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Formation of starch films with varying crystallinity

Åsa Rindlav[a], Stephan H.D. Hulleman[b] and Paul Gatenholm[a]*

[a]*Department of Polymer Technology, Chalmers University of Technology, S-412 96 Göteborg, Sweden*
[b]*ATO-DLO, P.O. Box 17, 6700 AA Wageningen, The Netherlands*

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Self-supporting, smooth and translucent films were prepared by drying starch gels at various temperatures and air humidities. Light microscopy showed different structures among the films dried at elevated temperatures compared with those dried at room temperature. B-type crystallinity, varying from almost none to 23%, developed upon film formation, as determined by wide-angle X-ray diffraction. Attenuated total reflectance infrared spectroscopy (ATR-FTIR) revealed an increasing absorbance ratio of the peaks at $1047\,\mathrm{cm}^{-1}$ and $1032\,\mathrm{cm}^{-1}$, which correlates with an increasing crystallinity in the films. The water content of the films was found to increase with increasing B-type crystallinity, which is partly explained by the higher water content of the B-type crystalline areas as compared with the amorphous areas. The glass transition temperature, T_g, decreased linearly as a calculated amount of water in the amorphous phase increased. An interesting observation was made in the second DSC scan, where the T_g decreased relative to the first scan. This decrease was found to be proportional to the amount of crystallinity in the films. © 1997 Published by Elsevier Science Ltd. All rights reserved

INTRODUCTION

The large volumes of plastics produced have resulted in environmental problems, as they are used to a large extent as packaging materials and after a very short time of use are deposited in landfills. Scientists have thus begun to seek alternative sources for plastic materials that combine renewability with biodegradability. Among the biopolymers investigated as potential alternative raw materials for plastics, starch has drawn a great deal of attention. Starch is a polysaccharide and consists of the linear D-glucan amylose and the highly branched amylopectin. As early as 1951, Wolff *et al.* prepared self-supporting amylose films with and without glycerol plasticization (Wolff *et al.*, 1951). Although most of the recent research has been focused on the conversion of starch into thermoplastic material by the extrusion process, another means of preparing films, i.e. from solution or gel, has been used (Lourdin *et al.*, 1995; Bader & Göritz, 1994) as an attractive alternative.

One important application of thermoplastic synthetic polymers is as barrier coatings on paper substrates. Starch films are known to exhibit very low oxygen permeability (Tomka, 1991). However, the barrier properties of starch films are greatly affected by air humidity. In industrial barrier applications, the starch films must be made less water-sensitive or be protected from water contact. For synthetic polymers, an increased crystallinity is known to increase the barrier properties of the material. This has also been shown for drawn starch films (Arvanitoyannis *et al.*, 1994).

Native granular starch is semi-crystalline and can adopt different crystalline structures consisting of packed double helices. Cereal starches have an A-type crystalline structure, while tuber starches such as the potato have a B-type crystalline structure. Recrystallization or retrogradation of starch after melting or gelatinization is known to occur in food as well as in thermoplastic materials. The spontaneous recrystallization in excess water is in the form of the B-type structure (Katz, 1930).

The aim of this study was to prepare and characterize potato starch films with varying crystallinity by controlling the film formation conditions.

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*Author to whom correspondence should be addressed.

MATERIALS AND METHODS

Preparation of films

The potato starch used was food grade from AVEBE, The Netherlands. Starch gels were made from a dispersion of starch in deionized water (5 w/w%) using a Brabender Viscograph E. The temperature in the viscograph was increased at a rate of 2°C/min from 20 to 95°C and kept at 95°C for 30 min before the temperature was decreased to 20°C at 2°C/min. Maximum torque was 129–137 cm g^{-1} at 72–73°C. The gels were poured onto polystyrene petri dishes and dried to films at various temperatures and relative air humidities (%RH). Some films were formed at 20°C in 92, 58 or 25%RH. Other films were formed at 50 or 68°C in almost closed petri dishes in which the air humidity decreased during drying from approximately 100%RH to a low level. The films had a final thickness varying between 70 and 100 μm. All films were reconditioned at 20°C and 58%RH for at least one week before any measurements. To reveal their structure, the films were stained with Lugols iodine solution and photos were taken in a Nikon FXA light microscope. To determine the water content triplicate samples were dried in a vacuum oven at 60°C for 24 h and the weight % water was calculated from the measured weight loss.

