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Properties of starch based blends. Part 2. Influence of poly vinyl alcohol addition and photocrosslinking on starch based materials mechanical properties

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Abstract

Mechanical properties of starch/PVA blends (maximum 5% wt PVA), with or without crosslinking, have been analyzed in order to study how the increase in the linear to branched chain can improve the material's performances. As a result, elongation is enhanced without significant strength decrease for both casting and extrusion processes. Water sorption and photocrosslinking ability have also been measured showing a fairly good compatibility between the two macromolecular components: PVA and starch. For example, a decrease in water sorption on PVA addition was observed which could not simply be related to additivity between the two polymers. Finally, systems composed of pure glycerol plasticized starch blends were photocrosslinked at very low rates in order to 'lengthen' the macromolecules. The results of the mechanical tests on these materials showed an enhancement of the elongation at break.

These results highlighted the fact that a modification of the molecular weight distribution (or linear long chains ratio, i.e. PVA) led to the development of entanglements or long distance interactions (strain at break increase).

Keywords: Starch; Polyvinyl alcohol; Crosslink; Water sorption; Mechanical properties

1. Introduction

The end of 20th century has seen extensive work aimed at replacing petrochemical-based plastic materials by renewable bipolymers. Since the seventies, starch has been considered a good candidate in thermoplastics technology (Doane, 1992; Griffin, 1977; Swanson, Westhoff, & Doane, 1988) for the production of biodegradable plastics. Starch is a low cost renewable agro-resource composed of amylose and amylopectin polysaccharides. To compete with the existing thermoplastics, starch-based materials should have similar thermo-mechanical characteristics in order to be processable in existing standard plastics equipment, and end use properties comparable to synthetic plastics. These requirements are not realistic because the major disadvantages of these starch based biodegradable materials are the particularly poor mechanical properties, generally attributed to the very branched structure of amylopectin along with their intrinsic hydrophilicity. Nowadays, only applications that do not require high stress and strain at break such as pharmaceutical capsules (Stepto, 1997) and biodegradable packaging chips (Bastioli, 1998) are amongst the few commercialized starch based products.

In the first part of this study, we reviewed the mechanical properties of plasticized starch based materials from the literature (Follain, Joly, & Dole, accepted). The methodology relied on the use of a strength/strain at break graph allowing the direct comparison of materials mechanical performances at a given relative humidity (RH). Moreover, the mechanical properties were compared with glycerol plasticized starches in order to highlight any specific mechanical behavior which could not be explained by plasticization. Surprisingly, on the graphics, materials mechanical performances were often located close to the

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ones obtained by simple glycerol content variation. In the light of these observations, most of the starch-based systems seemed to be roughly equivalent, whatever the numerous strategies reported in the literature for these materials. Based on these results several starch development approaches were then proposed by the authors (Follain et al., accepted) depending on the required performance at break. This paper deals with one of the proposed strategies based on long distance interactions (entanglements), which will play a major role in improving the elongation at break. In this respect, it appears that the geometry of native starch macromolecules is not tailored to fulfill such interactions. The starch macromolecule's architecture has to be modified in order to increase the linear to branched chain ratio. In the present study we investigate the influence of (i) the addition of long PVA chains to starch systems (i.e. polymer blends) (ii) the starch/PVA chains grafting to starch and (iii) 'lengthening' starch by controlled crosslinking, on the material's properties. Polyvinyl alcohol (PVA) was chosen because starch/PVA blends have demonstrated excellent compatibility (Kondo, Sawatari, Manley, & Gray, 1994; Nwufo & Griffin, 1985). All measurements were made on glycerol plasticized wheat starch systems. The present study essentially deals with economically viable materials that is to say materials formulated with a large amount of renewable and low cost native starch: blends made with high PVA contents were excluded.

In the case of a blend composed of two hydrophilic polymers, when one of the polymer is at low concentration (PVA in our case), water is an efficient probe, able to investigate polymer/polymer interactions. Therefore the water sorption properties of these blends reflect the compatibility. Chemical reactivity of starch/PVA blends was studied in order to analyze the influence of PVA's presence on the efficiencies of the photocrosslinking reaction. Controlled photocrosslinking (at very low crosslinking rates) was also performed in order to obtain a modified starch, lengthened by starch/starch interlinkages.

