Available online at www.sciencedirect.com
SCIENCE DIRECT®

Carbohydrate Polymers 53 (2003) 373–381

Carbohydrate Polymers
www.elsevier.com/locate/carbpol

Influence of photocrosslinking on the retrogradation of wheat starch based films

J. Delville[a], C. Joly[b,*], P. Dole[b], C. Bliard[a]

[a]*Laboratoire de Pharmacognosie, UMR URCA/CNRS 6013, Bât 18 Moulin de la Housse BP 1039, 51687 Reims cédex 2, France*
[b]*UMR URCA/INRA FARE, Equipe emballage, CPCB Moulin de la Housse BP 1039, 51687 Reims cédex 2, France*

Received 17 June 2002; revised 30 October 2002; accepted 19 February 2003

Abstract

The ageing of wheat starch based materials was followed as a function of time for different systems suitably hydrated to be in the rubbery state. In particular, one aspect of retrogradation, that is to say the development of crystallinity is analysed in order to study the influence of a specific crosslinking treatment of starch films made by UV irradiation (photocrosslinking). Mechanical and thermal properties showed that an important limitation on this particular ageing occurs after photocrosslinking at room temperature. A process of accelerated ageing, monitored by modulated DSC, was also performed at 60 °C in order to increase retrogradation kinetics. The results showed a recrystallisation decrease and it appeared that the presence of the plasticiser enhances retrogradation. For a plasticised sample (17% glycerol), a decrease of 30% of the melting enthalpy was observed compared to 91% for an unplasticised one. A modification in the nature of the melting peaks, as recorded by modulated DSC, allowed us to propose a model for amylopectin retrogradation after crosslinking.

Keywords: Crosslinked starch; Retrogradation; MDSC

---

1. Introduction

Wheat starch is a blend of amylopectin and amylose (75 and 25%, respectively). When starch is destructured prior to storage at high relative humidity or high plasticiser contents, retrogradation (or recrystallisation) occurs (Forssell, Hulleman, Myllärinen, Moates, & Parker, 1999; Rindlav, Hulleman, & Gatenholm, 1997; Van Soest, Hulleman, De Wit, & Vliegenthart, 1996a,b; Van Soest, & Knooren, 1997). Under these storage conditions, starch-based materials are in a rubbery state. This rubbery state allows the development of crystallinity by increasing macromolecular mobility.

Generally, during starch storage, amylose crystallisation occurs within hours (Van Soest et al., 1996a,b). Then, a slower development of the crystallinity occurs, a process, which has been essentially attributed to amylopectin (Morris, 1990). Moreover, the crystallinity types can change during storage (Duprat, Gallant, Guilbot, Mercier, & Robin, 1980; Forssell et al., 1999; Rindlav et al., 1997; Van Soest & Knooren, 1997). Different types of crystallinity have been revealed by X-ray diffraction depending on the amylose content of starch (Van Soest et al., 1996a,b), the starch origin (Forssell et al., 1999), the transformation process used (Miles, Morris, & Ring, 1985; Rindlav-Westing, Stading, Hermanson, & Gatenholm, 1998; Van Soest et al., 1996a,b) (thermomoulding, extrusion or casting), and the additives. Van Soest et al. (1996a) have shown the evolution of the degree of crystallinity for a starch-based material as a function of the relative humidity chosen for ageing. As expected, only rubbery materials (above 60% RH for the chosen systems) have shown diffractograms revealing macromolecular organisation.

The degree of crystallinity and the kinetics of crystallisation increases with the water content (Jouppila & Roos, 1997; Rindlav et al., 1997) for materials at the rubbery state. The presence of a conventional plasticiser content (glycerol) has also been studied. As opposed to water, glycerol plasticised amorphous rubbery amylopectin systems have shown slower crystallinity kinetics with an increasing level of plasticiser (Van Soest, de Wit, Tournois, & Vliegenthart, 1994). It appears that glycerol is able to stabilise amylopectin by both the development of specific interactions decreasing local macromolecular mobility necessary for crystallites formation (Van Soest et al., 1994) and, as

---

[*] Corresponding author. Fax: +33-3-26-91-39-16.
E-mail address: catherine.joly@univ-reims.fr (C. Joly).

0144-8617/03/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0144-8617(03)00141-3

expected, by limiting the crystallinity rate since enriched glycerol phases are unable to crystallise.

The recrystallisation of rubbery starch based materials plays an important role in the life span of these materials whatever their initial shape or geometry: (powder, films or more bulky samples for mechanical testing, plasticised or not): as expected, the mechanical properties are directly influenced by retrogradation (Kuutti, Peltonen, Myllärinen, Teleman, & Forssell, 1997; Van Soest et al., 1996a,b; Van Soest & Knooren, 1997). Tensile strain at break decreases drastically as stress and Young's modulus increase. Crystallites may be acting as physical crosslinking points which generate internal stresses or cracks which in turn lead to the damage of the samples.

In order to counteract and study this detrimental effect, a crosslinking process has been devised. In a previous paper (Delville, Joly, Dole, & Bliard, 2002), we described a new crosslinking process occurring in the solid state, using UV irradiation on sensitised starch films. Sodium benzoate was chosen as water-soluble photo additive for its good ability to crosslink extruded starch films. In those crosslinked films, the macromolecular movements are limited and the retrogradation phenomenon appears to be delayed and limited.

Moreover, crosslinks may act as structural flaws tending to decrease the crystallinity rate at equilibrium. This paper presents a study of the influence of photocrosslinking treatment on the retrogradation of starch films. Films were used to permit a good penetration of the UV radiation to allow a homogeneous crosslinking (Delville et al., 2002).

