

Structure, mechanical and barrier properties of amylose and amylopectin films

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Abstract

The effect of film formation conditions on structure, mechanical properties and barrier properties of amylose and amylopectin films was studied. The films were prepared by solution-gel-casting of amylose and amylopectin from potato, with or without the addition of glycerol as plasticizer. Transmission electron micrographs showed that the network structure characteristic for the amylose gel was also found in the film state. The amylose films without glycerol plasticization exhibited a relatively high degree of B-type crystallinity, as revealed by wide-angle X-ray diffraction, whereas the unplasticized amylopectin films were amorphous. Although the addition of glycerol did not affect the crystallinity of the amylose films, glycerol-plasticized amylopectin formed B-type crystallinity, and the degree of crystallinity was dependent on the air humidity during film formation. The degree of crystallinity affected the mechanical properties of the amylopectin films, whereas the mechanical properties of the amylose films were influenced by the network microstructure. Oxygen and water vapour permeabilities were dependent neither on the degree of crystallinity in the films nor on the network structure. © 1998 Elsevier Science Ltd. All rights reserved

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1. Introduction

There is an increased interest in the utilization of renewable resources for the preparation of such disposable materials as food packaging. Among natural polymers, starch has been considered as one of the most promising candidates for future materials primarily because of attractive combination of price and performance (Doane et al., 1992; Tomka, 1991). Starch consists of two polysaccharides, the linear D-glucan amylose and the highly branched amylopectin, which, in their native form, are organized in semicrystalline granules. Native starch can have A-, B- or C-type crystalline structures consisting of double helices. The conversion of starch into a thermoplastic material by extrusion or by gel-casting into films leads to a loss of the natural organization of the starch polymers. Extrusion has, for example, been shown to induce single helical crystal structures of V_H-, V_A- or E_H- types (van Soest et al., 1996a,b).

It was previously shown that, during gelation and ageing of starch gels, a crystalline X-ray diffraction pattern of the B-type develops slowly with time (Katz, 1930). The

polymer crystal growth theory was applied to the formation of B-type crystallinity in wheat starch gels by Marsh and Blanshard (1988). During storage of extruded potato starch samples, crystallinity developed with time (Arvanitoyannis et al., 1994). The development of crystallinity in an amylose solution has also been investigated. Miles et al. (1985) proposed that an interconnected gel network was formed in the polymer-rich regions provided the solution concentration was sufficiently high. Crystallization in these regions of the gel occurred subsequently. On the basis of ¹³C CP/MAS NMR studies of monodisperse amylose in solution, Gidley (1989) proposed that the origin of amylose gelation lies in the formation and subsequent aggregation of inter-chain B-type double helices. The amylose gel was suggested to contain rigid, crystalline, double-helical junction zones connected by more mobile amorphous, single-chain segments. Transmission electron micrographs of starch and amylose gels show networks of interconnected strands (Hermansson and Svegmarm, 1996; Hermansson et al., 1995; Leloup et al., 1992). The network was shown to be open and composed of stiff, rod-like strands 10–40 nm in diameter. Leloup et al. (1992) suggested a model for amylose gels where a network strand would consist of contiguous associated blocks of double helices, aligned along,

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and oriented perpendicularly to, the length axis of the strand. Loops of amorphous amylose segments would then link the double helices. The crystallinity detected by wide angle X-ray diffraction originates from the ordered arrays of B-type helices, which in that case would be located in the strands. The structure of the amylose gels was shown to be very consistent and not particularly influenced by the cooling rate, the presence of salts or by amylose concentrations in the range of 4–10% (Hermansson and Svegmarm, 1996).

Several studies have been made on starch-based films cast from a solution or gel. As early as the 1950s, self-supporting amylose films were prepared with and without glycerol plasticization and evaluated as regards their mechanical and barrier properties (Wolff et al., 1951; Rankin et al., 1958). The influence of amylose content on the mechanical properties of cast films was studied by Lourdin et al. (1995). The mechanical properties of starch based materials have also been investigated by a number of researchers (Lloyd and Kirst, 1963; Healy et al., 1974; Ollet et al., 1991), as well as by Bader and Göritz (1994a, b) in connection with studies on the crystallinity of high amylose films. We have recently showed that the conditions during film formation affect the crystallinity of starch films (Rindlav et al., 1997). However, we were not able to point out which of the starch polymers, or to what extent it contributed to the starch crystallinity that was developed upon drying of the starch into films.