2. Materials and methods

2.1. Components

Native wheat starch (27% amylose and 73% amylopectin) was provided by the Chamtor company (Pomacle, France). It was stored at 57% relative humidity prior to use. Polyvinyl alcohol polymers having different molecular weights ($\bar{M}w$) and acetyl groups hydrolysis rates (noted l, h and H for 80, 88 and 99% hydrolysis, Table 1), were purchased from Aldrich.

Sodium benzoate and glycerol, used respectively as photosensitizer and plasticizer, were both purchased from Avocado Research Chemical Ltd.

Table 1
Characteristics of selected polyvinyl alcohols

Molecular weight range ($\bar{M}_w$)	Acetyl hydrolysis rate (%)	Designation
13,000–23,000	99	PVA 13.H
13,000–23,000	88	PVA 13.h
124,000–186,000	99	PVA 124.H
124,000–186,000	88	PVA 124.h
9000–10,000	80	PVA 9.l

2.2. Film designation

The film nomenclature is referenced as follows:

SG17 for a wheat starch film plasticized with 17% wt glycerol.

SG17 + x% PVA w.h is used for a starch film plasticized with 17% wt glycerol, containing x% wt PVA of 10^3 weight average molecular weight. Two hydrolysis rates were employed and noted as h for 88% and H for 99%.

The weight percentages of glycerol and PVA were calculated on the dry starch basis. All films contain photosensitizer (1% wt with respect to the dried starch + glycerol contents), necessary to the crosslinking reaction (Delville, Joly, Dole, & Bliard, 2002) and also used as preservative.

2.3. Film preparation

2.3.1. By casting

Wheat starch aqueous suspensions, 4% weight, 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 (photosensitiser, polyvinyl alcohol and plasticizer) were added. The solutions were spread on a hot anti-adhesive coated mould maintained at 60 °C. This stage speeds up water evaporation and avoids extensive starch retrogradation. The films obtained were transparent with a 80 μm average thickness. All films were stored under constant relative humidity (RH) for one week before testing. The atmosphere's humidity was controlled by salt saturated aqueous solutions at 20 °C.

2.3.2. By extrusion

Starch 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 dissolved sensitizer and polyvinyl alcohol). The mixture obtained was processed in a single screw extruder (SCAMIA, France). The barrel was heated in three zones (110, 115, 120 °C) and equipped with a slit die heated to 125 °C. The mixing screw diameter was 2 cm in diameter, had a 11 L/D ratio and was operating at 40 rpm. Water content was 20% on a dry starch basis.

Extruded ribbons (150 μm thick) were stored under constant RH at 20 °C before mechanical testing.

2.4. Storage conditions

Films were stored at 57% RH in closed chambers over saturated sodium bromide solution at 20 °C. Each sample was tested after 1 week of storage to ensure water sorption equilibrium.

2.5. Ultraviolet irradiation

Before being conditioned, films were irradiated, when necessary, under atmospheric conditions at 40 °C for 2 h with a FUSION UVF 1000 mercury lamp (emitting mainly at λ max 365 nm and delivering 34 mW/cm^2) as described by Delville (Delville et al., 2002).

2.6. Gel fraction and swelling degree measurements

The gel fraction was determined as the insoluble part of the film immersed in dimethylsulfoxide (DMSO) in which starch was originally soluble.

Irradiated or non-irradiated formulated films were conditioned at 57% RH for 5 days before being immersed in DMSO (10 ml) at 25 °C for 24 h (at this stage the films' DMSO sorption was considered to be at equilibrium). The soluble part and additives were extracted. The insoluble part corresponding to the swollen film was gently wiped, weighed (m_s) and thoroughly washed, by immersion in water first and then in ethanol, in order to remove the DMSO. The insoluble part was then dried at 80 °C in an oven for 24 h and reconditioned at 57% RH before weighing (m_d). The final conditioning allowed to have a controlled moisture absorption at a controlled relative humidity to be achieved.

The gel fraction GF and the swelling degree SD were given by:

$$\mathrm{SD} = \frac{m_s - m_d}{m_d} \approx \frac{m_s}{m_d}$$

with $m_d \ll m_s$ for low crosslinking density

$$\mathrm{GF} = \frac{m_d}{m_c} \times 100$$

where m_c is a film weight at 57% RH.

