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Compatibilization of starch–zein melt processed blends by an ionic liquid used as plasticizer

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ABSTRACT

An ionic liquid (1-butyl-3-methyl imidazolium chloride [BMIM]Cl) was used as a plasticizer in starch, zein and their blends; and compared to glycerol, a classical plasticizer of starch. Thermoplastic plasticized biopolymer materials were obtained by melt processing using a twin screw microcompounder. Such a device allows simulating a twin screw extrusion process on small batches of a few grams, and to evaluate the necessary specific mechanical energy input for native starch destructurization; and the final apparent melt viscosity. Both were shown to be significantly reduced for starch in presence of [BMIM]Cl (compared to glycerol), while zein processing behavior was less sensitive to the plasticizer used. This induces significant starch/zein viscosity ratio differences, which affect melt mixing of the starch zein blends. In starch rich blends, this results in smaller zein aggregates in the case of [BMIM]Cl.

The characterization of the materials indicates that, compared to glycerol, the use of [BMIM]Cl leads to less hygroscopicity, a more efficient plasticization of both starch and zein phases and a compatibilization of starch/zein blends.

1. Introduction

From simple grains to wood, many vegetal structures involve combinations of different biopolymers. Using the vocabulary of polymer materials scientists, one could say that nature has developed highly efficient alloys of biopolymers (Utracki, 2002). From this perspective, perhaps the most striking point is that in many cases, those alloys involve the interfacial compatibilization of blends of hydrophobic and hydrophilic biopolymers.

Inside an maize grain, in which starch granules are embedded in a continuous protein rich minor phase, the interfacial adhesion between starch (hydrophilic) and proteins (mostly hydrophobic) phases are strong enough to ensure cohesive breaking of the material: when a grain is broken, most cracks propagate through the starch granules, not at the interface between starch and proteins! In that particular example, the nature of the interfacial interactions between the hydrophobic and hydrophilic polymer phases remains poorly understood. Nevertheless, since the work of Barlow, Buttrose, Simmonds, and Vesk (1973), the main assumption is the presence of an interphase containing water soluble proteins and partially water soluble polysaccharides. When cereal flour is melt processed to obtain a bioplastic, this complex interphase between starch and proteins is destroyed, resulting in an incompatible blend with poor mechanical properties. In addition, starch becomes the continuous phase giving to the material its strong sensitivity to moisture.

The current scientific state of art points out that the main problem is the thermodynamic incompatibility between starch and proteins. Chanvrier, Colonna, Dellavalle, and Lourdin (2005) and Chanvrier, Dellavalle, and Lourdin (2006) have been studying the structure and mechanical properties of glassy materials obtained by melt processing of corn flour and starch/zein model blends (zein being the main protein present in corn flour) in presence of water. Chanvrier et al. (2006) showed that mechanical properties of processed corn flour and starch/zein model blends are lower than those of both pure starch and pure zein based materials. The starch/protein interface was shown to play a major role due to the incompatibility between starch matrix and zein dispersed particles that are both in the glassy state at room temperature, with almost identical glass transition temperatures. For the same system, Guessama, Sehaki, Lourdin, and Bourmaud (2008) obtained a map of mechanical properties around zein particles (inside the starch matrix) by nanoindentation experiments. Mechanical properties of the continuous and the dispersed phase show a systematic collapse of mechanical modulus and hardness close to the interface. This behavior can be interpreted as a lack of adhesion between the matrix and particles. It suggests that the high fragility of corn flour-based materials is due to matrix–particle debonding effect under mechanical solicitation (Guessama et al., 2008).

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Blends of starch and zein, plasticized by glycerol have also been studied by Corradini, de Medeiros, Carvalho, Curvelo, and Mattoso (2006), Corradini, Carvalho, Curvelo, Agnelli, and Mattoso (2007), Habeych, Dekkers, van der Goot, and Boom (2008) and Habeych, van der Goot, and Boom (2010). Corradini et al. (2006) showed that contrary to water plasticized starch–zein blends, in presence of glycerol (23% and above), the continuous starch matrix is in the rubbery state at room temperature, while the zein dispersed phase is in the glassy state. The glass transition temperatures measured in dynamic mechanical analysis for the two phases differ by 40 °C or more, depending on the starch/zein ratio. They conclude that the starch phase is more plasticized than the zein phase and suggest a partition of the plasticizer between the two phases.

As for unplasticized blends, Habeych et al. (2008) showed that the absence of adhesion between glycerol plasticized starch and zein phases, results in poor mechanical properties. In a later work, Habeych et al. (2010) showed that compatibilization can be obtained by grafting reactions between the two phases, during melt mixing. Nevertheless, their results also show a degradation of the starch matrix properties due to the necessary chemical modification.

If we look at the toolbox developed during the last decades for the compatibilization of synthetic polymer blends (Utracki, 2002). The various compatibilization strategies used involve an interphase between the two polymers. Most of the time, an organic phase (surfactants, third polymer, graft or bloc-copolymer of the 2 polymers) introduced in the form of an additive or synthesize during reactive melt mixing as applied by Habeych et al. (2010).

In a recent work on starh/polyethylene blends, Taguet, Huneault, and Favis (2009) proposed a new strategy for compatibilization in which small molecules such as a plasticizer are involved. In their case, a glycerol rich layer located between starch and polyethylene phase is formed during melt processing. It is shown to reduce interfacial tension, allowing the compatibilization.

In the present work, we propose to use of an ionic liquid as co-plasticizer of starch and zein. Recently, we showed that starch can be efficiently thermoplasticized by 1-butyl-3-methyl imidazolium chloride ([BMIM]Cl) (Sankri et al., 2010), leading to water sensitivity and thermomechanical properties significantly different from those of classical glycerol plasticized starch. The same ionic plasticizer will be used to plasticize zein and starch zein blends. Effectively, Biswas, Shogren, Stevenson, Willett, and Bhowmik (2006), showed that both starch and zein are soluble in [BMIM]Cl.

2. Materials and methods

2.1. Materials

Maize starch was purchased from Tate & Lyle (Meritena 100) and Zein from Aldrich. Their initial moisture contents were 12 wt% and 6 wt%, respectively. Plasticizers used were glycerol (Aldrich), [BMIM]Cl, purchased in crystallized form under argon atmosphere (Solvionic, France).

2.2. Processing

Thermoplasticization of starch, zein and their blends, by the two plasticizers, was performed in a laboratory scale microcompounder (Fig. 1) allowing the preparation of batches of typically 5–10 g. The Minilab microcompounder (Thermo Haake) is a conical twin screw system with a backflow channel. This allows using the Minilab as a batch mixing reactor given that the material can be recirculated rather than exiting through the die. The conical twin screw system allows simulating the performance of a co-rotating or a counter rotating twin screw extruder. In all operations, the co-rotation operation was applied.