The aim of this study was to prepare films of amylose and amylopectin with or without the addition of glycerol as a plasticizer and to elucidate firstly how the film formation conditions affected the crystallinity and secondly how the mechanical and permeability properties were influenced by film crystallinity and microstructure.

2. Material and methods

2.1. Materials

Amylose (104561, batch 209861511) from potato was purchased from Merck (Darmstadt, Germany). The amylopectin was kindly supplied by Lyckeby Stärkelsen (Kristianstad, Sweden) in the form of granular amylopectin potato-starch. This potato was developed by Lyckeby Stärkelsen and Svalöv Weibull (Svalöv, Sweden) using genetic engineering to suppress amylose synthesis (Hofvander et al., 1992).

2.2. Film preparation

5%w/w amylose was dispersed in distilled water, degassed and heated to 150°C. The amylose solution was then cooled to 95°C and glycerol (2%w/w) was added to the plasticized samples. The solution was poured on a PVC dish and allowed to gel at 23°C.

3%w/w amylopectin was dispersed in distilled water, degassed and heated to 90°C in a Brabender Amylograph and was kept at 90°C for 15 min. Warm glycerol (1.2%w/w) was added to the plasticized samples. The solution was poured on a PVC dish and cooled to 23°C.

The plates with amylose or amylopectin were then dried at a constant relative air humidity (RH) of 20%, 50%, 70% or 90%RH at 23°C for 3 days. The films were peeled off and reconditioned for at least 2 days at 50%RH before measurements. All films containing glycerol are referred to as plasticized film. The thickness of the films was measured using a digital indicator (Mitutoyo IDC-112CB, Mitutoyo Corp, Japan) with an accuracy of $\pm 3 \mu\text{m}$. The films were 70–100 μm thick.

2.3. Wide angle X-ray diffraction

The films were ground in liquid nitrogen and reconditioned in 50%RH before measurements were made in triplicate. Wide-angle X-ray diffractograms of the powdered samples were recorded in the reflection geometry on a Siemens D5000 diffractometer using nickel-filtered CuK_α ($\lambda = 0.154178 \text{ nm}$) radiation. A variable divergence slit was used, giving an irradiated area with a diameter of 20 mm as the sample holder was rotated with 30 rpm. An antiscatter slit of 0.6 mm, a detector slit of 0.2 mm and a scintillation detector were used. Diffractograms were taken between 5 and 30°(2 θ) at a rate of 1°(2 θ) per min and a step size of 0.1°(2 θ). The background was subtracted from the diffractogram by drawing a straight baseline at 7°(2 θ). The relative crystallinity was calculated by dividing the area of the peak at approximately 17°(2 θ) by the total area (Hermans and Weidinger, 1948). The diffractograms were smoothed. The error bars in the figures show the scatter as a 90% confidence interval.

2.4. Mechanical properties

The tensile properties were studied using an Instron 1122 (Instron Ltd., High Wycombe, UK) in accordance with ASTM D882-91, but with sample strips 6 × 50 mm. The strips of the films were cut and clamped between pneumatic grips. Force and elongation were recorded during extension at 10 mm min⁻¹ up to break, and stress and strain were calculated. The parameters used were Young's modulus, E , stress at break, σ_b , and strain at break, ϵ_b . The two latter are often also referred to in the literature as tensile strength and elongation. The error bars in the figures show the scatter as a 90% confidence interval.

2.5. Gas permeability

The oxygen transmission was measured in accordance with ASTM D3985-81 using Mocon Oxtran 2/90 equipment (Modern Controls Inc., Minneapolis, USA). The permeability

was calculated from the transmission and the measured thickness of the films, and was presented in the units $\text{cm}^3 \mu\text{m}/(\text{m}^2 \text{ d kPa})$ where $d = 24 \text{ h}$. All films were measured at 50%RH.

