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Quaternary starch based blends: Influence of a fourth component addition to the starch/water/glycerol system

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Abstract

This paper deals with the effects of the addition of a fourth component to the starch glycerol/water/system used in thermoplastic starch materials on the basis of starch sorption site availability. These sites can sorbed both water and glycerol depending on the glycerol content and the chosen relative humidity. Starch sorption sites are saturated by specific glycerol + water concentrations, which defined the starch saturation point. The addition of a fourth component before, near or after this starch saturation point is a potentially interesting concept because of its effect on the mechanical properties of the whole system (quaternary system). This was illustrated with various types of fourth components introduced at low concentrations. The addition of maltose led to an efficient coplasticizing effect only after the saturation point. The addition of a polar polymer led to a strain increase (at break) before and at the saturation point, and to a strain decrease after the saturation point. The addition of fillers at the saturation point led to an unattempted plasticizing effect.

Keywords: Starch; Glycerol; Water; Maltose; Coplasticizer; Saturation point; Mechanical properties

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1. Introduction

Starch based material formulations generally contain more constituents than the starch/water/glycerol ternary systems well studied in the literature. Materials are either blended with fillers (De Carvalho, Curvelo, & Agnelli, 2001), fibers (Averous, Fringant, & Moro, 2001; Angles & Dufresne, 2001; Dufresne & Vignon, 1998; Wollerdorfer & Bader, 1998), polar synthetic polymers or biodegradable polymers (Ratto, Stenhouse, Auerbach, Mitchell, & Farrell, 1999; Seidenstucker & Fritz, 1998; Shogren, Lawton, Doane, & Willett, 2000; Walia, Lawton, Shogren, & Felker, 2000a,b; Wang, Sun, & Seib, 2002; Wang, Shogren, & Carriere, 2000). The plasticizing system can also be constituted of two components (Krogars, Heinämäki, Karjalainen, Niskanen, Leskelä and Yliruusi, 2003).

In a recent paper (Godbillot, Dole, Joly, Rogé, & Mathlouthi, to be published), we proposed a simple model of interaction between starch, glycerol and water. The saturation of starch sorption sites by both glycerol and water can be investigated on the basis of sorption stoechiometry. Indeed, the starch monomer can be considered as a trifunctional molecule; and water and glycerol as bifunctional molecules (Fringant, Desbrieres, Milas, Rinaudo, Joly and Escoubes, 1996; Joly, Gauthier, & Escoubes, 1996). The functionality was related to the ability to establish hydrogen bonds and was not simply related to the hydroxyl group number, i.e. glycerol, which was considered as bifunctional. Saturation of amorphous starch sorption sites by water/glycerol couple was obtained for several glycerol concentrations depending on the relative humidity: 23% glycerol at 0% RH, 20% glycerol at 11% RH, 17% glycerol at 58% RH and 13% glycerol at 80% RH for example (Godbillot et al., to be published). For glycerol concentrations above these saturation points, the glycerol was assumed to be sorbed in a multilayer form or to make clusters. It has been previously suggested that these glycerol clusters are responsible for the decrease in material cohesion (Follain, Joly, Dole, & Bliard, 2005a).

Generally, starch formulations are made with glycerol contents around 15-25%, i.e. in the range of the critical saturation point, in order to facilitate the extrusion process and to obtain soft materials (low elastic modulus). Unfortunately,

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Table 1
Commercial characteristics of polymers used as additives

Name	Molecular weight (g/mol)	Designation
PAA	$\overline{Mw}$ 1 250 000	PAA
PEG	$\overline{Mn}$ 10 000	PEG 10k
PVA/hydrolysis rate 99	$\overline{Mw}$ 13 000–23 000	PVA 13.H
PVA/hydrolysis rate 88	$\overline{Mw}$ 13 000–23 000	PVA 13.h
PVA/hydrolysis rate 99	$\overline{Mw}$ 124 000–186 000	PVA 124.H
PVA/hydrolysis rate 88	$\overline{Mw}$ 124 000–186 000	PVA 124.h

phase separation phenomenon (clusters) may appear and leads to weaker mechanical properties at break, which are already intrinsically low due to the starch structure (Tharanathan, 2003). Consequently, industrial applications use a fourth component in the formulation in order to improve mechanical properties. Depending on the content and the affinity of the fourth component towards starch/glycerol/water system, and depending on the starch and initial water content (above or below the saturation point), the position and the nature of the saturation point should vary. In this paper, we would like to illustrate the drawbacks and the advantages in introducing a fourth component before, after or around this saturation point.