2. Experimental

2.1. Materials

Wheat starch was provided by the Chamtor Company (Pomacle, France) and was stored under constant hygrometry prior to use (57% relative humidity, RH). This starch was chosen for regional economical reason (local production, lower cost than other starch origins). The plasticisers used were sorbitol or glycerol. The photosensitiser (sodium benzoate) was provided by the Avocado Company and used without further purification.

2.2. Films preparations

Films were extruded in a single screw extruder. Glycerol was added to starch (13% moisture) and the mixture heated for 45 min at 170 °C for plasticiser absorption and water evaporation. A dry blend was then obtained. (The initial water content of the weighed starch was accounted for in the final calculation of the percentages). Subsequently, water (20% dried starch basis) containing an adequate amount of dissolved sodium benzoate (3% dried starch + glycerol basis) was added while the dry blend was being stirred. The final mixture was then extruded into a ribbon by one run through a three-zone SCAMIA extruder (respectively, heated at 100, 110 and 115 °C) equipped with a slit die heated to 115 °C. The mixing screw had a 2 cm diameter, an 11 L/D ratio and was operating at 60 rpm. The extruded ribbon (100 μm thick, 3 cm wide) was then conditioned for one week under 57% RH before irradiation.

2.3. Films designation

Formulated films are referenced as illustrated in the following example:

> *G*17 for a starch film plasticised with 17 wt% *G*lycerol. Glycerol is noted **G**, sorbitol **S** and sodium hydroxide **s** when employed.

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

2.4. Ultraviolet irradiation set-up

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

2.5. Crosslinked sample characteristics

The networks, created by UV irradiation, were characterised in DMSO (dimethylsulfoxide), which is an efficient solvent for starch. Gel fraction (or GF) and swelling degree (SD) were both determined systematically for all tested samples and described in details elsewhere (Delville et al., 2002).

GF and SD expressions are given as following:

The SD is 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, where

m_s = weight of swollen sample,
m_d = weight of dried sample

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

with $m_d \ll m_s$ for low crosslinking density

The gel fraction GF is given by:

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

where m_c is a corrected weight (i.e. dry starch weight) because of simultaneous glycerol extraction during immersion in DMSO.

Table 1
Gel fraction and swelling degree of samples

	Samples		
Samples	G0[a]	G17[b]	S20s2[c]
Gel Fraction (GF)	90	90	95
Swelling degree (SD)	15	15	4

[a] Sample without plasticiser, containing photosensitiser (3%).

[b] Sample containing plasticiser (glycerol 17%) and photosensitiser (3%).

[c] Sample containing plasticiser (sorbitol 20%), photosensitiser (3%) and sodium hydroxide (2%).

m_c is the calculated weight obtained after subtracting the plasticiser amount introduced initially. This calculated weight mc has been validated with an experimental correction made after water extraction of glycerol prior to DMSO extraction. The sensitiser can also be extracted but its content was considered low enough to be negligible.

The GF and SD values are listed in Table 1 for the starch systems used in this study.

As seen in Table 1, all the created networks revealed a low crosslinking density compared to classical synthetic thermosets which present usually a SD ten times lower, but films remained nearly totally insoluble (GF near 100%).

2.6. Tensile testing

Tensile tests were performed on a tensile testing machine at 80% RH (Test 110 from GTTest, France), with a crosshead speed of 10 mm/min. and a pressure transducer of 2 kN. The films were cut into standard tensile samples from a dumbbell-shaped knife (H3 type). Ten samples for each composition were tested after a suitable ageing period at 80% RH and 23 °C. Young's modulus, ultimate tensile strength, and elongation at break were obtained. The maximum tensile strength is calculated from the initial sample section systematically measured before testing.

2.7. Thermal analysis

Thermal analysis were performed on a TA Instruments 2920 DSC with MDSC TM option and equipped with a refrigerated cooling system (RCS). Temperature and enthalpy were calibrated using indium. The same pan type and thermal programme (heating rate and modulation), as in the corresponding experiments, were used for the calibrations.

Samples were ground, pressed as pellets and then sealed into pans as specified later (depending on the performed experiment) always under the relative humidity corresponding to ageing conditions in order to prevent any water desorption. These operations were all made prior to ageing. Sealed pans were aged after a previously thermal treatment at 170 °C for 5 min, in order to eliminate their own thermomechanical history. This temperature was chosen to be above the melting point previously recorded or estimated from literature when it was possible (Savary & Colonna, 1993). Indeed, a second run recorded just after this thermal treatment has shown the absence of any endotherm initially present. The absence of leakage (or water permeation) was ensured by weighing the pans after this first temperature scan. The sample weights were typically15–50 mg according to the pans used.

2.7.1. Conventional DSC

Conventional DSC was used to determine the melting endotherm of aged samples heating at 5 °C/min from −40 to 200 °C. Hermetic Setaram pans with a metal seal (single use) were used.

2.7.2. Isothermal modulated DSC

Isothermal modulated DSC was used to record in situ sample crystallisation, i.e. starch crystallisation inside the pan during the ageing period. To accelerate the phenomenon (i.e. macromolecular movements), an isothermal experiment was performed at 60 °C with a modulation 0.5 °C/min and a 100 s period as already performed by De Meuter, Rahier, & Van Mele, 1999b. Polyethylene samples were used for the calibration of heat capacity, with the same modulation parameters as for experiments and according to the indications given by the DSC constructor (TA instruments).

Hermetic steel pans (TA instruments) equipped with viton® seal were used. These pans are designed to be hermetic up to a pressure of 25 bars. The initial weight of the sample was typically 50 mg.

2.7.3. Non-isothermal modulated DSC

This thermal analysis was used to record the melting endotherms of the samples artificially aged through MDSC's isothermic conditions as described in Section 2.7.2. The experiments were run with a modulation 0.5 °C/min a 100 s period, with a heating rate of 1 °C/min, from −40 to 200 °C.

