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Note

Enhanced stability of rubbery amylose-rich maize starch films plasticized with a combination of sorbitol and glycerol

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Abstract

Well known aging problems with rubbery starch films are the migration of plasticizer and increased crystallinity leading to embrittlement. The effects of a combination of sorbitol and glycerol used as plasticizers on mechanical, moisture permeability and solid-state properties of rubbery amylose maize starch (Hylon VII) films were studied. The films were prepared by casting and were exposed to conditions of 25 °C/60% relative humidity (RH) and 40 °C/75% RH for 9 months. The starch films plasticized with a combination of sorbitol and glycerol (1:1) at equal amount to the polymer weight, were shown to be the most stable alternative of the studied films during the 9 months storage period. The water vapor transmission (WVTR) of the films did not change during the period of storage and neither did the elongation at break, but the tensile strength increased. X-ray diffraction (XRD) results showed that during storage no crystallization had occurred. The combination of sorbitol and glycerol prevented the migration of the plasticizer molecules out of the film.

Keywords: Plasticizer; Sorbitol; Glycerol; High amylose maize starch; Film properties

Starch and especially amylose-rich maize starch (A-RS), is known to have good film forming properties (Friedman et al., 1999). Small molecular materials such as glycerol (Lourdin et al., 1995), sorbitol (Gaudin et al., 1999), and different mono- and disaccharides (fructose, glucose and sucrose; Arvanitoyannis et al., 1994), have been studied as plasticizers for starch films.

Starch is a renewable and biodegradable polymer. Therefore, there has been an increased interest for the utilization of different starches as adjuvants in the food and pharmaceutical industry. However, a major limitation of the application of rubbery starch films as e.g. film coating material is aging (Van Soest and Knooren, 1997). It has been reported that there were marked changes in the stress–strain behavior of films formed by

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thermoplastic barley and oat starches during 2 months of storage (Forssell et al., 1999). The authors concluded that crystallization and/or re-orientation of amylopectin and amylose caused the aging. Migration of the plasticizer to the surface of the starch films has also been reported (Kuutti et al., 1998).

In the present study, the physical stability of A-RS (Hylon VII) films plasticized with non-traditional levels of sorbitol and glycerol (and combinations of them) was studied with free films. The crystallinity, water vapor transmission (WVTR) and stress–strain behavior were evaluated with fresh films and films exposed to long-term storage conditions for 9 months.

The A-RS (Hylon VII, National Starch, Germany; 70% amylose and 30% amylopectin) solution was prepared in a high-pressure reactor (100 rpm, 160 ± 1 °C and pressure 4 bar), after which the solution was cooled to 95 ± 2 °C and removed from the reactor. The final A-RS content of the solution was 5% w/w and the plasticizer content was varied (50, 100, 120% of the polymer weight). Plasticizers glycerol and sorbitol (1:1) were added and mixed with the solution. The hot solution (80 ± 2 °C) was poured into Teflon moulds, which were kept in an oven for approximately 2 h at 70 °C. The films containing 50 or 120% of plastisizer combinations were of poor quality after aging and could not be studied (Table 1). Films with only one plasticizer (i.e. sorbitol or glycerol at levels of 50 and 100%) were also prepared. However, none of these films could be studied after a storage period of 9 months (at 25 °C/60% relative humidity (RH)), due to marked changes in the films (Table 1). The films had shrunk and hardened, and with some films aging had led to spontaneously formed film defects (i.e. 'waves' and cracks). In the case of films with ≥ 50% sorbitol, sorbitol had crystallized on the surface. Glycerol was found as droplets on the surface of the films plasticized with 100% of glycerol.

Films were held for 24 h (mechanical properties) or 2 days (other properties) at 25 °C (60% RH) (initial) and subsequently for 9 months at storage conditions of 25 °C (60% RH) and 40 °C (75% RH) before examining. Samples were analyzed by means of X-ray diffraction (XRD). XRD analyses measurements were performed in symmetrical reflection mode with CuK$_\alpha$ radiation (angular range 2–60° (at 2θ), steps of 0.02° and measuring time 20 s per step).

The mechanical and stress–strain properties of free films were determined using a material testing machine (Lloyd LRX, Lloyd Instruments Ltd., UK). The films were cut into strips and mounted on the material-testing machine. The initial position of the grips was 40 mm from each other. The extension speed was 10 mm/min. The thickness of the films was typically about 100 μm (average of three points). The measurements were carried out at ambient temperature and humidity.

For the WVTR studies the films were cut to a suitable size and fixed onto glass bottles containing calcium chloride ($CaCl_2$) and immediately sealed with metal rings. The exposed surface area was 1.23 cm^2. The bottles were held at 25 °C and 60% RH and were weighed several times during 28 h ($n = 3$). The WVTR was calculated according to Nagasenker and Hegde (1999).

After 9 months of storage the A-RS films plasticized with sorbitol–glycerol ratio 1:1 (100% of polymer weight) were transparent and flexible when handled. Visually it seemed that these films

Table 1
Appearance of A-RS films stored for 9 months at 25 °C and 60% RH

Plasticizer(s)	Total plasticizer content[a]		
	50%	100%	120%
Glycerol	Hard and wavy	Glycerol droplets on film surface	–
Sorbitol	Sorbitol crystals on film surface	Sorbitol crystals on film surface	–
Glycerol:Sorbitol (1:1)	Hard and wavy	Appearance as the initial film	Opal and tacky film

[a] w/w on the basis of polymer content.

had not aged significantly. These films were chosen for further studies.