Starch properties depend on many parameters including molecular interactions (the topic of this paper) and microstructure. In this paper we deliberately chose an interpretation at the molecular level, and thus discussion about structural effects have been disregarded when possible because

(i) we tried to work with a fully destructured starch (evaporation at high temperature for casting, use of preplasticised blends for extrusion
(ii) all systems were systematically compared to references obtained from the same process, which only differed by a small additional quantity of a fourth component; a quantity not supposed to affect processing behavior
(iii) all samples were tested after a quick water sorption equilibration (thin film) in order to avoid amylopectin recrystallisation.

2. Materials and methods

Native wheat starch was provided by Chamtor Company (Pomacle, France), contained 27% amylose and 73% amylopectin. It was stored under constant hygrometric conditions prior to use (57% relative humidity or 57% RH).

Glycerol (plasticizer), maltose (coplasticizer) and sodium benzoate (preservation agent) were all purchased from Avocado Research Chemical Ltd.

2.1. The fourth component:

Water-soluble polymers were used as additives-polyethylene glycol (PEG), polyvinyl alcohol (PVA) and polyacrylic acid (PAA) (Table 1)—were all purchased from Aldrich Chemical Company.

Inorganic fillers, titanium dioxide (TiO_2) and calcium carbonate ($CaCO_3$), were purchased from Prolabo. Wood cellulose fibers (Table 2) were purchased from JRS society.

2.2. Casting method:

Wheat starch aqueous suspensions, 4 wt%, were heated in a high pressure reactor at 120 °C for 20 min as described by Lourdin (Lourdin, Della Valle, & Colonna, 1995). Precise amounts of additives (plasticizers) were added. The solutions obtained were spread on a hot anti-adhesive coated mold maintained at 60 °C. This process speeds up water evaporation and avoids extensive starch retrogradation. The films obtained were transparent with a 80 μm average thickness.

For thermoplastic starch films prepared in the presence of a fourth component, the process was quite similar. Convenient amount of additives (maltose, water soluble polymers, fibers) were added in the suspension as described above. For water-soluble polymers (PVA, PEG, PAA), starch was added after the whole polymer dissolution in the appropriate amount of water to keep a 4 wt% starch aqueous suspension.

All films were stored under constant relative humidity (57% RH) for one week at 20 °C before testing. The ambient humidity was controlled by salt saturated aqueous solutions at 20 °C.

2.3. Extrusion method

Starch based films filled with inorganic fillers were obtained by the following extrusion process to avoid filler deposition of the suspension during the casting step. Hydrated starch (13 wt% water) and glycerol were premixed and heated for 45 min at 170 °C for plasticizer absorption and water evaporation. The dry blend was stirred while additives were added (water containing adequate amount of fillers). Water content was 20% on a dry starch basis. The mixture obtained was processed in a single screw extruder (SCAMIA, France). The barrel was heated in three zones (110, 115, 120 °C) and

Table 2
Commercial characteristics of cellulose fibers

Trade name	Length (μm)	Diameter (μm)	Designation
B600	60	20	SF
B400	900	20	LF

equipped with a slit die heated to 125 °C. The mixing screw diameter was 2 cm with a 11 *L/D* ratio and was operated at 40 rpm.

Extruded ribbons (150 μm thick) were stored at a controlled RH (57%) at 20 °C before mechanical testing.