X-ray diffraction

The films were milled with the addition of liquid nitrogen in a mortar and reconditioned at 20°C and 58%RH for five days before measurements. Diffractograms of powdered samples were recorded on a Philips PC-APD diffractometer, consisting of a PW1830 generator operated at 40 kV and 50 mA, a PW3710 mpd control and a PW3020 goniometer. Diffractograms were recorded in the reflection geometry. Nickel-filtered CuK_α ($\lambda = 0.1542$ nm) was used. The diffractometer was equipped with a 1° divergence slit, a 15 mm beam mask, a 0.2 mm receiving slit and a 1° scatter slit. Scattered radiation was detected in the angular range of 4–40°(2θ) at a speed of 2°(2θ)/min with a step size of 0.1°(2θ) using a proportional detector. Diffractograms were baseline corrected by drawing a straight line at 7°(2θ). Crystallinity was calculated by dividing the area of the diffraction peak at approximately 17°(2θ) between the diffraction angles 15.6–18.0°(2θ) by the total area under this peak relative to the drawn baseline (Hermans & Weidinger, 1948). Measurements were performed in triplicate.

Attenuated total reflectance infrared spectroscopy (ATR-FTIR)

Spectra were measured on a Digilab FTS-60A spectrometer (BioRad Laboratories) at 4 cm^{-1} resolution. The spectrometer was equipped with a horizontal ATR accessory with a 45° ZnSe crystal and a liquid-nitrogen-cooled MCT detector. Conditioned films were placed on the crystal and pressed onto the surface using a pressure plate. Measurements were done in triplicate. 64 scans were averaged for each measurement. Deconvolution was made with a half bandwidth of 15 cm^{-1} and an enhancement factor of 1.5 with triangular apodization.

Differential scanning calorimetry

The differential scanning calorimetry (DSC) analysis was performed on a Perkin Elmer DSC-7 equipped with a robotic system. Calibration was carried out with indium ($\Delta H = 28.6$ J g^{-1}, $T_o = 156.6$°C) and gallium ($\Delta H = 79.9$ J g^{-1}, $T_o = 29.8$°C). The films were ground in liquid nitrogen and reconditioned at 20°C and 58%RH before the measurements. Triplicate samples of 28–32 mg were weighed into stainless steel cups and sealed hermetically. An empty cup was used as reference. Scans were recorded from 0 to 160°C with a rate of 10°C/min, followed by quenching to 0°C at 200°C/min and rescanning. The maximum of the first derivative of the curve was taken as the glass transition temperature, T_g.

RESULTS AND DISCUSSION

Film formation

Native potato starch was gelatinized and dried into films in different relative air humidities and temperatures. All gels formed self-supporting, smooth, clear and translucent films. Light microscopy of iodine-stained films revealed different structures between the films formed at 20°C and the films formed at elevated temperatures, 50 and 68°C, as can be seen in Fig. 1. The films formed at elevated temperatures were more inhomogeneous and showed more light areas, which may be the result of thickness inhomogeneities or more pronounced phase separation. Both kinds of films had small domains with darker colouring and some fragments of granules were present.

