was added to the hydroxide solution. The solution was stirred at room temperature for 1 h. Ethanol was evaporated under vacuum. The compound obtained was the ionic liquid.

Tricholinium citrate ([Chol][Cit]), cholinium furoate ([Chol][Fur]) and cholinium lactate ([Chol][Lac]) were synthesized according to this method. After synthesis, ionic liquids were hermetically packaged and stored at 4 °C without further purification.

^{1}H-NMR analysis. NMR spectra were recorded on a Bruker Avance III 400 MHz NMR spectrometer. The chemical shifts are reported in parts per million, where s is a singlet, d a doublet, t a triplet, and m a multiplet. Unless otherwise specified, all the spectra were recorded at 30 °C from D_2O solutions.

The NMR spectra of [Chol][Lac] and [Chol][Cit] have already been described.[32]

[Chol][Fur]: ^{1}H NMR (400 MHz, D_2O, TMS): $\delta = 3.13$ (s, 9H, $-NCH_3$), 3.39 (m, 2H, $-NCH_2$), 3.95 (m, 2H, $-OCH_2$), 6.50 (m, 1H, $OC(COO^-)CHCHCH$), 6.97 (m, 1H, $OC(COO^-)CHCHCH$), 7.55 (m, 1H, $OC(COO^-)CHCHCH$).

Differential scanning calorimetry (DSC). Differential scanning calorimetry (DSC) analyses of the BioILs were performed with a Mettler Toledo DSC 1 STARe System DSC apparatus calibrated with indium. All samples were conditioned in 100 μL sealed aluminum pans. The following temperature program was used: precooling to −70 °C, temperature ramp from −70 to 120 °C at 10 °C min^{-1}, followed by cooling from 120 to −70 °C at 10 °C min^{-1} and, finally, heating from −70 to 120 °C at 10 °C min^{-1}. The melting point (T_m) values were determined at the onset of the peak during the second temperature ramp. In some cases, no melting peak was observed, or a cold crystallization was observed during the cooling step.

Thermogravimetric analysis (TGA). The thermal stability was investigated by two types of experiments under a nitrogen atmosphere:

(1) Anisothermal tests (temperature ramp from 30 °C to 750 °C at a heating rate of 10 °C min^{-1}) were performed on a LABSYS TGA/ATD (SETARAM). The mass loss curves were used to evaluate the onset of thermal degradation and the content of volatile compounds (% of volatile compounds, *i.e.*, the residual solvent from synthesis and water), which was defined as the weight loss between 30 °C and 100 °C.

(2) In addition, the static thermal stability at 130 °C (a temperature typically used in starch extrusion) was estimated using a TGA 2050 (TA Instruments). A temperature ramp from room temperature to 130 °C at 10 °C min^{-1} was applied, followed by an isotherm at 130 °C for 24 h. An initial mass loss was observed corresponding to the release of volatile impurities (like in non-isothermal experiments), followed by a slow decrease of mass at 130 °C. The slope of this second mass loss associated with the isothermal degradation of the ILs was measured in wt% per hour.

Chloride titration. The amount of residual chloride was obtained by potentiometric titration using an Ag-electrode (Orion®) and an Hg/Hg_2SO_4 reference electrode. Silver nitrate (0.1 mol L^{-1}) was used as titrant. Ionic liquid was dissolved and then diluted in deionized water until reaching an equivalence point at around 10 mL (estimated chloride concentration: approximately 0.01 mol L^{-1}). The amount of potassium (or sodium) chloride in the ionic liquid was deduced in wt%. A blank test (without ionic liquid) and a standard test (with a standard NaCl solution) were made to check the analysis.

Processing and characterization of thermoplastic starch films

Film casting. Films were obtained by the casting method.[4] Native starch was solubilized in a high-pressure stirred reactor at 130 °C for 20 minutes using 300 mL of ultrapure water, 12 g of starch and 3.6 g of plasticizer (BioIL, glycerol, *etc.*) representing 30 wt% of plasticizer in starch (dry basis). The procedure was performed under a nitrogen atmosphere to limit thermal degradation. The solution was evenly spread on a Teflon®-coated hotplate maintained at 70 °C until the film no longer adhered to the plate and edge curling occurred.