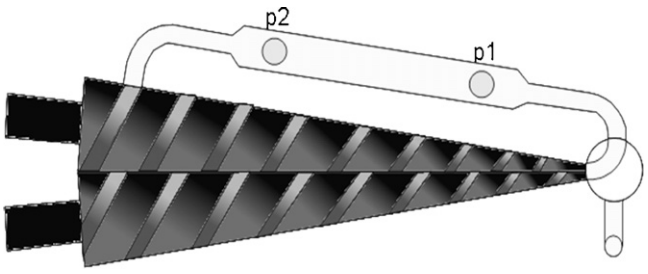

Fig. 1. Schematic view of the microcompounder Haake Minilab. The conical screws have a length of 12 cm. The melt can be extruded (continuous mode) or recirculated (batch mode). The total volume of the loop is 7 cm^3. The feeding zone is located in the large side of screws, with a piston system, perpendicular to the plane of the loop.

The following procedure was used: starch or/and zein powders (12% and 6% water, respectively) were premixed with the plasticizer (23 wt% in all formulations) in a mortar less than 5 min before melt processing. The following starch/zein ratio have been prepared: 100/0; 90/10; 70/30; 50/50; 30/70; 10/90 and 0/100. The starch/zein ratio 90/10 is assumed to be representative of the composition of corn flour.

The powder mix obtained was then introduced in the microcompounder at 130 °C (this temperature was chosen due to the low moisture level), at low rotation speed (50 rpm) of the twin co-rotating screws. The introduction into the microcompounder is done by pushing the powder with a piston. The filling of the machine required proceeding in 3 steps; introducing each time approximately 2–3 g of powder mix, pushed inside the recirculating cavity. This filling operation could be done reproducibly in 100–140 s for all the formulations. After complete filling, the (recirculating) mixing was continued for 60 s at 50 rpm and then the TPS was extruded through the exit die.

For each formulation, 3 batches were prepared in order to ensure the reproducibility of the mixing conditions and of the melt behavior, which were characterized by recording the torque signal and the pressure drop in the recirculating channel on the machine.

The specific mixing energy (SME) was defined as follow:

$$\mathrm{SME} = \int_0^t \frac{T \cdot 2\pi \cdot n}{M \cdot 60} \cdot dt \tag{1}$$

where T is the torque signal at mixing time t, n is the (constant) screw speed (rpm) and M is the loaded mass.

Note that due to the fact that the introduction of the material into the machine is done in 3 steps (as described above), this calculated SME can only be used for comparisons between different formulations and should not be regarded as the exact mixing energy received by the material.

The apparent viscosity of the melt was obtained assuming that the volume flow rate Q (m^3/s) through the recirculating capillary channel is proportional to the screw speed, n (rpm), following the approach proposed by the microcompounder manufacturer, described by Chabrat, Rouilly, Evon, Longieras, and Rigal (2010). The shear stress (τ), the apparent shear rate ($\dot{\gamma}$) in the capillary and the resulting capillary viscosity are given by:

$$\tau = \frac{h}{2 \cdot \Delta L} \Delta P \tag{2}$$

$$\dot{\gamma} = \left(\frac{6}{w \cdot h^2}\right) \cdot Q = \left(\frac{6}{w \cdot h^2}\right) \cdot C \cdot n \tag{3}$$

$$\eta = \frac{\tau}{\dot{\gamma}} = \left(\frac{w \cdot h^2}{12 \Delta L}\right) \cdot \frac{1}{C \cdot n} \cdot \Delta P \tag{4}$$

where h and w are the depth and the width of the recirculating channel, respectively; ΔL is the distance between the pressure sensors in the channel and ΔP is the (constant) pressure drop in the recirculating channel.

C is a calibration constant, equal to 8×10^{-7} according to the microcompounder manufacturer. This value has been calculated for a polyolefin material and is not valid for the starch and protein materials we have been studying. Nevertheless, assuming that the order of magnitude of C should not undergo strong variations from one material to another, we have been using this value for all calculations. Consequently, in the discussion the apparent viscosity values will only be compared between the different formulations studied. In all our experiments, the screw speed was constant (50 rpm), so that the calculated apparent shear rate was 173 s^{-1}.

After melt mixing, all samples were thermomolded into films at 110 °C for 5 min and the cooled down to 60 °C under pressure (20 MPa). The films obtained had a typical thickness of 500 μm. They were stored at 25 °C under a controlled relative humidity of 50%. The increasing weight of each film (due to water uptake) was measured regularly. No more variations were observed after 3 days, showing that the equilibrium water uptake (at 50% RH) was reached, allowing the characterization of the samples.

2.3. Characterization

2.3.1. Composition

The *water content* of the films was measured by weight loss after drying on samples of 1 g in an oven at 90 °C under vacuum during 4 h. No significant additional weight losses were observed for longer drying times.

2.3.2. Confocal scanning laser microscopy (CSLM) and image analysis

CSLM (NIKON A1) was used for examining the organization of the protein in extruded and molded corn flour and starch–zein blends. For each sample, three sections of different strips were prepared using a cryotome (20 μm section thickness). The sections were placed on flat glass slides and protein coloration was performed by staining for 2 min in a 0.01% (w/v) acid fuchsin solution diluted in 1% acetic acid (v/v).

Sections were rinsed with distilled water: using a Pasteur pipette, a water drop was put on the section surface and removed after approximately 1 min. This allowed the excess of fuchsin dye to migrate in the water drop and to be removed. This operation was repeated four times. The sections were subsequently dried on their glass slides at 25 °C (50% RH) during one week before observation.

For the observation, water and a coverslip were added. Samples were examined in the epifluorescence mode of the microscope, excited by a laser beam at 561.6 nm and the emitted light was selected by a band-pass filter (595 ± 25 nm). Images were acquired with CSLM parameters of pinhole (20), objective (20) and zoom (1.5).

Image analysis for particles sizes evaluations are generally developed with a segmentation step in order to obtained binary images (white particles with a black background). This was not possible with our images, on which the gray level of particles varies a lot. Therefore, the image analysis was performed directly. Considering the gray level variations, small particles produce more changes than large particles. This image texture evaluation was evaluated by mathematical morphology, as described by Devaux et al. (2006). Mathematical morphology is a set of operations which compare each portions of image to a structuring element, erosions and dilations are the basics ones (Serra, 1982). Erosion causes a reduction of white objects. Dilation is the dual operation. Opening is a combination of an erosion and a dilation. The effect of an opening is to remove white objects considering their morphology without modify others object's area. Objects disappear if one of their dimensions is smaller than the structuring element width. The effect of an opening is comparable of a sieving. A series of opening of increasing sizes are applied and the sum of gray level (V) is calculated at each step. The V decreasing depends on the sizes of the objects affected at each opening. The V variation curve obtained is normalized according to the initial value and derived to obtain a curve comparable to a particle size distribution. Image analysis routines were developed with Matlab 7.9.0.