Crystallinity of films

The relative crystallinity of all films was determined using wide-angle X-ray diffraction and the spectra are shown in Fig. 2. The films formed in 20°C show a clear B-type crystalline structure. The films formed in 92%RH possessed the highest crystallinity, followed by the films formed in 58%RH and the films formed in 25%RH. Films formed in 50°C had a very low crystallinity and films formed in 68°C were almost amorphous. The relative crystallinities, calculated

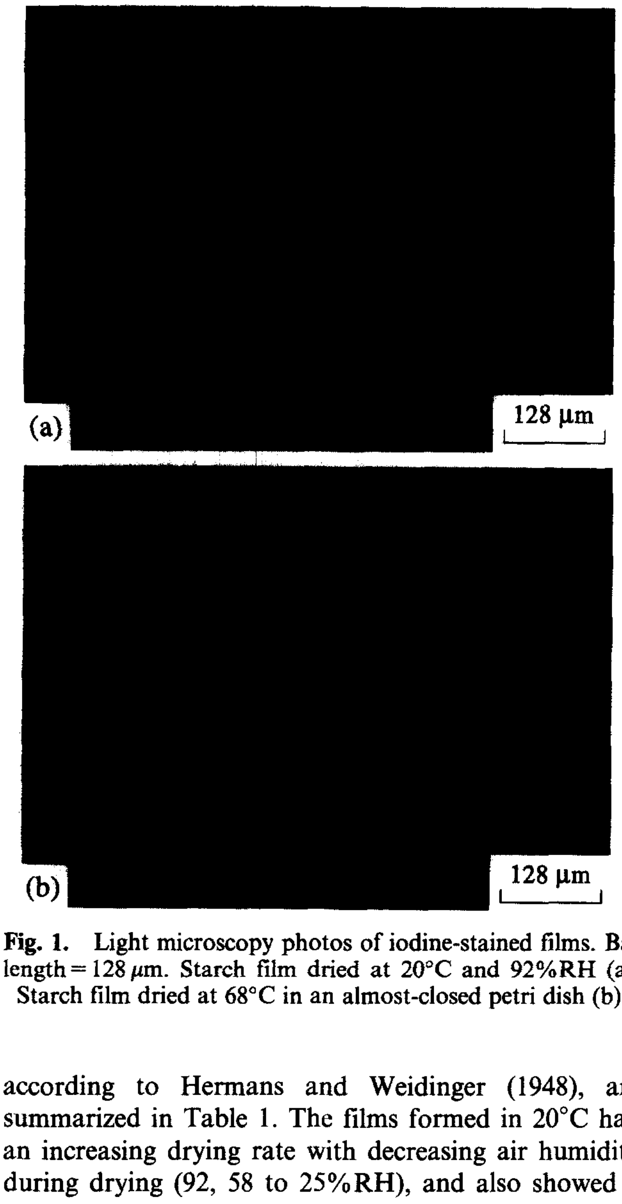

Fig. 1. Light microscopy photos of iodine-stained films. Bar length = 128 μm. Starch film dried at 20°C and 92%RH (a). Starch film dried at 68°C in an almost-closed petri dish (b).

according to Hermans and Weidinger (1948), are summarized in Table 1. The films formed in 20°C had an increasing drying rate with decreasing air humidity during drying (92, 58 to 25%RH), and also showed a decreasing relative crystallinity (23, 16 to 13%). This is because water plasticizes starch and increases the mobility of the starch polymer chains. A lower drying rate gives the chains a longer time to arrange into more favourable conformations, i.e. in the form of crystals, and a higher crystallinity is thereby achieved for films formed in the higher air humidities. The crystallinity in polymeric materials is generally dependent on the crystallization rate, which follows a bell-shaped curve between the temperatures T_g and T_m (Fatou, 1989). Apparently, in the cases where the temperature is increased from 20 to 50 and 68°C, the rate of nucleation is decreased and the overall rate of crystallization is thereby also low. The temperature of 68°C is close to the gelatinization temperature of native potato starch in excess water and crystals are not easily formed at all.

