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Elodie Chabrat, Houssein Abdillahi, Antoine Rouilly, Luc Rigal. Influence of citric acid and water on thermoplastic wheat flour/poly(lactic acid) blends. I: Thermal, mechanical and morphological properties. *Industrial Crops and Products*, 2012, vol. 37 (1), pp. 238-246. 10.1016/j.indcrop.2011.11.034 . hal-00865719

**HAL Id: hal-00865719**

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Submitted on 25 Sep 2013

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**To link to this article** : doi:10.1016/j.indcrop.2011.11.034  
URL : <http://dx.doi.org/10.1016/j.indcrop.2011.11.034>

<p><b>To cite this version</b> : Chabrat, Elodie and Abdillahi, Houssein and Rouilly, Antoine and Rigal, Luc Influence of citric acid and water on thermoplastic wheat flour/poly(lactic acid) blends. I: Thermal, mechanical and morphological properties. (2012) Industrial Crops and Products, vol. 37 (n° 1). pp. 238-246. ISSN 0926-6690</p>
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# Influence of citric acid and water on thermoplastic wheat flour/poly(lactic acid) blends. I: Thermal, mechanical and morphological properties

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## Keywords:

Citric acid

Starch

Flour

Poly(lactic acid)

Extrusion

Wheat flour was plasticized with glycerol and compounded with poly(lactic acid) in a one-step twin-screw extrusion process in the presence of citric acid with or without extra water. The influence of these additives on process parameters and thermal, mechanical and morphological properties of injected samples from the prepared blends, was then studied.

Citric acid acted as a compatibilizer by promoting depolymerization of both starch and PLA. For an extrusion without extra water, the amount of citric acid (2 parts for 75 parts of flour, 25 parts of PLA and 15 parts of glycerol) has to be limited to avoid mechanical properties degradation. Water, added during the extrusion, improved the whole process, minimizing PLA depolymerization, favoring starch plasticization by citric acid and thus improving phases repartition.

## 1. Introduction

Wheat flour is mainly constituted of starch and proteins (Saiah, 2007). Starch, which is a natural renewable polysaccharide, is considered to be a promising raw material for the production of bioplastics. However, it needs intense transformation to disrupt its native structure and to become thermoplastic. It is also possible to plasticize flour to make thermoplastic flour. In low moisture conditions used for thermoplastic processing, the influence of wheat proteins has been shown to be minor, the proteic phase is dispersed in the starch matrix (Chanvrier et al., 2007) and no significant differences were noticed in terms of mechanical and thermal properties between flour and starch (Leblanc et al., 2008). This material shows very similar properties and the same limits as thermoplastic starch. Thermoplastic starch (TPS) is indeed a very interesting product for

making non-durable objects. However, its water sensitivity and limited mechanical properties make it only useful for specific applications (Forssell et al., 1999). Citric acid could be a good candidate to increase the range of reachable properties. To our knowledge, there is no study concerning the addition of citric acid in thermoplastic wheat flour. Nevertheless, it has been added to thermoplastic starch in different studies.

Several authors (Shi et al., 2007; Wang et al., 2007a, 2009) have reported that citric acid could form ester bond with starch. The esterification could take place between the carboxyl groups on citric acid and the hydroxyl groups on starch. Nevertheless when glycerol was present, it reacted preferentially with the hydroxyl groups of the glycerol (Wang et al., 2007a). The formation of glycerol citrate esters has been studied by Differential Scanning Calorimetry (DSC) and Fourier Transform Infrared Spectroscopy (FTIR) (Holser, 2008). Even if no ester bond was formed between citric acid and starch, it has been reported that citric acid could form strong hydrogen bond interactions with starch, stronger than glycerol. The thermal and water sensitivity of thermoplastic starch was then improved and retrogradation was inhibited (Holser, 2008; Shi et al., 2007; Yu et al., 2005). Crosslinking of starch films has been performed using citric acid and a catalyst (sodium hypophosphite) (Reddy and Yang, 2010), citric acid bearing three carboxyl groups. Free citric acid, which was not involved in any crosslinking interaction could act as a plasticizer (Shi et al., 2008). Citric acid has also been added to thermoplastic starch to modify its

*Abbreviations:* DMTA, dynamic mechanical thermal analysis; DSC, differential scanning calorimetry; FTIR, Fourier Transform infrared spectroscopy; PLA, poly(lactic acid); SEM, Scanning Electronic Microscopy; TPS, thermoplastic starch; UTS, ultimate tensile strength.

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physical performance by controlled degradation of starch through an acid-catalyzed hydrolysis of the ether linkages in the polysaccharide chains (Carvalho et al., 2005; Hirashima et al., 2005; Wu et al., 2010). The viscosity of starch was then reduced without relevant changes in water affinity or in dynamic mechanical properties (Da Roz et al., 2011).

Citric acid has been reported to increase the plasticization and melt processing properties of TPS (Ronasi et al., 2010; Shi et al., 2007). It might accelerate the fragmentation and dissolution of starch granules. It could help starch plasticization, even when additives such as montmorillonite are added which normally hinder the plasticization (Wang et al., 2009). The fluidity of TPS was also improved using citric acid. This decrease was explained by some authors by an acid hydrolysis of starch (Ke and Sun, 2003). So, co-plasticizing starch with a mixture of glycerol/citric acid is interesting because it increases starch plasticization, partial esterification can happen, and chains with lower molecular weight are obtained. In wheat flour, addition of citric acid can lead to a decrease in the cross-linking degree of the protein network during extrusion. It has been stated, according to a study of thermo-mechanical behavior of wheat gluten materials (Gomez-Martinez et al., 2009), that an acidic environment might prevent aggregation of gluten protein.

Blending poly(lactic acid) (PLA) with thermoplastic starch has become widespread in the bioplastics community in the last 10 years, in order to reach different properties and decrease the price of bioplastics. But PLA and TPS are known to be non-miscible, and non-compatibilized blends exhibit weak properties (Martin and Avérous, 2001).