2.4. Tensile test set up

A TEST 108 2kN (GT-TEST) equipped with a load cell of 500 N was used for tensile measurements. Tensile failure stress and strain were measured with a crosshead speed of 10mm/min under constant storage conditions (57% RH) and at 20 °C in an environmentally controlled instrument room. Dumbbell-shaped specimens of H_3 type were cut from the extruded and casted plates. Ten replicates were tested for each material and the average value of each quantity reported. The parameters used were strength and strain at break, often referred to in the literature as tensile strength and elongation. The maximum tensile strength was calculated from the initial sample section and was systematically measured before mechanical testing.

2.5. Water sorption measurements

The water uptake was studied over a period of 2 months. The starch film samples (~300 mg, 80 μm thick) were dried under vacuum for 2 h at 60 °C and weighed (m_{dry}). The samples were then stored at 20 °C in controlled equilibrium relative humidity in separate containers. The chosen humidity was 57% RH. Samples were periodically weighed and water sorption equilibrium was considered to be reach when no weight change occured m_{moist} (±0.001 g).

The water uptake was given by:

$$\text{water uptake (\%)} = 100\frac{m_{\mathrm{moist}} - m_{\mathrm{dry}}}{m_{\mathrm{dry}}}$$

3. Results and discussions

3.1. Coplasticization with maltose

In previous work, which focused on lignin plasticization (Bouajila, Dole, Joly, Lemaitre, & Limare, submitted for publication), we demonstrated that the plasticizing efficiency was differently controlled before and after the lignin saturation point. Before the saturation point, the key factor was the functionality of the plasticizer. After the saturation point, the plasticizer efficiency was mainly governed by the solubility parameter, which must be close to that of the polymer matrix. For example, water had the highest plasticizing efficiency below the saturation point and the lowest above saturation. Because of the semi polar character of lignin, this earlier study involved plasticizers with a large range of solubility parameters. This is not the case for polysaccharides, which solubilize only polar species. Nevertheless, this assumed double plasticizing mechanism can be applied to starch: after saturation of sorption sites, the plasticizer should act more as a chain extender than as an H bond inhibitor. Glycerol is far from being the best candidate for this second function, because of its incompatibility with starch. Consequently, it would be interesting to investigate the action of a coplasticizer, characterized by (i) a high compatibility with starch (ii) a steric hindrance inhibiting the competition with glycerol for the sorption on starch. Maltose was first selected. Fig. 1 show the variation of the mechanical properties as a function of maltose contents gradually added to an initial 10% glycerol plasticized system. As a reference, a glycerol plasticized system is systematically represented in the same way (quantity of glycerol added to an initial 10% glycerol system). The initial glycerol content increases from 10 to 20% from Fig. 1a–f.

For a 10% initial glycerol content (Fig. 1a and b), the plasticizing effect of maltose addition is very low compared to that of glycerol, which exhibits a conventional behavior: a strength decrease associated with a strain increase as a function of glycerol content.

The strain increase due to maltose addition is very low even at high additional levels. A small antiplasticizing effect of maltose (strength increase) at low contents is observed. This was previously described with sorbitol (Gaudin, Lourdin, Le Botlan, Ilari, & Colonna, 1999) and others polyols (Lourdin, Bizot, & Colonna, 1997) at low contents (well below the saturation point). Local interactions between the polymer network and the plasticizer decrease local macromolecular mobility, leading to an irregular evolution of mechanical properties with plasticizer content.

For a 15% initial glycerol content (Fig. 1c and d), the plasticizing effect of maltose at low contents remained lower than that of glycerol. However, at a high maltose content (27%), a non-negligible plasticizing effect was obtained (increase of strain and decrease of strength).

For a 20% initial glycerol content (Fig. 1c), the maltose plasticizing effect was the same as the glycerol one on the basis of the strain property. However, the loss of strength at break was much lower than in the case of the glycerol reference.

