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Some effects of processing on the molecular structure and morphology of thermoplastic starch

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Abstract

Hydroxypropylated and oxidised potato starch (HONPS) was used together with glycerol and water to produce thermoplastic starch. The amount of glycerol was kept constant at 22 parts by weight per 100 parts of dry starch. The thermoplastic starch was converted into films/sheets using three different processing techniques; casting, compression moulding and film blowing. The last two methods represent typical thermoplastic conversion techniques requiring elevated processing temperatures. By means of size-exclusion chromatography, it was found that compression moulding and film blowing led to some degradation of high-molecular weight amylopectin as well as of high-molecular weight amylose-like molecules. The degradation was significantly less pronounced for the cast films. The morphology of the specimens was quite complex and phase separations on different levels were identified. In the cast films and, to a lesser extent, in the compression-moulded specimens, a fine network structure could be distinguished. Such a structure could however not be ascertained in the film-blown material and this is discussed in terms of the thermo-mechanical treatment of the starch materials.
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1. Introduction

Starch is often mentioned as one of the polymers originating from a renewable source that could replace some of the synthetic polymers used today, especially for products with a limited life time. One possible processing technique for converting starch, when combined with a plasticizer such as e.g. glycerol, into a final product is extrusion where the potential thermoplastic properties of starch are taken advantage of. During the extrusion, melting and sufficient mixing, resulting in a homogenous melt and thus final product, while avoiding degradation is aimed for.

It can be mentioned that films and similar structures based on starch are not expected to exhibit the same mechanical properties as e.g. low density polyethylene which is common in packaging applications. Thunwall, Boldizar, and Rigdahl (2006) reported a strain at break of the order of 40–50% for sheets of thermoplastic starch. These figures are comparatively low and this must be accounted for when using the material in practice.

The melting or the disruption of the initial crystalline structure of the starch material requires in principle a high processing temperature but this can be facilitated at a lower temperature using a higher moisture content which reduces the softening temperature (Biliaderis, Page, Slade, & Sirett, 1985). Since the melting point of, for instance amylose complexes, is believed to be rather high (Shogren, 1992), the required processing

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temperatures could be in a range where degradation of the starch molecules may be expected. It is well known that polymers may degrade upon combined heating and shearing but, in the case of thermoplastic starch, less is known about the detailed mechanisms involved and how to control the degradation. Earlier studies on extrusion of starch have correlated the required specific mechanical energy (SME) during the process with the resulting changes in molecular structure (Brümmer, Meuser, van Lengerich, & Nieman, 2002; Willet, Millard, & Jasberg, 1997). The results mainly refer to so-called extrusion cooking, which is a rather quick and intense (high screw velocity) extrusion process using substantial amounts of water, by which a foamed structure is created. The extrusion used in the case of classical plastics processing is normally carried out at lower flow rates leading to lower shear rates, but also longer residence times in the extruder. It has been suggested that it is in the first hand the high shear stresses that lead to the molecular breakdown (van den Einde et al., 2004) and since a high SME is normally associated with such high shear stresses, it also follows that high SME correlates with a higher degree of degradation.

A complete melting of any initial crystalline structure of the starch material and subsequent homogenisation of the melt is desirable since remaining crystals will have a crucial negative impact on the extensibility of the polymer melt. A highly extendable extrudate with a high melt tenacity is desired in a processes like film blowing or extrusion coating. In a previous work, it was assumed, but not confirmed in detail, that thermoplastic processing of starch and glycerol with moisture contents of about 15 weight-% at temperatures of 140 °C produced a more or less amorphous extrudate (Thunwall et al., 2006). However, with the X-ray diffraction technique used, the limit for detection of crystalline structures might be as high as 15% (Lourdin, Della Valle, & Colonna, 1995).

In the present work the influence of different processing on the molecular structure and morphology of hydroxypropylated and oxidised potato starch, plasticized with glycerol, was investigated to some extent. Thus, in contrast to most other types of thermoplastic starch, this material was thus based on a chemically modified starch instead of native starch. However, despite this modification, it is expected that the starch morphology will exhibit several of the characteristics known to exist with native starch. Homogenisation of the material is desired since this will promote the processing behaviour of the starch melt. It is expected that phase separation with regard to amylose and amylopectin will take place as well as with regard to glycerol-rich and glycerol-poor regions. Such phase separations will affect processability of the material (often in a less favourable manner) and also the physical properties of the final properties of the product. Similarities between the morphology of systems based on native potato starch and modified grade used here will be discussed.