2.3.3. Dynamic mechanical thermal analysis

A DMTA apparatus (MKIV, Rheometrics Scientific, USA) was used in the tensile mode at a frequency of 1 Hz with a deformation amplitude of 0.1%. This value is in the range of linear viscoelasticity, and any deviation from this domain during heating was discarded and assumed to be the same for all samples tested. The heating rate was set at 3 °C min^{-1}. Prior to DMTA trials, films were coated with a silicone-based hydrophobic grease to limit dehydration during experiments above room temperature. It has been previously shown that such a thin coating of grease has no effect on the thermomechanical properties (Chanvrier et al., 2005).

The following starch/zein ratio plasticized by glycerol or [BMIM]Cl have been characterized: 100/0, 90/10, 50/50, 10/90 and 0/100.

Mechanical tensile tests were conducted on ASTM D412 type dogbone sampled cut from the films, using an INSTRON 1122 universal press at 10 mm/min. No extensometer could be used due to the sticky behavior of the samples. The strain was defined as the ratio of the displacement of cross head × to the initial length of the sample l_0.

$$\varepsilon = \frac{x}{l_0} \tag{5}$$

The true stress was defined has the ratio of the force F to the effective cross section of the sample. Assuming that the material has a Poisson coefficient of 0.5 (rubbery behavior) this is obtained by dividing the initial cross section S_0 by $(1+\varepsilon)$:

$$\sigma = \frac{F}{S_0} \cdot (1+\varepsilon) \tag{6}$$

Note that this correction of the stress is only significant for large deformations.

The stress–strain curved were analyzed in order to obtain the elongation at break (%), the breaking stress (MPa) and the elastic modulus (MPa) defined as the secant modulus at 5% elongation.

3. Results

3.1. Processing

As stated in Section 2, the mixing time was arbitrarily fixed to 200 s for all other formulations. This total mixing time was chosen after a preliminary study on glycerol plasticized starch, taken as a reference. Fig. 2 shows, the typical curves obtained for this formulation for a mixing time of 300 s, putting in evidence that the torque and pressure drop values reached before 200 s remain constant afterwards, indicating complete melting of starch and no loss of plasticizer, or degradation of the material.

Figs. 3 and 4 show the recirculating channel pressure drop signals obtained for starch, zein and their blends, plasticized by glycerol and [BMIM]Cl, respectively. The apparent viscosities calculated for plasticized starch and zein are reported in Table 1.

For all formulations, the torque signal evolution with time showed similar behavior to that of the pressure drop. It was not reproduced here, the pressure drop signal being more sensitive, especially for high zein content blends which have very low melt

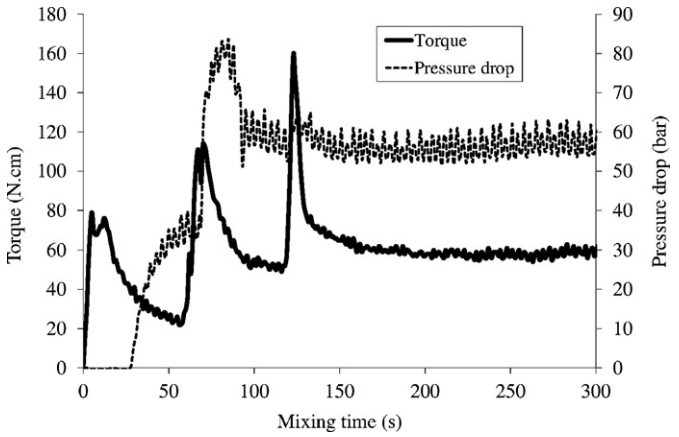

Fig. 2. Typical curves obtained for the torque and recirculating channel pressure drop signals for glycerol plasticized starch. The 3 peaks observed on the torque curve correspond to the 3 steps introduction of the powder premix with the piston of the machine.

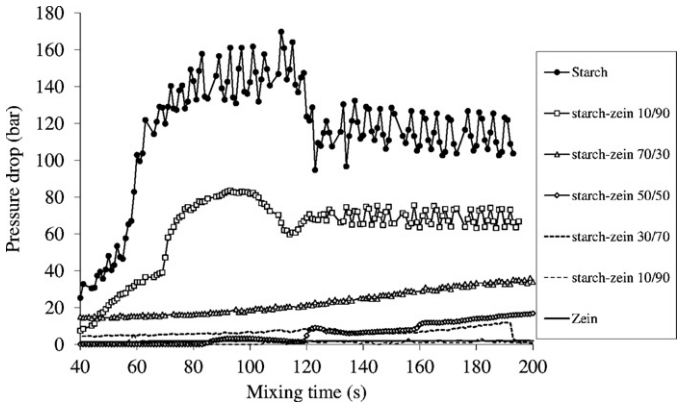

Fig. 3. Pressure drop curves for glycerol plasticized blends recorded during melt mixing in the twin screw microcompounder.

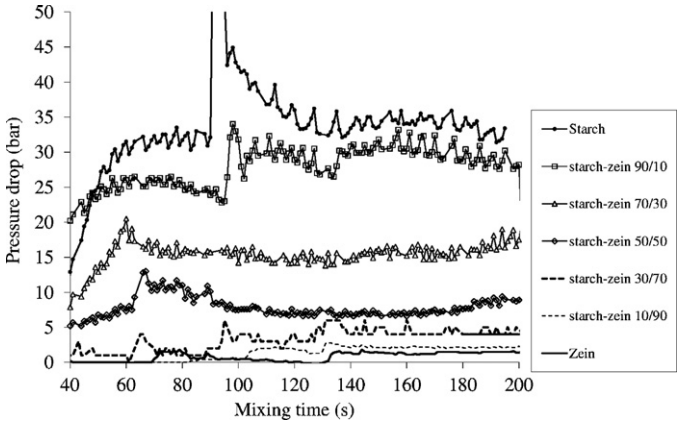

Fig. 4. Pressure drop curves for [BMIM]Cl plasticized blends recorded during melt mixing in the twin screw microcompounder.

Table 1
Specific mechanical energy inputs and melt viscosities of starch and zein, in presence of glycerol and [BMIM]Cl.