The influence of citric acid on TPS/PLA blends has thus been reported in different studies (Ke and Sun, 2003; Wang et al., 2007b, 2010). It has been established that even without water, plasticization of starch with glycerol was possible when citric acid (0–4%) was present. When water was present, the blend was more homogeneous but thermal stability was decreased. In both cases, a better interaction between PLA and TPS has been found (Wang et al., 2010).

Citric acid has also been used as an additive to starch-PVA (poly(vinyl alcohol)) films (Park et al., 2005). It was reported that adding citric acid decreased the strength of the films but provided better strength than glycerol-added films. This was attributed to the better hydrogen bonding between citric acid and starch-PVA molecules than with glycerol. Citric acid is composed of carboxyl and hydroxyl groups which increase the different interactions between the components of the blend (Yoon et al., 2006; Yun et al., 2006). When added to thermoplastic starch/LDPE blends, citric acid improved starch plasticization and increased the mechanical properties of the blend (Wang et al., 2007b).

Citrate esters are known to plasticize PLA (Ke and Sun, 2003; Labrecque et al., 1997). Moreover, citric acid is inexpensive, non-toxic and considered nutritionally harmless as approved by FDA. Indeed, it is a metabolic product of the body (Krebs cycle). Citric acid, when concentration is less than 20%, shows no significant toxicity effect on the cell proliferation (Shi et al., 2008).

In order to improve thermoplastic wheat flour properties, and so to reach new application fields, it was chosen to be blended with a small amount of poly(lactic acid). Three additives were used for the compounding in an industrial-size twin-screw extruder: water, glycerol and citric acid. Water is the most known starch plasticizer. Glycerol is commonly used as a plasticizer to obtain thermoplastic starch. Citric acid, which is a natural occurring organic acid, was chosen to improve starch plasticization and the phases miscibility. The obtained compounds have then been molded in dumbbell-shape specimens to assess their mechanical, thermal and morphological properties. The influence of water and citric acid, in a wide range, on material properties has been studied.

## 2. Experimental

### 2.1. Materials

Wheat flour was supplied by Gers Farine (France). It is mainly made up of starch (65%). Secondary components were water (13%), proteins (13%), fibers, essentially hemicelluloses (2%) and lipids (1%). Poly(lactic acid) is an extrusion grade. Glycerol (purity 99%) was used as starch plasticizer and was supplied by Gaches Chimie (France). Citric acid was obtained from Sigma-Aldrich (France).

### 2.2. Thermoplastic starch/PLA blends extrusion

In this study, ten different blends were extruded in an industrial-size twin-screw extruder (Evolum HT53, Cleextral (France) with L/D = 36) at a temperature of 60–140 °C and screw rotational speed of 250 rpm. The screw profile was divided into two main zones, a plasticization zone composed of kneading elements and reverse screw elements in the first half of the barrel and a mixing zone composed of kneading elements in the second half of the barrel. Poly(lactic acid) was introduced at the beginning of the second zone, i.e. after starch plasticization. A cylindrical die with 6 holes was fixed at the end of the extruder. The compositions of the blends can be understood from their names. First, wheat flour (extruded at its equilibrium humidity (13%)), poly(lactic acid) and glycerol ratio were kept constant at 75 parts, 25 parts and 15 parts respectively. The only variables were water and citric acid ratios. The generic name for the formulations is CA $x$ . When a  $W$  is present before this name, it means that 10 parts of extra water was present in the formulation during the extrusion. This water was added to help processing and to study the behavior between water and citric acid.  $x$  indicates the concentration of citric acid, with values between 0 and 20 parts. The formulation WCA5 contained thus 10 parts of water and 5 parts of citric acid.

### 2.3. Injection-molding

After stabilization at 60% RH and 25 °C, the plastics pellets were injection-molded into dumbbell-shaped specimens using a Negri Bossi VE160-720 injection molding machine (Italy). Molding temperature profile was defined as following: 80/125/130/145 °C and backpressure was 10 bar. The holding pressure was 300 bar during 1 s. For experimental reasons, WCA2 was not injected; no results from injection-molded specimens are available for this formulation.

### 2.4. Tensile testing

A Tinius Olsen H5kT (UK) universal testing machine was operated at a crosshead speed of 5 mm/min and used for tensile testing. Young's modulus, ultimate tensile strength, elongation at break and toughness were recorded for each specimen. Toughness represents the energy by volume unit necessary to break the dumbbell specimen. It was calculated from the area under the force–displacement curve. Injection dumbbell specimens were conditioned at 60% RH and 25 °C for 3 weeks prior testing. Each mechanical parameter was averaged from 5 to 10 specimens.

### 2.5. Dynamic mechanical and thermal analysis

Dynamic mechanical and thermal analyses (DMTA) of the samples were performed with a Tritec 2000 DMA (Triton Technology, UK) in a multi-frequency mode over the temperature range –80 to 180 °C with a scanning rate of 2 °C/min. The amplitude and frequencies were kept constant at 25  $\mu$ m and 1 and 10 Hz, respectively. The geometry used was the single cantilever bending mode with one extremity of the bar fixed, while the other one was

bended with the amplitude and frequencies indicated above. On glycerol-plasticized starch-based materials, two relaxations are usually observed attributed to plasticizer rich phase (T1 around  $-50^{\circ}\text{C}$ ) and to starch rich phase (T2 around  $40^{\circ}\text{C}$ ) (Lourdin et al., 1997). In this work, the first relaxation was not observed in the analytical conditions used and the discussion is then focused on the second one, appearing just before the glass transition of PLA.

## 2.6. Scanning Electron Microscopy (SEM)

The sections of the dumbbell specimens were examined using a JEOL JSM-700F (Tokyo, Japan) scanning electron microscope, with a 5 kV accelerating voltage. The dumbbell-shape specimens were cooled in liquid nitrogen and then broken. The PLA phase was etched by stirring the sample in chloroform (99.5% purity) at room temperature. The samples were then vacuum-coated with palladium for observation to avoid charging under the electron beam. The size of the holes was directly measured with the Jeol software. Average value was calculated from 10 measurements.