The XRD pattern of fresh films (Fig. 1) resembled that of the hexagonal starch structure (B-polymorph). B-type crystallinity is, indeed, rapidly formed in amylose-rich materials (Van Soest and Essers, 1997). The diffraction patterns of the 9-month old A-RS films were rather similar to the diffraction pattern of the fresh films and only small differences could be seen (Fig. 1). The embrittlement on aging of starch films has been explained by loss of plastisizing water by evaporation, physical aging (glassy state; Shogren, 1992) or increase in crystallinity of starch (Van Soest and Knooren, 1997). In this study the degree of crystallinity of the AR-S films did not increase during storage, instead the crystallinity of the films stored for 9 months at 40 °C/75% RH had slightly decreased (Table 2), which may be due to incorporation of some water molecules into the film during storage.

Stress–strain properties of films are a sensitive measure of the aging of starch films (Van Soest and Knooren, 1997). As seen in Table 3, the elongation at break (%) for the A-RS starch films did not change during storage. According to the literature, the changes in elongation are clearly related to the changes in starch structure and B-type crystallinity (Van Soest and Knooren, 1997). However, the XRD measurements of our stored A-RS films showed that no crystallization had occurred, which probably explains why the elongation had not changed. Amylose-rich starch is less sensitive to aging phenomena than amylopectin-rich starch (Van Soest and Essers, 1997). The tensile strength of the films, however, increased over the 9 months (Table 3), which cannot be explained by change in crystallinity but can indicate a slight loss of plasticizing water.

Starch films are known to be poor water vapor barriers. In this study the measured WVTR-values of the amylose-rich films were $40 \pm 6 \times 10^{-11}$ g/m s Pa. In an earlier study the WVTR values of maize starch films were between 0.3 and 15×10^{-11} g/m s Pa, with WVTR values augmenting with increasing plasticizer content (0–40% glycerol) (Arvanitoyannis et al., 1996). The WVTR results of the current study supports the finding that higher

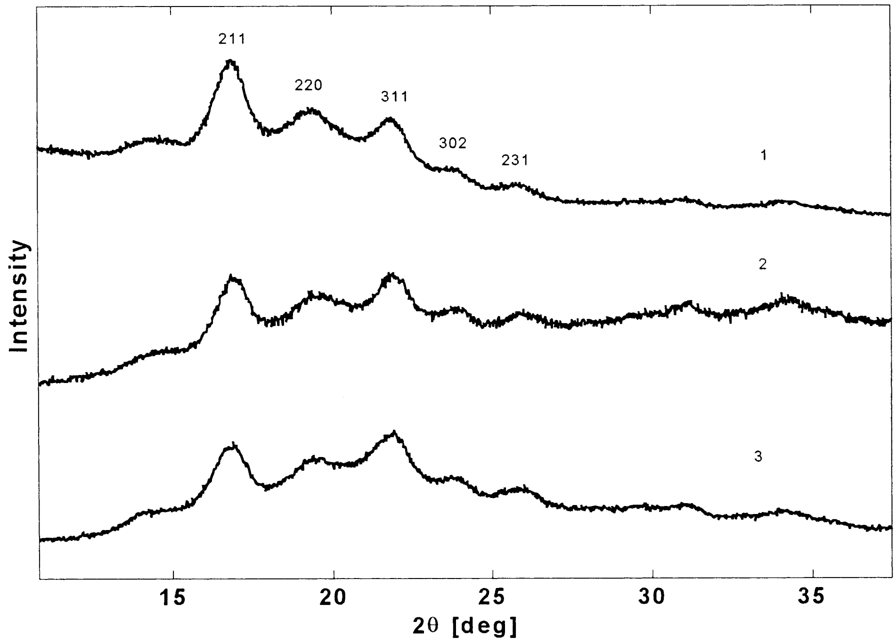

Fig. 1. Measured XRD intensity curves of the starch films. The intensity curves from top to bottom: films stored for 9 months at, (1) 40 °C, 75% RH; at (2) 25 °C, 60% RH; and (3) fresh film.

Table 2
The effect of storage time and conditions on crystallinity and crystal size of A-RS films plasticized with a combination of sorbitol and glycerol (1:1)

Storage time	Storage conditions		Crystallinity (%)	Crystal size (Å)
	RH (%)	Temperature (°C)		
Initial	60	25	24	65
9 months	60	25	25	68
9 months	75	40	21	72

Table 3
Mechanical properties of free A-RS films (glycerol:sorbitol 1:1, 100%; $n = 3$–6)

Composition	Tensile strength (MPa) mean ± S.D.	Elongation at break (%) mean ± S.D.
Initial	4 ± 1	14 ± 2
9 months at 25 °C/60% RH	7 ± 1	15 ± 2

plasticizer content gives higher WVTR. The A-RS films in the current study were stable with respect to WVTR. The WVTR-values did not change during the 9 months of storage.

With this film preparing condition the films with 100% plasticizer level (with plasticizer combination) were more stable than films with 50 and 120%. The films with 120%-plasticizing level were over-plasticized, and opal initially. The hardening and shrinking of films with 50% plasticizing level indicates loss of plasticizer, i.e. plasticizing water, whereas with 100% plasticizing level the role of water as a plasticizer seems to be less significant (the results were not, however, verified by moisture content measurement).

Improved stability in rubbery A-RS films seems to be obtained by using a combination of sorbitol and glycerol as plasticizers (at 100% level) compared with using these plastisizers solely. The combination of two different sized plasticizers seems to induce more interactions between the components and thereby, keep the plasticizers more tightly bonded, hindering them from migrating out of the film.

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