The water vapour permeability (WVP) was measured in accordance with the gravimetric method described in ASTM E96-90. Films with a diameter of 25 mm were placed on top of a cup and tightly sealed with a lid. The bottom of the cup was filled with water and the distance to the film was 13 mm. This device was placed in a climate chamber at 23°C and 50%RH and the weight loss owing to evaporation was monitored. The WVP was calculated as described in the ASTM standard and presented in the units $\text{g mm}/(\text{m}^2 \text{ d kPa})$. The error bars in the figures show the scatter as a 90% confidence interval.

2.6. Microscopy

The microstructure of the amylose films was studied using transmission electron microscopy (TEM) on a JEOL microscope (STEM-JEOL 100 CX-II). Small pieces of the films were prepared by fixation in 2% glutaraldehyde and stepwise dehydration in an ethanol series. The ethanol was then replaced in steps, first by propyleneoxide and thereafter by a cured epoxy resin (Polybed, Polyscience Inc.). The embedded samples were sectioned in $\sim 70 \text{ nm}$ thick slices using a diamond knife in a Reichert-Jung Ultracut E. The sections were transferred on to Formvar-supported gold grids and stained with periodic acid, thiosemicarbazide and silver-proteinase (PA-TSC-SP) by the method described by Thiéry (1967).

Confocal laser scanning microscopy (CLSM) was used to study the microstructure of the amylopectin films on a Leica TCS 4D microscope (Leica, Heidelberg, Germany). Small pieces of the film were cut and directly stained with a 0.01% Rhodamine 6G solution (Molecular Probes European BV, Leiden, The Netherlands) without further preparation. The stained samples were directly inserted in the microscope and examined at a wavelength of 590 nm. The entire procedure was carried out within less than 5 min.

3. Results and discussion

3.1. Microstructure

The films were prepared by casting water solutions of amylose and amylopectin, with or without the addition of glycerol as a plasticizer. The amylose solutions formed gels immediately on cooling. All films were formed by drying at controlled air humidity. The microstructure of the amylose gels and corresponding films was studied by TEM, and the microstructure of the amylopectin films was studied by CLSM. Fig. 1a shows a TEM micrograph of a thin section of a 5% amylose gel with 2% glycerol. The section is only about 60 nm thick, which means that the network strands go

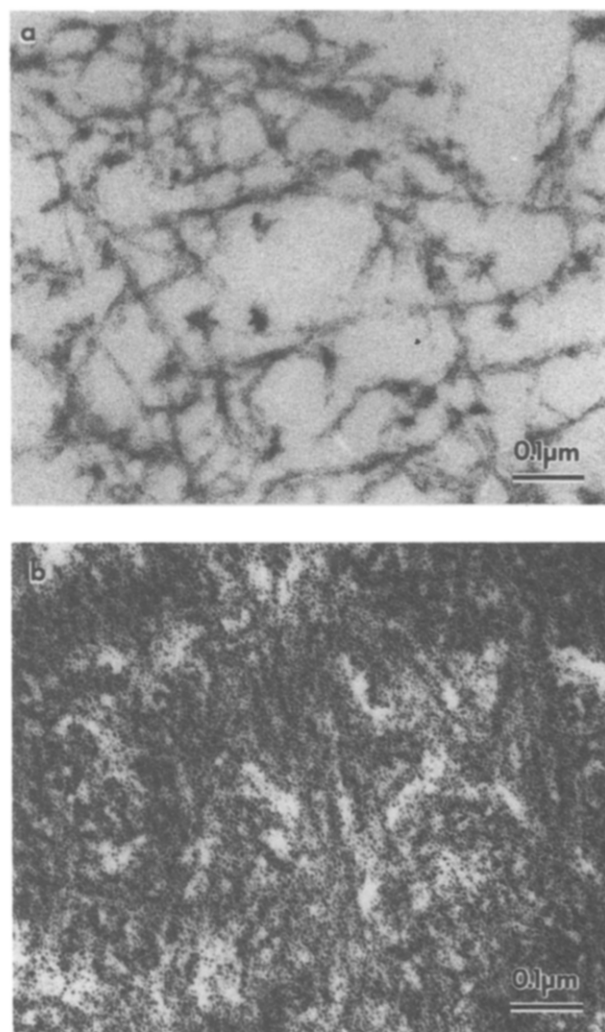


Fig. 1. TEM micrographs of (a) 5% amylose gel with 2% glycerol and (b) the corresponding amylose film.