The transparent film obtained had a mean thickness of approximately 100 μm. In some cases, the film was too brittle to be removed and manipulated for further testing. Therefore, the corresponding couples of IL/starch were considered to be "non film-forming". For the film-forming systems, the stable films obtained were equilibrated at 21 °C and 57% relative humidity (RH) (saturated sodium bromide solution) for at least 2 weeks before being tested.

Water content in films. Water content in films was evaluated by Karl Fischer analysis (KF analysis). Before analysis, the films were immersed in methanol under stirring in order to extract water. Afterwards, the water content in the methanol was determined by the Karl Fischer method.

X-ray diffraction. In order to determine the crystallinity of the plasticized starch, diffraction diagrams were recorded using a Bruker D8 X-ray diffractometer (Karlsruhe, Germany) equipped with a GADDS detector. The following parameters were used: supply voltage: 40 kV; current intensity: 40 mA; characteristic radiation wavelength for a coordinated copper lamp: 0.1542 nm (Cu $K_{\alpha1}$). Measurements were conducted after 2 and 8 weeks at 21 °C and 57% relative humidity (RH).

Differential scanning calorimetry (DSC). Glass transition temperatures of the cast films were determined by differential scanning calorimeter on a Q100 apparatus (TA Instruments, New Castle, DE, USA). Stainless steel sealed pans were used in order to avoid water loss during tests. A scan was then performed from −60 to 100 °C at 10 °C min^{-1}. The glass transition temperature (T_g) was evaluated from the thermogram defined as the onset of the heat capacity increase.

Dynamic mechanical analysis under controlled relative humidity. RH-DMA measurements were made on a Metravib DMA 50 analyzer. The tensile mode was used at a frequency of 1 Hz, with a deformation amplitude of 0.01%, which is in the range of linear viscoelasticity. Measurements were performed on a piece of film measuring approximately 20 × 10 mm and with a thickness of about 100 μm. Simultaneously to the dynamic solicitation, a static force of 0.5 N was applied in order to maintain the film under tension. The storage modulus was measured under controlled atmosphere from approximately 5 to 95% relative humidity. The humidity was obtained by mixing a dry air flow with a water-saturated air flow, thermostated by a circulating water bath at 22 °C. The measurement temperature was kept constant at 22 ± 1 °C and the relative humidity was also measured using a humidity sensor close to the sample.

Results and discussion

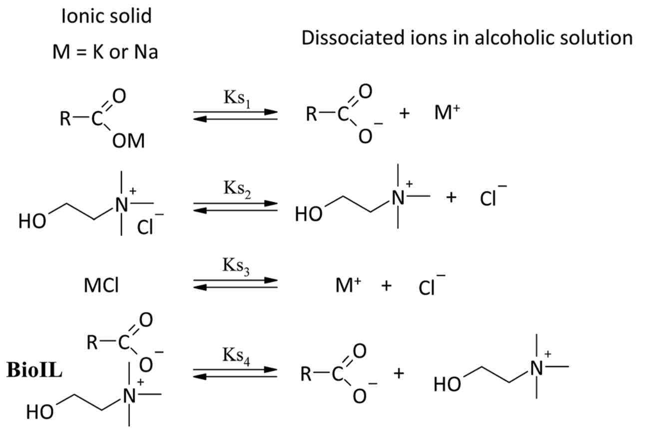
Synthesis and characterization of ionic liquid

The synthesis of cholinium-based ionic liquids has already been described by Fukaya *et al.*[34] However, this process requires the use of ion exchange resin made using several elutions and a large amount of solvent. Our synthesis method is adapted from the Nockemann method[31] based on metathesis. The equilibrium of ion solubility is used in this case. NaCl and KCl are known to be very slightly soluble in ethanol,[35] contrary to cholinium chloride.[36] When the alcoholic solution of the carboxylic acid compound (or alcoholic potassium hydroxide) and the cholinium chloride compound were mixed, KCl (or NaCl), precipitate formation was observed. The partial dissociation of the ions in ethanol seems to be sufficient to bring together the two cations and two anions and, therefore, the establishment of four solubility equilibria (Scheme 1).