2.7. Water sorption properties

The water uptake was studied over a period of 2 months. The starch films samples (about 100 mg, 80 μm thick) were dried under vacuum for 2 h at 60 °C and weighed (m_{dry}). Then, samples were stored at 20 °C in equilibrated controlled relative humidity in separate containers. The chosen humidities were 15, 32, 43, 58, 75, 84, 88 and 98% RH. Samples were periodically weighed and water sorption equilibrium was considered to be reached when no weight change occurred m_{moist} ($\pm$0.001 g).

The water uptake was given by:

$$\text{Water uptake} = \frac{m_{moist} - m_{dry}}{m_{dry}}$$

2.8. Mechanical properties

A TEST 108 2 kN (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 10 mm/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 or casted films. Ten replicates were tested for each material and the average value of each quantity reported. The parameters used were strength and strain at break. The tensile strength was calculated from the initial sample section systematically measured before mechanical testing.

3. Results and discussions

3.1. Starch/PVA blends

3.1.1. Mechanical properties

In order to study starch films mechanical properties, i.e. tensile strength and elongation at break, were recorded. To compare the results, an internal reference curve was obtained for starch films plasticised with several glycerol contents as shown in Fig. 1 (5, 17, 22 and 30% by weight) (Follain et al., accepted). This curve (dotted line) presents a typical plasticizing behavior i.e. strength decreases and strain

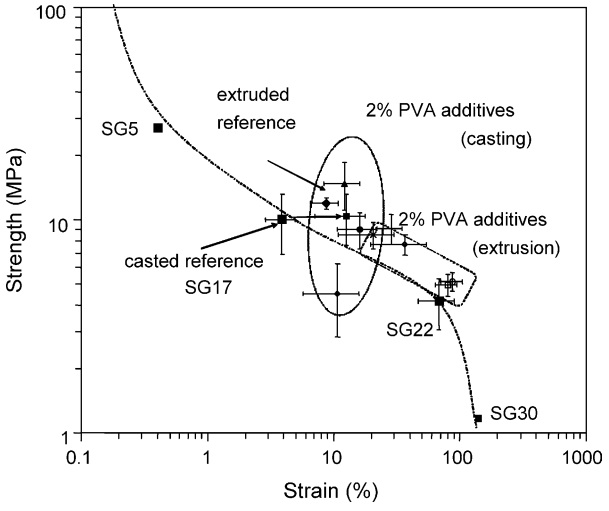

Fig. 1. Strength versus strain at 57% RH and 20 °C for starch+PVA blends containing 17% wt glycerol. The dotted curve represents the evolution of starch plasticized with increasing glycerol amounts (5, 17, 22 and 30% wt). Casted and extruded references are shown in the graph. Casted blends: ▲: SG17+2% PVA 9.l, ■: SG17+2% PVA 124.h, ♦: SG17+2% PVA 124.H, ●: SG17+2% PVA 13.h, +: SG17+2% PVA 13.H. Extruded blends: □: SG17+2% PVA 124.h, ◇: SG17+2% PVA 124.H, ○: SG17+2% PVA 13.h, ×: SG17+2% PVA 13.H.

increases at break with the increasing plasticizer content (without antiplasticizing effect). The log/log presentation is used for clarity. Useful new properties are obtained for a material presenting properties above the starch/plasticizing dotted curve.

In this figure, the mechanical properties evolution (at break) is represented in comparison with two starch systems taken as references, i.e. extruded and casted references films. Since film preparation procedures can affect mechanical properties (Rindlav-Westling, Stading, Hermansson, & Gatenholm, 1998) selected plasticised PVA/starch systems obtained through both casting and extrusion processes were tested.

3.1.1.1. Casted samples. Compared to the reference (casted PVA free sample—casted SG17), materials (positioned in the circle in Fig. 1) showed that the presence of 2% PVA systematically led to a *strain increase* (from 4 to 30% depending on the systems) generally obtained *without* any strength decrease. No significant differences were observed by varying the PVA characteristics except for the longer PVA (PVA 124.H) which showed less interesting properties.

3.1.1.2. Extruded samples. Taking the extruded PVA free sample as a convenient reference, extruded materials (located in the rectangular shape) presented higher strains at break than those obtained by casting (the increase being from 8 to about 90% depending on the systems).

