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Solid state photocrosslinked starch based films: a new family of homogeneous modified starches

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Abstract

A new family of crosslinked starches were synthesised in the solid state by UV irradiation. The crosslinking treatment is novel because starch is treated in the solid state and no crosslinking agent is used. The original photosensitisers used were water soluble and members of the benzoic acid family. They were able to crosslink starch even at concentrations as low as 0.1%. The crosslinking kinetics were established by the determination of both the swelling degree and the gel fraction in order to characterise the network created. Crosslinking densities can be varied by altering the UV exposure time (1–10 min). Although the final crosslinking density is relatively low, it is still sufficient to render starch nearly insoluble in DMSO. The reactivity is discussed (i) as a function of the plasticisers content (water, glycerol, sorbitol), which can modify both the macromolecular mobility and the material density and (ii) as a function of the presence of a destructuring agent (NaOH) which favours starch accessibilites to the reactants. Mechanical properties were measured. Due to the relatively low crosslinking rate, only a slight increase is observed for crosslinked samples.

Keywords: Starch; Crosslink; UV irradiation; Sodium benzoate; Plasticisation

1. Introduction

Wheat starch is a low-cost renewable material containing of two polymers (25% amylose and 75% amylopectin). Thermoplastic starch (TPS) is usually obtained through an extrusion process by adding water and plasticisers (Shogren, Swanson & Thompson, 1992; Van Soest, De Wit & Vliegenthart, 1996b). Both decrease the glass transition and melting temperatures (Donovan, Lorentz & Kulp, 1983; Lourdin, Coignard, Bizot & Colonna, 1997a; Shogren, 1993; Zeleznak & Hoseney, 1987). Numerous starch mixtures based on this process have been investigated in order to replace synthetic polymers and promote new biodegradable materials.

Nevertheless, no starch-based materials have found application in the polymer market except for loose filler materials. A possible explanation for this situation may be explained by the short shelf time of starch materials, their mechanical weakness and the fact that they are swollen by water the extent of which depends on the relative humidity (RH). Moreover, it is well-known that the ageing of hydrophilic polymers causes damage (cracks or crazes) at low and high partial water vapour pressures. Except for the lower water contents (Seow, Cheah & Chang, 1999), ageing can be explained by molecular motion enhanced with sorbed water, inducing macromolecular reorganisations. This phenomenon leads to crystallisation (also called retrogradation) at temperatures above the glass transition (T_g) and/or physical ageing by densification of microdomains below T_g (Forssell, Hulleman, Myllärinen, Moates & Parker, 1999; Shogren, 1992; Thiewes & Steeneken, 1997; Van Soest & Knooren, 1997).

Chemical modifications such as grafting or crosslinking are able to limit excessive water swelling and macromolecular motions. Up to now, many chemical treatments have been made in order to limit hydration or preserve starch from ageing (Fringant, Debrieres, Milas, Rinaudo, Joly & Escoubes, 1996a; Fringant, Debrieres & Rinaudo, 1996b; Gros & Feuge, 1962; Laignel, Bliard, Massiot & Nuzillard, 1997).

Classical treatments lead to the modified starches used in food or paper additive applications in which crosslinking occurs in heterogeneous media using dry or semidry blending processes. For example, starch networks are usually performed by treating granular starch with the following

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crosslinking agents in heterogeneous media: sodium trimetaphosphate (Woo & Seib, 1997), epichlorohydrin (Kuniak and Marchessault, 1973), phosphoryl chloride (Jane, Xu, Radosavljevic & Seib, 1992; Yook, Pek & Park, 1993).

Radiative treatments, in the solid or liquid states such as gamma irradiation (Fanta, Burr, Doane & Russell, 1974; Kiatkamjornwong & Meechai, 1997; Reyes, Syz & Huggins, 1968) or electron beam (Olivier, Cazaux, Gors & Coqueret, 2000; Ruckert, Cazaux and Coqueret, 1999) have been used to modify starch especially in grafting processes. In general, no crosslinking takes place as far as we know (except for the polymerisation of added monomers which modifies the biodegradability and involves the use of high yields of synthetic chemicals). Irradiation often causes significant degradation at ambient temperature (Bertolini, Mestres, Raffi & Colonna, 2001; Fiedorowicz, Tomasik, You & Lim, 1999; Greenwood & MacKenzie, 1963; Ruckert, Cazaux & Coqueret, 1999; Sokhey & Hanna, 1993).

In order to find a way to crosslink starch using irradiation, approaches applied to other polymers were examined. As far as we know, the radiative grafting process used with starch has only been applied to vinyl monomers (Ghosh & Paul, 1986; Hérold & Fouassier, 1981; Merlin & Fouassier, 1981). Previous studies have reported ultraviolet-induced crosslinking or grafting with no crosslinking agent. Benzophenone is a current sensitiser used, for example, in the crosslinking of poly(ethylene oxide) or polyphosphazene (Doytcheva, Stamenova, Zuetkov & Tsevetanov, 1998; Graves & Pintauro, 1998). The sensitised irradiated films are rendered insoluble in the solvents in which they were originally soluble. In solvent media, many authors (Marsano, Gagliardi, Ghioni & Bianchi, 2000; Portnoy, Nelson, Margavio & Arthur, 1974; Zhang & McCormick, 1997) synthesised modified cellulose with unsaturated esters moieties, thus leading to insoluble products after UV exposure.