Plasticizer	Glycerol	[BMIM]Cl
SME (kJ/kg) (starch)	85	47
SME (kJ/kg) (zein)	5	3
Viscosity (Pa s) (starch)	784	236
Viscosity (Pa s) (zein)	5	7
Viscosity ratio	0.005	0.030

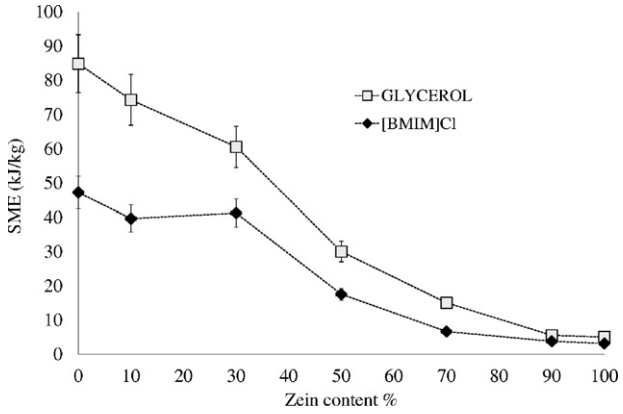

Fig. 5. Influence of the zein content on the specific mechanical energy received by the glycerol and [BMIM]Cl plasticized blends. The zein content is calculated with respect to starch. (10% zein means a blend of 90 part of starch, 10 parts of zein and 30 parts of plasticizer).

viscosities. The torque signal was used to calculate the SME values, plotted in Fig. 5 and reported in Table 1.

After processing into films, all plasticized starch samples were translucent, without any coloration; while the plasticized zein samples were yellow/brown colored and more or less opaque. All starch–zein blends showed intermediate appearance, with a more pronounced loss of translucent character above 50% of zein.

3.2. Laser confocal scanning microscopy

In all LCSM micrographs, the starch rich phase appears in black and the zein rich phase in white. The size of the micrographs shown in Figs. 6 and 7 is 425 μm × 425 μm. Fig. 6 allows to compare the morphology of the starch rich blends (90/10; 70/30 and 50/50 starch/zein ratio) with glycerol and [BMIM]Cl. For both plasticizers, an apparently co-continuous morphology is observed for the 50% zein blends. For the blends with lower zein content, a dispersion of zein aggregates in the continuous starch matrix is observed. For a zein content of 30%, fibrillar like aggregates of zein can be observed in presence of [BMIM]Cl. Fig. 7 Shows an example for zein contents above 50%, dispersion of large starch aggregates into a continuous zein matrix can be observed. The two micrographs correspond to the same sample (starch/zein 30/70 with [BMIM]Cl) as a topography of the sample can be observed, allowing to confirm the presence of very large starch aggregates. Fig. 8 shows the result of the image analysis performed on the micrographs by mathematical morphology. The decay of the percentage of surface variation vs. the increase of the opening size, gives information about the zein domains size distribution. For starch rich blends containing 10% zein which clearly has a nodular morphology, it can be seen that the blends containing [BMIM]Cl (1090b) presents more smaller zein nodules than the blends plasticized by glycerol (1090g). Very fine zein particles can be observed with sizes below 1 μm.

Table 2
Water contents of all extruded samples equilibrated at 50% RH.

Zein/starch ratio	Water content (%) with glycerol	Water content (%) with [BMIM]Cl
0	12.9 ± 0.2	10.0 ± 0.2
10	12.9 ± 0.2	9.7 ± 0.2
30	12.3 ± 0.2	10.0 ± 0.2
50	12.1 ± 0.2	9.9 ± 0.2
70	11.5 ± 0.2	9.8 ± 0.2
90	11.5 ± 0.2	9.4 ± 0.2
100	10.4 ± 0.2	9.0 ± 0.2