A plasticizing effect with maltose was observed only when hydroxyl site saturation was assured, this being the case for: (i) a 20% glycerol content. Because mechanical properties are measured at 57% RH, the theoretical glycerol concentration at saturation is near 17-18%; (ii) a 15% glycerol +13–27% maltose. This maltose concentration, equivalent to a smaller percentage of glycerol, seems very high. However, maltose was selected because of its difficulty in establishing hydrogen bonds. Moreover, maltose addition can shift the saturation point to higher glycerol contents (interaction between glycerol and maltose).

The fact that maltose and glycerol present exactly the same plasticizing effect in Fig. 1c (on the basis of strain property) validates the assumption of a physical plasticizing mechanism above the saturation point. This mechanism involves only the steric (/volumetric) effect of the molecules, acting as a chain extender.

If only the strain at break is considered, there is no advantage in using a fourth coplasticizer component (20%

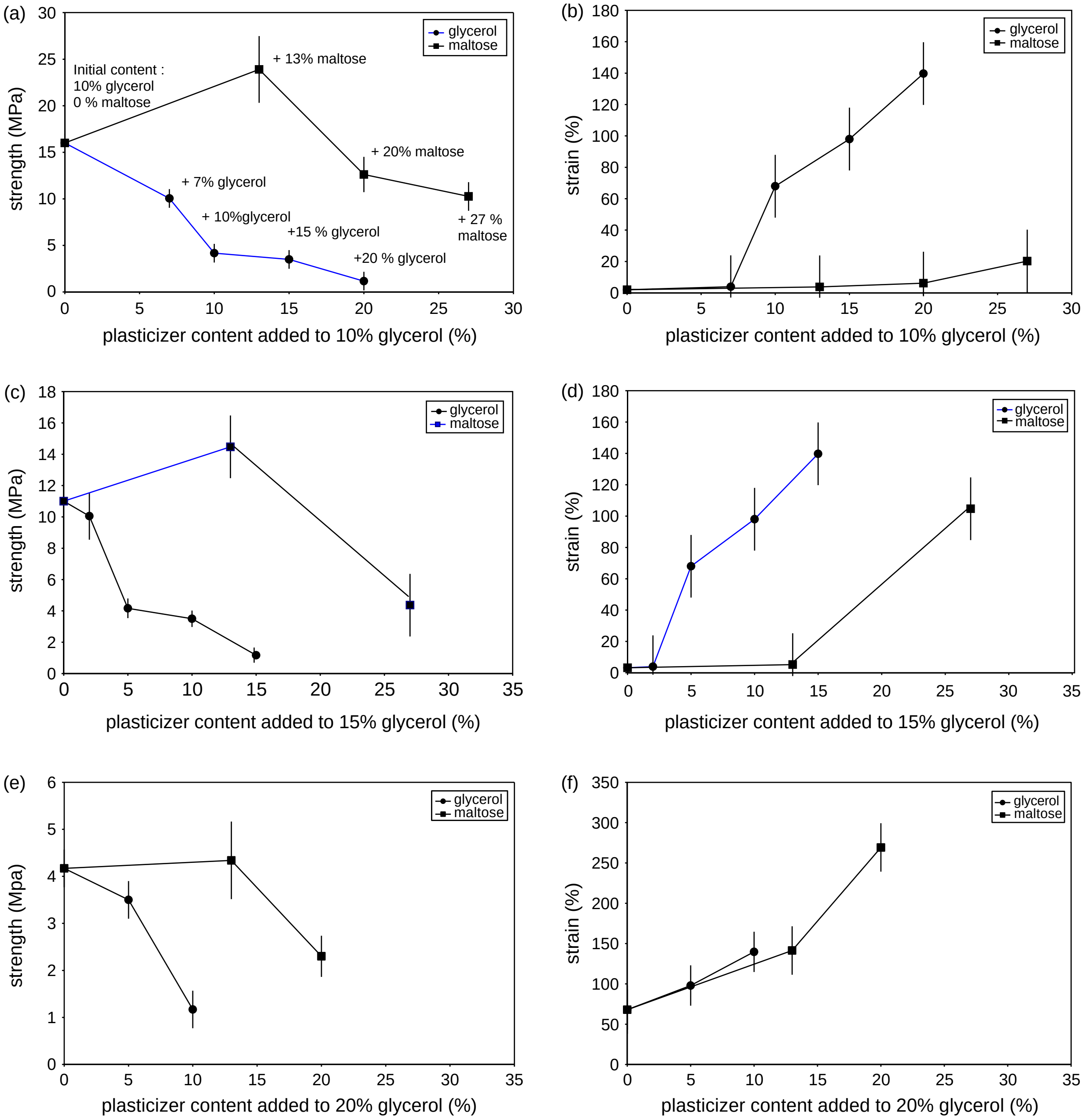

Fig. 1. Evolution of strength and strain at break for plasticized starch based films. Glycerol or maltose (coplasticizer) were added to films initially plasticized with 10% glycerol (a) and (b), with 15% glycerol (c) and (d), with 20% glycerol (e) and (f).

glycerol + 13% maltose = 30% glycerol). But the strategy presented here leads to higher strength (2 to 3 times better when compared to the glycerol reference). Multilayer glycerol and/or glycerol clusters have a negative impact on material resistance. On the contrary, free maltose, more compatible with amylose and amylopectin, should be better solubilized, even at concentrations higher than the saturation point.

The improved properties obtained by coplasticizing strategy illustrate the benefits of complex plasticizer systems. Maltose is highly compatible with starch but further studies are necessary to explore the characteristics of a good coplasticizer for natural (hydrophilic) polymers like volume or shape. For example, the higher the volume, the better the extender property, and the lower the plasticizer efficiency (assuming Couchman type relations). In this way, glucose, oligosaccharides and also cyclic oligosaccharides should be tested.

3.2. Polymer blends