Takakura, Takayama and Ukida (1965) used photo-additives such as benzoic acid derivatives for poly(vinyl alcohol) crosslinking. In the present study, benzoic acid sodium salt was used in the same manner for starch films.

This paper presents an original study of solid state photo-crosslinking by the combination of extrusion and UV-irradiation of sensitised starch film. No crosslinking agent was used. The process consists of two steps: (i) extruding a thermoplastic starch-based (TPS) film which includes a low percentage of sensitiser (ii) using UV exposure to crosslink this film. This method leads to homogeneous starch crosslinking.

2. Experimental

2.1. Materials

Wheat starch was provided by the Chamtor company (Pomacle, France), and amylose was purchased from Aldrich. Both were stored under constant at 57% RH prior to use. Amylose was dissolved in DMSO to remove as much as possible of complexed *n*-butanol and then washed in water and ethanol to remove DMSO. The plasticisers used were sorbitol and glycerol. The photosensitisers were provided by the Avocado and Aldrich companies and used without further purification.

2.2.1. Films preparations

Films were cast in aqueous medium or extruded in a single screw extruder.

(1) Casting method: Native starch aqueous suspensions, 4% weight (dry basis), were heated in a high pressure reactor at 120°C for 20 min according to a previously described procedure (Lourdin, Della Valle & Colonna, 1995). Precise amounts of platiciser and photosensitiser were added. The solutions obtained were spread on a hot anti-adhesive coated mould maintained at 60°C to speed up water evaporation and avoid extensive starch retrogradation. The films obtained were transparent with a 80 μm average thickness. All films were stored for one week before testing in a 57% RH atmosphere controlled by a saturated sodium bromide solution at 25°C (CRC Handbook of Chemistry and Physics, Weast and Astle, 1979).

(2) Extruded films: glycerol was added to starch while vigorously stirring, and then heated for 45 min at 170°C for plasticiser absorption and water evaporation. (The initial water content of the weighed starch was accounted for in the final calculation of the percentages.) Subsequently, the dry blend was stirred while water containing an adequate amount of dissolved sensitiser (20% dried starch basis for water) was added. The final mixture was then gelatinised into a ribbon by one run through a SCAMIA three zone extruder (respectively heated at 100, 110 and 115°C) equipped with a slit die heated to 115°C. The mixing screw diameter was 2 cm in diameter, had a 11 L/D ratio and was operating at 60 rpm. The extruded ribbon was then conditioned for one week at 57% RH before irradiation.

2.2.2. Films designation:

Formulated films are referenced as illustrated in the following example:

G17B3 for a starch film plasticised with 17% wt Glycerol and sodium Benzoate 3 wt%,

Glycerol is designated G, sorbitol S, sodium benzoate B, and sodium hydroxides when employed.

The weight percentages are calculated on a dry starch basis for glycerol and on a dry (starch + glycerol) basis for the sensitiser.

2.2.3. Ultraviolet spectrophotometry

A UV-2401 PC spectrophotometer from Shimadzu was used to analyse the films formulated with 0.5% sodium benzoate (G17B0.5) allowing convenient absorbency of the UV light for 60 μm thick films. The reference is the same as for sensitised starch film before irradiation. Absorbency ratio was calculated as follows: A/A_0 where A is the film absorbency for exposure time t and A_0 for the unirradiated reference.

2.2.4. Ultraviolet irradiation set up

After being conditioned at 57% RH, films were irradiated under normal atmospheric conditions at 40°C with a FUSION UVF 1000 mercury lamp (emitting mainly at λ max 365 nm). The distance from the lamp was chosen relative to the delivered intensity as measured by a radiometer (at 365 nm) at 34 and 100 mW/cm^2 in this study.

2.2.5. Swelling measurements in dimethylsulfoxide

The gel fraction was determined from the insoluble part of the film immersed in dimethylsulfoxide (DMSO) in which TPS is originally soluble. The method is as follows:

Formulated films are irradiated and conditioned at 57% RH before immersion in DMSO (10 ml) at 25°C for 24 h (sorption equilibrium). The soluble part and the additives were extracted. The insoluble part (swollen film) was then wiped lightly, weighed (ms) and thoroughly washed, first by immersion in water and then in ethanol in order to remove the DMSO. The insoluble part was then dried at 80°C under vacuum for 24 h and reconditioned at 57% RH before weighing (md). Conditioning at 57% RH prior to all weighings was necessary to avoid any experimental error caused by uncontrolled moisture absorption in films at various ambient relative humidities.

The swelling degree SD is given by:

$$\mathrm{SD} = \frac{m_\mathrm{s} - m_\mathrm{d}}{m_\mathrm{d}} \approx \frac{m_\mathrm{s}}{m_\mathrm{d}} \qquad \text{with } m_\mathrm{d} \ll m_\mathrm{s}$$

for low crosslinking density

The gel fraction GF is given by:

$$\mathrm{GF} = 100\frac{m_\mathrm{d}}{m_\mathrm{c}}$$

where m_c is a corrected weight (i.e. only starch weight content) because of simultaneous glycerol extraction during immersion in DMSO, m_c is then a calculated weight obtained with respect to the plasticiser amount introduced initially. This calculated weight m_c has been validated with experimental correction made by water extraction of glycerol prior to DMSO extraction. The sensitiser can also be extracted but its content is low enough to be negligible.