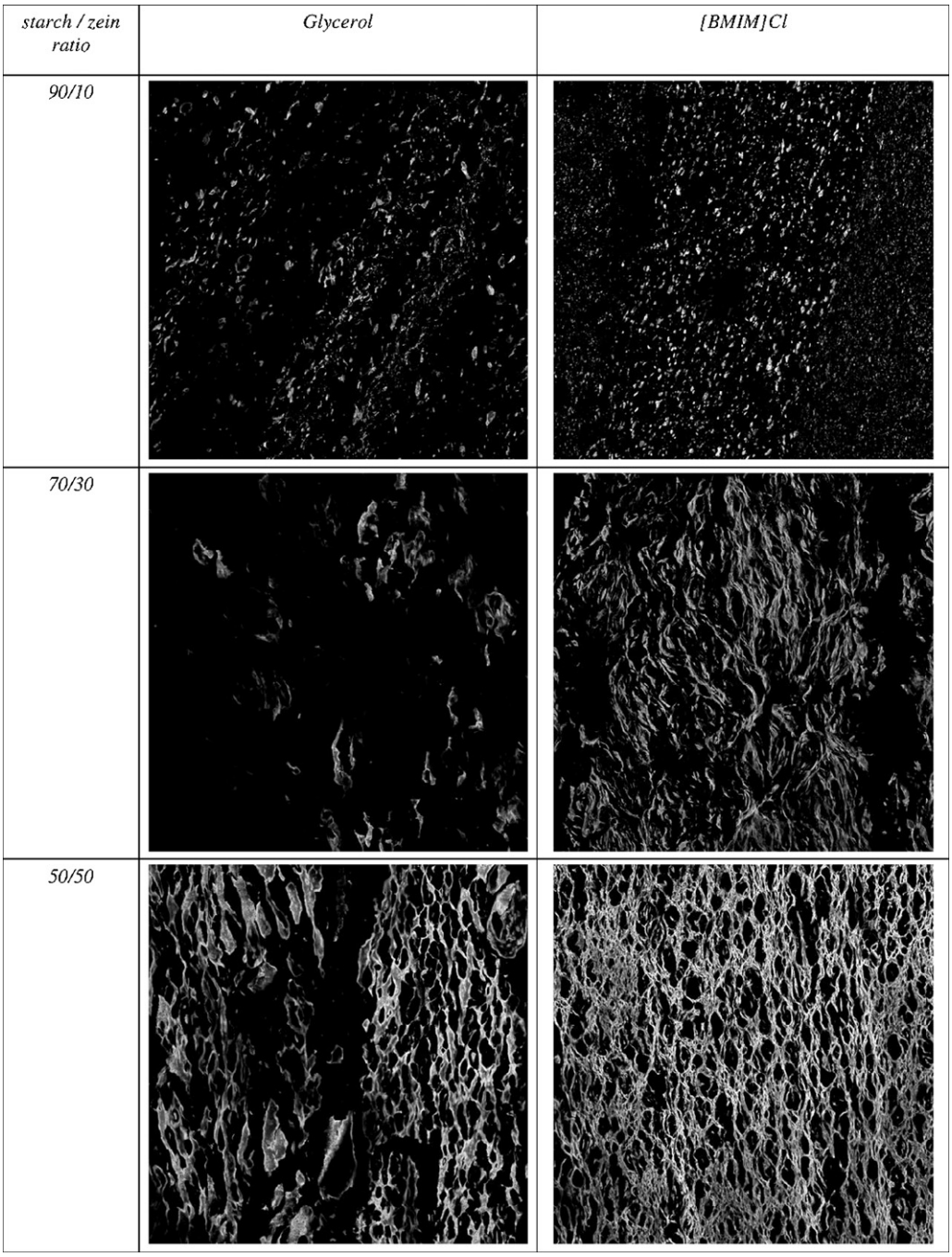

Fig. 6. Morphologies of starch/zein blends below 50% zein, plasticized by glycerol and [BMIM]Cl.

For higher zein contents, especially at 50% where the morphology is co-continuous it can be seen that the depth of the zein domains is also smaller in presence of [BMIM]Cl, which indicates that the surface area between starch and zein phases is increased compared to glycerol plasticized samples. For zein contents above 50%, the image analysis, confirms the presence of large starch aggregates.

3.3. Water content and thermomechanical transitions

Table 2 gives the water content of samples equilibrated at 50% RH. Water content from about 10 to 13% for glycerol plasticized samples are significantly higher than in samples containing [BMIM]Cl which are from about 9 to 10%. For glycerol plasticized zein samples, a significant exudation of the plasticizer was observed, while this did not occurred with [BMIM]Cl.

Dynamic mechanical analysis results are shown in Fig. 9 and temperatures corresponding to the maximum of the mechanical relaxations are reported in Table 3. For plasticized starch and plasticized zein, the relaxation associated to the glass transition, named 2nd and 3rd peak respectively, can be observed. The relaxation temperatures obtained for samples plasticized with [BMIM]Cl are significantly lower than relaxation temperatures obtained for samples plasticized with glycerol. In the case of the blends, two main relaxations are associated to the glass transitions of two co-existing domains.

Table 3
Relaxation temperatures measured by DMA respectively with their water content.

	Zein/starch ratio	1st peak (tan δ) glycerol rich phase	2nd peak (tan δ) starch rich phase	3rd peak (tan δ) zein rich phase	Water content (%)
Glycerol	0/100	−51	41	–	12.9 ± 0.2
	10/90	−60	42	81	12.9 ± 0.2
	50/50	−60	10	83	12.1 ± 0.2
	90/10	−55	−15	79	11.5 ± 0.2
	100/0	–	–	76	10.4 ± 0.2
[BMIM]Cl	0/100	–	30	–	10.0 ± 0.2
	10/90	–	14	69	9.7 ± 0.2
	50/50	–	5	67	9.9 ± 0.2
	90/10	–	−30	52	9.4 ± 0.2
	100/0	–	–	53	9.0 ± 0.2

According to Corradini et al. (2006, 2007), they are attributed to the starch rich and the zein rich phases, for the low temperature (2nd peak) and the high temperature (3rd peak) respectively.

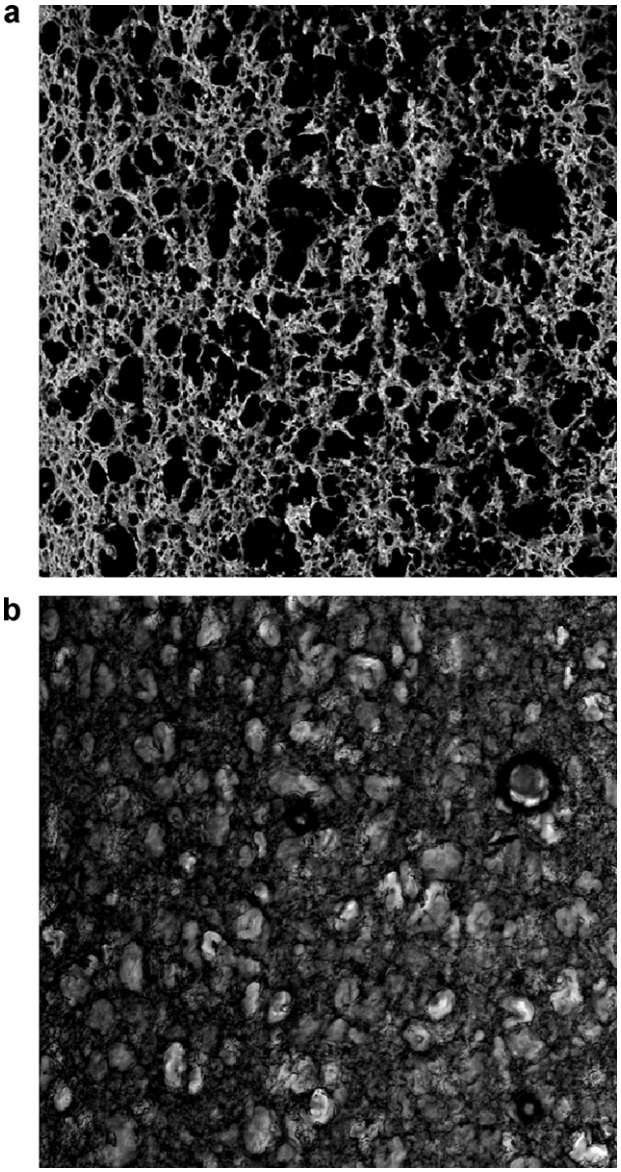

Fig. 7. Example of morphology of a zein rich blend (70% zein with [BMIM]Cl). On micrograph A, starch appears in black and zein in white, while micrograph B, shows the relief.

For glycerol plasticized samples, an additional relaxation, named 1st peak, is observed at low temperature, associated to a glycerol rich starch/glycerol phase.

3.4. Large deformations (tensile tests)

Fig. 10 shows the influence of the different plasticizers on the tensile modulus, the elongation at break and the maximum stress; for starch, zein and their blends. Due to the significant difference in modulus, the properties of the blends plasticized by glycerol and by [BMIM]Cl are presented with different scales. The maximum of tensile modulus is obtained for starch/zein 50/50 at 25 MPa in the case of [BMIM]Cl. In the case of glycerol the maximum of tensile modulus is obtained for pure zein at 350 MPa. For both plasticizers, a complex behavior of elongation at break is observed with zein content increase. The curves show a minimum at about 40–50% and a maximum at about 70–80% zein. The main characteristic is the very high deformation of about 600% obtained for starch/zein 30/70 plasticized by [BMIM]Cl compared to the maximum value obtained at about 100% in the case of starch plasticized by glycerol. For glycerol the maximum stress decreases until 50% zein content compared to a maximum stress quite constant at about 4 MPa for [BMIM]Cl. For higher zein content, maximum stress increases until 9–10 MPa.