2. Materials and methods

2.1. Materials

Hydroxypropylated and oxidised normal potato starch (HONPS) was supplied by Lyckeby Stärkelsen, Kristianstad, Sweden. According to Jansson and Järnström (2005), this grade had an average number of carboxylic acid groups per anhydroglucose unit of 0.04 and its degree of substitution with regard the hydroxypropyl groups was 0.11. Glycerol (Rectapur from Prolabo, Sweden) was used as plasticizer for the starch together with water.

2.2. Preparation of films and sheets

Three different routes were used to produce films or sheets (see Fig. 1); film casting, compression moulding and film blowing. The dry starch to glycerol ratio was in all cases 100 parts to 22 parts (by weight). Films or sheets of the thermoplastic starch were here produced by three different techniques described below and schematically shown in Fig. 1. The techniques employed were casting, compression moulding and film blowing.

Casting was done from a solution of HONPS and glycerol in distilled water. An amount of 14 g HONPS (containing 15% moisture) and 2.64 g glycerol was dispersed in 386 g distilled water. The dispersion was heated from 20 to 97 °C at 1.5 °C/min and held at 97 °C for 30 min in a Brabender Viscograph (Brabender OHG, Duisburg, Germany). Evaporated water was compensated for and the solution was further mixed for 50 min at 97 °C. The warm solution was cast in Petri dishes (90 mm diameter) to form approximately 100 μm thick films after solvent evaporation at constant conditions of 23 °C and 50% relative humidity (RH).

The compression-moulded sheets were manufactured in basically two steps; starch and glycerol was first pre-melted in a Brabender chamber mixer (Brabender OHG, Duisburg, Germany) at 90 °C and 50 rpm for 3 min and then the molten material was compression moulded into sheets with a Bucher heated hydraulic press (Bucher–Guyer AG, Niederweningen, Switzerland) at 140 °C and 9 MPa for 5 min. No water was added to the mixture but with an initial moisture content of about 15 weight-% of the starch material, the starch/glycerol blend had a water content of about 12 weight-% when transferred to the chamber mixer. The material was cooled under pressure to 30 °C, which took

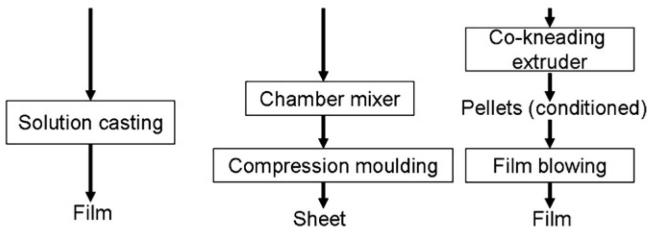

Fig. 1. Schematic illustration of the different processing techniques used.

approximately 15 min. The pressure was then released and the sheet was peeled away from the press plates. The compression-moulded sheet had a thickness of 0.55–0.60 mm.

The film blowing was also carried out in two steps; first a compounding step and then the actual film blowing. In the compounding step, starch and glycerol were premixed by hand and then fed into a Buss co-kneading extruder (Buss PR 46, Switzerland, diameter $D = 46$ mm and length $L = 11D$). The screw speed was 24 rpm and the barrel and die temperature were both set to 90 °C. Starch and glycerol was mixed in the weight proportions 100:22 (dry starch:glycerol) with no additional water. This meant that the blend only contained water absorbed from the environment; amounting to about 12 weight-%. The extruded strands were cut into pellets and conditioned at 53% RH, using a $Mg(NO_3)_2$-solution (Greenspan, 1977), and 23 °C prior to any further processing. The equilibrium water content of the specimens was measured gravimetrically by exposing the samples to a temperature of 105 °C in a ventilated oven. The moisture content of the pellets was 10 weight-% after the conditioning.

The film blowing was accomplished using a Brabender compact extruder (Brabender OHG, Duisburg, Germany, screw diameter $D = 19$ mm and screw length $25D$) with three individually controlled temperature zones. A screw with a compression ratio of 4:1 was used in all experiments. The extruder was equipped with a conventional temperature-controlled film-blowing die with a diameter of 24 mm and a film-blowing tower with a calendering nip and take up-rolls. The velocity of the take-off rolls and the pressure inside the film “bubble” were adjusted in order to achieve as good results as possible, meaning a stable process with a bubble diameter greater than two times the die diameter. The temperature profile along the barrel of the extruder was 90, 120, 115 and 95 °C (from hopper to die) and the screw speed was kept constant at 30 rpm resulting in a film thickness between 0.17 and 0.22 mm.