2.2.6. Tensile testing

Tensile tests were performed on a tensile testing machine at 57% RH, with a crosshead speed of 6 mm/min. The films were cut into standard tensile samples from a dumbell shaped knife (H3). Ten samples for each composition were tested after a suitable conditioning period at 57% RH and 23°C. Young's modulus, ultimate tensile strength, and elongation at beak (EB) were obtained. The maximum tensile strength is calculated from the initial sample section systematically measured before testing.

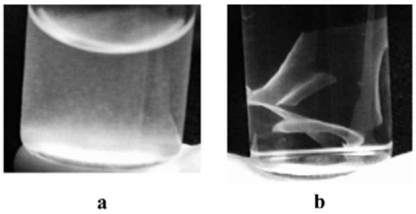

Fig. 1. Starch films immersed in water before (a) and after irradiation (b). Before irradiation, films disintegrate (a) and after irradiation, films only swell (b).

3. Results and discussion

Non-irradiated starch films disaggregate when immersed in water and are completely soluble in DMSO. Fig. 1 shows the results after 6 months of immersion in water on G17B3 starch films with no UV treatment (a) and after irradiation (b): the crosslinked films are only swollen; the linkages created appear to remain stable in water over time. In DMSO, the irradiated films also remain insoluble.

In this study, photocrosslinking kinetics were systematically recorded. Typical curves are given in Fig. 2: the swelling degree (SD) decreases and the gel fraction (GF) increases with irradiation, which is characteristic of network formation. At time 0, the films are entirely soluble in dimethylsulfoxide (DMSO) and the swelling degree is infinite. As a function of time, the GF increases until it reaches a plateau and the SD decreases at about the same time.

The following parameters are considered:

Time to reach the plateau
Final GF value
Final SD value

3.1. Influence on the nature of the sensitiser: benzophenone and aromatic carboxylic acid derivatives

Benzophenone sensitised films are obtained by extrusion prior to crosslinking (casting is not possible, benzophenone being water insoluble). The crosslinking kinetics shown in Fig. 2 lead to a relatively low gel fraction at the plateau (65%) compared to the sodium benzoate system (85%).

The SD at the plateau (measured from the insoluble part) exhibits no important difference between the two systems but the kinetics are dramatically accelerated using sodium benzoate: 30 after 3 min versus 7 min in the case of benzophenone.

It is well-known that the efficiency of a photosensitiser is based on its chemical affinity with the monomers to polymerise (Decker, Thi Viet & Le Xuan, 1996; Moussa

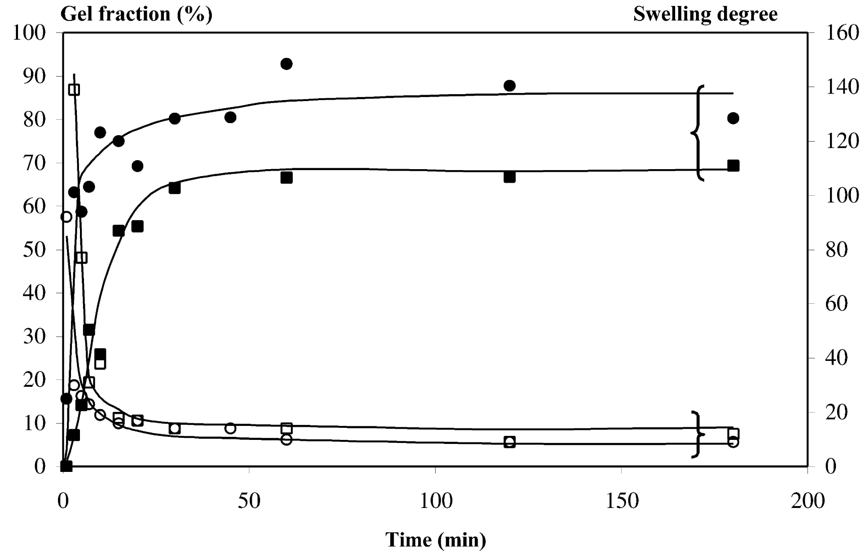

Fig. 2. Comparison of the crosslinking kinetics obtained for starch films as a function of two different sensitisers: benzophenone sensitised film: GF (■), SD (□); and sodium benzoate sensitised film: GF (●), SD (○).

& Decker, 1993) and in this case with the matrix to crosslink. In native starch, water soluble photoadditives are supposed to be more efficient because of (i) to a high affinity with hydrophilic starch and (ii) easy introduction as an aqueous solution during film preparation leading to a homogeneous distribution in the extrudable starch dry blend.

The final degree of swelling corresponds to a very low crosslinking density compared to synthetic thermosets. For example, the swelling values determined from swelling studies in water of the polymeric gels of cinnamoyloxyethylacrylates are typically around 0.1 and 0.4. (Ali & Srinivasan, 1995).