4. Discussion

4.1. Influence of plasticizers on blends' processing

For glycerol plasticized blends (Fig. 3), only the torque and pressure drop curves obtained for the blend containing 10% of zein, were similar to those of the reference glycerol plasticized starch (Fig. 2). A constant pressure drop is obtained before 200 s (Fig. 3). For increasing zein contents (30% and above), the pressure drop (Fig. 3) slowly increased with time and did not reach a plateau within the imposed mixing time. Corradini et al. (2007) observed a similar behavior for starch–zein blends plasticized by glycerol in a brabender type mixer with a torque rheometer. For a zein content of 20% the torque typically increased progressively during several minutes. They assume that the thermoplasticization of starch is affected by interactions with the hydrophilic portions of the protein. For zein contents of 50% and above, they observed very low torque values. The torque signal they recorded for plasticized zein being almost flat. In our case also, for zein content above 50%, the pressure drop signal (Fig. 3) recorded were very low. For plasticized zein, the apparent viscosity calculated from the pressure drop was much lower than that of plasticized starch (Table 1). The calculated SME values gradually decrease with increasing zein content up to 30% (Fig. 5) confirming a strong influence of zein on the thermoplasticization of starch by glycerol. Between 30 and 50% zein content, the SME decreases sharply suggesting a phase inversion.

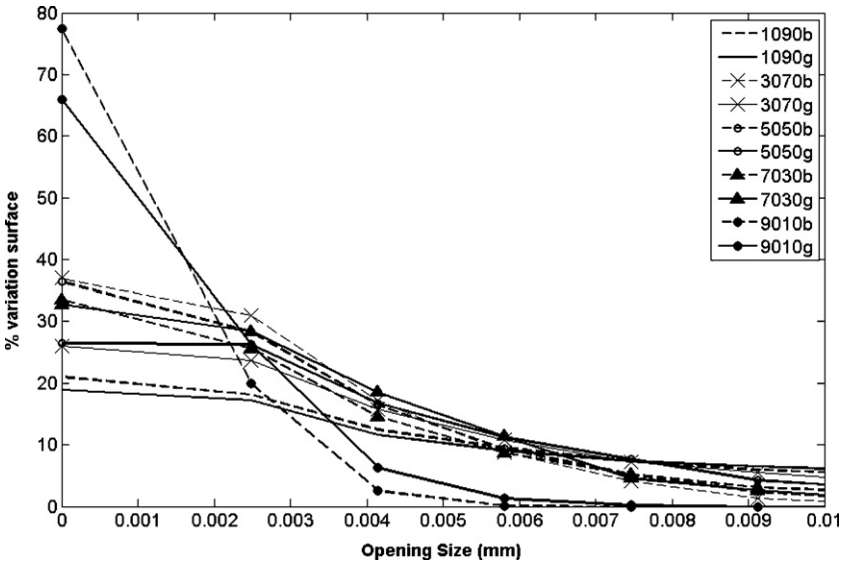

Fig. 8. Zein domains size characterization by image analysis results (1090b corresponds to a blend containing 10% of zein, plasticized by [BMIM]Cl).

For [BMIM]Cl plasticized blends (Fig. 4), all the torque and pressure drop curves were similar to those obtained for the starch/glycerol reference. Nevertheless, the steady pressure drop values obtained were significantly lower for starch rich blends. The viscosity of [BMIM]Cl plasticized starch is approximately a third of that in presence of glycerol (Table 1). Concurrently, the SME values for [BMIM]Cl are also much lower and less sensitive to zein content up to 30%. These observations suggest that [BMIM]Cl is more efficient than glycerol to obtain the melting of starch, allowing to reduce the necessary mechanical energy input and to reduce the influence of zein. Our previous work (Sankri et al., 2010) had shown that the hydrogen bonding interactions of starch with [BMIM]Cl in the solid state were stronger than with glycerol, in the solid state, strongly modifying the mechanical properties. These interactions at molecular level may also be the cause of the modified melting behavior observed. For zein contents above 50%, the behavior is similar to that of glycerol plasticized blends. Nevertheless, the viscosity of [BMIM]Cl plasticized zein is significantly higher (Table 1).

4.2. Influence of plasticizers on blends' morphologies

For a nodular morphology in the melt, the capillary number Ca is defined as the ratio between viscous forces tending to deform and break the droplets and the counteracting interfacial tension:

$$Ca = \frac{\dot{\gamma} \cdot \eta_c \cdot D}{2 \cdot \Gamma} \quad (8)$$

where $\dot{\gamma}$ is the shear rate, η_c is the viscosity of the continuous phase, D is the diameter of the droplet and Γ is the interfacial tension.

The critical capillary number Ca^* above which the droplet is broken by fibrillation and rupture under shear, depends on the viscosity ratio between the dispersed phase and the continuous phase $p = \eta_d/\eta_c$. As it has been shown by Grace (1982) for shear flow and later by Wu (1987), in twin screw extrusion conditions, the minimum value of Ca^* is obtained for a viscosity ratio close to unity. For a growing viscosity ratio (above 1), Ca^* increases very sharply and diverges, so it is unlikely to obtain droplet breakup. While for a decreasing viscosity ratio (below 1) the increase of Ca^* is more progressive, making possible the breakup of droplets for high values of Ca. That is to say for small interfacial tensions if the other parameters: $\dot{\gamma}$, η_c and D are unchanged.

The calculated viscosity ratio between starch and zein are reported in Table 1. Despite the values are higher in presence of the ionic plasticizers, they are still much smaller than 1. Consequently, the fibrillation and breakup under shear in starch rich blends is possible, but probably only if the interfacial tension is low. The absence of large aggregates and the presence of a large number of small particles 10% of zein in presence of [BMIM]Cl as observed in image analysis (Figs. 6 and 8). The apparent presence of a fibrillar structure for 30% of zein in presence of [BMIM]Cl is also consistent with this mechanism (Fig. 6).

As an opposition, for zein rich blends it is unlikely that any deformation of the starch dispersed phase could occur. This is consistent with the observation of very large starch aggregates in Fig. 7, confirmed by image analysis (Fig. 8).

4.3. Influence of plasticizers on water uptake and thermomechanical properties

As observed by Corradini et al. (2007), the water uptake of glycerol plasticized starch/zein blends decreases with zein content (Table 2). The behavior in presence of [BMIM]Cl is similar, although with a smaller amplitude. For all starch/zein ratio, the water uptake is lower than with glycerol, which could be an advantage.