The low solubility of KCl (or NaCl) shifts the equilibrium until the total precipitation of KCl (or NaCl) and, thus, the formation of the ionic liquid (or [Chol][OH]) in the supernatant. However, the success of the synthesis depends on the solubility of the starting carboxylate reagent. When its solubility is partial, the reaction is often unsuccessful. NMR analysis allows us to check the success of the reaction (Table 1). Moreover, by-product analysis (weighing, FTIR, calcination) confirms this. It should be noted that many tests were performed and the result is binary: either it works or it does not work at all, *i.e.*, the tripotassium citrate synthesis failed.

Chloride titration quantifies the residual salt (Table 1). The measured amount is around the same as in the Ma study,[37] which shows that this amount of salt limits starch recrystallization, which is positive.

Ethanol is used because it is potentially bio-based, easy to remove by evaporation (unlike water) and recyclable for many syntheses without any noticeable difference. According to the type of carboxylate, the carboxylate solution can be concentrated (*i.e.*, potassium acetate) without modifying the yield.



Scheme 1 Synthesis of BioIL.

Table 1 Composition of the synthesized BioILs

Synthetic route	BioIL	NMR ^{1}H anion/cation ratio (target)	Titration NaCl or KCl residual (wt%)	TGA residual volatile impurities (wt%)
Ion exchange	[Chol][Ace]	1.02 (1)	2.5	7
	[Chol][Sac]	0.78 (1)	3.0	4
	[Chol][Sal]	1.01 (1)	3.0	6
Acid–base reaction	[Chol][Cit]	2.83 (3)	2.5	14
	[Chol][Lac]	0.92 (1)	2.5	8
	[Chol][Fur]	1.01 (1)	2.0	4

Table 2 Thermal properties of the synthesized BioILs

Synthetic route	BioIL	DSC T_m (°C) (cold crystallization)	TGA (non-isotherm at 10 K min^{-1}) degradation onset temperature (°C)	TGA (isotherm at 130 °C) mass loss (wt%/per hour)
Ion exchange	[Chol][Ace]	51 (yes)	190	2.04
	[Chol][Sac]	40 (no)	250	0.02
	[Chol][Sal]	/(Liquid) (no)	241	0.05
Acid–base reaction	[Chol][Cit]	/(Liquid) (no)	194	0.72
	[Chol][Lac]	/(Liquid) (no)	213	0.29
	[Chol][Fur]	/(Liquid) (no)	226	0.41

When the ion exchange reaction fails or if the carboxylate compound is much more expensive than the carboxylic compound, the acid–base method is used and requires two synthesis steps (1st step: synthesis of [Chol][OH]; 2nd step: synthesis of BioIL). The [Chol][OH] solution can't be concentrated otherwise it will undergo partial degradation (color evolution observed in the final ionic liquid).

The volatile content shows that the evaporation step can be improved because we have limited the time and temperature of this evaporation step to avoid thermal degradation.

Regarding the melting temperatures (Table 2), all the BioIL synthesized meet the definition of an ionic liquid ($T_m \leq 100$ °C). Some of them even remain liquid despite low storage temperatures.

Thermal stability was considered both in non-isothermal conditions for a heating rate of 10 K min^{-1} and in isothermal conditions at 130 °C (temperature typically used for starch extrusion).

The onset temperatures of degradation for non-isothermal tests range between 190 °C and 290 °C. Moreover, the isothermal tests show that the BioILs are not completely stable at 130 °C. However, the mass loss per hour is lower than 1% for all the samples, except for [Chol][Ace] with a value of 2%.

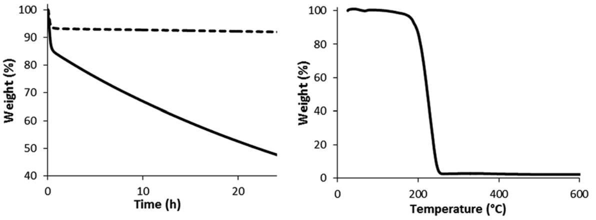


Fig. 1 TGA results of [Chol][Ace]: (right) at 10 °C min^{-1}; (left) isotherm at 130 °C; [Chol][Ace] (solid line); [Chol][Sal] (dotted line).

The BioILs with an aromatic structure (saccharin and salicylate) display the highest thermal stability (Fig. 1). This is not surprising since the salicylate group is known for its antioxidant effect.[38] Our BioILs clearly appear to be less thermally stable than imidazolium-based IL.[39] However, their thermal stability remains compatible with their use for producing plasticized starch by extrusion at temperatures close to 130 °C, since the typical residence times for that process are lower than 10 minutes. In the case of the less stable BioIL ([Chol][Ace]), this would result in a degradation/mass loss of 0.3%.