3. Results and discussion

The crystallisation of an amorphous solid is a phenomenon occurring above glass transition (T_g). This phenomenon implies a reorganisation of the macromolecules. The first part of this paper describes the evolution of the mechanical properties with ageing and the second part deals with thermal analysis of samples after ageing at room temperature and then in situ (in the DSC pans) with accelerated ageing.

3.1. Evolution of mechanical properties with ageing

Fig. 1 shows a picture of samples (G17) used for tensile testing after 6 weeks of ageing at 80% RH Crosslinked

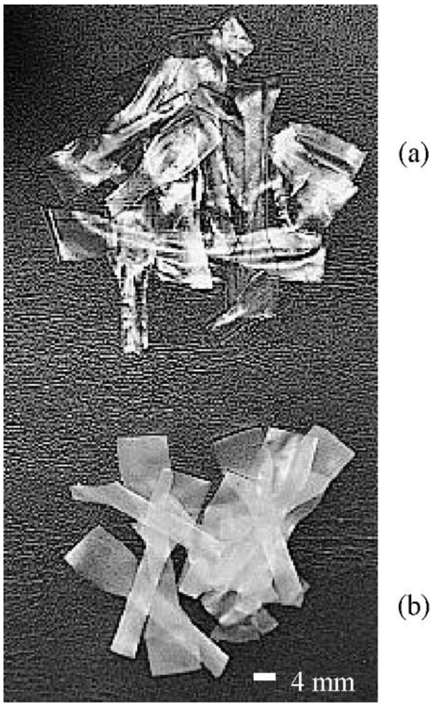

Fig. 1. Irradiated films (a) and unirradiated G17 films (b) aged for 6 weeks (H3 standard samples).

samples (a) (top of the picture) remained nearly transparent whereas uncrosslinked samples (b) became nearly opaque. It is well known that the development of opacity is often related to the formation of ordered zones (Karim, Norziah, & Seow, 2000; Miles et al., 1985; Ring et al., 1987). This qualitative observation strongly suggests that crosslinking treatment has stabilised starch films, thus limiting crystallisation: crosslinked samples remained transparent (Fig. 1(a)).

Figs. 2 and 3 show the evolution of the ultimate mechanical properties, elongation (ε) and stress (σ) at break, and of the Young's modulus for crosslinked (Fig. 2(a) and solid lines in Fig. 3) and uncrosslinked (Fig. 2(b) and dotted lines in Fig. 3) materials during ageing. The tested starch films were plasticised with glycerol (G17) and contained 3 wt% of photoadditive. The uncrosslinked sample was prepared exactly the same way except for the irradiation part. The crosslinking treatment caused the strain at break (ε) to be slightly different after one week, time considered as the time zero of ageing (in fact, one week minimum is required to assure moisture equilibrium inside films). The drop in elongation was 75% for the untreated sample as compared to 40% for the crosslinked one. Ageing tended to obliterate the difference due to the crosslinking treatment. Stress and modulus increased during storage, but samples showed different ageing kinetics depending on the crosslinking treatment. Uncrosslinked samples, initially have the same mechanical properties as the crosslinked ones, presented higher properties after 15 days. At the end of ageing (6 weeks), uncrosslinked samples showed values of around 40% higher.

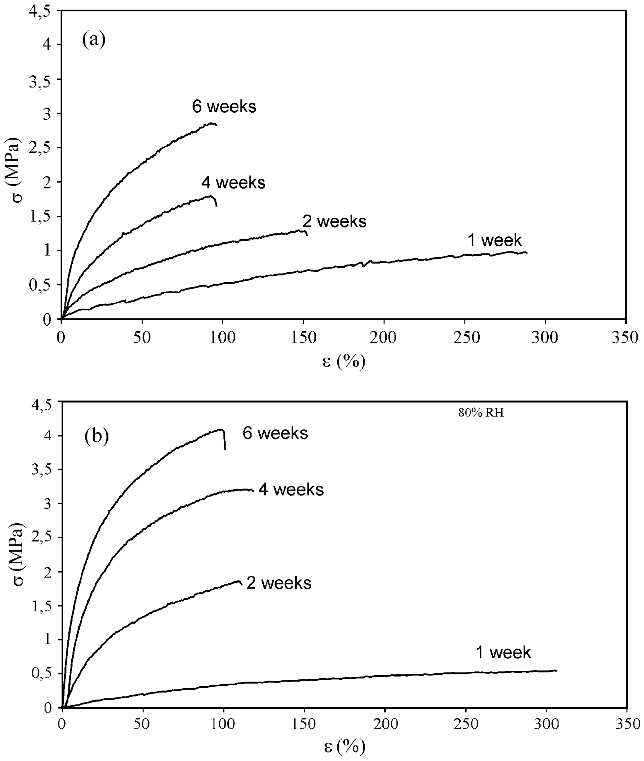

Fig. 2. Evolution of the stress/strain curves as a function of ageing at 80% RH for (a) crosslinked film and (b) uncrosslinked film plasticised with glycerol (17 wt% or G17).

These results suggest that the crosslinking treatment partially prevented starch from retrogradation because crystallinity development is well known to increase the mechanical properties and more specifically the Young's modulus E and stress σ as shown in Figs. 2(b) and 3(b) for uncrosslinked samples. After 6 weeks of ageing, evolution was still noticeable and there was no well-defined plateau value showing that the ageing was not complete. In Fig. 3, one can suppose that the curves begin to level off but the magnitude of the experimental errors do not make it possible to be dogmatic.