in and out of the plane of the micrograph and only the ones parallel to the plane appears as strands. The network was open and composed of stiff rod-like strands 10–30 nm in diameter and had the same structure as previously published for amylose gels without glycerol (Hermansson and Svegmarm, 1996; Hermansson et al., 1995). Fig. 1b shows a micrograph of a film formed from the amylose gel which is given in Fig. 1a. It shows a network much denser than the one present in the gel, but the basic characteristics of the amylose network could still be detected and the rod-like strands were also found in the films. This suggests that a compaction of the already formed network took place during the drying process.

The film and gel structures presented in this study, together with earlier published results, show that the amylose network structure is very stable, with strong molecular orientation responsible for the characteristic superstrands. The network structure observed was, as far as could be told from the micrographs, consistent with the model proposed by Leloup et al. (1992). It was not possible to use the

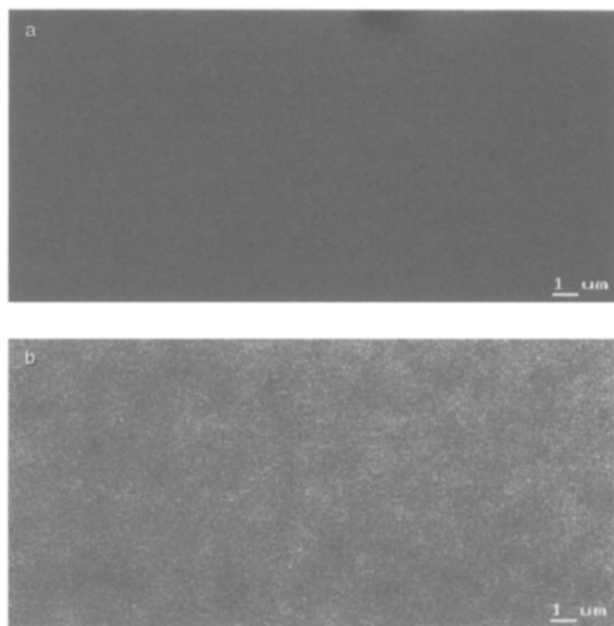


Fig. 2. CLSM micrographs of amylopectin films with glycerol formed at (a) 20%RH and (b) 90%RH.

same TEM preparation technique for the amylopectin films, since the embedded amylopectin films could not be sectioned.

Fig. 2 shows confocal laser scanning micrographs of amylopectin films with glycerol formed at 20%RH and 90%RH. The micrographs show a plane from the interior of the film parallel to the surface. The 20%RH film (Fig. 2a) did not show any structure at this magnification. The 90%RH film (Fig. 2b) showed fluctuations in density, which must be studied further to understand its origin. The amylose films were denser than the amylopectin films and did not show any structure at the resolution of CLSM.

3.2. Crystallinity

The relative crystallinities of the films were investigated with wide-angle X-ray diffraction. Fig. 3 shows the effect of air humidity during film formation on the relative crystallinity of films without addition of glycerol. Amylose developed a relative crystallinity of a B-type to about 34%, and the crystallinity did not vary consistently with the air humidity during film formation. Contrary to amylose films, all amylopectin films without glycerol were shown to be amorphous irrespective of the air humidity during film formation. Fig. 4 shows X-ray diffractograms of glycerol-plasticized amylopectin films formed at various air humidities. The films formed at low air humidity were almost amorphous, while an increased air humidity during film formation resulted in a gradually increased B-type crystallinity. A diffractogram of glycerol-plasticized amylose is shown for comparison on the top of this figure. The addition of glycerol did not significantly affect the degree of crystallinity of amylose films. The differences in relative