The thermomechanical behavior of starch, zein and their blends in presence of glycerol (Fig. 9) is similar to that observed by Corradini et al. (2006). The mechanical relaxation associated to the glass transition of starch (Fig. 9a) occurs in a very broad range of temperature and the rubbery plateau level is about 10 MPa. Such a value relatively high for a rubbery state could be due to the presence of crystalline domains, appeared during the storage of samples. For zein, the transition is sharp and the rubbery plateau at about 1 MPa is typical of an amorphous polymer (Fig. 9b). For blends, the temperature of the two relaxations associated to the starch rich and zein rich phases (Fig. 9c) decrease with increasing zein content (Table 3). Corradini et al. (2006) assume that this is due to a migration of glycerol (and/or water) from the zein phase to the starch phase. The fact that we observe some exudation on glycerol plasticized samples support this assumption of a better affinity of glycerol with the starch phase.

As Corradini et al. (2006), we also observe the relaxation of glycerol rich phase at low temperature (around −60 °C) for all samples (Table 3), due to limited miscibility with starch. As an opposition, such a relaxation was not observed for [BMIM]Cl plasticized starch, zein and blends. The relaxation associated to the glass transition of

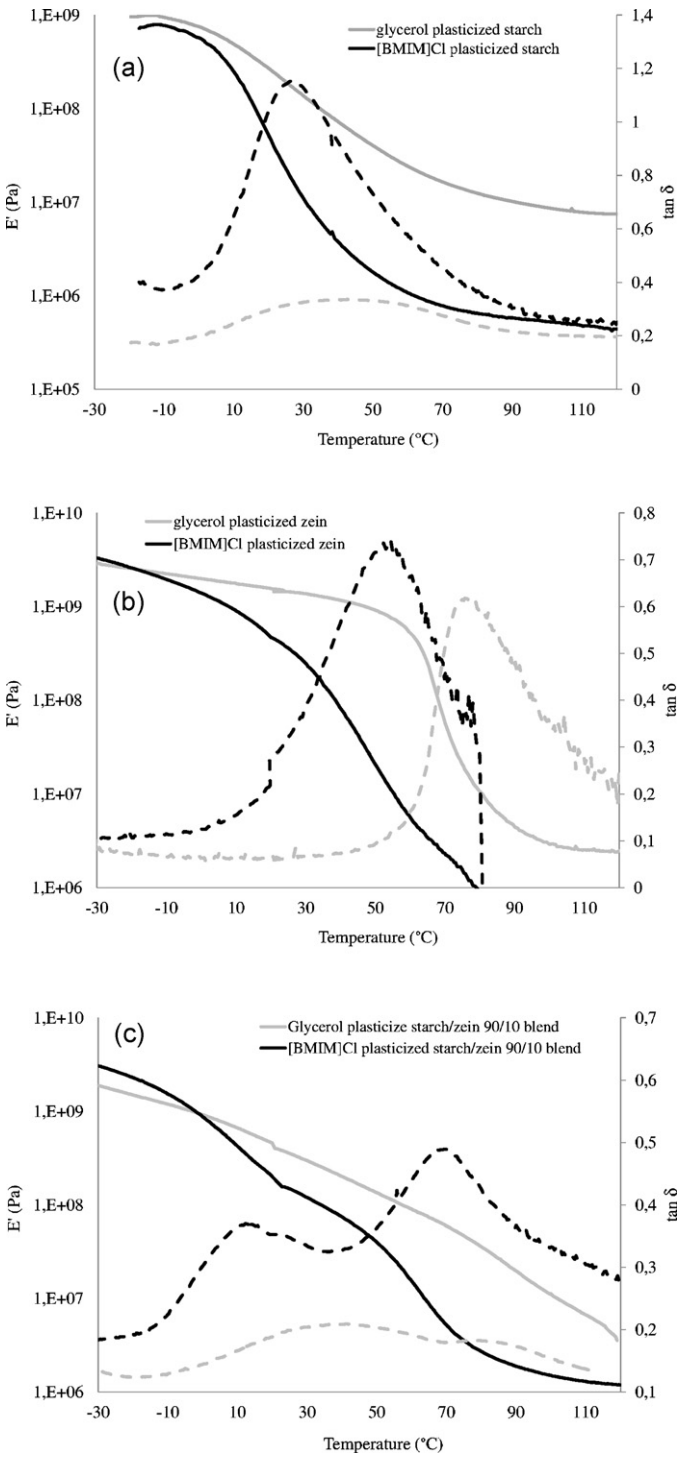

Fig. 9. Dynamic mechanical behavior of starch (a), zein (b) and a 90/10 starch/zein blend, plasticized by glycerol and [BMIM]Cl.