2.3. Molecular characterisation by fractioning and iodine-staining

The as-received HONPS and the three different starch-based films were dissolved to a concentration of 5 mg/ml in 0.1 M NaOH and fractionated by size-exclusion chromatography (SEC). Samples (1 ml) were injected onto a Sepharose CL-2B (Amersham Biosciences, Uppsala, Sweden) column (80 × 1.6 cm) and separated using 0.01 NaOH as eluent at a flow rate of 0.4 ml/min (Lloyd, Hedley, Bull, & Ring, 1996). Fractions of 2 ml were collected.

Amylose and amylopectin were detected by iodine-staining essentially according to Morrison and Laignelet (1983). To each fraction 100 µl I_2–KI-solution (2 mg I_2 and 20 mg KI/ml) was added and 15 min after addition a spectrum of each fraction was measured between 300 and 800 nm using a UV-2101PC Spectrophotometer from Shimadzu, Kyoto, Japan. Iodine forms coloured complexes with α-1,4 linked glucan chains by binding to the hydrophobic cavity of the glucan helices. The wavelength corresponding to maximum absorption is denoted λ_{max}. A typical λ_{max}-value for amylopectin is around 540 nm, showing a red-brown colour. With increasing chain length, λ_{max} increases and the colour changes towards deep blue for long chains as in amylose, which can have a λ_{max} as high as 640 nm (Banks & Greenwood, 1975).

2.4. Freeze etching and transmission electron microscopy (TEM)

Three different starch films/sheets containing 22 parts of glycerol were prepared for freeze etching; cast HONPS, compression-moulded HONPS and film-blown HONPS. The films were placed in a cryo-mount and momentarily freezed in liquid propane and then placed in a pre-cooled, −170 °C, freeze-etching device, Balzers BAF400 (Balzers Union Gesellschaft, Balzers Lichtenstein). The films were fractured at −100 °C and then etched for 3 min in order to enhance the structures in the cross-section of the films. The etched surfaces were replicated with evaporated platinum and carbon. Each film was freeze-etched at two to three occasions. The freeze-etched replicas were analysed in a transmission electron microscope (TEM), LEO 906e (LEO Electron Microscopy Ltd., Oberkochen, Germany).

3. Results and discussion

3.1. Effects of processing on molecular structure

The as-received HONPS and the three different films were dissolved as described and fractionated by SEC and amylopectin and amylose were detected by iodine-staining. The first peak in the chromatograms, between 50 and 65 ml, corresponds to the large amylopectin molecules (Fig. 2). This is emphasised by the low λ_{max} between 540

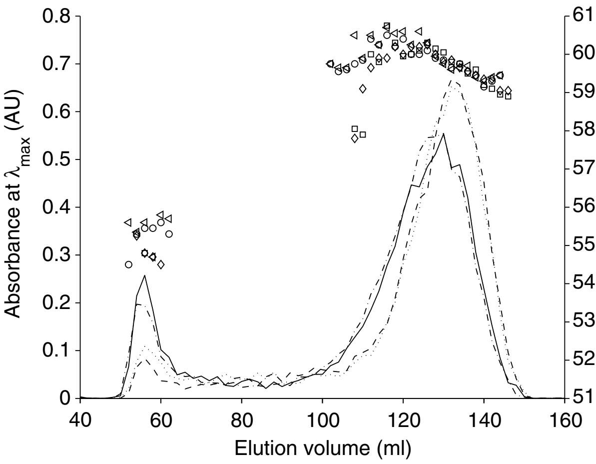

Fig. 2. Chromatograms (lines) and λ_{max} (open symbols) for as-received HONPS (solid line and circles), film-blown HONPS (dashed line and squares), compression-moulded HONPS (dotted line and diamonds) and cast HONPS (dash dotted line and triangles) fractionated on Sepharose CL-2B and detected by iodine staining.

and 560 nm in this region. The large second peak, roughly between 100 and 150 ml, corresponds to partially degraded amylopectin and amylose. The rise in $\lambda_{\max}$ between the two main peaks indicated an increase in the proportion of amylose, which was expected. For the second peak, the $\lambda_{\max}$ values are similar between the different samples, but not as high as expected for pure amylose. This indicates a presence of amylopectin fragments from the degradation. In addition, $\lambda_{\max}$ decreased over the second peak, also indicating a decreasing glucan chain length with decreasing molecular size.