## 2.7. Molecular weight distribution

A Dionex (Voisins le Bretonneux, France) Size Exclusion Chromatography (SEC) equipped with a Iota2 refractive index (RI) detector was used to measure the molecular weight distribution of the samples.

Both phases were studied separately and the extraction was processed in a Soxhlet apparatus. PLA phase was extracted with chloroform during 8 h and then solvent was removed by evaporation. Extracted mass was compared to theoretical PLA mass in the sample to give an extracted percentage of PLA.

To analyze the starchy phase, two PLgel 5  $\mu\text{m}$  mixed-D columns, and a PLgel precolumn were purchased from Polymer Laboratories (Church Stretton, UK). The columns were connected in series along with the precolumn. The temperature of the columns was set to  $80^{\circ}\text{C}$ . DMSO was used as the solvent for dissolving the starchy sample, and as the eluent. Sample concentration in DMSO was approximately 5 mg/mL. Samples were prepared at ambient temperature and stored in an oven at  $60^{\circ}\text{C}$  for a few days for the dissolution. The liquid part was then removed with a syringe, leaving the insoluble part in the vial. No molecular weight was calculated from this experiment because of the non-linear structure of amylopectin and of the lack of total dissolution. Some molecules which were not soluble in DMSO, were not analyzed in the samples. Elution times were directly analyzed, corresponding to hydrodynamic volumes.

To analyze the PLA phase, three PLgel columns were associated in series of  $10^3$ , 500 and 100  $\text{\AA}$  along with a precolumn. The temperature of the columns was set to  $30^{\circ}\text{C}$ . Chloroform was used both as the solvent for dissolving the PLA sample and as the eluent. Sample concentration in chloroform was approximately 5 mg/mL. Samples

were prepared from what has been extracted with chloroform in Soxhlet apparatus. PS standards were used for the calibration.

## 2.8. FTIR spectroscopy

FTIR spectra were collected from the part of the blend which cannot be dissolved in chloroform. KBr disks were prepared by mixing approximately 300 mg of sample in KBr. 64 scans were collected with a Spectrum 65 apparatus (Perkin Elmer, USA) for each sample between 4000 and  $400\text{ cm}^{-1}$ .

## 3. Results

### 3.1. Process parameters

The extrusion of the different blends is really dependent on the citric acid ratio and on the presence of extra water. Different process parameters were followed (Fig. 1) throughout the extrusion to understand the influence of citric acid. These parameters were the Specific Mechanical Energy (SME) needed for the extrusion, the matter temperature in the plasticization zone (reverse screw elements) (plasticization temperature) which was followed to detect an eventual warm-up of the matter and the pressure in the die. This last parameter gives information about molten blend viscosity.

Globally, the SME decreased significantly with increasing citric acid concentration (Fig. 1a). However, for formulations extruded with extra water, SME was maximum for 2 parts of citric acid and then decreased for higher citric acid ratios. For the formulations without extra water, a local maximum of SME was observed for formulations with 10 parts of citric acid. A specific change occurred at these concentrations, also visible on the die pressure curve (Fig. 1c) which could be attributed to a viscosity change of the blend.

Die pressure (Fig. 1c) was higher for the formulation extruded without water. It decreased from 36 bar to 13 bar when adding 10 parts of citric acid in the blend without water. It decreased from 18 bar to 9 bar when 10 parts of citric acid were added in the blend with extra water.

The barrel temperature of the plasticization zone was set to  $100^{\circ}\text{C}$ . When looking at Fig. 1b, the matter was self-warmed-up of  $10^{\circ}\text{C}$  for the formulation with water, and of more than  $20^{\circ}\text{C}$  for the formulation without extra water. This confirms the idea that water helps for the process, promoting starch gelatinization. Adding citric acid limits this self-warming up. For formulations with 10 parts of citric acid, the temperature in the plasticization zone was  $105^{\circ}\text{C}$ . So, globally, as the citric acid concentration increased, the extrusion parameters (SME, plasticization temperature, die pressure) decreased.

### 3.2. Materials properties

Mechanical properties are presented in Table 1. For comparison, mechanical properties of PLA and F75G25 (75% of wheat flour (at

**Table 1**  
Mechanical, DMTA and extractability properties of the different blends compared to PLA and F75G25.

Blends	Young's modulus (MPa)	Ultimate tensile strength (MPa)	Elongation at break (%)	Tan delta shoulder	Tan delta peak	% Extracted PLA
CA0	709 (33)	9.6 (0.3)	7 (1)	45	65	111
CA2	189 (26)	3.1 (0.2)	34 (6)	33	66	84
CA5	46 (9)	1.0 (0.1)	69 (17)	32	65	88
CA10	29 (5)	0.4 (0.1)	109 (20)	33	66	63
CA20	3 (1)	0.2 (0.1)	57 (11)	32	67	53
WCA0	715 (20)	10.0 (0.2)	6 (1)	43	65	101
WCA2	n.d.	n.d.	n.d.	n.d.	n.d.	112
WCA5	66 (18)	1.4 (0.1)	41 (8)	22	66	60
WCA10	69 (18)	1.6 (0.2)	58 (4)	25	67	61
WCA20	24 (7)	1.3 (0.1)	64 (12)	20	67	46
PLA	1806 (74)	52.4 (10.3)	4 (1)	n.d.	n.d.	95
F75G25	15 (3)	1.8 (0.1)	58 (10)	n.d.	n.d.	n.d.