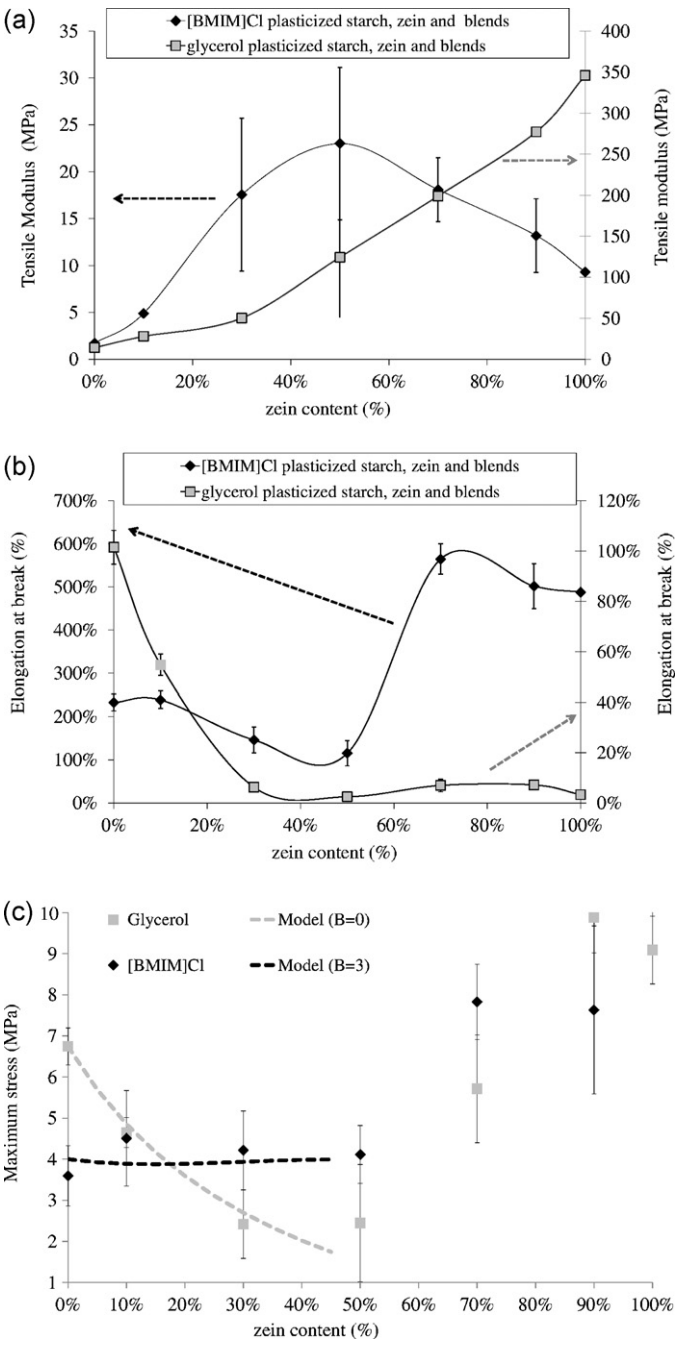

Fig. 10. Tensile large deformation mechanical properties of starch, zein and their blends, plasticized by glycerol and [BMIM]Cl: (a) elastic modulus, (b) elongation at break, (c) stress at break.

starch in presence of the ionic liquid is also much sharper (Fig. 9a). These two characteristics indicates a better miscibility and plasticizing efficiency of [BMIM]Cl.

The rubbery plateau of [BMIM]Cl plasticized starch is also much lower and typical of an amorphous polymer (Fig. 9a). In the case of zein, the glass transition occurs at a significantly lower temperature than with glycerol (Fig. 9b). It is also broader and no rubbery plateau is observed (the material flows). That suggest that [BMIM]Cl has limited miscibility with zein. The variations of the temperatures of the relaxations associated to the starch and zein phases in the blends (Fig. 9c, Table 3) support this assumption, with a possible migration of [BMIM]Cl between the zein and starch as for glycerol, but resulting in stronger variations of the glass transition temperatures.

4.4. Influence of plasticizers large scale deformations

In agreement with DMTA results, the tensile mechanical properties (Fig. 10) of glycerol and [BMIM]Cl plasticized starch are significantly different. The modulus of [BMIM]Cl plasticized blends is typically divided by a factor of 10 compared to glycerol plasticized blends, while the elongation at break is strongly increased. Nevertheless, taking into account the corrections of Eq. (6), the

maximum stress values are relatively close with the two plasticizers.

As observed by Corradini et al. (2006), glycerol plasticized zein is brittle, with a very low elongation at break and high modulus. In agreement with their results and those later data published by Habeych et al. (2008, 2010), the behavior of glycerol plasticized blends containing up to 50% of zein is typical of an incompatible blend, with a strong decrease of the maximum stress. In the meantime, the elongation at break also decreases dramatically. In order to characterize this behavior, Habeych et al. (2008) applied the model (Turcsanyi, Pukanszky, & Tudos, 1988):

$$\frac{\sigma_{\text{blend}}}{\sigma_{\text{matrix}}} = \frac{1-\Phi}{1+2.5\cdot\Phi}\cdot e^{B\Phi} \quad (9)$$

where Φ is the volume fraction of dispersed phase (zein) and B is a parameter linked to the transmitted load to the dispersed phase.

For glycerol plasticized starch/zein blends, we obtain the same result as Habeych et al. (2008): $B = 0$ (Fig. 10), which is typical of blend without adhesion between the phases.

As an opposition, when [BMIM]Cl is used as a plasticizer, the parameter B is equal to 3 (Fig. 10), which indicates an adhesion between the starch and zein plasticized phases. That suggests a compatibilization of the blend involving [BMIM]Cl.

Assuming that, as in the work of Taguet et al. (2009) on starch/polyethylene blends, a plasticizer rich phase is formed at the interface between starch and zein, the occurrence of compatibilization should be directly related to the interfacial tension between the zein dispersed phase and the plasticizer. The exudation observed for glycerol plasticized zein samples suggest that the interfacial tension should large, impeding compatibilization. As an opposition [BMIM]Cl is an efficient and compatible plasticizer for both starch and zein. Nevertheless, according to DMTA results, there was no evidence of the presence of a [BMIM]Cl rich phase; but the assumption of a decrease of interfacial tension for [BMIM]Cl plasticized blends is consistent with the morphologies observed.

Such a result opens new perspectives for the elaboration of bioplastics such as blends from unrefined natural polymer (eg. corn flour) or composites (starch/cellulose, etc). For potential applications such as packaging, but also solid electrolytes since the materials are electrically conductive due to the presence of the ionic liquid (Sankri et al., 2010), it is interesting to note that biodegradable ionic systems with properties close to ionic liquids called deep eutectic solvents (Abbott, Boothby, Capper, Davies, & Rasheed, 2004) can be used as plasticizers for starch (Abbot & Ballantyne, 2011). Preliminary results (Jacquet, Coativy, Lourdin, & Leroy, 2011) tend to show that compatibilization of starch/zein blends also occurs when such biodegradable ionic plasticizers are used.

5. Conclusions

In the present work, our goal was to evaluate the potential of an ionic liquid (1-butyl-3-methyl imidazolium chloride [BMIM]Cl) (used as a multifunctional plasticizer) for starch and its blends with zein, taken as a model of corn flour. [BMIM]Cl was shown to be a more efficient plasticizer than glycerol. During melt processing, the necessary specific mechanical energy input for native starch destructurization; and the final melt viscosity are significantly reduced for starch, while zein processing behavior was less sensitive to the plasticizer used. This results in a decrease of starch/zein viscosity ratio, which affects mixing efficiency in the starch/zein blends. Smaller zein aggregates were observed in the case of [BMIM]Cl plasticized blends.

In addition, mechanical testing show that a compatibilization of starch/zein blends takes place in presence of [BMIM]Cl, while those plasticized by glycerol are incompatible. Such a result opens new perspectives for the elaboration of bioplastics such as blends from unrefined natural polymer (ex: corn flour) or composites (starch/cellulose, etc). For potential applications such as packaging, but also solid electrolytes since the materials are electrically conductive due to the presence of the ionic liquid (Sankri et al., 2010), it is interesting to note that biodegradable ionic systems with properties close to ionic liquids called deep eutectic solvents (Abbott et al., 2004) exist and can be used as plasticizers for starch (Abbot & Ballantyne, 2011).

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