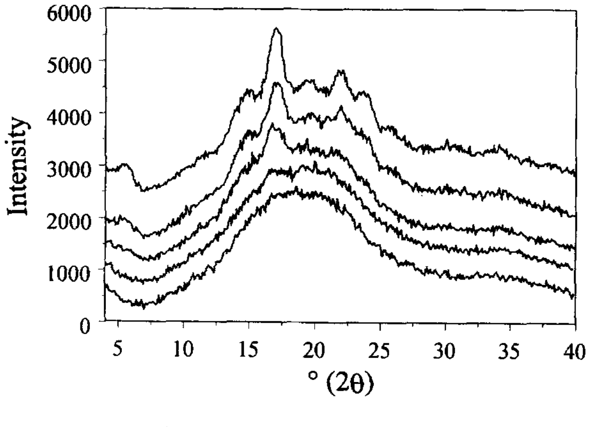

Fig. 2. X-ray diffraction spectra of potato starch films dried under various conditions. Top to bottom: 20°C and 92%RH, 20°C and 58%RH, 20°C and 25%RH, 50°C in an almost-closed petri dish, 68°C in an almost-closed petri dish.

The films were also investigated with ATR-FTIR. The differences in polysaccharide conformation in solution as well as in the solid state yield differences in the region between 1400 and 800 cm^{-1} in FTIR spectra (Belton *et al.*, 1986). The peaks in this region originate from C–C and C–O stretching. Previous studies have shown that an increased crystallinity, achieved by starch gel retrogradation, gave rise to band narrowing and changed absorbance ratios for certain peaks (Wilson *et al.*, 1987; van Soest *et al.*, 1995). In this study, the absorbance ratio of the deconvoluted peaks at 1047 and 1032 cm^{-1} was found to be sensitive to the degree of crystallinity of potato starch films, as determined by X-ray diffraction (Figs 3 and 4). The absorbance ratio increased with increasing crystallinity (Table 1) and this result is in good agreement with the results of van Soest *et al.*, (1995) for retrograded potato starch gels.

Water content

The water contents of the reconditioned films were determined by vacuum drying and the results are shown in Table 2. The water present in the amorphous phase and in the crystalline phase was removed during vacuum drying. X-ray diffraction spectra revealed that no B-type crystallinity was present in the sample immediately after drying. The water contents in the reconditioned films increased linearly with the crystallinity. This is believed to be partly owing to the water incorporated in the B-type crystalline structure, which in this case is higher than in the amorphous phase. The channel between six double helices contains about 36 water molecules per three-glucose unit rise in the B-type crystalline structure (Wu & Sarko, 1978). This gives a water content of 25 weight % in the crystalline structure. A theoretical value for the water content in the amorphous phase can be calculated from:

$$W_{\mathrm{total}} = X_c \times W_{\mathrm{cryst}} + (1 - X_c) \times W_{\mathrm{amorph}} \qquad (1)$$

where W_{total} is the total water content of the sample, X_c

Table 1. The effect of drying conditions on the relative crystallinity, X_c, and on the absorbance ratio obtained with ATR-FTIR

Drying condition	X_c	Standard deviation of X_c	Absorbance ratio, $1047\,cm^{-1}/1032\,cm^{-1}$	Standard deviation of absorbance ratio
20°C, 92%RH	0.23	0.02	1.026	0.012
20°C, 58%RH	0.16	0.01	0.927	0.045
20°C, 25%RH	0.13	0.01	0.885	0.013
50°C	0.02	0.03	0.826	0.009
68°C	0.01	0.01	0.806	0.004