Properties of IL-plasticized starch films

Casting tests were conducted to identify BioILs that could be used as starch plasticizers (Table 3). Glycerol is used as a reference starch plasticizer. From a qualitative point of view, only three BioILs ([Chol][Ace], [Chol][Cit] and [Chol][Lac]) make it possible to obtain a comparable quality of films such as glycerol-based film. Film quality is qualified as “good” if the film is homogeneous and easy to handle. For other BioILs, the films obtained, which were fragile and less homogeneous, are qualified as “medium”. Finally, one BioIL did not make it possible to obtain films and so its film-forming properties are therefore qualified as “poor”.

At this time, it is difficult to qualify the influence of the anion structure on film quality because not enough different structures were studied. Nevertheless, this approach could be easily applied to a larger screening campaign.

Table 3 Properties of starch/BioIL films obtained by casting (equilibrium conditions: 21 °C, 57% RH)

Compound: starch (77 wt%)/ BioIL (23 wt%)	Film-forming	Recrystallization after 8 weeks	Moisture content (% wet basis)	T_g by DSC (°C)
Starch/[Chol][Ace]	Good	B-Type	15.2 ± 0.2	7 ± 0.5
Starch/[Chol][Sac]	Poor	None	11.7 ± 0.2	20 ± 0.5
Starch/[Chol][Sal]	Medium	None	11.9 ± 0.2	9 ± 0.5
Starch/[Chol][Cit]	Good	None	16.7 ± 0.2	17 ± 0.5
Starch/[Chol][Lac]	Good	None	16.8 ± 0.2	-6 ± 0.5
Starch/[Chol][Fur]	Medium	None	12.8 ± 0.2	2 ± 0.5
Starch/glycerol (reference)	Good	B-Type	11.6 ± 0.2	-5 ± 0.5

Evolution of crystallinity of starch/BioIL film

X-ray diffraction analyses were made after 2 and 8 weeks of conditioning at 21 °C and 57% relative humidity (RH) (saturated sodium bromide solution).

These measurements highlight the disappearance of the native crystal structure (A-type for corn starch) during the solubilization of starch before the casting process. Furthermore, we did not observe V-type emergence for any of the samples.[40]

However, depending on the BioIL used, B-type recrystallization may occur. In Fig. 2, two cases can be observed: on one hand, [Chol][Ace] seems to promote the B-type recrystallization with the presence of a characteristic peak at 2θ 17° after only 2 weeks (behavior similar to that of starch/glycerol films). On the other hand, the use of [Chol][Lac], [Chol][Cit], [Chol][Fur], [Chol][Ace] and [Chol][Sal] seems to preserve the amorphous structure of plasticized starch films as demonstrated by the absence of a diffraction peak, at least for the investigated storage time of 8 weeks. Nevertheless, slow recrystallization cannot be excluded.

This confirms the strong interest in ionic liquids for the limitation of starch recrystallization, which had already been reported for imidazolium-based systems.[13,16] However, the influence of the ionic liquid structure on this effect seems difficult to predict.

Glass transition temperature of starch/BioIL film (DSC)

The glass transitions of films containing different ionic liquids were determined from the thermograms shown in Fig. 3 for some of the examples. They are reported in Table 3 and plotted in Fig. 4 as a function of water content. Water content results from conditioning at a relative humidity of 57% and also strongly depends on the type of ionic liquid. The figure clearly shows that the type of ionic liquid is the first-order parameter controlling the decrease in T_g, *i.e.*, the "efficiency of the plasticizer".

Fig. 4 highlights the influence of the BioIL anion on the T_g and water content of the film. However, glycerol seems to be the most efficient T_g depressor compared to all of the BioILs. Indeed, starch/glycerol film has the lowest T_g and the lowest water content. If we consider only these glass transition values, the influence of BioIL on starch thus seems to be similar to a conventional plasticizer such as glycerol, but less efficient.