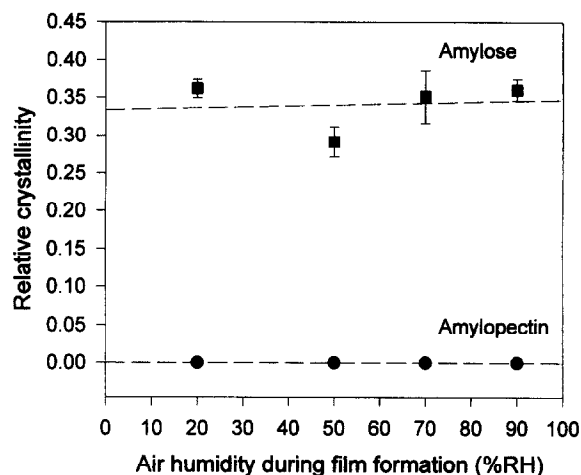


Fig. 3. Relative crystallinity of amylose and amylopectin films without glycerol as a function of air humidity during film formation.

crystallinity between the glycerol-plasticized films of amylose and amylopectin are quantified and presented in Fig. 5. The crystallinity of the amylopectin films with glycerol did not increase after they were dried and reconditioned at 50%RH. This was verified by X-ray diffractograms taken 6, 9 and 13 days after preparation. The granular amylopectin potato starch used in this study had a relative crystallinity of 44% and a B-type crystalline structure. At this point it should be stressed, however, that under the current film forming conditions the degree of crystallinity in the amylopectin films did not reach such a high level.

Amylose and amylopectin are known to recrystallize in the B-type crystalline form from a dilute solution (Katz, 1930; Miles et al., 1985). The observed B-type crystalline structure in the films should be attributed to the fact that crystallinity was developed in the early stage of film formation. The final degree of crystallinity in a polymer sample is dependent on the ability of the chains to form crystals as well as the mobility of the chains during the crystallization process. A higher air humidity during film formation will

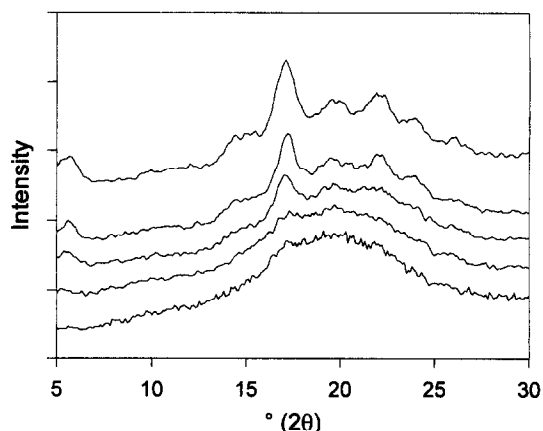


Fig. 4. Wide-angle X-ray diffractograms of amylopectin films with glycerol formed at 20%RH, 50%RH, 70%RH and 90%RH and of amylose film with glycerol formed at 90%RH (bottom to top).

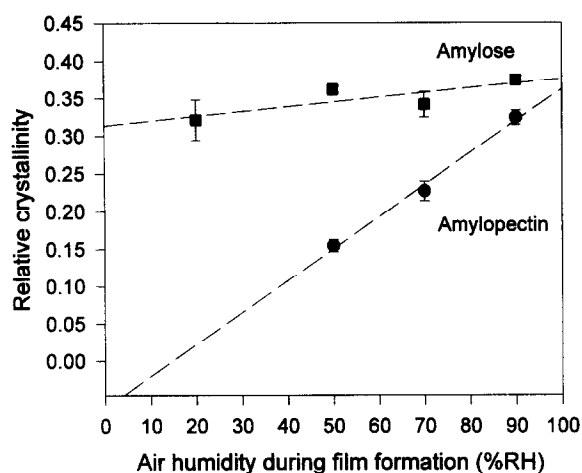


Fig. 5. Relative crystallinity of amylose and amylopectin films with glycerol as a function of air humidity during film formation.