Concerning the references (casted or extruded SG17) and the starch/PVA blends, it is to be noticed that extrusion systematically lead to materials with a slightly higher elongation at break. Since all systems were identically formulated, this increase would be mainly due to the extrusion step. Several hypotheses can be made in order to explain that phenomenon: the casting method involves a drying step at high temperature (60–70 °C) during which starch is at the rubbery state for a sufficiently long time to enable macromolecular reorganization (recrystallization to occur). This starch retrogradation could explain the differences observed between the references' mechanical performances (casted and extruded SG17), i.e. the recorded elongation of the extruded sample is double for an identical strength (Fig. 1) (Rindlav, Hulleman, & Gatenholm, 1997; Rindlav-Westling et al., 1998).

Concerning the blends, the lower elongation increase obtained with the casting method with respect to the extrusion process could be explained by the conformation of macromolecules: the casting process can favor self associations between PVA macromolecules (random coil chain) instead of the desired starch/PVA interactions. On the contrary, the extrusion technique can force the PVA macromolecules to be stretched out in a linear conformation, thus interacting with starch chains (H bonds). It is interesting to notice the difference in the mechanical properties observed with the various PVA's acetyl hydrolysis rate (88 or 99%). The more hydrolysed samples showed an earlier break. The starch+PVA systems (88%, 124 h and 13 h) are close to those obtained for starch alone when plasticized with 22% glycerol: the addition of 2% PVA seems to be 'equivalent' to 5% glycerol (with respect to the reference SG17). The presence of long PVA chains in starch systems seems to lead to the required properties.

3.1.2. Water sorption properties

3.1.2.1. Unplasticized samples. In Fig. 2, the water uptake of several cast starch based systems was recorded as a function of PVA's content (2% wt) and type (13,000 and 124,000 g/mol, 99% hydrolyzed). In order to compare the water sorption properties with reference systems, pure PVA and starch only films were prepared using the same procedure as for starch/PVA blends (casting) and their water uptake analyzed. Pure PVA films gave a much lower water uptake

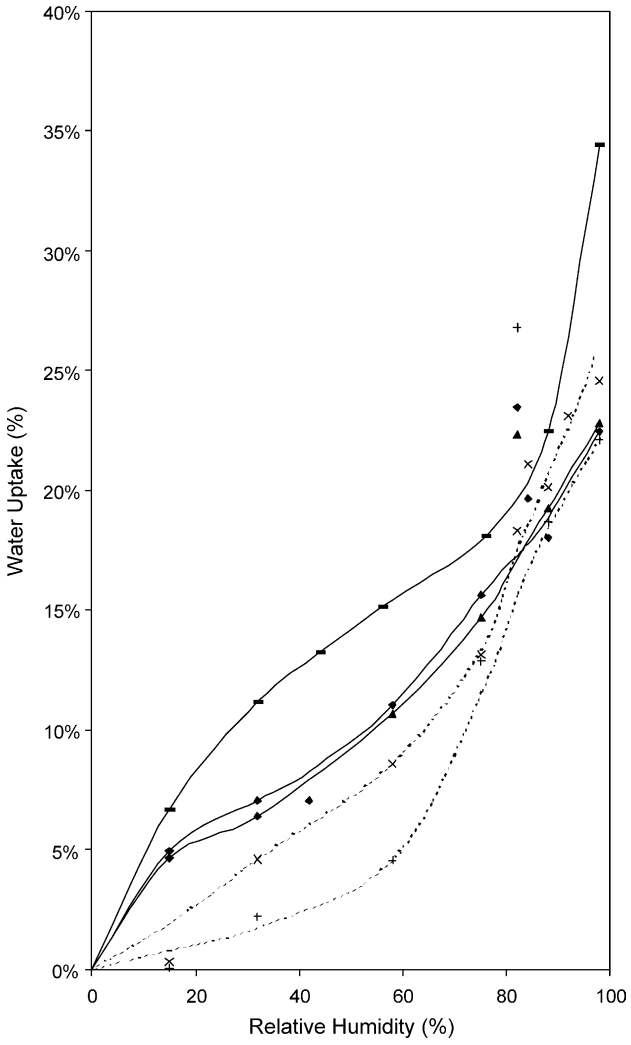

Fig. 2. Water sorption isotherms at 20 °C of unplasticized materials: −; starch reference, ×: PVA 124.H reference, +: PVA 13.H reference and non plasticized starch-based materials containing 2% wt of PVA (◆: 2% PVA 124.H, ▲: 2% PVA 13.H).

than that of starch films, but the differences in water uptake are more pronounced for low and medium RH.