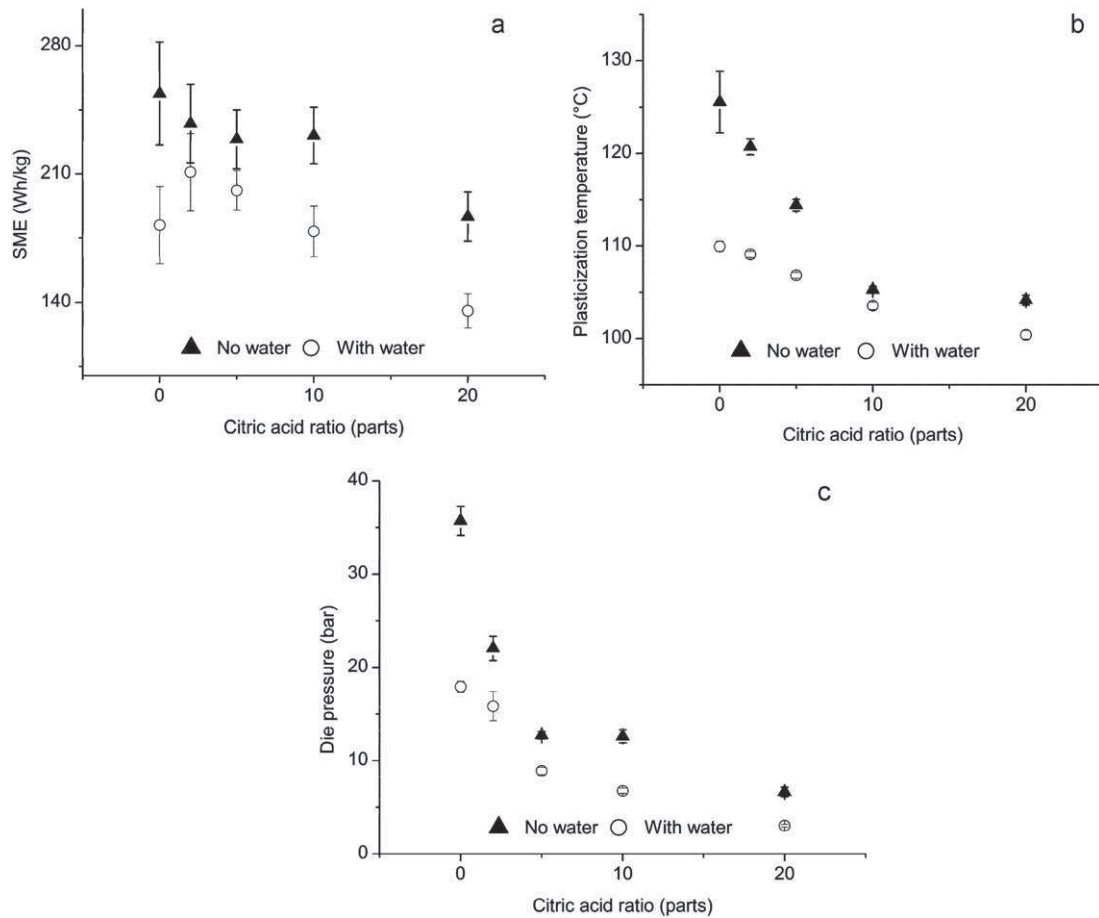


Fig. 1. Process parameters read for the different blends with increasing citric acid concentration, with (○) or without (▲) extra water.

its equilibrium humidity, i.e. 13%) and 25% of glycerol) are also presented. Plasticized flour composition is not the same as the one of the plasticized flour of the study (75/25 for F75G25 and 83.3/16.7 for the study). Because mechanical properties are directly dependent on plasticizer ratio, comparison cannot be done. However, values of F75G25 are given to present an order of magnitude of the mechanical properties of a plasticized flour. Plasticized wheat flour (F75G25) is a ductile material with a Young's Modulus of 15 MPa and an elongation at break of 58%, whereas PLA is brittle with a Young's Modulus of 1806 MPa and an elongation at break of 4%. Adding 20 parts of PLA to plasticized wheat flour (83.3% of wheat flour (at its equilibrium humidity) and 16.7% of glycerol) increased its Young's Modulus up to 709 MPa and decreased its elongation at break to 7%. The two blends without citric acid (with or without water) present the same mechanical properties: Young's Modulus reached 700 MPa, ultimate tensile strength was close to 10 MPa but elongation at break was 6–7%. This low value can be explained by the low glycerol ratio (15 parts of the blend).

As soon as some citric acid was added (2 parts), Young's Modulus and ultimate tensile strength (UTS) decreased drastically. Their values were very low as soon as citric acid ratio reached 5 parts (Young's Modulus of 46 and 66 MPa and UTS of 0.97 and 1.43 MPa). However, this decrease when adding citric acid was accompanied by an important increase of the elongation at break. With 5 parts of citric acid, the elongation at break was close to 50% and it is the same for 20 parts of citric acid. Elongation at break reached even values close to 100% when 10 parts of citric acid were added to the blend extruded without extra water. There could be a competition between glycerol and citric acid for the plasticization. Toughness decreased a lot when adding citric acid in the blends extruded

without water but was more stable for the blends which contained extra water for the extrusion (Fig. 2). This is an interesting observation. It is then possible to think that there is a better dispersion in the blends with water.

SEM images are presented in Fig. 3 to better understand the phases repartition (thermoplastic wheat flour and PLA) of the different blends. PLA which was etched with chloroform is represented by dark holes on the images. These observations will enable us to make a correlation between structure and properties. The SEM image of CA0 (not shown) was similar to that of WCA0 and was not as smooth as the ones of the blends in which citric acid was added.