lead to a longer time in contact with water and thereby a longer time with a high mobility of the starch polymer chains. The linear amylose and the branched amylopectin polymers exhibit different behaviour with regard to gelation and development of crystallinity. For synthetic polymers, it is well known that a linear polymer crystallizes more easily than a branched polymer based on the same monomer. X-ray diffraction of amylose solutions in the study of Miles et al. (1985) showed that the development of crystallinity though fast in the beginning was levelled off approximately 1 day after preparation. In our case, it is assumed that the crystallinity in the amylose gel is fully developed during the first period of drying when the water content is still very high, and thereby also the mobility. The crystallinity of amylose films will, therefore, be only slightly affected by the air humidity during film formation or the addition of glycerol. In amylopectin solutions, the development of crystallinity is much slower than in amylose solutions, and it has

been shown to develop over a period of several days (Ring et al., 1987; Durrani and Donald, 1995). In this study, the amylopectin, in the absence of glycerol, did not have sufficient time to crystallize before the water content reached very low values during the drying process. Thus, these films became totally amorphous. The addition of glycerol facilitated the mobility of the amylopectin polymer over a prolonged time so that crystallization could gradually start. An increase in air humidity leads to an increase in the time available for crystallization and results in a higher degree of crystallinity. The crystallinity of amylopectin films is thereby affected both by the presence of glycerol and the air humidity during film formation. In a study by Arvanitoyannis et al. (1996), a higher content of plasticizer (sugars or glycerol) in the corn starch material also increased the crystallization rate. The rate of crystallization in starch gels is also dependent on the crystallization temperature and was found, in theoretical calculations by Marsh and Blanshard (1988), to follow a bell-shaped curve between the temperatures of glass transition and melting.

3.3. Mechanical properties

The amylose and amylopectin films were strong and had a Young's modulus, E , and stress at break, σ_b , comparable to, for example, low density polyethylene (LDPE), as shown in Table 1. All films exhibited yield at strain $\epsilon \approx 2.5\%$. The amylose films were stiffer and ultimately stronger than the amylopectin films, as shown in Figs. 6 and 7. The values of σ_b and E strongly depended on the film-forming conditions, and on plasticization as well. The strain at break, ϵ_b , was substantially lower than for LDPE. Early published mechanical measurements gave similar results for less plasticized amylose films, thus with slightly higher σ_b and lower ϵ_b (Wolff et al., 1951). Lourdin et al. (1995) studied mixed amylose–amylopectin films and also found slightly higher

Table 1
Mechanical properties of amylose and amylopectin films

Polymer	Stress at break, σ_b (MPa)	Strain at break, ϵ_b (%)	Comments
Amylose	20	31	Present study, glycerol/amylose = 0.4, films formed at 50%RH and measured at 50%RH
Amylopectin	6	29	Present study, glycerol/amylopectin = 0.4, films formed at 50%RH and measured at 50%RH
Amylose	20	46	Wolff et al. 1951, glycerol/amylose = 0.3, films formed at 65%RH
Amylose	23	10	Lourdin et al., 1995, glycerol/amylose = 0.2, films formed at room conditions
Amylopectin	5	25	Lourdin et al., 1995, glycerol/amylose = 0.2, films formed at room conditions
High-amylose corn starch ~50% amylose	50	2.5	Lloyd and Kirst, 1963, no glycerol, films formed at 50%RH
High-amylose corn starch ~55% amylose	38	9	Bader and Göritz, 1994b, no glycerol, films formed at 60%RH
Low density polyethylene, LDPE	7–16	100–800	Doak, 1986, Young's modulus E = 100–240 MPa

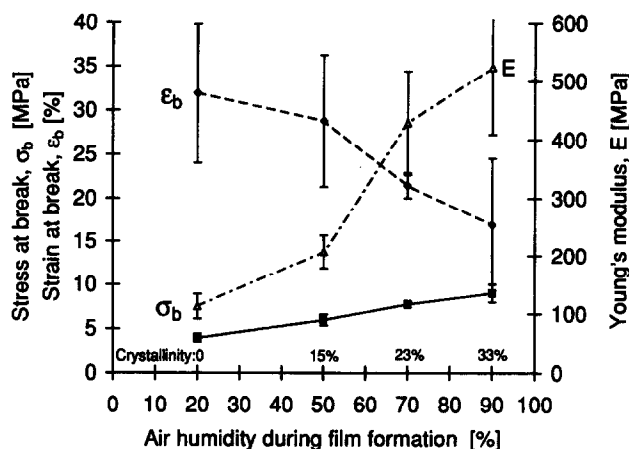


Fig. 6. Mechanical properties of plasticized amylopectin films.