3.2. Thermal analysis: conventional DSC

The samples tested for their mechanical properties (G17, stored at 80% RH) were analysed by differential scanning calorimetry. The resulting thermograms are shown in Fig. 4 as a function of ageing for the crosslinked and uncrosslinked films. Generally, the starch thermal events have been shown to present two endotherms. The first event occurring between 50 and 120 °C was attributed to amylopectin melting, and the second endotherm occurring between 120 and 170 °C was attributed to the melting of amylose (Silverio, Svensson, Eliasson, & Olofsson, 1996). In our experiments, the thermograms obtained appear to correspond to the melting of amylopectin (Fig. 4) in the ageing conditions chosen in this study. The thermograms shown in Fig. 4 are presented from 30 °C to 140 °C for clarity reasons

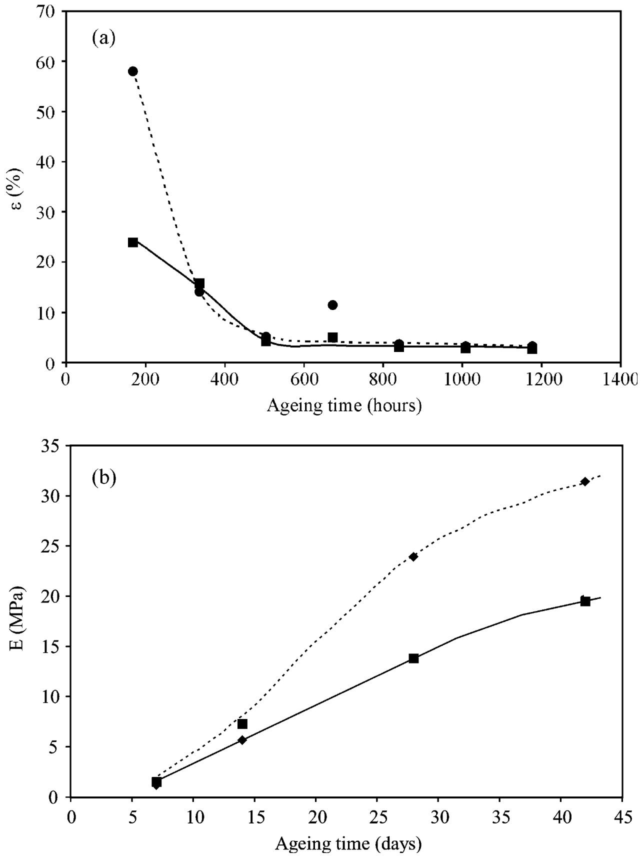

Fig. 3. Evolution of the mechanical properties: (a) Strain ε and (b)Young modulus *E* for uncrosslinked film (dotted line) and crosslinked film (bold line). Films are plasticised with 17% glycerol (G17) aged at 80% RH for 1–6 weeks.

because no thermal event was detected above this temperature despite previously discussed literature. This large peak (from 50 to 130 °C) was bimodal (one peak at 70 °C and the second at 110 °C), as already reported elsewhere by other authors—(De Meuter, Amelrijckx, Rahier, & Van Mele, 1999a; Fredriksson, Silverio, Anderson, Eliasson, & Åman, 1998). Two hypotheses have been proposed to explain this phenomenon: (i) the first one involves an amylopectin specific macromolecular reorganisation during storage: the melting at lower temperature would be characteristic of lower ordered zones, less organised than other crystallites melting at higher temperature (De Meuter et al., 1999a). De Meuter et al. (1999a) proceeded to isothermal crystallisation of waxy maize starch (starch/water: 76/24 wt%) at different temperatures but always 10° below the onset value of the melting peak. The melting event remained bimodal but the first peak was shifted to the higher temperatures as the storage temperature increased. This annealing allowed the formation of more ordered regions which subsequently melted at higher temperature. (ii) The second hypothesis invokes an amylopectin macromolecular reorganisation during the thermal analysis (Fredriksson et al., 1998). In this hypothesis the population of crystallites responsible for

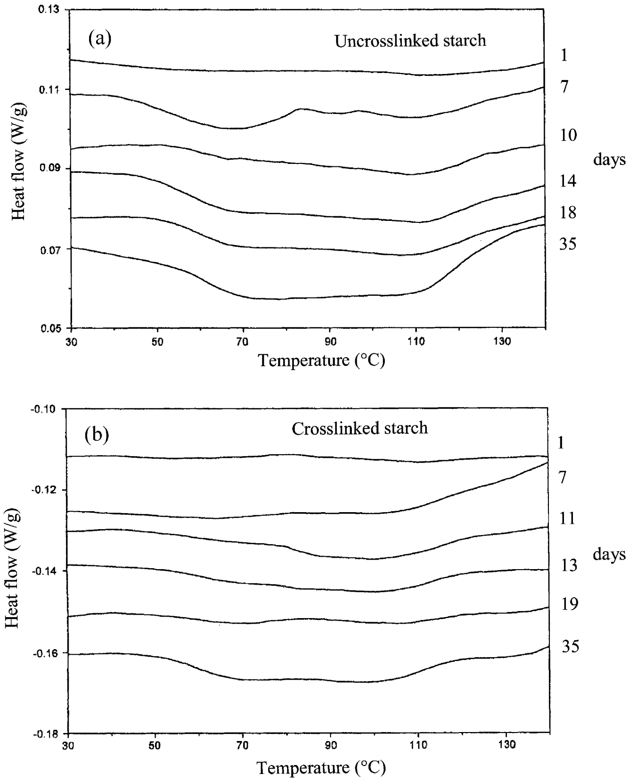

Fig. 4. Standard DSC. Melting endotherms evolutions for uncrosslinked film (a) and crosslinked film (b). Films (G17) aged at 80% RH for 1–35 days.