After the addition of 2% wt PVA, the starch/PVA isotherms show a much lower water uptake than the one recorded for pure starch. This effect is particularly pronounced in the specific water sorption region (from 0 to 70% RH). A 30% difference is observed at 57% RH (Fig. 2). In the water hydration area (higher RH), this decrease is less pronounced, but still noticeable. No significant difference could be observed with PVA type (molecular weight or hydrolysis rate) considering S + 2% PVA 13.H or S + 2% PVA 124.H (Fig. 2).

A theoretical sorption isotherm of starch/PVA blend was calculated taking into account the calculated contributions of both components (98% of the water uptake of starch + 2% for PVA). As expected, this calculated isotherm, based on the linear contribution of both components, superimposes with the starch isotherm because the contribution of such low PVA concentration on the blend's isotherm is not noticeable. Thus, the drastic sorption decrease observed for starch systems in the presence of 2% PVA is not simply related to the PVA content.

3.1.2.2. Plasticised samples. In Fig. 3, the effect of a 17% wt glycerol addition to the systems previously shown in Fig. 2 is presented. It is well known that the presence of glycerol decreases water sorption as already reported (Gaudin, Lourdin, Le Botlan, Ilari, & Colonna, 1999; Lourdin, Coignard, Bizot, & Colonna, 1997) and this phenomenon can be explained as follows: water bonding sites occupied by glycerol are unavailable for water. Between 40 and 80% RH, a slight decrease is noticed between the plasticized starch reference (SG17) and plasticized systems filled with 2% of low molecular weight PVA (13,000 g/mol). However, such a difference is not in relation with the much more significant water uptake decrease observed in the unplasticized systems. The presence of glycerol appears to cancel the previously observed hydrophilicity decrease. Moreover, as previously described for unplasticized systems, no significant differences were observed using PVAs having different characteristics.

The water uptake decrease observed in unplasticized systems after the addition of 2% wt PVA can not only be explained by the consumption of starch water binding sites as in the case of plasticizers. One of the possible explanation for these unusual results could be that the presence of PVA in the blend induces a conformational modification of the amylose/amylopectin blend. Raj, Raj, Madan, and Siddaramaiah (2003) reported that PVA/starch systems in opposite proportions (small amounts of starch in PVA matrix) displayed a similar discrepancy between theoretical and experimental water uptake values as a function of the starch content. The addition of 10% wt starch led to a decrease of nearly 40% of PVA's water uptake. This unexpected decrease was attributed to the formation of hydrogen bonds between the two polymers which reduced its capacity to absorb water.

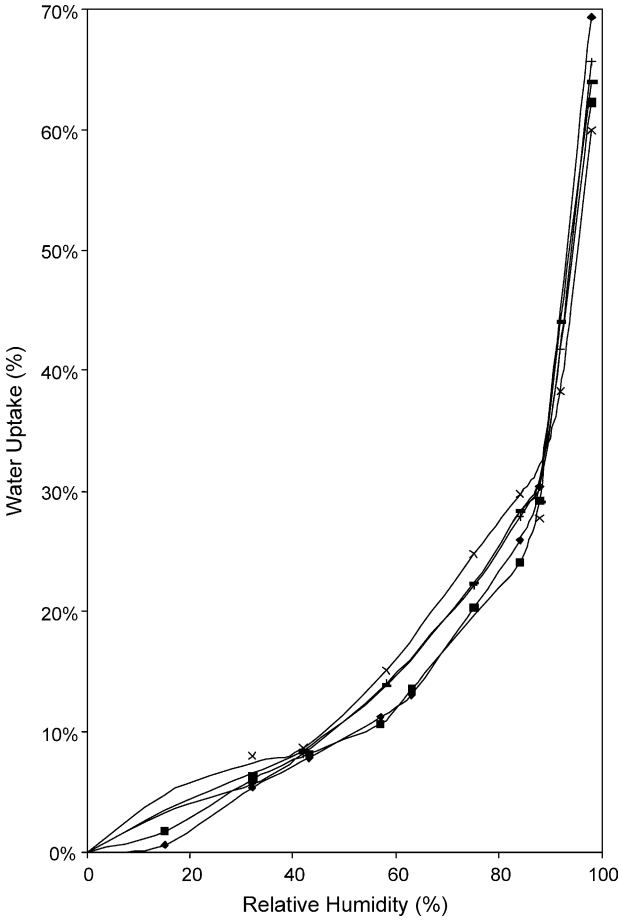

Fig. 3. Water sorption isotherms at 20 °C of plasticized materials: −: starch reference (SG17) and starch/PVA blends: ×: SG17 + 2% PVA 124.H, +: SG17 + 2% PVA 124.h, ♦: SG17 + 2% PVA 13.H, ■: SG17 + 2% PVA 13.h.