All three forming processes were found to have a degrading effect when compared with the as-received material, even though the effect of film casting was very small. Both the compression moulding and the film blowing resulted in a more noticeable effect, roughly to the same extent. This is seen by the change in chromatographic profiles in Fig. 2. The amylopectin peaks (eluting around 50–60 ml) for the film-blown and compression-moulded specimens were significantly smaller than for the as-received material, indicating a decrease in the content of intact amylopectin. Concomitantly, the second peaks for both samples had increased and shifted towards the lower molecular weight region at the end of the chromatogram compared with the as-received HONPS. Hence, a degradation of high-molecular weight amylopectin as well as of high-molecular weight amylose-like molecules (eluting around 100–120 ml) appears to have taken place. Moreover, $\lambda_{\max}$ for the film-blown and compression-moulded specimens were lower in the material eluting between 100 and 110 ml, indicating a smaller proportion of amylose in this region compared to the as-received material. As mentioned, the chromatographic profiles for the compression-moulded and the film-blown samples were quite similar. The elongational- and shear-related deformation rates during the processing are likely to be significantly higher in the latter case, which indicates that the degradation in the present case is to an appreciable extent triggered by the high temperatures used with these techniques.

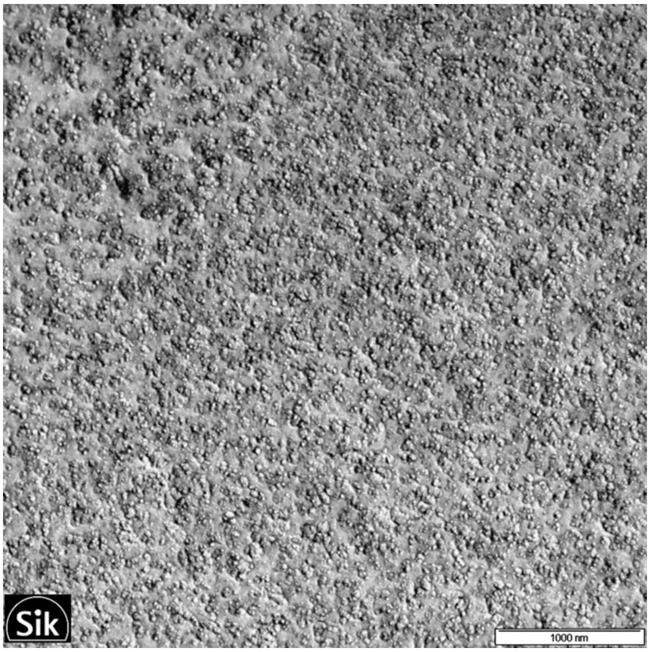

Fig. 3. Overview TEM micrograph of cast HONPS (scale bar 1000 nm).

For films produced by casting, the chromatographic profile in large part resembles the one for the as-received material. A slight decrease in amylopectin content was detected, which is in concurrence with the small increase of the peak eluting at around 120–130 ml. The weak effect of the casting on starch structure is most likely due to the mild processing conditions used.

3.2. Effects of processing on morphology

The cast HONPS had a rather homogenous structure with only a few remaining starch granules; see the TEM micrograph in Fig. 3 obtained at a low magnification. Two type of structures where found, one fine network structure as seen in the left micrograph of Fig. 4 and one