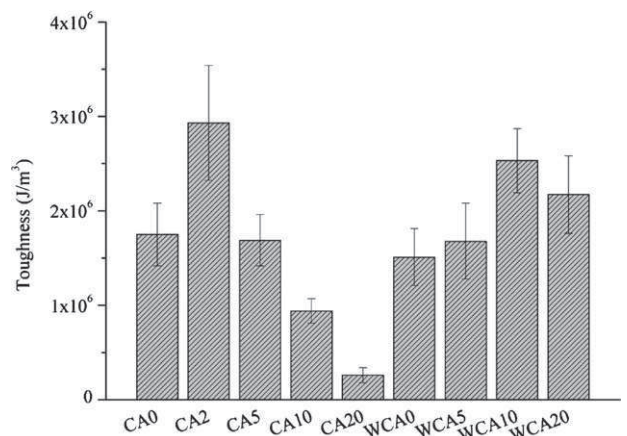
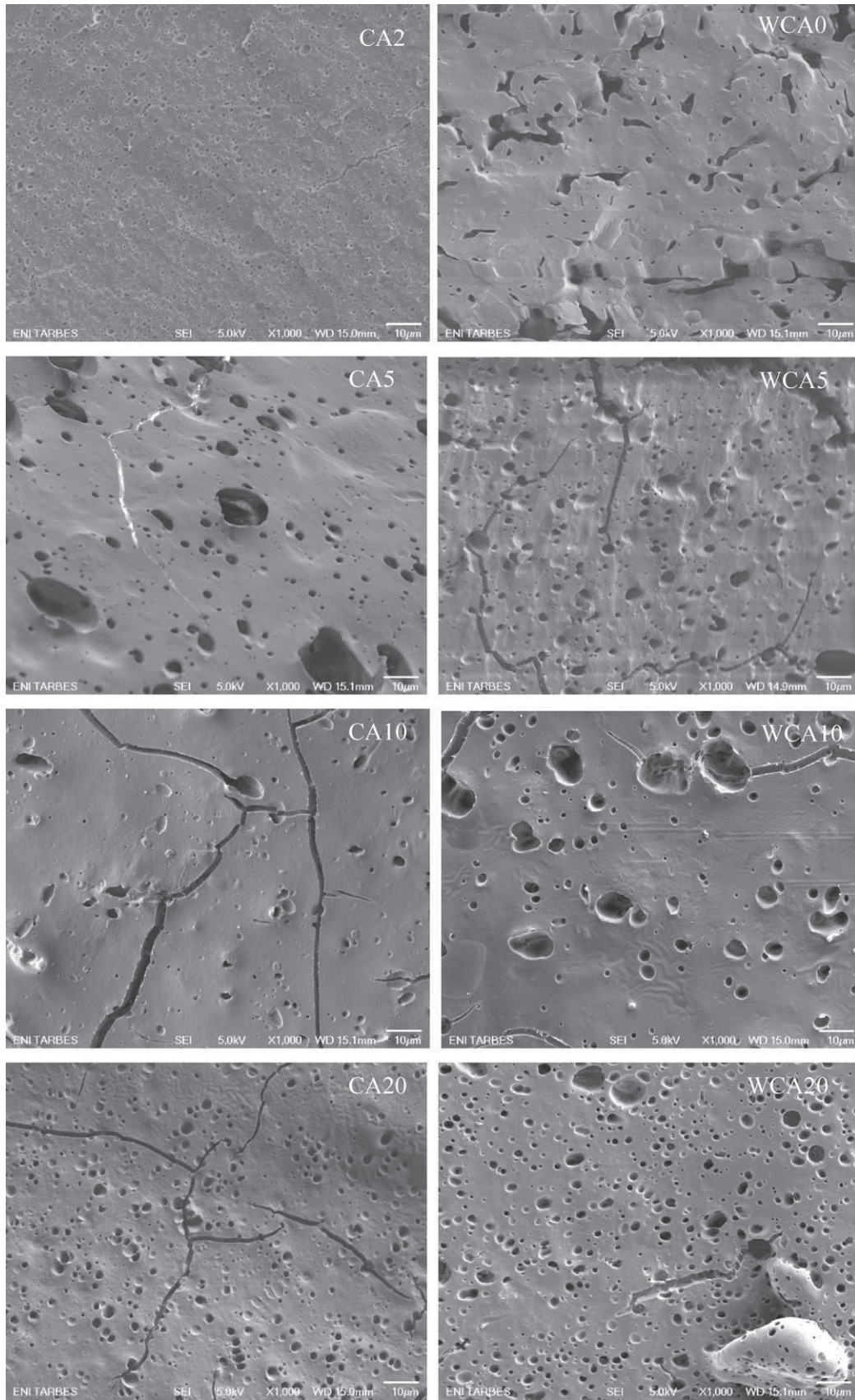


Fig. 2. Toughness for the different blends.



**Fig. 3.** SEM images of the fractured section after PLA etching for the different blends (magnification 1000×, left: blends without water and right: blends extruded with extra water).

PLA holes were not well-defined holes but more like canals. When 2% of citric acid was added, the PLA repartition was completely different. CA2 presents a multitude of really small holes with a diameter comprised between 1 and 5  $\mu\text{m}$ . Then, when increasing citric acid ratio to 5 parts, the repartition was not the same. PLA holes were bigger (6–30  $\mu\text{m}$ ) and not so well-distributed. The size of the holes decreased when the citric acid ratio was increased to 10 parts and to 20 parts. A lot of cracks between the holes were observable for the blend with 20 parts of citric acid.

Looking at the SEM images, there was not much structural difference between the blends extruded with or without extra water. For the blends extruded with water (Fig. 3), the structure change was nearly the same as that previously observed for the blends without extra water. Canals were transformed into holes with citric acid and the size of the holes decreased when citric acid amount was increased. This observation is shifted compared to the blends extruded without extra water. For the blends extruded with extra water, PLA domains were still small for WCA5 and were bigger for WCA10 then smaller for WCA20. The distribution of the holes is finer for the blends extruded with extra water (diameter of holes for WCAx: 2–6  $\mu\text{m}$ , whereas for CAx: 3–22  $\mu\text{m}$ ). SEM image for WCA2 is not available; due to a lack of pellets, WCA2 was not injection-molded.