Nevertheless, networks formed from modified biopolymers present swelling degrees comparable to those obtained with our systems although the reported results are difficult to compare with ours because in the literature, crosslinking treatment occurs in heterogeneous media with granular starch (Inagaki & Seib, 1992; Tsai, Li & Lii, 1997; Wurzburg, 1986). Nevertheless, the lowest swelling value in water is around 8 for corn starch with 220 glucose units/crosslink and around 20 for waxy corn starch with 940 glucose units/crosslink (Tsai et al., 1997; Wurzburg, 1986). These authors obtained a swelling value of 20 with rice starch and 1% W/W of epichlorohydrin. In these modified starches, reactions yields are calculated on the basis of the initial reactives amounts added at the beginning of the reaction and are not the result of structural characterisation. Moreover it should be noted that the given swelling degrees are obtained in water and not in DMSO: for example, with our systems a SD of 15 obtained in DMSO corresponds to a SD of 5 in water. This suggests that, as far as we know, our systems are among the most crosslinked ones obtained for starch.

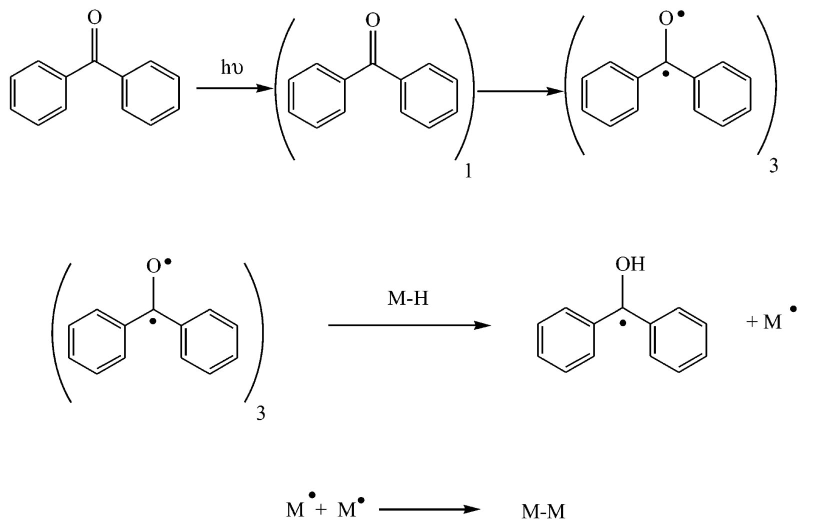

Fig. 3. Mechanism involved in benzophenone sensitised film.

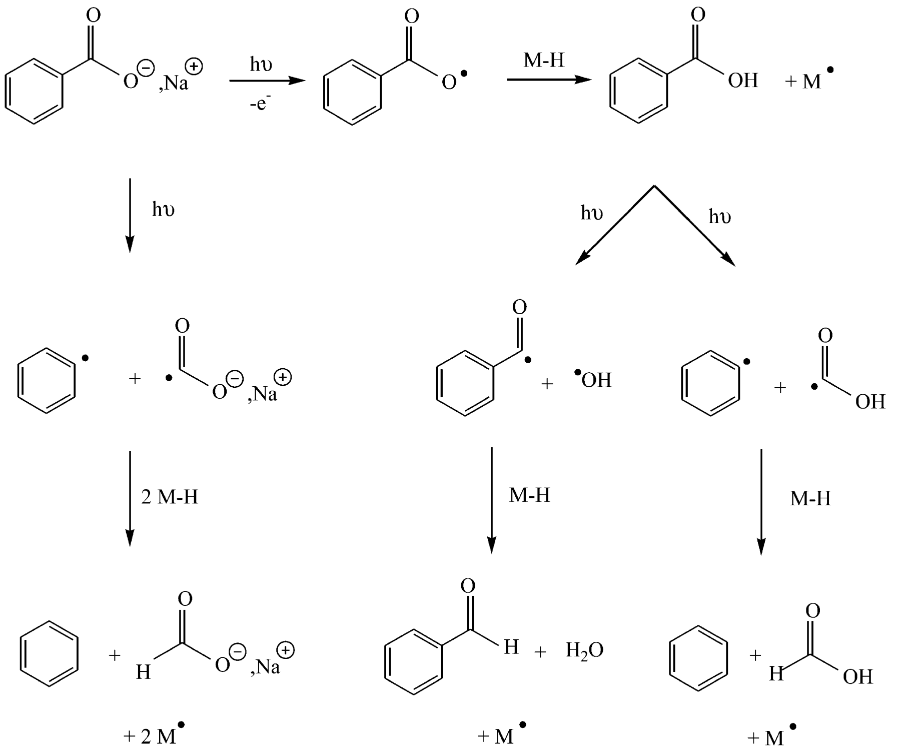

Fig. 4. Mechanism involved in sodium benzoate sensitised film.

Several sodium benzoate derivatives have also been tested as potential photoinitiators in order to improve kinetics and/or crosslink density: sodium salicylate, sodium ferrulate, sodium *o*-coumarate, *m*-coumarate, *p*-coumarate and sodium resorcylate. The chemical structures of these sensitisers differ from the sodium benzoate in the presence of hydroxyl group(s) or conjugated double bonds. The results are the following: sodium ferrulate, *m*-and *p*-coumarate show no crosslinking effect and the films remain soluble in DMSO. The action of sodium *o*-coumarate is limited to GF 20 and SD 150 and it is slightly higher for sodium resorcylate (GF 35, SD 100). Sodium salicylate gave final values close to those recorded for sodium benzoate though with much slower kinetics (30 min to obtain the final values instead of 15).