3.2. Starch PVA blend crosslinking

In this study some of the starch materials underwent a photochemical treatment as a result of UV curing in the solid state (film) (Delville et al., 2002). Sodium benzoate was used as the UV sensitiser and was added to all systems (3% wt). Previous work (Delville et al., 2002) has demonstrated a network structure formation occurring during UV irradiation. Such networks are characterized by the Gel Fraction (GF) and Swelling Degree (SD) measurements in DMSO. GF is directly related to the macromolecules' crosslink degree and SD to the density of the newly created network. These values allow the recording of the crosslinking kinetics as a function of the UV exposition time.

In Fig. 4, the starch blend crosslinking kinetic (S + 5%PVA 124.H) is represented in comparison with the one of pure materials (starch and PVA). After 120 min of UV exposure, both starch and PVA gel fractions reach,

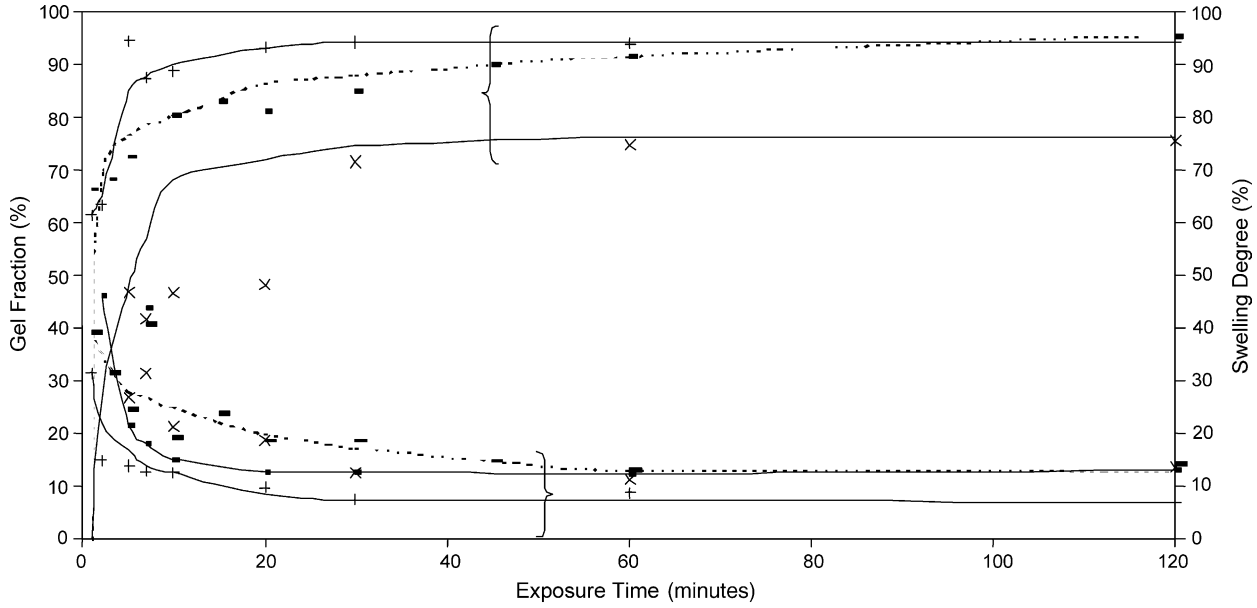

Fig. 4. Crosslinking kinetics of non plasticized starch based systems. −: starch reference, ×: PVA 124.H reference and +: starch+2% PVA 124.H

respectively, 95 and 75%. In addition, the PVA GF kinetics are slower than those recorded for starch+PVA blend and pure starch. This phenomenon can be related to the notion of a critical molecular mass introduced by Takakura (Takakura, Takayama, & Ukida, 1965). On the other hand, starch/PVA blend system reached the highest GF plateau value (99% from 20 min of irradiation).