the peak observed at lower temperature, would develop during storage and the more ordered ones would have been formed during the DSC heating. This assumption appeared unverified in this study because no exothermic peak was observed during heating even at different heating rates. Nevertheless such a phenomenon could only be detected if the crystallisation kinetics were fast enough and had sufficient amplitude. As previously reported the melting endotherms increased as a function of storage time (Fig. 5) (Forssell et al., 1999; Jouppila & Roos, 1997) showing that the retrogradation of the samples is roughly linear for

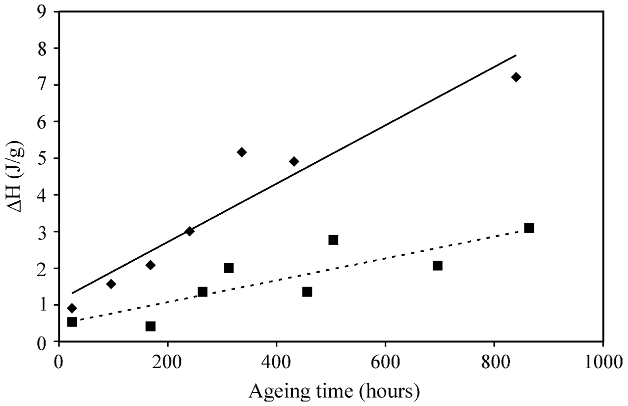

Fig. 5. Standard DSC. Melting enthalpy evolution of an uncrosslinked G17 film (◆) and crosslinked G17 film (■) stored at 80% RH versus ageing time.

the crosslinked samples and may begin to level off for the uncrosslinked one as already reported in Fig. 3. It is to be noted that the enthalpy values obtained were difficult to compare with the literature as the systems (water and/or plasticiser contents), ageing and thermal analysis conditions are very variable.

In Fig. 4, the melting endotherms of crosslinked and uncrosslinked samples can be qualitatively compared. At first, since both irradiated and non-irradiated films present melting endotherms, it is clear that the crosslinking treatment did not totally prevent the samples from crystallisation. Other authors (Le Bail, Morin, & Marchessault, 1999) working on chemical crosslinking, have come to the same conclusion. However, endotherms corresponding to irradiated samples are smaller. More quantitatively, Fig. 5 shows the evolution of enthalpies as a function of ageing time for the two systems, before and after UV exposure. The comparison of the two curves clearly shows that the crosslinked samples present lower crystallisation kinetics. The calculated crystallinity kinetics were 0.192 J/g 24/h for the uncrosslinked sample against 0.072 J/g 24/h for the crosslinked one. Therefore the decrease in ageing kinetics due to crosslinking is about 60%, but at this stage, it is not possible to conclude whether the effect of crosslinking acts on the recrystallisation rate alone or on the final plateau as well.

Finally, it is very clear from the mechanical properties, and the thermal analysis, that ageing by recrystallisation is not complete at the end of the storage period used under the chosen conditions. Therefore accelerated ageing was performed in order to achieve the nearly completed retrogradation.

3.3. Isothermal retrogradation at 60 °C

In order to accelerate the ageing kinetics, and since storage, temperature and humidity directly influence the development of crystallinity (rate and order degree) of a crystallisable material (Jouppila & Roos, 1997), the different tested systems were stored at 88% RH, humidity chosen to study the samples above T_g at this relatively high temperature (60 °C). A standard DSC scan was performed to verify the T_g position. Samples were not tested with conventional DSC but with modulated DSC (MDSC) using an isothermal temperature program. De Meuter et al. (1999b) have been the first authors, to our knowledge, who have applied such analysis to starch. MDSC allowed the in situ starch crystallisation to be recorded. This method is based on monitoring the complex heat capacity (Cp^*) decrease while the sample crystallises in situ (i.e. into the DSC pan) (De Meuter et al., 1999a,b). The temperature choice in this study (60 °C) is a compromise between two points: the temperature had to be high enough to give a crystallisation time in the DSC apparatus short enough so as not to immobilise the machine for long periods. Secondly, the pans used were impermeable enough against water for a higher temperature to be maintained for a long time.

Fig. 6 displays the obtained Cp^* evolution for crosslinked and uncrosslinked G17 samples. Tested samples also underwent the first scan to 170 °C, previously described, in order to cancel their thermo-mechanical history. The curves show the Cp^* drop during the isothermal crystallisation at 60 °C and even though the signal was very noisy, the results were significantly different. This drop in Cp^* occurred immediately (without any induction period) and then reached a plateau value. This value is well defined for the crosslinked samples (Fig. 6(b)). In Fig. 6(a), the system seems not to be at equilibrium. As the crystallisation proceeded, the Cp^* decrease (ΔCp^*) as well as the time to reach the plateau (t_f) were recorded by simple linear extrapolation of plateau or quasi-plateau values. Crosslinked films present a lower and slower retrogradation (or ΔCp^*) as shown in Fig. 6. The noisy curves do not allow further quantitative investigation of such phenomenon. However, the obtained curves were reproducible for G17 samples (in Fig. 6) and other systems.

Using non-isothermal modulated DSC, we analysed samples that had been previously retrograded in situ at 60 °C. The same bimodal peak, as discussed before (c.f.