The crosslinking reaction occurs through a radical mechanism, the sensitizers (benzophenone and aromatic carboxylic acid derivatives) are excited or decompose to produce radicals upon irradiation with UV light.

For benzophenone, a probable reaction mechanism given

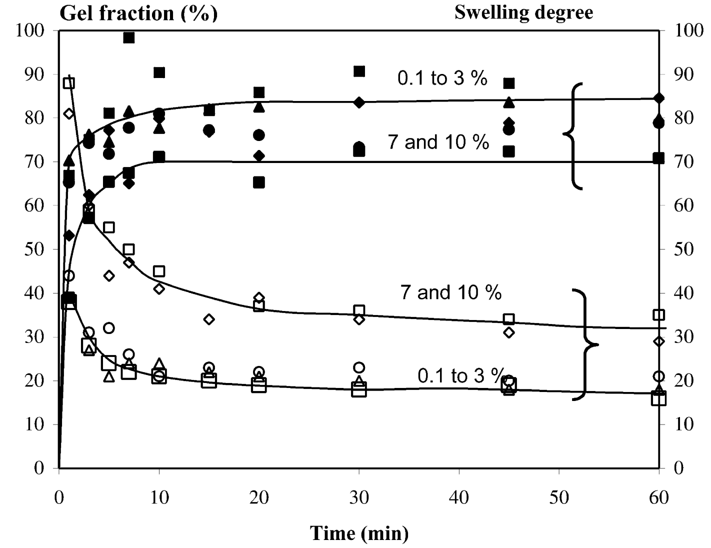

Fig. 5. Crosslinking kinetics of starch based film plasticised with glycerol (25 wt%) as a function of soldium benzoate contents (0.1–10 wt%).

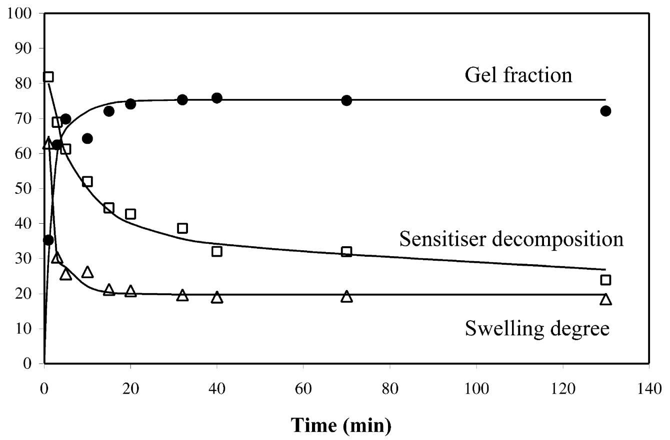

Fig. 6. Relationships between swelling degree (Δ), gel fraction (●) and photodecomposition of sodium benzoate (□) included in starch film (0.5%) — thickness of 60 μm. Sodium benzoate decomposition is recorded by UV absorption of a specific band ($A/A_{0225\ \mathrm{nm}}$).

by Rabek (1987) is described as being a hydrogen abstraction followed by a macroradical combination (Doytcheva et al., 1998; Graves & Pintauro, 1998): a macroradical can react on another macroradical for a termination reaction creating a crosslink (Fig. 3).

The most effective sensitiser, sodium benzoate, is known to be photolysed by UV irradiation as described by the Fig. 4 (Ghosh & Gangopadhyay, 2000; Wells, 1972) and also leads to macroradical combination by hydrogen abstraction.

For the other tested sodium benzoate derivatives bearing hydroxyls on the aromatic ring, the very low GF and SD obtained can be explained by the assumption that the radicals created are more stable and less prone to create macroradicals thereby inhibiting crosslinking.

For the cinnamic acid derivatives used, the lack of starch crosslinking reactivity could be due to possible photodimerization (Kamath, Kincaid & Mandal, 1996; Wang & Azuma, 1996).

Finally, among all tested photoadditives, sodium benzoate appeared to be the most effective sensitiser and no further investigations were made with other materials.

3.2. Influence of the photoadditive content (sodium benzoate)

In Fig. 5, the gel fraction final values vary from 70 to 80 wt% and are roughly independent of the initial sodium benzoate contents varying from 0.1 to 10 wt%. This result differs from the ones obtained with comparative systems made of 20 μm thick PVA, poly(vinylalcohol) films (Takakura, Takayama & Ukida, 1965). In the case of PVA, the insoluble fractions are strongly dependent on the sensitiser content: GF varies from 40 to 90% respectively for 0.65 and 2% sensitiser contents. Nevertheless, a direct comparison is difficult: although sodium benzoate is also used as a sensitiser, the PVA structure is very different from the one of starch and the crosslinking mechanisms could be different.

For swelling degree kinetics and final values, two groups are distinguished as shown in Fig. 5. One group is representative of the low sensitiser contents (0.1–3%) with faster kinetics and lower degrees of swelling: 15 times instead of 30 times for the second group for higher sodium benzoate amounts (7–10%). An excessive amount of the photochemical additive increases UV absorption and acts as a photochemical filter which limits UV penetration into the exposed film, thus leading to a lower crosslinking density, characterised by a crosslinking gradient (Decker & Moussa, 1990). Final crosslinking values for these sodium benzoate contents (7 and 10%) are not reached after 120 min of exposure (data not shown), but the kinetics are very low: the photodegradation of sodium benzoate would appear to be the limiting factor in the reaction kinetics.