σ_b for plasticized amylose films but lower σ_b for plasticized amylopectin films with glycerol/polymer = 0.2. The mechanical properties vary between the different studies owing to several factors. The conditions during casting differ, as do the polymer sources and molecular weight. The molecular weight has been shown to have a pronounced influence on the mechanical properties of amylose films (Wolff et al., 1951). Published results (Table 1) show that films cast from high-amylose corn starch have σ_b and ϵ_b in the same range as amylose films (Lloyd and Kirst, 1963; Bader and Göritz, 1994b). Also glycerol plasticized thermoplastic starch show stress and strain values similar to those found in this study (van Soest et al., 1996a).

The increase in relative crystallinity of the amylopectin films with increased relative air humidity during film formation had a clear impact on the mechanical properties. Fig. 6 shows E, σ_b and ϵ_b for the plasticized amylopectin films. An increase in crystallinity made the films more brittle, with increased E and σ_b and decreased ϵ_b . This may be expected from an increase in crystallinity, since

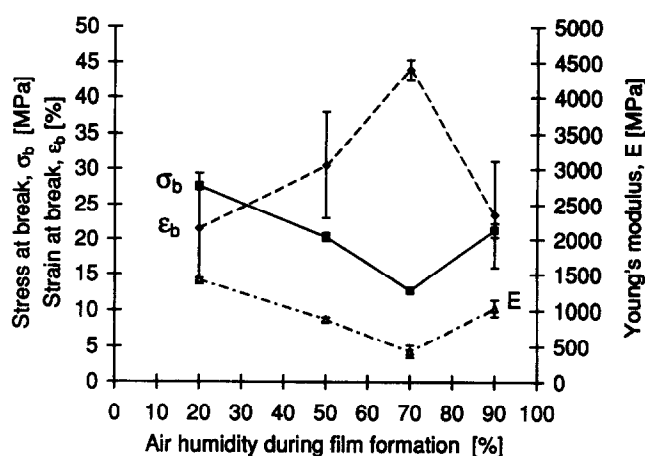


Fig. 7. Mechanical properties of plasticized amylose films.

the crystalline parts are dense and have a high modulus, while they also make the network less extendible, thus causing a decrease in ϵ_b .

Amylose films with corresponding plasticization were stronger than amylopectin films with higher σ_b and E, but had a lower ϵ_b , which is shown by a comparison of Fig. 7 and Fig. 6. The amylose films had an almost constant degree of crystallinity, independent of the relative air humidity during film formation. On the other hand, the microstructure probably changed with different relative air humidity during film formation. The mechanical properties of the amylose films showed the opposite behaviour, compared with the amylopectin, up to a relative humidity of 70%, where there was a minimum in E and σ_b and a maximum in ϵ_b . The extreme behaviour at 70% RH is suspected to be related to the microstructure, which will be studied further. Healy et al. (1974) studied the tensile properties of corn starch films at varying surrounding humidity and found that σ_b showed a maxima for very low humidities, ~10%, and then decreased at higher humidity. This was attributed to the moisture content of the films and could be a parallel

Table 2

Oxygen and water vapour permeability of films of amylose, amylopectin and some common packaging plastics

Polymer	Oxygen permeability (cm ³ μ m m ⁻² d kPa)	Water vapour permeability (g mm m ⁻² d kPa)	Comments
Amylose	7	103	Present study, glycerol/amylose = 0.4 WVP: 50–85%RH over the film OP at 50%RH
Amylopectin	14	124	Present study, glycerol/amylopectin = 0.4 WVP: 50–85%RH over the film OP at 50%RH
Amylose	n.d.	4.7	Rankin et al., 1958, glycerol/amylose = 0.4 WVP: 1–53%RH over the film
Amylose	n.d.	23	Rankin et al., 1958, glycerol/amylose = 0.4 WVP: 29–81%RH over the film
Compression molded thermoplastic potato starch	—	6.3	Arvanitoyannis et al., 1996, no glycerol, 85% starch, 15% water
Compression moulded thermoplastic potato starch	6.4	13	Arvanitoyannis et al., 1996 glycerol/starch = 0.4 5% water in the film
LDPE	1900 ^a	0.079 ^a	McHugh and Krochta (1994)
EV0H	0.1–12 ^a	0.25 ^a	McHugh and Krochta (1994)