FTIR analyses of the non-soluble part in chloroform of the different blends revealed the same spectra as starch. The main absorption bands were observed at 3400–3450  $\text{cm}^{-1}$  (hydroxyls groups), 2880–2900  $\text{cm}^{-1}$  (C–H stretching) and 1150–1085  $\text{cm}^{-1}$  (ether band) (Da Roz et al., 2011). One absorption band was different from starch, the area of which is increasing with citric acid concentration: the absorption band at 1759  $\text{cm}^{-1}$ . It is characteristic of the stretching of the carbonyl bonds. The presence of carbonyl bonds can have different causes: residual citric acid, poly(lactic acid) presence, starch or glycerol esterification.

PLA was effectively more and more present in the part of the blend which has not been dissolved in chloroform when citric acid concentration is increased (Table 1). Extraction rate was calculated from theoretical PLA concentration resulting from compounding and is then not very accurate resulting in values higher than 100%. For the formulation WCA10 for example, only 61% of the PLA was extracted. The 39% left were not carried away by chloroform. Interactions could thus form between PLA and wheat flour. The rate decreased with the increase of citric acid ratio and this decrease was even more marked for the blends extruded with extra water, falling to only 46% for WCA20.

There is a priori no free residual citric acid in the analyzed part because important vibration bands of citric acid were missing, for example at 2635  $\text{cm}^{-1}$  and 2555  $\text{cm}^{-1}$ . Citric acid still in the blends probably participates in low energy interactions with the biopolymers. For the esterification, we do not have enough clue to argue around a possible esterification at this stage, as the one observed by Shi et al. (2007) for example.

## 4. Discussion

### 4.1. Citric acid influence

Citric acid can be seen as a compatibilizer (esterification, hydrogen bonding), as a starch plasticizer and as a depolymerization agent for starch and PLA in thermoplastic wheat flour/PLA blends. It could also play a role in gluten disaggregation.

Gluten disaggregation is assumed, because it has already been observed in the literature (Gomez-Martinez et al., 2009) that the cross-linking degree of the protein network can be decreased during the processing, by adding 3% of citric acid. This phenomenon could be one explanation among others for the viscosity decrease in

the extruder. However, since proteins represent only 13% of wheat flour, which represent at maximum 65% of the blend itself, proteins represent at maximum 8% of the blend. As no specific effect of these proteins can be seen on either thermal or mechanical analyses, and as other authors have shown their minor participation in wheat flour-based materials properties (Chanvrier et al., 2007; Leblanc et al., 2008), their influence will not be specifically developed in this study. Starch molecular weight reduction, which is probably the main explanation of the viscosity decrease, is considered later in this discussion.

The compatibilization effect of citric acid is visible on the mechanical properties, especially when looking at the toughness, which represents the energy needed for the sample to break. When no water was added during the extrusion, citric acid seemed to be effective only in small amounts, while with water, the effect was noticed on the whole range of concentration (Fig. 2). Adding a small amount of citric acid changed in a considerable way the phase repartition of the blend, from PLA canals to PLA holes (Fig. 3). The same effect was observed by Wang et al. (2007a) on pure TPS/PLA blends. PLA was also less extractable by chloroform for blends containing citric acid (Table 1). The more the citric acid, the less PLA was extracted. With high ratio of citric acid, the non-extracted PLA, which is supposed to interact more with the other components of the blend, accounted for 40% and more. Esterification has not been proved but all these observations at least show a better affinity between the phases.

DMTA analyses on injected samples clearly showed the relaxation peak corresponding to PLA glass transition around 65 °C. They showed also another relaxation shoulder between 20 and 45 °C (Fig. 4 and Table 1), which has been attributed to the glass transition of the starch backbone or starch-rich phase (Lourdin et al., 1997). PLA glass transition temperature stayed constant whatever

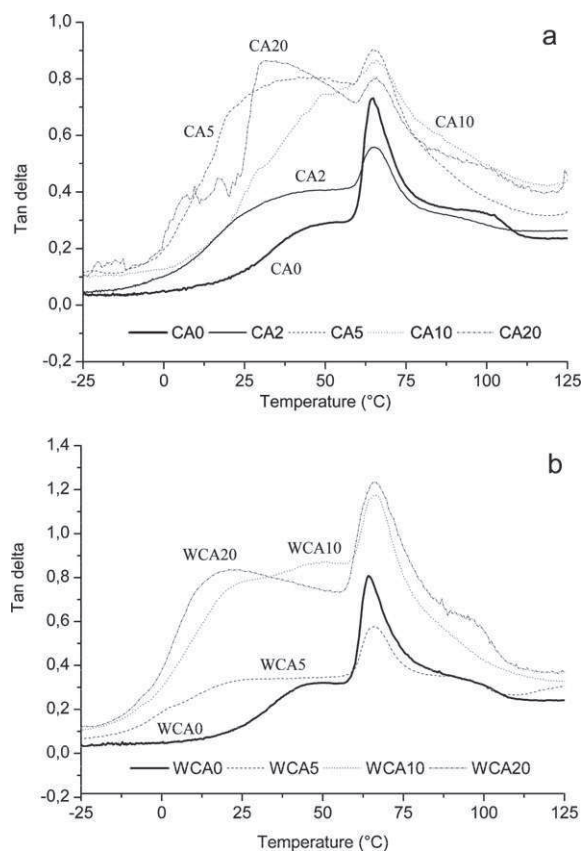


Fig. 4. Damping factor the blends extruded without extra water (a) and with extra water (b).



the amount of citric acid in the blend and the presence of water during the extrusion. Citric acid did not plasticize PLA in these conditions. Moreover, citrate esters, the proposed product of the reaction between citric acid and glycerol (Holser, 2008), also known as a PLA plasticizer (Ke and Sun, 2003; Labrecque et al., 1997), did not form. Also, the possible esterification of glycerol with citric acids as proposed by Shi et al. (2007) to form citrate esters did not occur in this experiment. However, damping factor intensity seemed to be weaker for small amounts of citric acid (CA2 and WCA5), meaning that chains would be less mobile and that better interactions were created between the chains. On the contrary, for higher citric acid amount, mobility would be better because damping factor intensity was higher. The shoulder corresponding to starch-backbone glass transition temperature (T2) was shifted to lower value when citric acid was added but the value stayed constant whatever its concentration (i.e. 32–33 °C for CAx and 20–25 °C for WCAx). This shift could be due to the plasticizing effect of citric acid on carbohydrates, water improving the access in the polymer network thanks to a swelling effect and lowering even more the glass transition temperature. The expected behavior for compatibilized phases, involving glass transition peaks moving towards each other, is not observed. Fig. 5 presents the storage modulus of the analyzed blends in a logarithmic scale. Blends without citric acid (CA0 and WCA0) show the higher storage modulus for the whole temperature range. Storage modulus is kept at a high value

