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► **To cite this version:**

J. Delville, Catherine Joly, P. Dole, C. Bliard. Ageing of solid state photocrosslinked starch based films. Physical and Chemical News, 2004. hal-02074497

**HAL Id: hal-02074497**

**<https://hal.science/hal-02074497>**

Submitted on 20 Mar 2019

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(Version finale)

## Ageing of solid state photocrosslinked starch based films

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### ABSTRACT

A new family of crosslinked starch was synthesised in the solid state by UV irradiation without the use of any crosslinking agent. The original photosensitiser used was sodium benzoate. Although the final crosslinking density is relatively low, it is still sufficient to render starch nearly insoluble and to modify the “ageing” behaviour. Physical aging (at  $T < T_g$ ) is only slightly affected by the crosslinking bonds whereas recrystallisation (also called retrogradation) is highly modified.

**Keywords** : starch, crosslink, UV irradiation, sodium benzoate, ageing.

### INTRODUCTION

The development of biodegradable thermoplastic starch is considered important in order to reduce the total amount of plastic waste. In the literature, a wide range of studies on the processing of starch have yielded numerous starch based materials, all of them presenting a deterioration of their mechanical properties during storage.

Ageing is due to the movements of the macromolecular components (amylose and amylopectin) in starch based materials. The ageing phenomenon leads to crystallisation (called retrogradation in the case of starch) when happening at the rubbery state ( $T > T_g$ ) or physical ageing by densification of microdomains when happening in the glassy state below  $T_g^{\ddagger, \ddagger, \ddagger, \ddagger, \ddagger}$ . The ageing of hydrophilic natural polymer such as starch is specific compared to common synthetic polymers. Since water plasticises starch, ageing (type, kinetics...) is governed by starch water content (except in the case of very low water contents<sup>††</sup>). It is known that the amount of sorbed water is depending on to the ambient relative humidity. The varying humidity conditions during storage will govern the aging characteristics of starch based materials.

Chemical modifications such as crosslinking are able to limit (reduce) macromolecular motions. As far as we know, there has been no study dealing with starch crosslinking *in the solid state* (after achieving the material final shape). This paper presents an original study of solid-state photocrosslinking process using the combination of extrusion and UV-irradiation on sensitised starch

film. No crosslinking agent was used. The hydrosoluble photoadditive used was sodium benzoate, already known to photocrosslink polyvinyl alcohol for example<sup>‡‡</sup>. The process consists in two steps: i) extruding a thermoplastic sensitised starch film ii) using UV irradiation to crosslink this film.

### EXPERIMENTAL

*Materials and Films preparation* : Wheat starch was provided by the Chamtor Company (Pomacle, France). Glycerol and sodium benzoate were provided by the Avocado Company and used without further purification. Films were extruded in a single screw extruder : glycerol (17 wt%) was added to starch, heated for 45 min at 170°C and stirred while water (20 wt%) containing dissolved sodium benzoate was added (3 wt%). The mixture was gelatinised into a ribbon by one run through a SCAMIA monoscrew three zone extruder (heated at 100, 110 and 115°C, slit die 115°C, screw diameter: 2 cm, 11 L/D ratio). The weight percentages were calculated on a dry starch basis for glycerol and on a dry (starch + glycerol) basis for the sensitiser.

*Ultraviolet irradiation set up* : after being conditioned at 57% R.H. (1 week), films were irradiated at 40°C with a FUSION UVF 1000 mercury lamp (34 mW/cm<sup>2</sup> at 365 nm).

*Modulated Differential Scanning Calorimetry (MSCD)*: a TA Instruments 2920 DSC was used. A standard heating ramp of 5°C.min<sup>-1</sup> was chosen and a modulation period of 60s with an amplitude of 0.8°C. Hermetically sealed pans (25 bars proof) were used and a classical ramp of 10°C.min<sup>-1</sup> was used in order to record melting endotherms. The samples were hydrated at constant RH over adequate saturated aqueous salt solutions. A 5 minutes preliminary heating period at 170°C was used with all the samples and the pans weights were measured before and after this thermal treatment in order to check that there was no water lost.

### RESULTS AND DISCUSSION

The network characterisation is described in details elsewhere<sup>§§</sup>. The measurement of the swelling degree (SD) and the gel fraction (GF) in DMSO (definitions are given in annexe) allowed the characterisation of the created network. Before irradiation, the films were entirely soluble in dimethylsulfoxide (DMSO), i.e. the swelling degree is infinite. As exposure time increases, the GF increases until it reaches a plateau (after 10 minutes of exposure) and the SD decreased correspondingly. The final values for SD and GF are 15 and 85 %, respectively. SD values revealed a low crosslinking degree compared to thermosets, but this crosslinking degree was still sufficient to render starch nearly totally insoluble.

The photocrosslinking mechanism is still uncertain and the elucidation of the obtained structure is under investigation. It appears that this mechanism involves macroradical recombinations since sodium benzoate is known to be photolysed by UV<sup>\*\*\*,†††</sup> leading to radical formation after hydrogen abstraction.

The influence of UV treatment on both physical ageing and retrogradation was studied by measuring thermal properties as determined by modulated DSC.