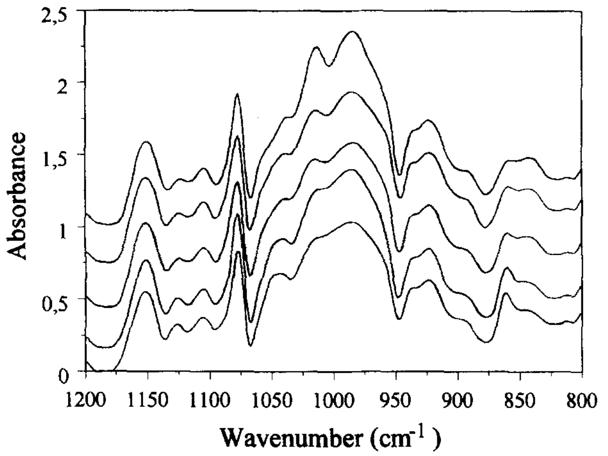

Fig. 3. Deconvoluted ATR-FTIR spectra of potato starch films with increasing crystallinity from top to bottom. Spectra normalized at the $1147\,cm^{-1}$ peak.

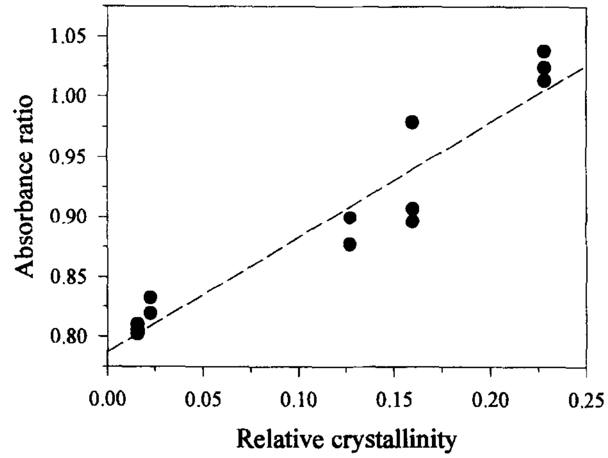

Fig. 4. Absorbance ratio of peaks at 1047 and $1032\,cm^{-1}$ of potato starch films as a function of crystallinity.

is the crystallinity, W_{cryst} is the water content in the crystalline phase, which is assumed to be 0.25 according to Wu and Sarko (1978), and W_{amorph} is the water content in the amorphous phase. As seen in Table 2, the calculated water content in the amorphous phase is not the same for all samples and this is believed to be a consequence of the water vapour sorption hysteresis phenomena. Films formed at 20°C in 58 and 92%RH desorbed water, while films formed at 50, 68 and 20°C in 25%RH sorbed water during reconditioning. Sorption of water leads to a lower water content than desorption of water as a consequence of hysteresis phenomena (Slade & Levine, 1991). The films formed at elevated temperatures, 50 and 68°C, had a different structure as revealed by light microscopy, which may also explain the lower water content in these films as compared with the films formed at 20°C.

Thermal transitions

DSC measurements were performed on reconditioned films and the spectra are shown in Fig. 5. A sub-T_g endotherm at about 50°C is observed for all films. This endotherm is seen at the same temperature for all polysaccharides when T_g is above this temperature (Appelqvist *et al.*, 1993). The endotherm has been considered to result from carbohydrate–water interactions (Appelqvist *et al.*, 1993; Yuan & Thompson, 1994). Other reports refer to the endotherm as being a free volume relaxation phenomena (Shogren, 1992). As seen in Fig. 6, the T_g in the first DSC scan is decreased with the amount of water in the amorphous phase, which is calculated from equation (1). A free volume relaxation seems to be present immediately after the T_g, but is in some samples overlaid by a broad endotherm with a maximum at about 110°C (Fig. 5). This endotherm has an increasing enthalpy with increasing crystallinity and appears only in the first DSC scan. In the second scan, made immediately after the first heating scan to 160°C, the T_g was found to be lower than the T_g observed in the first scan. The decline in T_g was proportional to the initial degree of crystallinity in the sample and thereby also to the water content. At first, a possible explanation of this behaviour seemed to be that the water released by the melting of the B-type crystalline structure plasticized the sample, causing this decrease in T_g. However, further investigation showed that the decline appeared before that, after heating just through the T_g in the first scan. X-ray diffraction of a sample heated to the same temperature above T_g (100°C) showed no decrease in crystallinity. This decline in T_g is an interesting observation and the reasons for it may be related to differences in 'order' in the amorphous glassy phase. Further investigation is needed, however.