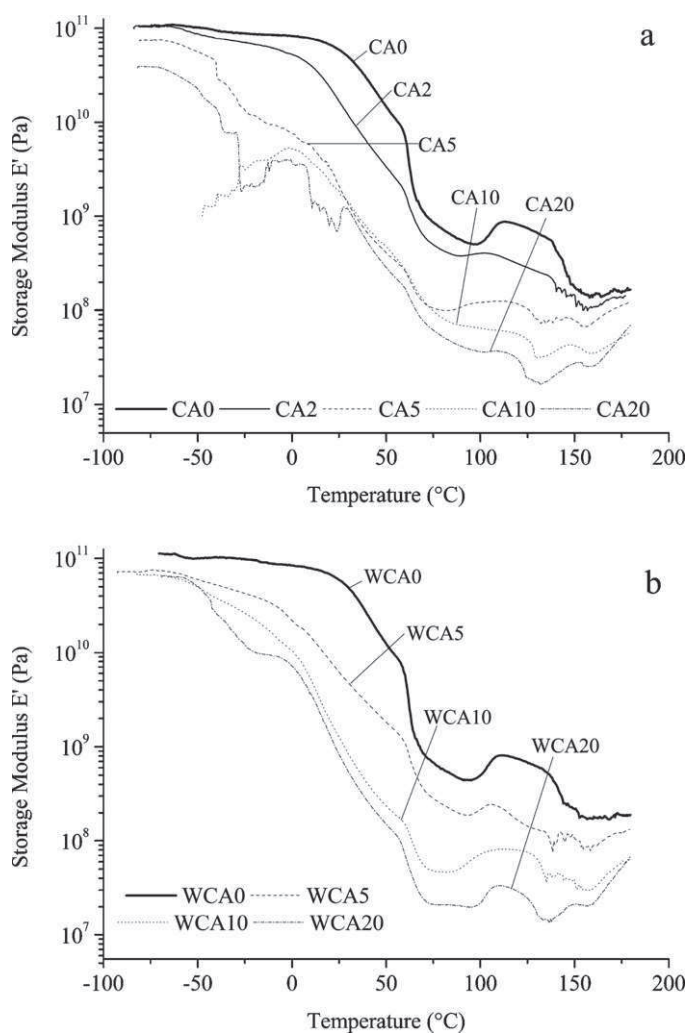


Fig. 5. Storage modulus for the blends extruded without extra water (a) and with extra water (b).

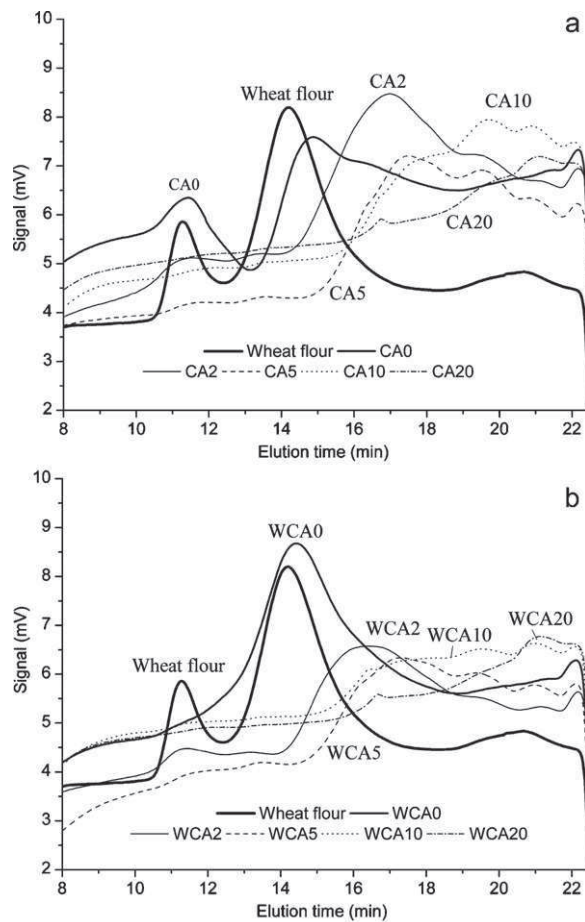


Fig. 6. Molecular mass distribution of starch for the different blends.

for higher temperature compared to blends with citric acid. However, for small amounts of citric acid (CA2 and WCA5), the slope of the decreasing curve between 0 and 50 °C is smaller than the one of the blends without citric acid. This observation confirms the observation of the damping factor intensity; interactions between chains may be more important when a small amount of citric acid is added. For all the blends, storage modulus increases a little bit between 100 and 110 °C. This can be due to water evaporation at 100 °C or a crystallization event.

Another possible explanation for the shift of the damping shoulder associated to the starch phase would be depolymerization (Wang et al., 2007a). To confirm this hypothesis, SEC experiments were performed separately for the PLA phase extracted by chloroform and for the starchy phase dissolved in DMSO. Both PLA and starch showed a lowering of their molecular weight when citric acid was added in the blends (Figs. 6 and 7).