To compare our results with the previous study[9] on [Bmim][Cl], we prepared an additional casted sample with this ionic liquid, confirming the better plasticizing properties of [Bmim][Cl] compared to glycerol. This suggests that the T_g and water uptake values of plasticized starch films are mainly influenced by the type of cation. Nevertheless, the results obtained for the present series of BioILs also show that the type of anion makes it possible to modulate these properties.

Moreover, the evolution of the mechanical properties of the starch/BioIL films with relative humidity (Fig. 5) shows that both the type of anion and cation greatly affect the thermo(hydro)mechanical behavior of starch.

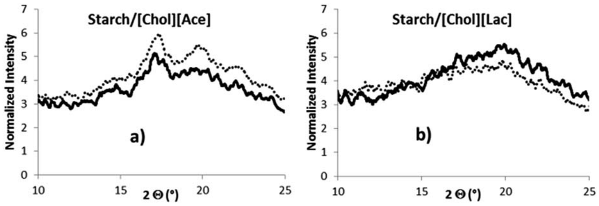


Fig. 2 XRD diffractograms of plasticized starch-casted films using: (a) [Chol][Ace] and (b) [Chol][Lac] as plasticizers; after 2 week conditioning (solid line) and after 8 week conditioning (dotted line).

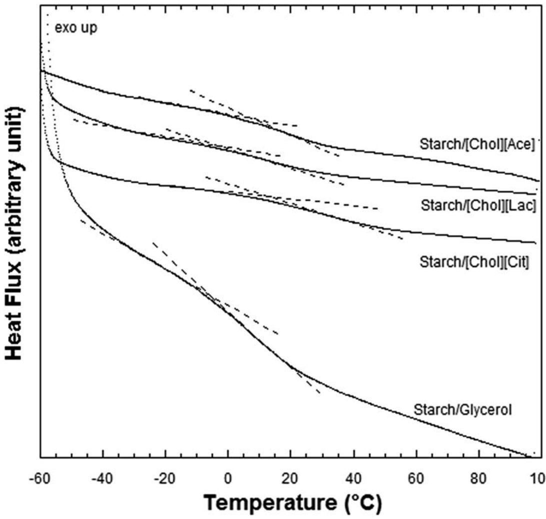


Fig. 3 Examples of DSC thermogram of BioIL–plasticized starch films (dotted lines indicated the glass transition onset).

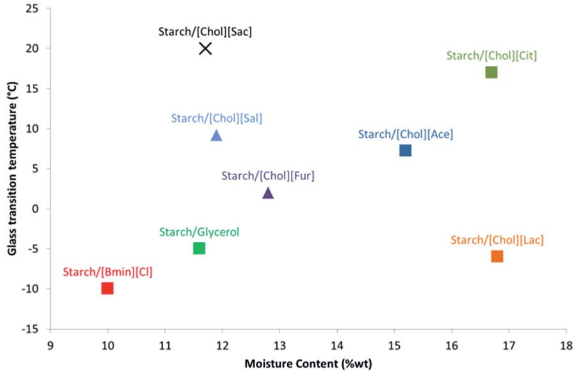


Fig. 4 Glass transition temperature of starch/BioIL film according to moisture content. Squares (■) represent starch/BioIL mixtures with good film-forming properties, triangles (▲) represent medium film-forming properties, and crosses (×) represent poor film-forming properties. Starch/[Bmim][Cl] and starch/glycerol mixtures were used as references (the precision of the measurements is ±0.5 °C for T_g values, and ±0.2% for moisture content).

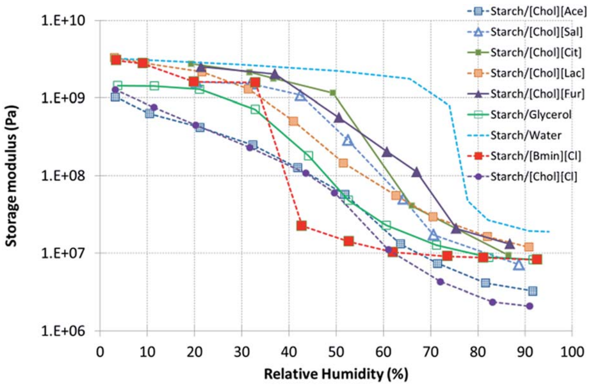


Fig. 5 Influence of the relative humidity on the thermomechanical properties of starch/BioIL films.