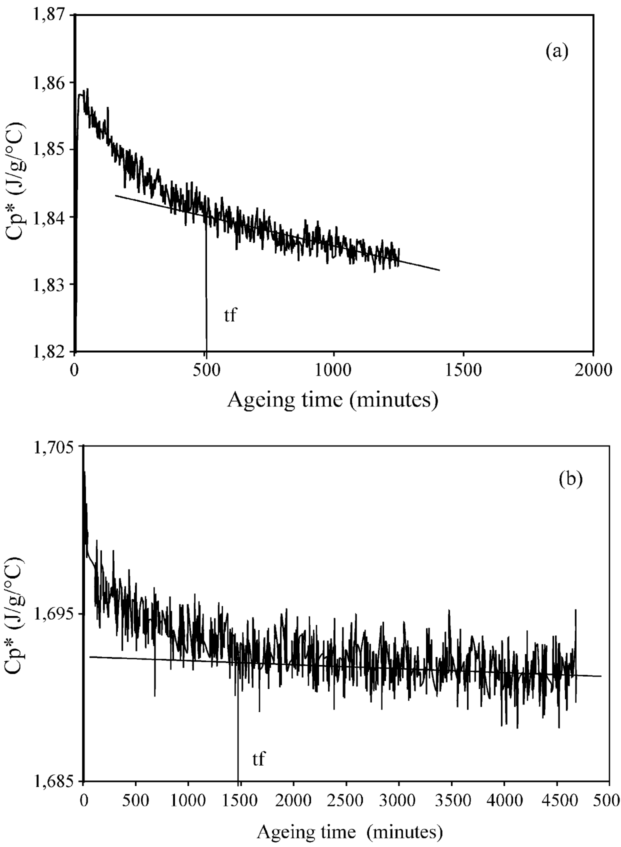

Fig. 6. MDSC. Complex heat capacity evolution as a function of ageing time for a G17 film. (a) uncrosslinked and (b) crosslinked films. Plateau value are extrapolate linearly to indicate the t_f (time to reach the final value).

Table 2
Peak positions of melting endotherms

Samples	Melting temperature of the first peak (°C)	Melting temperature of the second peak (°C)
G0[a]	91	133
Crosslinked G0	89	131
G17[b]	79	115
Crosslinked G17	80	108
S20s2[c]	86	116
Crosslinked S20s2	85	110

[a] Sample without plasticiser, containing photosensitiser (3%).
[b] Sample containing plasticiser (glycerol 17%) and photosensitiser (3%).
[c] Sample containing plasticiser (sorbitol 20%), photosensitiser (3%) and sodium hydroxide (2%).

conventional DSC paragraph), was found for all samples. Table 2 displays the measured maximum peak temperature. The first peak appears to be unchanged after crosslinking treatment but the position of the maximum of the second peak (at higher temperature) is slightly decreased, suggesting a loss of crystallite perfection. Crosslinking appears to partially prevent retrogradation, specifically within the more organised zones.

From modulated DSC, bimodal endotherms (as already discussed for the conventional DSC paragraph) were always obtained in the literature. There is a substantial interest in studying the nature of the melting endotherm of previously retrograded samples. From this point of view, interpretation of heat flows (reversing and non-reversing signals) was not easy because both non-reversing and reversing flows contain endothermic signals. Two hypotheses can be made. In the first one, both the chosen amplitude modulation and temperature ramp may not have been well adapted to these samples and subsequently the reversible and non-reversible part of the total signal would not be very well separated. In the second one, since this phenomenon has already been reported in the field of synthetic thermoplastics such as polyesters (Sauer, Kampert, Blanchard, Threefoot, & Hsiao, 2000; Wang, Hsiao, Sauer, & Kampert, 1999), these results could be interpreted as follow:

(i) The non-reversing contribution of the total melting signal is usually attributed to the total melting of the well-ordered crystallites. In some cases, these perfect crystals cannot recrystallise fast enough because of the low recrystallisation kinetics.
(ii) The reversing endothermic signal is due to partial melting of crystals. The non-melted parts of the crystal acts as nuclei to allow heterogeneous recrystallisation of the melted part. In the case of starch, this signal could be related to the melting endotherm of the single clusters (less ordered lamellae). This contribution is not always easily detected and can be calculated by the difference between the total heat flow and the non-reversing one.

In our systems, the reversible endotherm was observed at low temperatures (Fig. 7) (around 85 °C) compared with the main non-reversing peak, recorded around 115 °C. This would confirm the attribution of the reversible signal to the less ordered crystallites. Quantitatively, Table 3 presents the melting enthalpy decrease due to the crosslinking treatment, and the contributions of the reversible and non-reversible enthalpies.

From data in Table 3, three points can be highlighted:

(1) The systems that were exempt from plasticisers were the most retrograded (or crystallised): 8.6 J/g for G0 against 6.4 for S20S2 and 3.4 for G17. It is known that the plasticiser is partially removed from crystallites for recrystallisation to occur. Moreover, glycerol plasticised samples are less retrograded than those plasticised with sorbitol.
(2) The crosslinking treatment has a strong influence on retrogradation properties. The enthalpy values decreased whatever the considered signal (total, reversible and non-reversible). The unplasticised samples presented a large recrystallisation decrease of 91%.
(3) A larger decrease was observed on the reversible heat flow peak, this peak was attributed to the less ordered crystals. The observed decrease was of 50% for glycerol-plasticised samples and up to 97% of the total heat flow with unplasticised samples. The crosslinking treatment seems to prevent the reorganisation of these less perfect crystalline regions.
(4) The influence of the crosslinking treatment on the non-reversing heat flow showed an enthalpy decrease varying from 26 and up to 79% depending on the formulation. Fig. 7 shows the comparison of retrograded crosslinked and uncrosslinked samples analysed by MDSC. From the non-reversing heat flow thermogram, the second melting peak seems to be weaker after crosslinking, indicating the limitation of

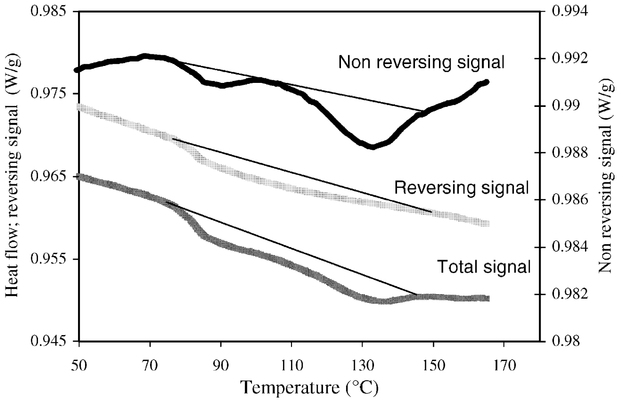

Fig. 7. Modulated DSC thermograms of unirradiated G0 sample.