In conclusion, a very low photoadditive content (0.1%) is sufficient to obtain crosslinked starch, and no improvement was observed by increasing the amount of photoadditive.

3.3. Sensitiser decomposition recorded by UV spectroscopy

Sodium benzoate included in starch film (G17B0.5) by the casting method shows absorption peaks as recorded by UV spectrophotometry: a major peak at 225 nm and 3 peaks centred at 270 nm. The decrease of the main peak at 225 nm during irradiation indicates sodium benzoate photo-decomposition. Simultaneously, peaks around 270 nm increase to a maximum after 10–20 min of UV exposure and then decrease to the previous value.

The ratio A/A_0 at 225 nm is calculated as a function of time and compared to the crosslinking kinetics in Fig. 6. Crosslinking and photolysis of sodium benzoate kinetic are similar thus these reactions appear to be correlated. Looking closely at Fig. 6, it appears that the sensitiser decomposition happens on a longer time scale: swelling degree reaches the final value after about 15 min although the absorption peaks ratio indicates a decomposition limited to 70%. After 140 min of exposure, the decomposition of sodium benzoate is not complete even for a low initial

Table 1
Evolution of the gel fraction GF (final value and time to reach the plateau) as a function of the glycerol content (0, 17 and 25%)

Sample	Time to reach the final value (min)	Final value of GF (%)
G0B3	40	90
G17B3	10	90
G25B3	5	80

concentration (0.5%). This result might explain the absence of a direct correlation between the final crosslinking density and the initial photoactivator concentration.

The presence of the 3 peaks centred at 270 nm is also of interest: irradiated films were extracted by water to remove the excess remaining sodium benzoate and then by DMSO to achieve a complete extraction. Extracted films show the presence of the same peaks: sensitiser reaction by-products appear to be grafted onto films after UV exposure. Further structural investigations are necessary in order to determine if grafted species participate in the crosslinking linkage or not.

3.4. Influence of plasticisers: glycerol or water

Starch macromolecular mobility is affected by both the plasticisers content (water and glycerol) and temperature. Crosslinking can be affected by the glass transition temperature (T_g) which defines the degree of starch mobility.

Table 1 shows the time required to reach the final values of GF as a function of glycerol content for 0, 17 and 25 wt% glycerol. It is obvious that increasing the glycerol amount accelerates the kinetics, the plateau being reached 8 times faster with 25% glycerol than without glycerol. However, a high glycerol content (>17 wt%) limits the final value of the GF. This result can be explained in terms of inter-chains distances, which are increased with the high plasticiser contents and limit the macroradical combinations.

Despite the use of an air cooling set up, the temperature of the film increased up to 40°C during irradiation. Water desorption occurred and dried films became brittle during UV exposure. Two sets of experiments were performed in order to study the role of water whilst the crosslinking process is taking place. In experiment A, starch samples were preconditioned at 93% RH: this initial high hydration content allowing longer desorption time. In experiment B, the limitation of water desorption during irradiation was assured by the realisation of a 3 layer composite film: a central conditioned starch layer (57% RH) being moulded between two UV transparent polyethylene sheets.

Samples in experiment A conditioned before irradiation at 93% RH initially contained 24% water, which is twice as high as for films conditioned at 57% RH.

The insoluble fraction reached only 36% with a SD of 45 after 10 min of irradiation for a G17B0.5 film. These values were compared with 80% GF and 10–15 SD for the same films conditioned at 57% RH. This result suggests that the effect of water content on the macromolecular behaviour is the same as for glycerol.

PE coated films remained soft after 120 min of UV exposure at 40°C, thereby indicating that the water desorption was sufficiently low. The final SD for sealed films was the same as in experiment A, but the kinetics were enhanced (after 3 min of irradiation SD is 30 in experiment B and 40 in experiment A). On the other hand, the photoinitiator decomposition (recorded by UV spectrometry) was lower in the case of PE sealed films. In fact, although less radicals might have been created, they seemed to lead to more efficient combinations for crosslinking. These results correspond well with both molecular mobility and reactivity,

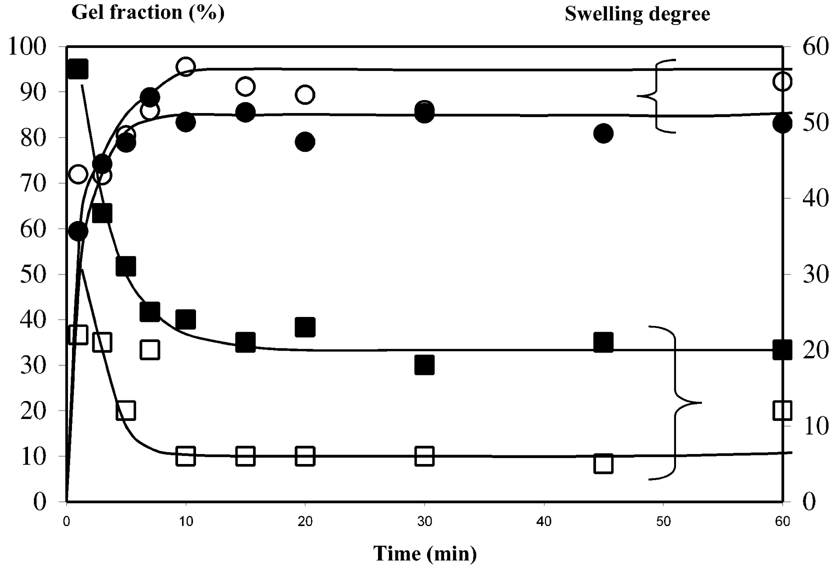

Fig. 7. Influence of sodium hydroxide (2%) on swelling degree (□) and gel fraction (○) for sorbitol plasticised sample. Full symbols are used for non alkali treated samples.