In general, commercial starch/polymer based blends are formulated with glycerol contents between 20 and 30%, i.e. at concentrations above the saturation point at 50% RH. The added polymer develops interactions with the saturated starch (glycerol + water) and 'free' glycerol. This is not an ideal situation for creating starch / added polymer interactions. However, such interactions are necessary to limit the formation of a totally immiscible two phases system. In this part, the addition of polar polymers above, around and below the saturation point is studied. In order to attribute the mechanical response to the properties of the continuous starch based phase, we chose to test low contents of added polymer. In order to simultaneously compare strain and strength, strength versus strain graphs were drawn (Follain et al., 2005a). The dotted line was obtained from the properties of glycerol plasticized systems, from 5% glycerol (noted SG5) to 30% (noted SG30) . In this previous paper, we demonstrated that most ternary, quaternary starch based systems presented in literature had the same mechanical properties as those described by this dotted line. To make innovative materials the mechanical properties must be located above the dotted line.

- Fig. 2a shows the variation of mechanical properties (strength + strain) resulting from the addition of 12% polyvinyl alcohol to a 5% glycerol plasticized system (noted SG5). The strain at break increases while the strength remains constant.
- Fig. 2b shows the variation resulting from the addition of 2% polyacrylic acid (PAA), polyethylene glycol (PEG), and polyvinyl alcohol (PVA) to a 17% glycerol plasticized system (noted SG17). A significant increase of strain at break is obtained, associated with a strength increase for PEG and PAA. Higher contents of PVA (up to 10%) lead to an additional strain increase at break as a function of the PVA (macromolecular weight), but with a minor amplitude.
- Fig. 2c shows the influence of the addition of PAA, PEG and PVA to a 22% glycerol plasticized system (noted SG22). An inverse effect is observed and depends on the nature of the added polymer. A 2% addition of PEG or PAA drastically decreased the strain at break, i.e. the properties at break are those obtained for SG17. The addition of only 2% PVA had no effect on the mechanical properties, but the increase of PVA content up to 10% gave similar effect to PEG and PAA but with a minor extend.