Physical ageing was monitored by recording endotherms (observed in the range of 40-60°C) over 7 weeks at 57 % RH. As expected, the ageing endotherms increased with time but remained roughly the same regardless of the sample. On the contrary, the temperature of the peak maximum, as shown in Figure 1, increased at different rates for crosslinked and uncrosslinked starch films.

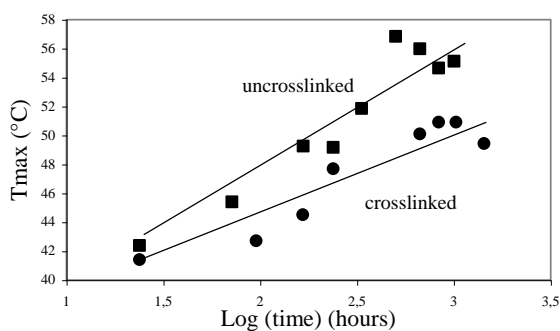


Figure 1. Temperature of the endotherm maximum as a function of ageing time for crosslinked and uncrosslinked samples.

From these data it is clear that crosslinked samples presented a slower ageing process. However, this limitation is not very intense; the low crosslinking degree obtained was not sufficient enough to prevent the local macromolecular movements causing physical aging.

On the other hand, samples were subjected to retrogradation in the rubbery state (80% R.H.). Figure 2 shows that the crosslinking treatment limits the starch recrystallisation kinetic and amplitude in the range of 30 to 50 % depending on the sample.

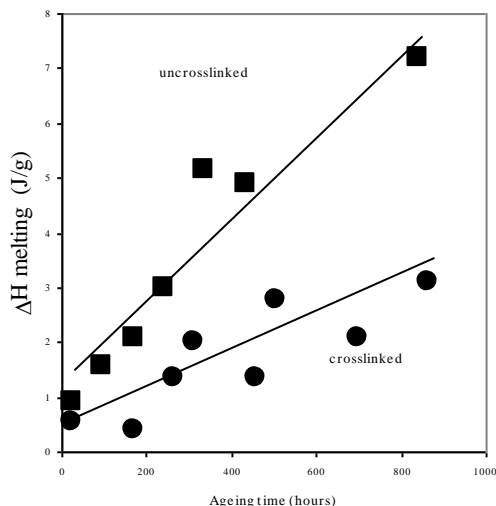


Figure 2. Comparison of the melting endotherms enthalpies of crosslinked and uncrosslinked samples as a function of time.

To achieve the retrogradation, samples were submitted to an accelerated ageing process at 60°C. The change of heat capacity occurring with the development of crystallinity was recorded *in-situ* (in the DSC chamber) by measuring the complex heat capacity ( $C_p^*$ ), as described by De Meter et al.<sup>†††</sup>. The retrogradation time was 3 times longer for the crosslinked sample (1500 minutes against 500 minutes) and the amplitude decreased down to 64% ( $\Delta C_p^*$ ) of the value recorded for the uncrosslinked film. The endotherm enthalpy of the crosslinked starch films was clearly smaller. Figure 3 shows the melting characteristics of the samples that had been submitted to accelerated ageing.

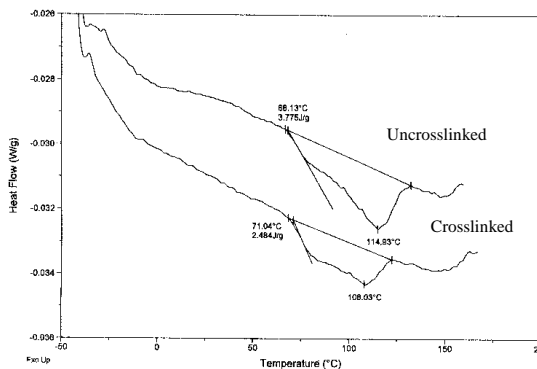


Figure 3. Melting properties of samples submitted to accelerated ageing at 60°C (i.e.; in the rubbery state).

In fact, the melting endotherm enthalpy was decreased by 30% for the chosen sample (17% of glycerol) until 90% for the unplasticised sample. The crosslinking treatment was able to prevent starch retrogradation (specifically in the most organised domains) by limiting the macromolecular movements, which are required for the development of the crystals.

## CONCLUSION

Extruded starch films were subjected to UV treatment in order to crosslink their macromolecular components. The influence of the photocrosslinking treatment on starch ageing showed that:

- The physical aging ( $T < T_g$ ) is only slightly limited
- The retrogradation ( $T > T_g$ ) presented a lower kinetic associated with a strong decrease of the crystallinity ratio (25 to 90 % of the melting enthalpy) as a function of the studied systems although the swelling degree were roughly the same. Unplasticised crosslinked sample presented nearly no retrogradation. The presence of the plasticiser seemed to “facilitate” the retrogradation.

Further experiments are under investigation to explain the role of glycerol in the aging process on one hand, and to enhance starch crosslinking degree by modifying the initial matrix or the irradiation conditions on the other hand.

## ANNEXE

The swelling degree SD and gel fraction GF are given by:

$$SD \approx \frac{m_s - m_d}{m_d} \approx \frac{m_s}{m_d} \quad m_d \ll m_s \text{ for low crosslinking density}$$

$$GF = 100 \frac{md}{mc}$$

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  $m_c$  was validated with experimental correction made by water extraction of glycerol prior to DMSO

extraction. The sensitiser is also extracted but its content is low enough to be negligible.

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

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