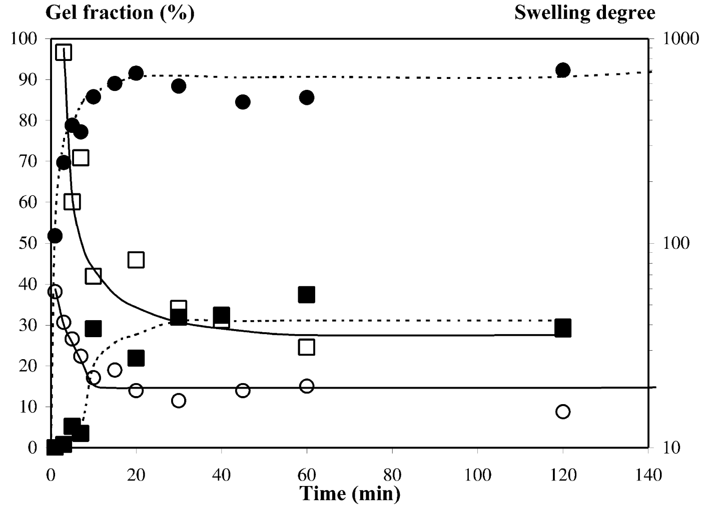

Fig. 8. Comparison on photocrosslinking kinetics for amylose: GF (●), SD (○), and amylopectin rich media GF (■), SD (□).

which increase in the absence of excessive swelling, as already discussed for glycerol.

Crosslinking necessitates a compromise between the macromolecular mobility enhanced by the presence of the plasticiser, especially for water (kinetic effect) and the probability of macroradicals combining. The probability of having two macroradicals combining decreases with higher amounts of plasticiser (swelling effect).

3.5. Influence of sodium hydroxide content: a destructuring agent?

Sodium hydroxide is widely used at concentrations as low as 10 mmol/l to help polysaccharide dissolution in aqueous solution (Be Miller, 1964).

Similarly, sodium hydroxide (2 wt%) can also be used as a destructuring agent in the solid state, breaking inter or intra-molecular hydrogen bonds, thus improving (i) macromolecular mobility and (ii) the sensitiser diffusion during mixing. The influence of alkali treatment was tested on both glycerol (G25B3s2) and sorbitol (S20B3s2) plasticised samples. In glycerol plasticised films, no effect on kinetics and swelling final values was found. However, the gel fraction increased from 80 to 95% in the presence of sodium hydroxide. On sorbitol plasticised samples (S20B3s2), alkali treatment led to faster kinetics and a much lower swelling degree (Fig. 7). A significant effect on crosslinking density (SD) occured with sorbitol but not with glycerol. This suggests that NaOH gives a dramatically enhanced co-plasticising effect in the films with sorbitol, the latter presenting a lower plasticising action than glycerol in starch (Gaudin, Lourdin, Forssell & Colonna, 2000). Moreover, by breaking hydrogen bond network, NaOH can also act as a sodium benzoate carrier, allowing the presence of the photo-additive into domains initially inaccessible. In the case of glycerol, the swelling degree remained unchanged (no co-plasticiser effect), but the insoluble fraction increased showing that part of the film components, which had not previously participated in the network in the reaction without NaOH, was now crosslinked. More macromolecules were covalently bounded within the tridimensional network but with the same crosslinking density as for the non-alkali treated samples. Since the plasticising effect of glycerol is greater than for sorbitol, the part of glycerol, which interacts strongly with starch could render these areas inaccessible to the sensitiser because of strong glycerol/starch interactions (Lourdin, Bizot & Colonna, 1997b) which are weakened by the presence of NaOH.

Unplasticised starch treated with NaOH has been tested and the results show slower kinetics and a GF limited to 70%. Therefore, NaOH seems to act as a co-plasticiser, the plasticiser presence remaining necessary to reach an optimised final value.

3.6. Influence of the amylopectin/amylose ratio

Crosslinking kinetics of pure amylose have been studied. Fig. 8 shows the comparison between the kinetics obtained with amylose and those of wheat starch, which can be considered as an amylopectin rich medium (75%). Kinetics obtained at time 0 with amylose showed the same behaviour as for the amylopectin rich medium studied before (infinite SD and total solubility when immersed in DMSO). Results show that wheat starch is more UV crosslinkable than amylose (gel fraction of 30% only for amylose). Amylose being constituted of essentially linear macromolecules, it seemed probable that intermolecular hydrogen linkages would be favoured as opposed to highly branched amylopectin where intramolecular bounds might be prevalent. However, (i) the very large difference in molecular weight between amylose and amylopectin is an important parameter to consider and (ii) amylose is likely to crystallise quickly both before and during irradiation, thus exhibiting lower mobility/reactivity, as well as decreasing the amount