Below and near the saturation point (Fig. 2a and b), the interactions between starch and added polymer can be established based on the availability of bonding sites, which are free of glycerol. At 17% glycerol, the added amount of a fourth component is limited, even if a saturation point shift is possible. Consequently, adding more than 2% PVA does not lead to a major change of the mechanical behavior, possibly due to phase separation. Theoretically, 17% glycerol is the exact saturation point, but sorption sites can be created either by glycerol moving or by the decrease of water content. Authors have previously demonstrated that the addition of PVA to starch decreases the water content, even at low PVA concentrations (Follain, Joly, Dole, & Bliard, 2005b).

Above the saturation point (Fig. 2c), polymer/starch phase separation cannot be avoided, even at low content. Free glycerol is available to interact in the dispersed phase, at the interfaces, and in the continuous starch phase. The concentration of glycerol in the continuous starch phase can thus be decreased, which explains the property shift towards a less plasticized starch system.

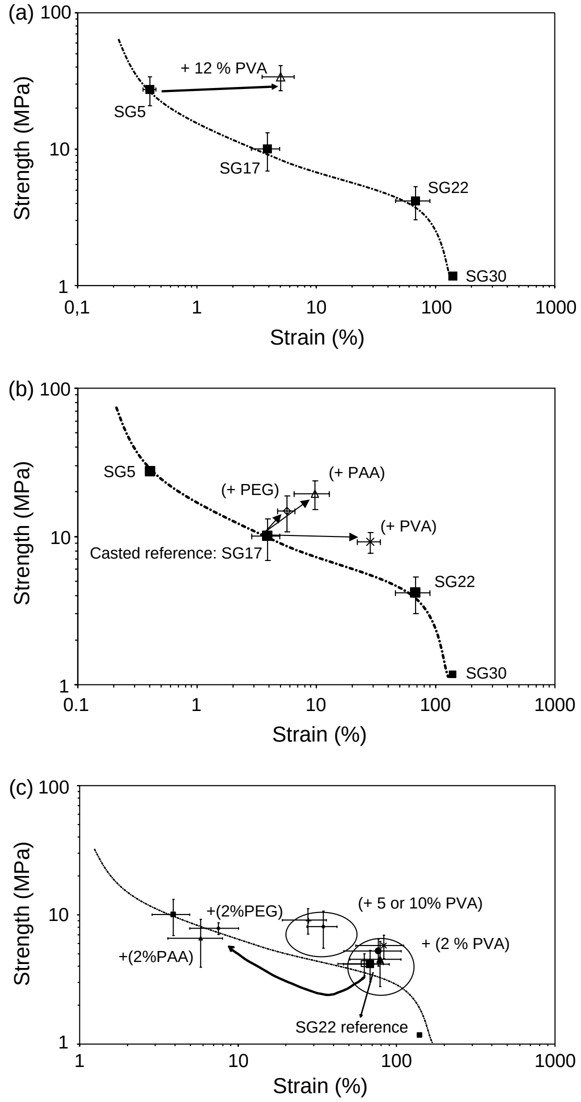

Fig. 2. Influence of polymer addition on the strength/strain properties of a starch/glycerol/water system before (a), at (b) and after (c) the saturation point. (a) Strength versus strain at 57% RH for plasticized starch materials. The dotted curve represents the evolution of starch plasticized with increasing glycerol amounts (5, 17, 22 and 30 wt%, noted SG5 to SG30). △, SG5 + 12% PVA 13.H. (b) Strength and strain at break properties for starch + polymers blends containing 17 wt% glycerol. The arrows represent the evolution of the mechanical properties after the polymer introduction in comparison with the reference SG17. Starch blends: △, SG17 + 2% PAA; ◇, SG17 + 2% PEG 10k; ∈, SG17 + 2% PVA 124.H. (c) Strength and strain at break properties for starch based films containing 22%wt glycerol after polymer introduction. △, SG22 + 2% PAA; ◇, SG22 + 2% PEG10 k; □, SG22 + 5% PVA 124.h; ▲, SG22 + 2% PVA 13.88; ●, SG22 + 2% PVA 12.h; ×, SG22 + 10% PVA 124.h; ♦, SG22 + 5% PVA 124.H; +, SG22 + 10% PVA 124.H.