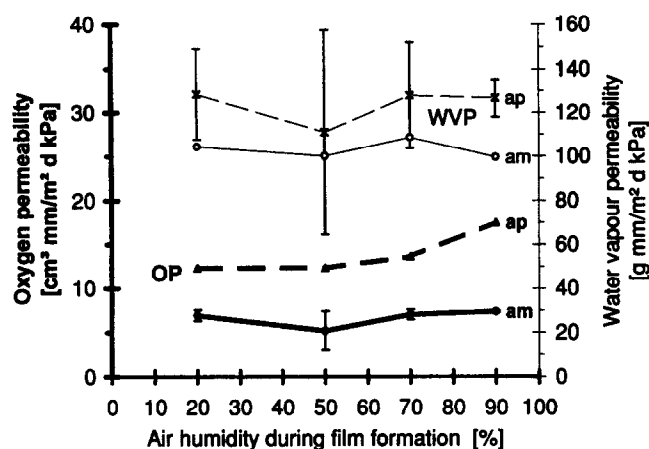


Fig. 8. Permeability properties of amylose and amylopectin films.

behaviour to the observed variation in σ_b with humidity during film formation in the present study.

3.4. Permeability properties

The permeability of oxygen and water vapour of plasticized amylose and amylopectin films was evaluated and is presented in Fig. 8. Both the oxygen permeability (OP) and the water vapour permeability (WVP) were higher for the amylopectin films than for the amylose films. Mean values of OP and WVP for amylose and amylopectin films are summarized and compared in Table 2 with the results of similar studies and with typical packaging plastics such as LDPE and ethyl vinyl alcohol (EVOH). It is seen that starch, and especially amylose, exhibits excellent oxygen barrier properties. The WVP is high, however, as a result of the hydrophilic nature of the starch polymers. The WVP has been published for thin (30 μ m) amylose films, where the air humidity difference over the film was varied (Rankin et al., 1958). The WVP increased with an increased surrounding air humidity during the measurements. This explains the higher WVP of the amylose films in the present study, which were measured in a higher average humidity, than has been used in other published studies.

In this study, the WVP was not affected by the relative air humidity during film formation, i.e. neither the differences in crystallinity in the amylopectin films nor the difference in network microstructure in the amylose films influenced the WVP. The OP of the amylose films was also unaffected by the relative air humidity during film formation. The OP of the amylopectin films may depend on the air humidity during film formation, but the accuracy of the measurements was not good enough to verify this. The gas permeability of compression-moulded, thermoplastic starch films has been shown to depend on the crystallinity of the films (Arvanitoyannis et al., 1994, 1996). It was found that the crystallinity developed during storage at temperatures above the glass transition temperature, and a decrease in

permeability was observed with increasing crystallinity. The microstructure of the compression-moulded, thermoplastic starch films was not presented, but may very well be different from the films presented in this study. The micrograph in Fig. 1b shows that the amylose films, which contained 10–15%w/w water, had pores in the order of 20–100 nm filled with water. The fine structure of the amylopectin films has not yet been revealed to the same resolution as amylose but, as seen in Fig. 2, the most crystalline amylopectin films show density fluctuations where pores may be present as well. Through these pores permeating gases could diffuse without being much influenced by the crystallinity present in the network strands. The permeability would, in this case, be more influenced by the microstructure than by the degree of crystallinity in the films.

4. Conclusions

- The relative crystallinity of glycerol-plasticized amylopectin films increased with increasing air humidity during film formation, whereas unplasticized amylopectin films remained amorphous independently of the humidity during drying from gel to film.
- The relative crystallinity of amylose films was about 34% and independent of both the addition of glycerol and the air humidity during film formation.
- The mechanical strength of glycerol-plasticized amylose and amylopectin films was dependent on the relative air humidity during film formation. The change in mechanical strength depended on the crystallinity for the amylopectin films, whereas the mechanical properties of the amylose films probably depended more on the network microstructure.
- The permeability of oxygen and water vapour of the films were higher for amylopectin than for amylose films, and for the amylose films remained constant and independent of both crystallinity and microstructure.
- The functional properties of amylose films are in general slightly better than those of amylopectin films regarding both film strength and barrier properties.

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