Measured SD (swelling degrees) are displayed in Fig. 4. Starch/PVA blend showed a larger kinetics of swelling and the results are closer to those already described for the gel fraction. The starch/PVA system presents a swelling degree of 5 (five times the initial weight), smaller than the ones observed for both pure polymers films (SD value of 12 at 120 min) which correspond to the higher crosslinking density.

Starch/PVA blend systems show a higher reactivity than the reference materials obtained in the same experimental conditions. This optimized network presents a high crosslinking density (low SD of 5, i.e. swelling 500%). This higher starch/PVA reactivity could be explained by privileged interactions development leading (i) to a denser material favoring the radicals combination occurring during the network creation (Delville et al., 2002) (ii) to a 'more amorphous' initial material taking into account that the presence of PVA can prevent starch retrogradation. Even if it was not possible to prove such a hypothesis, these results seem to be related to the previously described modification of water sorption properties.

3.2.1. Influence of crosslinking on starch/PVA blends mechanical properties

The crosslinking step leads to an insoluble macromolecular network. As in all other studied systems, at the end of the reaction films are nearly totally insoluble (except for pure PVA), starch/starch and starch/PVA chemical bonds are created. In order to investigate the influence of the PVA chains, grafted onto the starch skeleton, the mechanical behavior of such systems was measured and compared to the crosslinked blanks (PVA free samples). The blanks are shown in Fig. 5 and corresponded to the previous reference curve before and after irradiation. Irradiation systematically induced a 2–2.7 times strength increase but accompanied by a strain loss; except for one reference (SG17); this behavior is not particularly interesting, being a typical case of a conventional mechanical properties evolution achieved by a network creation.

Starch/PVA blends—comprising 2 and 5% wt (124,000 g/mol, 99% hydrolyzed) PVA—were also photocrosslinked and analyzed. The resulting materials presented

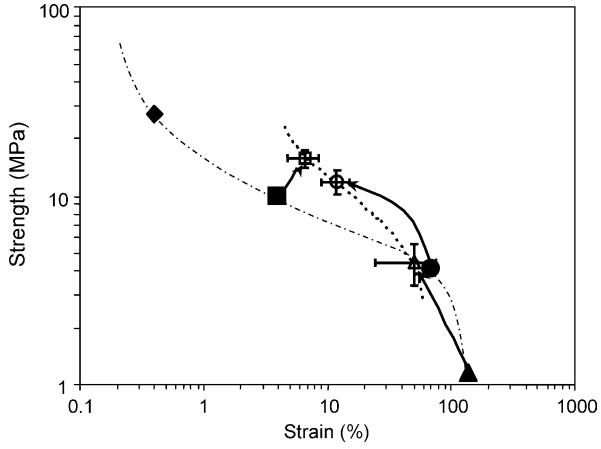

Fig. 5. Influence of photocrosslinking on the mechanical properties of plasticized starch based materials as a function of plasticizer content at 57% RH and 20 °C. Non irradiated starch materials: ■: SG17, ●: SG22, ▲: SG30. Irradiated starch materials: □: SG17, ○: SG22, Δ: SG30.

the same effect on the mechanical properties and are not shown. The PVA chains, probably grafted onto the starch structure, did not induce any noticeable specific behavior or this behavior could have been masked by starch crosslinking.

3.2.2. Influence of starch 'lengthening' on mechanical properties

The second strategy investigated was starch macromolecular weight distribution modification at very low conversion rate, using short UV exposure times, in order to keep the system soluble. The attempted effect was a chain 'lengthening' one as opposed to a crosslinked network.

An aqueous starch solution was pre-irradiated in a time scale ranging from 30 s until 30 min. These irradiated starches were then suitable for a further casting step and tensile testing. Photocrosslinking a solution allowed the appearance of the gel fraction to be observed at the end of the experiment.

In Fig. 6, the effect of starch pre-irradiation on mechanical properties (for short irradiation times) is presented:

- a five time strain increase was observed for the short exposure time, generally accompanied by a slight strength decrease as compared to the non-pre-irradiated reference (SG17). It can be assumed that the polysaccharide chains undergo a photo lengthening process, leading to an increase in chain entanglements.
- When the exposure time increased, strain at break decreased (see arrow bend in Fig. 6) and strength increased. The aqueous 'pre-irradiation' step led to the partial crosslinking of the macromolecules.