The aim of this part was not to focus on materials exhibiting optimized mechanical properties, i.e. involving higher contents of added polymer. By studying blends with low polymer content, we wished to look for starch formulations, which

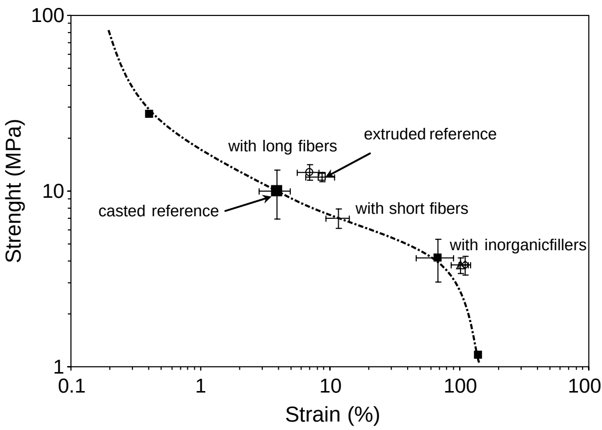

Fig. 3. Influence of filler and fiber addition to the strength/strain properties of starch based films plasticized with 17 wt% glycerol. Reference: ■, Casted reference; □, extruded reference, Starch systems: ○, SG17+5% LF; +, SG17+5% SF; △, SG17+5% TiO$_2$; ◇, SG17+5% CaCO$_3$.

would improve the interactions between starch and the added polymer. Interactions are possible for a glycerol concentration less than 20% (in classical conditions of ambient humidity, i.e., near 50% RH). The glycerol content in materials is usually equal to or higher than 20%, because around this concentration, and at 60% RH, starch glass transition is near room temperature. Two options are thus possible: either a ductile starch matrix and no interactions with added polymer, or a brittle starch matrix and good interactions with added polymer. A strategy of material formulation should systematically test both options. A third possibility is to work at the saturation point. In this condition, the starch matrix is almost ductile, and interactions are possible due to the displacement of the starch/water/glycerol equilibrium.

3.3. Inorganic fillers and natural fibres

We have demonstrated above that the introduction of an incompletely miscible fourth component shifted the interaction equilibrium between starch, water, and glycerol. In this part, we investigated the introduction of an immiscible species, one that cannot absorb significant amounts of glycerol or water due to a high cristallinity rate. Calcium carbonate, titanium dioxide, and commercial cellulose fibers were selected. These systems can only interact through interfaces. In order to observe a potential equilibrium change, we chose to work at the saturation point (17% glycerol, 57% RH, noted SG17). As previously discussed, low filler contents were introduced (5%), in order to measure properties mainly related to the starch/water/glycerol equilibrium. For practical reasons, cellulose filled systems were obtained by casting and inorganic filled systems were extruded. Fig. 3 shows the strength/strain graph of a filled thermoplastic starch as well as the two references of the unfilled materials. In both cases, the addition of fillers is associated with an increase of the strain at break. It should be emphasized that the evolution of properties was opposite to those expected, i.e. a strength increase and a strain decrease (at break). Indeed, the conventional description of a fibers/fillers reinforced composite is based (i) on the mixing law as the addition of a high modulus system increases the rigidity (ii) on the local matrix mobility decrease due to interactions at an interface. Fig. 4 shows the water content at 57% relative humidity of the filled materials. Two references are presented: the water uptake of the unfilled system and the underestimation of the water uptake of filled materials, assuming totally impermeable fillers and no interaction with the plasticized starch system. In all cases, the water content is lower than this last reference, suggesting a significant interaction between the fillers and the plasticized starch.