The dynamic mechanical analysis of BioIL/starch film makes it possible to measure the evolution of the storage modulus during a relative humidity moisture scan. Relaxation of mechanical stress is observed within a humidity range from 30 to 70%. These data are very informative and complementary to T_g data.

The modulus changes with humidity can be "flat" or "rough", depending on the type of plasticizer. Despite a quite high T_g and high water level for starch/[Chol][Ace], the modulus changes are more continuous in comparison with starch/[Bmim][Cl], which shows a very abrupt modulus change. In contrast, despite a low T_g of −6 °C for starch/[Chol][Lac], the modulus remains quite high over the domain of humidity. These results provide direct information on the behavior of films in conditions of use and under variations in humidity.

Conclusion

A family of biofriendly ionic liquids (BioIL) based on a food cation (cholinium) and low toxic anions with different structures was investigated for starch plasticization applications. To synthesize these BioILs, two easy and fast synthetic routes were selected: an ion exchange reaction, direct and economical, and a two-step acid–base reaction.

We studied the starch plasticizing properties of six BioILs: five of them made it possible to obtain plasticized starch films by casting. In comparison to the glycerol/starch film (reference), the BioILs led to a stronger water absorption and a smaller decrease in the glass transition temperature. The structure of the anion, however, had a great influence on thermo(hydro) mechanical behavior, as well as the recrystallization of the plasticized starch. Only [Chol][Ace] promoted the recrystallization of the film, while the other BioIL–plasticized starch remained amorphous upon aging for the studied period of 8 weeks.

The screening approach of starch plasticization properties described in the present work could be applied to other types of newly synthesized ionic liquids available in small quantities.

In a future paper, we will study the extrusion of starch/BioIL mixtures in more detail since they require larger quantities of ionic liquid.

Acknowledgements

We are grateful for the financial support provided by GDR BioMatPro and funded by INRA and the CNRS, and the LIMPONAN project funded by the "Région de Pays de la Loire" Council. We thank O. Camatte, M. Oxeant and B. Pontoire for their experimental contributions.

Notes and references

1 J. B. van Beilen and Y. Poirier, *Adv. Biochem. Eng./Biotechnol.*, 2007, **107**, 133–151.
2 H. Liu, F. Xie, L. Yu, L. Chen and L. Li, *Prog. Polym. Sci.*, 2009, **34**, 1348–1368.
3 J. W. Donovan, *Biopolymers*, 1979, **18**, 263–275.
4 D. Lourdin, L. Coignard, H. Bizot and P. Colonna, *Polymer*, 1997, **38**, 5401–5406.
5 A. L. Da Roz, A. J. F. Carvalho, A. Gandini and A. A. S. Curvelo, *Carbohydr. Polym.*, 2006, **63**, 417–424.
6 X. Ma and J. Yu, *Carbohydr. Polym.*, 2004, **57**, 197–203.
7 N. Follain, C. Joly, P. Dole and C. Bliard, *J. Appl. Polym. Sci.*, 2005, **97**, 1783–1794.
8 J. J. G. van Soest and F. G. Vliegenthart, *Trends Biotechnol.*, 1997, **15**, 208–213.
9 A. Sankri, A. Arhaliass, I. Dez, A. C. Gaumont, Y. Grohens, D. Lourdin, I. Pillin, A. Rolland-Sabate and E. Leroy, *Carbohydr. Polym.*, 2010, **82**, 256–263.
10 K. Wilpiszewska and T. Spychaj, *Carbohydr. Polym.*, 2011, **86**, 424–428.
11 F. Xie, B. M. Flanagan, M. Li, R. W. Truss, P. J. Halley, M. J. Gidley, T. McNally, J. L. Shamshina and R. D. Rogers, *Carbohydr. Polym.*, 2015, **122**, 160–168.
12 A. P. Abbott, A. D. Ballantyne, J. P. Conde, K. S. Ryder and W. R. Wise, *Green Chem.*, 2012, **14**, 1302–1307.