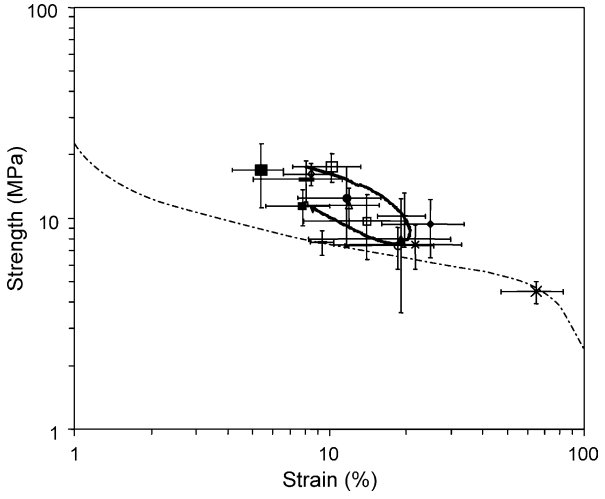

Fig. 6. Evolution of mechanical properties at break of low crosslinked starch ('lengthened' starch) subsequently plasticized with 17% of glycerol. The arrow represents increasing starch crosslinking degree. Starch materials: ■: 30 s of UV exposure in a 3 cm deep aqueous solution; ♦: 1 min of UV exposure in a 3 cm deep aqueous solution; ▲: 5 min of UV exposure in a 3 cm deep aqueous solution; ●: 10 min of UV exposure in a 3 cm deep aqueous solution; ✕: 10 s of UV exposure in a 3 cm deep aqueous solution; ○: 10 min of UV exposure in a 1 cm deep aqueous solution; △: 5 min of UV exposure in a 1 cm deep aqueous solution; ◇: 1 min of UV exposure in a 1 cm deep aqueous solution; □: 30 s of UV exposure in a 1 cm deep aqueous solution; +: 10 s of UV exposure in a 1 cm deep aqueous solution; −: 10 min of UV exposure in a 0.2 mm deep aqueous solution; ×: 5 min of UV exposure in a 0.2 mm deep aqueous solution; ▬: 1 min of UV exposure in a 0.2 mm deep aqueous solution; ▬: 30 s of UV exposure in a 0.2 mm deep aqueous solution; □: 10 s of UV exposure in a 0.2 mm deep aqueous solution

Adding PVA to these systems did not result in any additional properties and are not shown.

Size exclusion chromatography was used to observe molecular weight distribution modification. Preliminary results were not significant enough to be conclusive and further work is under investigation.

4. Discussion/conclusion

The aim of this study devoted to mechanical properties of starch based materials was to increase starch's average macromolecular weight in order to increase the elongation at break (without decreasing the strength). Physical blends (starch + PVA) and photo lengthened starch were made and tested. Results showed that an increase of strain was observed for the starch/PVA blends and for the photo-lengthened starch taking into account a noticeable effect of the process used in film making (the mixing efficiency): extrusion systematically led to a higher elongation increase compared to the casting method.

It is to be noticed that this interesting observed effect on elongation could be related to a delayed starch retrogradation effect compared to respective references (PVA free samples or uncrosslinked starch) performed by:

- the high interactions developed between starch and PVA (shown by water sorption, chemical reactivity)
- the introduction of structural defects on starch skeleton due to crosslinking

However, this assumption could not be verified since all tests were performed after very short ageing time and X ray measurements on these samples (not presented here) did not show any noticeable differences with the references.

In conclusion, long linear interacting polymers are required to achieve improvement of starch based materials' mechanical properties:

- with starch/PVA blends, the starch/PVA macromolecules developed specific interactions when samples were free of plasticizer
- with crosslinked starch (which obviously developed self-interaction), if the investigated process provided higher chain length, it did not appear to create the linearity of the molecules, necessary to achieve macromolecular entanglements.

Consequently, the perspectives for the development of this topic still relies on the blends by way of adding an interactive and linear polymer; and the optimized material would have to be processed by extrusion. 'Linear starch' would be one of the best candidate but native amylose, for example, did not fulfill the expected criteria (Follain et al., accepted) because of its too rapid crystallizability (leading to an elongation decrease) and its too short chain length. A longer amylose slightly modified to prevent crystallization would appear to be a more interesting candidate. Whether these substrates can be produced by plants or synthesized by chemical modification strategies would have to be determined since the required ratio of linear to branched chains need not necessarily be high.

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