Table 2. The effect of drying conditions on the water content as measured by weight loss

Drying condition	X_c	Measured water content, total(%)	Standard deviation of water content, total	Calculated water content in amorphous phase[a](%)
20°C, 92%RH	0.23	17.4	0.6	15.1
20°C, 58%RH	0.16	16.4	0.2	14.8
20°C, 25%RH	0.13	15.7	0.2	14.3
50°C	0.02	14.0	0.5	13.8
68°C	0.01	13.4	0.3	13.2

[a]The water content in the amorphous phase was calculated from equation (1).

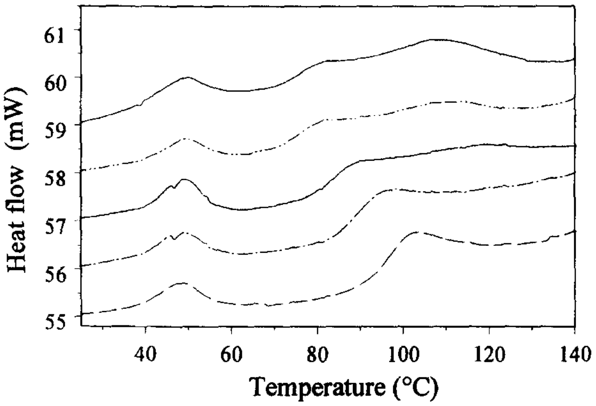

Fig. 5. DSC spectra of potato starch films dried in 20°C and 92%RH, 20°C and 58%RH, 20°C and 25%RH, 50°C in an almost-closed petri dish, 68°C in an almost-closed petri dish, from top to bottom.

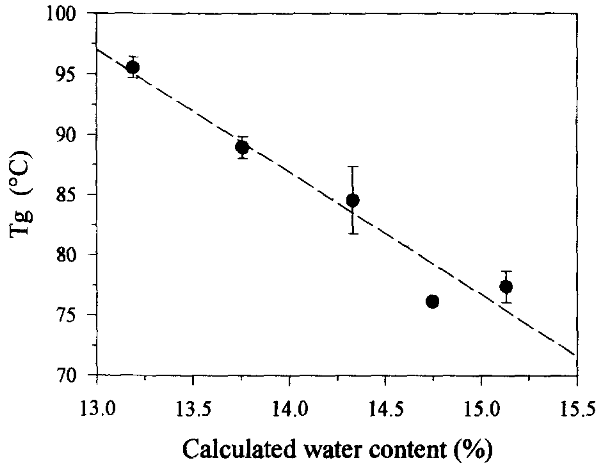

Fig. 6. Glass transition temperature of the first DSC scan as a function of the water content in the amorphous phase calculated from equation (1). Error bars show standard deviation of three samples.

CONCLUSIONS

This study demonstrates that it is possible to control the crystallinity of starch films. The degree of crystallinity depends on the temperature, the air humidity and the time that elapses during drying from gel to film. The films formed at elevated temperatures, 68 and 50°C, were almost amorphous. In films formed at 20°C, the final crystallinity was strongly dependent on the time required for drying, i.e. the time in contact with water, and a higher crystallinity was thereby observed in the films formed in high air humidity. The total water content of the films varied linearly with the crystallinity. This is believed to be partly a result of the water content in the crystalline areas being greater than in the amorphous areas, and partly as a result of water vapour sorption hysteresis and varying microstructure. A value for the water content in the amorphous phase was calculated and the glass transition temperature, T_g, decreased linearly with the increase in this value. The T_g in the second DSC scan was decreased relative to the first scan. The decline was proportional to the initial crystallinity in the samples as well as to the water content.

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