13 M. Zdanowicz, T. Spychaj and H. Maka, *Carbohydr. Polym.*, 2016, **140**, 416–423.
14 M. Zdanowicz and T. Spychaj, *Polimery*, 2011, **56**, 861–864.
15 M. Zdanowicz and C. Johansson, *Carbohydr. Polym.*, 2016, **151**, 103–112.
16 E. Leroy, P. Decaen, P. Jacquet, G. Coativy, B. Pontoire, A.-L. Reguerre and D. Lourdin, *Green Chem.*, 2012, **14**, 3063–3066.
17 A. Bendaoud and Y. Chalamet, *Carbohydr. Polym.*, 2013, **97**, 665–675.
18 F. Xie, B. M. Flanagan, M. Li, P. Sangwan, R. W. Truss, P. J. Halley, E. V. Strounina, A. K. Whittaker, M. J. Gidley, K. M. Dean, J. L. Shamshina, R. D. Rogers and T. McNally, *Carbohydr. Polym.*, 2014, **111**, 841–848.
19 N. Wang, X. Zhang, H. Liu and B. He, *Carbohydr. Polym.*, 2009, **76**, 482–484.
20 H. Wang, G. Gurau and R. D. Rogers, *Chem. Soc. Rev.*, 2012, **41**, 1519–1537.
21 D. J. Couling, R. J. Bernot, K. M. Docherty, J. K. Dixon and E. J. Maginn, *Green Chem.*, 2006, **8**, 82–90.
22 K. M. Docherty and C. F. Kulpa Jr, *Green Chem.*, 2005, **7**, 185–189.
23 T. P. T. Pham, C.-W. Cho and Y.-S. Yun, *Water Res.*, 2010, **44**, 352–372.
24 J. Pernak, K. Sobaszkiewicz and I. Mirska, *Green Chem.*, 2003, **5**, 52–56.
25 C. Pretti, C. Chiappe, I. Baldetti, S. Brunini, G. Monni and L. Intorre, *Ecotoxicol. Environ. Saf.*, 2009, **72**, 1170–1176.
26 C. Pretti, M. Renzi, S. Ettore Focardi, A. Giovani, G. Monni, B. Melai, S. Rajamani and C. Chiappe, *Ecotoxicol. Environ. Saf.*, 2011, **74**, 748–753.
27 J. Neumann, S. Steudte, C.-W. Cho, J. Thoeming and S. Stolte, *Green Chem.*, 2014, **16**, 2174–2184.
28 A. P. Abbott, T. Z. Abolibda, S. J. Davis, F. Emmerling, D. Lourdin, E. Leroy and W. R. Wise, *RSC Adv.*, 2014, **4**, 40421–40427.
29 S. Ramesh, R. Shanti and E. Morris, *Carbohydr. Polym.*, 2012, **87**, 701–706.
30 R. H. Broh-Kahn, *Int. Rec. Med.*, 1960, **173**, 217–233.
31 P. Nockemann, B. Thijs, K. Driesen, C. R. Janssen, K. Van Hecke, L. Van Meervelt, S. Kossmann, B. Kirchner and K. Binnemans, *J. Phys. Chem. B*, 2007, **111**, 5254–5263.
32 Z. Li, X. Liu, Y. Pei, J. Wang and M. He, *Green Chem.*, 2012, **14**, 2941–2950.
33 Y. Yu, X. Lu, Q. Zhou, K. Dong, H. Yao and S. Zhang, *Chem.–Eur. J.*, 2008, **14**, 11174–11182.
34 Y. Fukaya, Y. Iizuka, K. Sekikawa and H. Ohno, *Green Chem.*, 2007, **9**, 1155–1157.
35 S. P. Pinho and E. A. Macedo, *J. Chem. Eng. Data*, 2005, **50**, 29–32.
36 J. M. Lopes, A. B. Paninho, M. F. Molho, A. V. M. Nunes, A. Rocha, N. M. T. Lourenco and V. Najdanovic-Visak, *J. Chem. Thermodyn.*, 2013, **67**, 99–105.
37 X. Ma, J. Yu, K. He and N. Wang, *Macromol. Mater. Eng.*, 2007, **292**, 503–510.
38 A. B. Vipper, *Lubr. Sci.*, 1996, **9**, 61–70.
39 C. Maton, N. De Vos and C. V. Stevens, *Chem. Soc. Rev.*, 2013, **42**, 5963–5977.
40 J. J. G. van Soest, S. H. D. Hulleman, D. de Wit and J. F. G. Vliegenthart, *Ind. Crops Prod.*, 1996, **5**, 11–22.