Table 3
Melting enthalpy decreases due to crosslinking

Sample	Total ΔH (J/g)	Total ΔH decrease (%)	Reversing ΔH (J/g)	Reversing ΔH decrease (%)	Non-reversing ΔH (J/g)	Non-reversing ΔH decrease (%)
G0[a]	8.6	90.7	6.3	96.8	2.8	78.6
Crosslinked G0	0.8	90.7	0.2	96.8	0.6	78.6
G17[b]	3.4	29.4	0.8	50.0	2.7	25.9
Crosslinked G17	2.4	29.4	0.4	50.0	2.0	25.9
S20S2[c]	6.4	53.1	0.7	85.7	5.7	49.1
Crosslinked S20S2	3.0	53.1	0.1	85.7	2.9	49.1

[a] Sample without plasticiser, containing photosensitiser (3%).

[b] Sample containing plasticiser (glycerol 17%) and photosensitiser (3%).

[c] Sample containing plasticiser (sorbitol 20%), photosensitiser (3%) and sodium hydroxide (2%).

the more perfect crystallite development during retrogradation.

4. Conclusion

The properties of rubbery starch based materials (approximately 20–25 wt%) were followed as a function of time for different systems. In particular, crosslinked starch was synthesised in the solid state by UV irradiation and the influence of such a treatment on one aspect of retrogradation, the recrystallisation, was studied. Mechanical properties were recorded and showed an expected evolution due to the retrogradation. Photocrosslinking allowed a partial stabilisation of the samples during ageing. This result was shown qualitatively on samples: crosslinked samples remained nearly transparent whereas uncrosslinked samples became nearly opaque.

In order to more accurately study the crystallisation occurring during ageing, modulated thermal analysis was performed using a specific in situ ageing experiment inside the DSC pans.

The samples presented a large decrease in melting enthalpy after crosslinking, depending on the formulation. An unplasticised starch sample (water/starch) showed a decrease of 90% as compared to 30% for the glycerol plasticised sample (water, starch, glycerol). The presence of plasticiser probably affects the homogeneity of the created network. In fact, a probable heterogeneity of plasticiser repartition into starch can lead to heterogeneity of crosslinking degree (Delville et al., 2002) leading to a decrease of crosslinking efficiency on retrogradation.

Moreover, the results obtained through modulated DSC led to the elaboration of a hypothesis which describes the retrogradation according to the chronological events occurring during ageing. The first scheme on Fig. 8 presents the crystalline cluster formation of amylopectin, which constitutes the major component of wheat starch (Tester & Debon, 2000). The cluster formation begins with

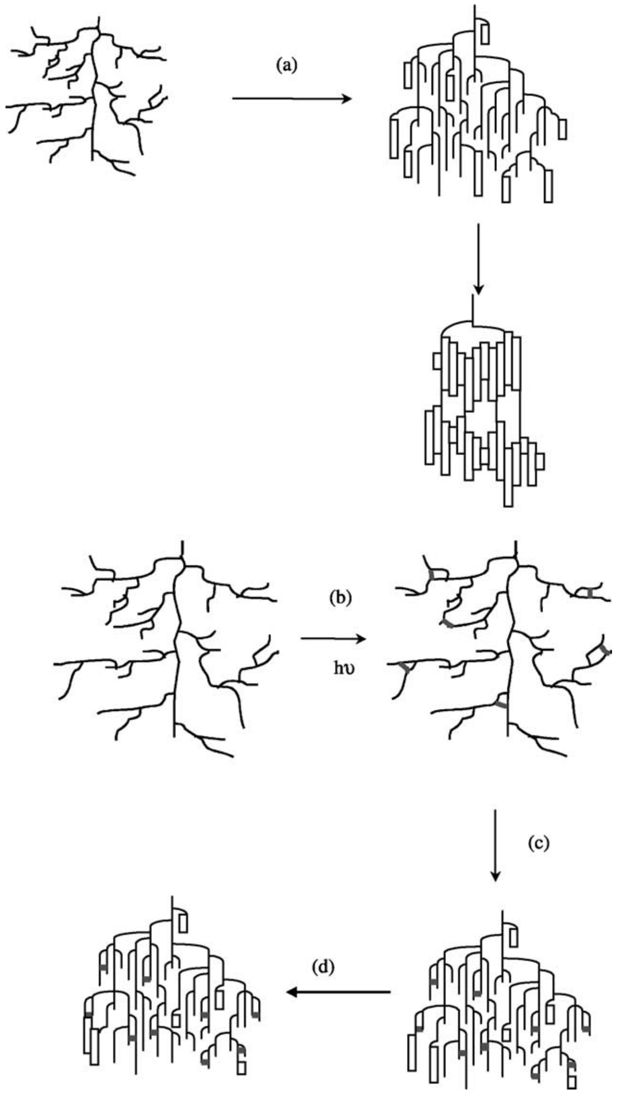

Fig. 8. Pictural representation amylopectin retrogradation at the rubbery state. (amylopectin double helices are represented as rectangles). (a) uncrosslinked amylopectin (b)–(d): crosslinked amylopectin.

the formation of the crystalline lamellae composed of double helical structure of amylopectin short chains (symbolised with rectangular boxes). Then, the packing of double helices forms crystalline clusters. This second step would be the one prevented by the crosslinking linkages even if the crosslinking rate is relatively low (Fig. 8(b)–(d)). It is difficult to use this scheme to explain the thermal behaviour of starch recorded by DSC. One can suppose the following idea that double helices could form but not associate in a crystalline register would be consistent with film clarity.