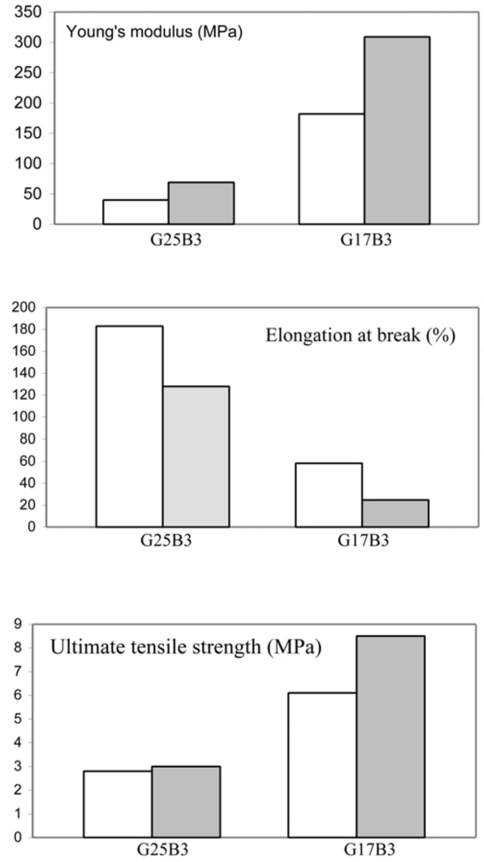

Fig. 9. Influence of irradiation on the mechanical properties of glycerol plasticised films: wheat starch film (glycerol 17%: G17B3) and pea starch film (glycerol 25%: G25B3). Crosslinked samples are coloured in grey.

of amorphous reactive zones. This fast recrystallization of amylose is a well-known phenomenon which occurs in starch–glycerol thermoplastic material (Van Soest, Hulleman, de Wit & Vliegenthart, 1996a).

3.7. Influence of irradiation intensity

UV induced crosslinking kinetics may be affected by radiation intensity (Decker & Moussa, 1988). Two intensities were investigated, 34 and 100 mW/cm^2. Results show that the final values are independent of the intensity but the kinetics are faster, suggesting, as expected, that conversion would be proportional to energy.

3.8. Influence of UV penetration in the sample thickness

The limitation of UV penetration has been well documented (Decker & Moussa, 1990). In order to roughly determine the thickness of the irradiated layer, films of various thicknesses were irradiated on both sides. They were swollen but remained cohesive when immersed in DMSO until 200 micrometers thick. Above this value the swollen films divided in to two slices held together by their edges (exhibiting a tube-like shape).

3.9. Influence of UV treatment on the mechanical properties

Mechanical properties obtained from tensile testing are given in Fig. 9. For each tested film, the sensitiser rate is of 3 wt% and the plasticiser is glycerol. Two starches have been tested: wheat starch (25% glycerol G25B3) and pea starch (17% glycerol G17B3).

After irradiation, the mechanical performances are higher as shown in Fig. 9. For example, for G17B3, Young's modulus is increased by 70%, and elongation at break is reduced by 107%.

This increase is relatively low compared to UV-cured synthetic thermosets. Thereby, it is to be related to the low crosslinking rate achieved by the photocrosslinking treatment. The samples containing sodium hydroxide and plasticised with sorbitol were also tested because they showed much lower swelling degree (3 times lower, Fig. 7). Unfortunately, the results lead to the same conclusion as before.

4. Conclusion

Extruded starch films were crosslinked by UV treatment. We believe this treatment has never been applied to starch and thus an innovative family of modified starches is reported (Delville, Joly, Dole & Bliard, 2000) which can be used, for example, as neutral hydrogels, thickeners or controlled drug release materials. Various crosslinking densities can be obtained by using different exposure time. The crosslinking treatment is original because it occurs in the solid state. The most efficient photoadditive, i.e. sodium benzoate, is a chemical product widely used as a preservative in drugs, cosmetics and foods (Pylypiw & Grether, 2000).

The crosslinking reactivity was discussed as a function of several parameters such as macromolecular mobility, film density or starch macromolecules accessibility, all modified by the presence of plasticisers (glycerol, sorbitol and water) and destructuring agent (NaOH). Mechanical performances were evaluated.

The results are the following:

1. Plasticisers accelerate the kinetics.
2. High contents of conventional plasticisers (water included) reduce the crosslinking efficiency at the end of the reaction probably because large intermacromolecular distances reduce the probability of macroradicals combinations.
3. Alkali treatment increases the reactivity of the crosslinking reaction: NaOH can be considered as a co-plasticiser able to enhance starch accessibility to the photoadditive, especially in the case of sorbitol plasticised sample.
4. Part of the sensitiser derivatives appear to be grafted onto the starch.
5. Crosslinked films have higher Young's moduli and ultimate strength. However, this increase is not sufficient

enough to be significant because of the relatively low crosslinking rate. The interesting properties of this new family of modified starch are the insolubility (gel properties) or the viscosity (for short time irradiation).

Further experiments are under investigation to elucidate the nature of the newly created bonds and to propose a mechanism for starch crosslinking. Since the product is insoluble, irradiated starch requires hydrolysis (acid or enzymatic), separation and then structure elucidation of the hydrolysis products. Further studies are aimed at improving mechanical properties by increasing the crosslinking rate and modifying the initial matrix.

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