Fig. 6 shows the molecular mass distribution of all the components of the blend soluble in DMSO. Amylose, amylopectin and proteins were the different polymers normally present in the analyzed samples. Wheat flour was analyzed as a reference. It presented two main peaks that should correspond to amylopectin (11.28 min) and amylose (14.20 min) (Liu et al., 2010). The intensity of the peaks did not correspond to the amylopectin/amylose ratio of 75/25 for wheat starch. The amylopectin peak was very small. It is well-known that the characterization of amylopectin by SEC is very difficult because of its low solubility and its size (Chen et al., 1997). Only a small part of amylopectin was probably dissolved, which explains the small amylopectin peak. Looking at the trace of CA0 (Fig. 6a), extruded formulation without water and without citric acid, both amylopectin and amylose peaks were still visible.

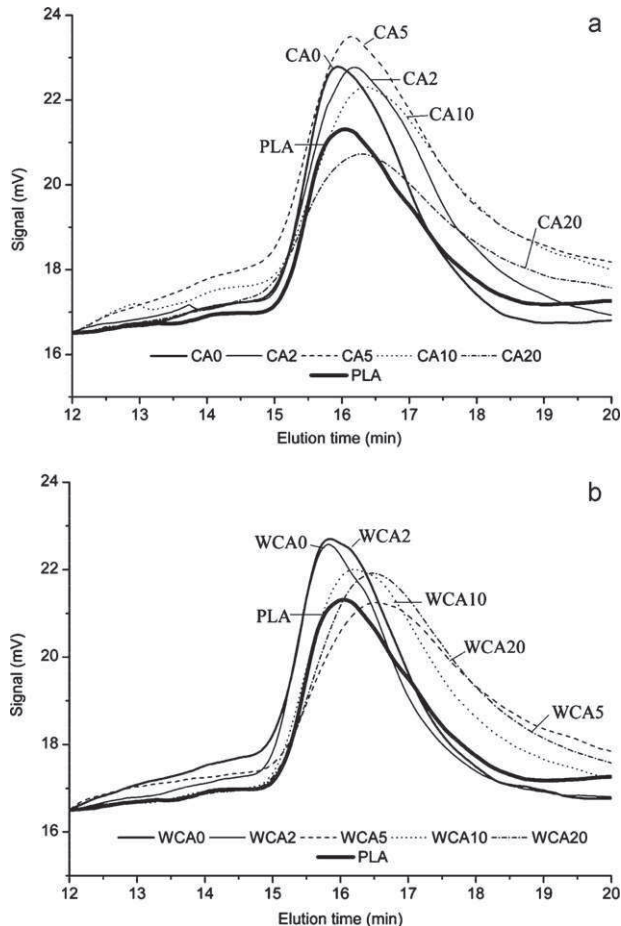


Fig. 7. Molecular mass distribution of PLA for the different blends.

They were nevertheless not as well-defined as they were for native wheat flour, and more spread over time. In spite of this molecular weight dispersion, a part of the amylopectin was still present. As soon as 2 parts of citric acid were added to the blend, molecular weight decreased a lot, and all the more as the citric acid concentration was increased. Different peaks of lower size than native amylose were visible.

PLA peak was shifted to longer elution time (smaller chains) (Fig. 7) when citric acid concentration increased for both types of blends (with or without water). This molecular weight decrease was not sufficient to impact the PLA glass transition temperature (Table 1). It is interesting to note that PLA molecular weight was kept when 2 parts of citric acid are added to a blend extruded with extra water (Table 1).

Citric acid ratio probably had an effect on the depolymerization mechanism. For low citric acid concentration (i.e. <5 parts), starch was preferentially hydrolyzed, as already seen on starch glass transition shift (Fig. 4), whereas for higher amounts both PLA and starch molecular mass distributions were reduced.

#### 4.2. Water influence

Without citric acid, both blends extruded with or without extra water showed the same properties (mechanical, thermal and morphological). Processing was clearly facilitated (Fig. 1); water is a process aid which did not impact on the material properties. Starch depolymerization might be weaker when the blends were extruded with extra water, as SEC peak corresponding to amylose did not move (Fig. 6). Unfortunately, weak amylopectin solubility did not allow a complete interpretation of the SEC traces.

With low citric acid amount, the use of water did not involve specific PLA hydrolysis (Fig. 7) as supposed. On the contrary, water might be completely mobilized within the starch phase (swelling), facilitating the citric acid penetration and inducing a slight increase of the SME during compounding. Citric acid penetration in the starchy phase was confirmed by a larger decrease of the damping factor peak for the starch phase, when compared to blends extruded without extra water (Table 1).

With more citric acid, water helped to preserve mechanical properties (Fig. 2); material elongation was higher without water but tensile strength was kept at acceptable level. This should be related to lesser extent of PLA depolymerization (Fig. 7). Moreover, the sizes of the PLA domains were smaller for blends extruded with water.

## 5. Conclusion

Wheat flour/PLA blends have been successfully produced on industrial equipments. The use of citric acid promoted the compatibility of the phases. Two different mechanisms have been enlightened depending on the use of extra water or not during the extrusion. With no added water, small amounts of citric acid tended to improve material properties, citric acid causing starch depolymerization and improving the PLA repartition in the matrix. When the citric acid ratio was increased, depolymerization of PLA and starch occurred and elongation at break increased drastically, but tensile strength decreased as well, leading to less tough materials. Adding small quantity of water during the extrusion was beneficial to the whole process, facilitating compounding, improving starch plasticization and lowering PLA depolymerization when small amounts of citric acid were used.

Blending thermoplastic wheat flour with PLA and citric acid led to highly deformable materials with an interesting toughness, thanks to the PLA, making them an interesting compromise between brittle PLA and very ductile glycerol-plasticized wheat flour.

Our group is currently working on the dynamic vapor sorption and permeability properties of these blends. The influence of citric acid on these properties will surely be discussed in another paper.

## Acknowledgements

We would like to thank Nathalie Aubezac and Joël Alexis (LGP) for their help for SEM images and Laure Candy and Jérôme Peydecastaing for their help for SEC analyses. The French Environment and Energy Management Agency (ADEME) and the "Conseil general des Hautes-Pyrénées" have participated to this work via financial support.

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