The irregular evolution of the mechanical behavior and the water uptake can be explained by strong interactions between starch and fillers, as previously described from viscoelastic measurements (Dufresne, 2000). The decrease of available sorption sites could lower the equilibrium water

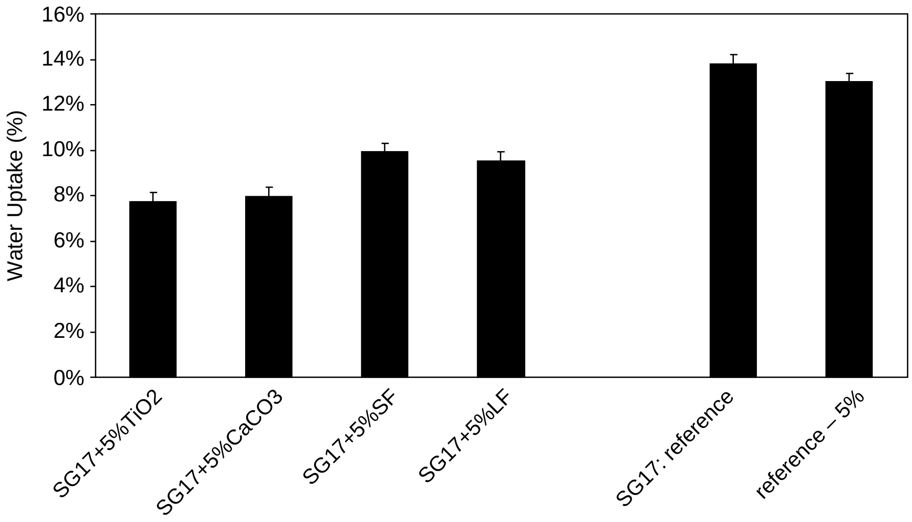

Fig. 4. Water uptake of filled materials shown in Fig. 3.

content as well as the critical glycerol concentration. This may explain the variation of mechanical properties, equivalent to an addition of 'free' glycerol. The introduction of fillers has thus the same effect as the introduction of polymers in the starch matrix.

The large evolution of physicochemical properties of starch materials formulated near the saturation point cannot be solely explained by sorption stoechiometry. For example, in a previous paper (Follain et al., 2005b) we observed a water content decrease of 3% at 57% RH after the introduction of 2% PVA. The high functionality of PVA cannot explain this decrease. Moreover, the number of sorption sites at a filler surface is not directly related to the decrease of 4% water content for cellulose fibers, and around 6% water content for inorganic fillers.

In the present paper, we studied starch based materials with a low crystallinity rate (retrogradation avoided by a quick equilibration of thin films) (Delville, Joly, Dole, & Bliard, 2003; Van Soest & Knooren, 1997) in order to assume starch hydroxyl site availability. This ignores the amylose crystalline fraction, which could be affected by a change of the starch environment (presence of fillers and additive polymer). Moreover, when a higher water sorption decrease was obtained for the inorganic filled materials, a higher degradation may probably occur during the extrusion process. As the macromolecular weight is related to the water sorption uptake, shorter macromolecules, being more tightly packed, partially inhibit hydration (Turner, 1987).

In spite of these arguments to the contrary, the general tendencies observed here cannot be questioned: the addition of polymer or fillers at a low content to starch at the saturation point leads to a plasticizing like effect. It is thus possible to obtain close interactions with starch at the saturation point. At this point, the matrix starts to be ductile, but still keeping the ability to develop interactions.

4. Conclusion

We have shown that the effect of a fourth component addition on the mechanical properties of a starch/glycerol/-water system depends on the starch sorption site availability. This was illustrated with various types of fourth component additions:

- the addition of maltose leads to an efficient coplasticizing effect only for a concentration of glycerol higher than the starch saturation point
- the addition of a polar polymer to starch leads to a strain increase at break before and at the saturation point, and to a strain decrease only above the saturation point.
- The addition of inorganic fillers and natural fibers gave a strength decrease and a strain increase at break instead of giving the expected filler/fiber reinforced composite.

Formulating starch materials at the saturation point is a potentially interesting strategy because:

- the matrix ductility is acceptable
- strong interactions can take place with the fourth component due to a change of the starch saturation point (water and glycerol motions)
- the addition of a coplasticizer is possible to avoid glycerol enriched domains, which decrease the materials cohesion.

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