Acknowledgements

This work was supported by Europol'Agro through a research program devoted to the development of materials derived from agricultural resources.

References

Delville, J., Joly, C., Dole, P., & Bliard, C. (2002). Solid state photocrosslinked starch based films: a new family of homogeneous modified starches. *Carbohydrate Polymers*, *49*, 71–81.

De Meuter, P., Amelrijckx, J., Rahier, H., & Van Mele, B. (1999a). Isotherm crystallization of concentrated amorphous starch systems measured by modulated differential scanning calorimetry. *Journal of Polymer Science: Part B: Polymer Physics*, *37*, 2881–2892.

De Meuter, P., Rahier, H., & Van Mele, B. (1999b). The use of modulated temperature differential scanning calorimetry for the characterisation of food systems. *International Journal of Pharmaceutics*, *192*, 77–84.

Duprat, F., Gallant, D. J., Guilbot, A., Mercier, C., & Robin, J. P. (1980). L'amidon. In B. Monties (Ed.), *Les polymères végétaux* (pp. 176–231). *Polymères pariétaux et alimentaires non azotés*, Paris: Gauthier Villars.

Forssell, P. M., Hulleman, S. H. D., Myllärinen, P. J., Moates, G. K., & Parker, R. (1999). Ageing of rubbery thermoplastic barley and oat starches. *Carbohydrate Polymers*, *39*, 43–51.

Fredriksson, H., Silverio, J., Anderson, R., Eliasson, A. C., & Åman, P. (1998). Methods for the study of starch retrogradation. *Carbohydrate Polymers*, *35*, 119–134.

Jouppila, K., & Roos, Y. H. (1997). The physical state of amorphous corn starch and its impact on crystallization. *Polymers*, *32*, 95–104.

Karim, A. A., Norziah, M. H., & Seow, C. C. (2000). Methods for the study of starch retrogradation. *Food Chemistry*, *71*, 9–36.

Kuutti, L., Peltonen, J., Myllärinen, P., Teleman, O., & Forssell, P. (1997). AFM in studies of thermoplastic starches during ageing. *Carbohydrate Polymers*, *37*, 7–12.

Le Bail, P., Morin, F. G., & Marchessault, R. H. (1999). Characterization of a crosslinked high amylose starch excipient. *Macromolecules*, *26*, 193–200.

Miles, M. J., Morris, V. J., & Ring, S. (1985). Gelation of amylose. *Carbohydrate Research*, *135*, 257–269.

Morris, V. J. (1990). *Trends in Foods Science Technology*, *1*, 2.

Rindlav, Å., Hulleman, S. H. D., & Gatenholm, P. (1997). Formation of starch films with varying crystallinity. *Carbohydrate polymers*, *34*, 25–30.

Rindlav-Westing, Å., Stading, M., Hermanson, A. M., & Gatenholm, P. (1998). Structure, mechanical and barrier properties of amylose and amylopectin film. *Carbohydrate Polymer*, *36*, 217–224.

Ring, S. G., Colonna, P., L'anson, K. J., Kalichevsky, M. T., Miles, M. J., Morris, V. J., & Orford, P. D. (1987). The gelation and crystallisation of amylopectin. *Carbohydrate Research*, *162*, 277–293.

Sauer, B. B., Kampert, W. G., Blanchard, E. N., Threefoot, S. A., & Hsiao, B. S. (2000). Temperature modulated DSC studies of melting and recrystallization in polymers exhibiting multiple endotherms. *Polymer*, *41*, 1099–1108.

Savary, C., & Colonna, P. (1993). Matériaux d'emballage à base d'amidon et de leurs dérivés. *Industrie des céréales*, 17–20.

Silverio, J., Svensson, E., Eliasson, A. C., & Olofsson, G. (1996). Isothermal microcalorimetric studies on starch retrogradation. *Journal of Thermal Analysis*, *47*, 1179–1200.

Tester, R. F., & Debon, S. J. J. (2000). Annealing of starch—a review. *International Journal of Biological Macromolecules*, *27*, 1–11.

Van Soest, J. J. G., de Wit, D., Tournois, H., & Vliegenthart, J. F. G. (1994). The influence of glycerol on stuctural changes in waxy maize starch as studied by Fourier transform infra-red spectroscopy. *Polymer*, *35*, 4722–4727.

Van Soest, J. J. G., Hulleman, S. H. D., De Wit, D., & Vliegenthart, J. F. G. (1996a). Changes in the mechanical properties of thermoplastic potato starch in relation with changes in B-type crystallinity. *Carbohydrate Polymers*, *39*, 225–232.

Van Soest, J. J. G., Hulleman, S. H. D., De Wit, D., & Vliegenthart, J. F. G. (1996b). Crystallinity in starch bioplastics. *Industrial Crops and Products*, *5*, 11–22.

Van Soest, J. J. G., & Knooren, N. (1997). Influence of glycerol and water on the structure and properties of extruded starch plastic sheets. *Journal of Applied Polymer Science*, *64*, 1411–1422.

Wang, Z. G., Hsiao, B. S., Sauer, B. B., & Kampert, W. G. (1999). The nature of secondary crystallisation in poly (ethylen terephtalate). *Polymer*, *40*, 4615–4627.