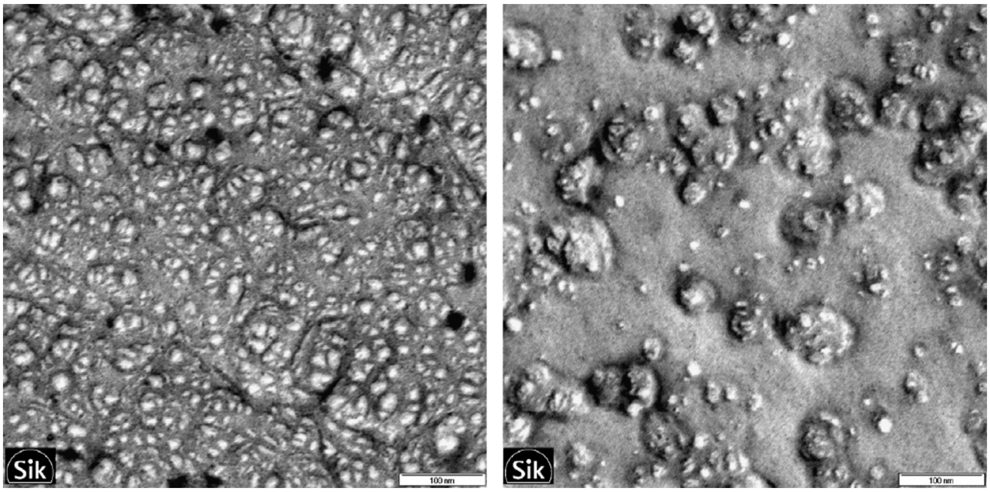

Fig. 4. TEM micrographs of the two different structures in cast HONPS (scale bars 100 nm).

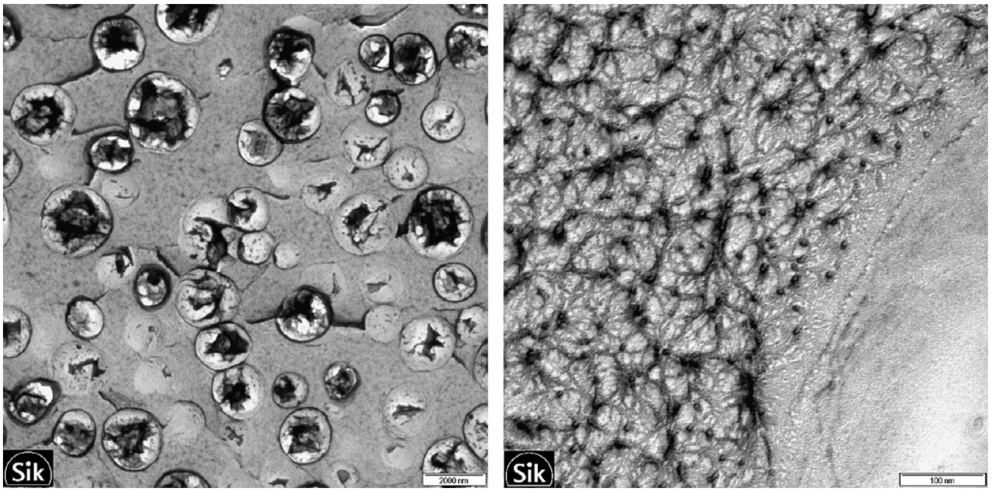

Fig. 5. TEM micrographs of compression-moulded (HONPS). The scale bars are 2000 and 100 nm in the left and right micrographs, respectively.

phase-separated structure with units of size up to 200 nm (right micrograph in Fig. 4).

In the compression-moulded films, numerous remaining starch granules were found embedded in a starch matrix. The left micrograph of Fig. 5 gives an overview of the structure where residual granules are clearly visible whereas the right micrograph shows a fine network structure with very small pores in the size of 10–50 nm typical of a freeze-etched biopolymer network (Hermansson, 1995). The network structure was very similar to that found in the cast film (Fig. 4, left).

Remaining starch granules were also found in the blown films but not to the same extent as in the compression-moulded specimens (Fig. 6, left). The starch structure appeared to be phase separated into a smooth region and a coarser one (right micrograph in Fig. 6). The smooth, dense region (or phase) could be a glycerol-rich phase and it did not have the same appearance as the fine network structure noted in cast HONPS (Fig. 4, left). The surfaces of the granules were covered with a layer which most likely is to be associated with amylopectin and/or amylose which has leached out from the granule during the processing.

It is well known that amylose and amylopectin in native starch are not compatible in an aqueous solution and could phase separate (Kalichevsky & Ring, 1987). This phase-separated structure has been subject of several studies, cf e.g. (Svegmark, Kidman, & Hermansson, 1993). Also films dried from aqueous solution are believed to exhibit a phase-separated structure (Rindlav-Westling, Stading, & Gatenholm, 2002). In addition to this kind of phase separation, starch containing glycerol, like thermoplastic starch can also exhibit a separation into glycerol-rich and glycerol-poor regions (Forssell, Mikkilä, Moates, & Parker, 1997; Moates, Noel, Parker, & Ring, 2001). The morphology of these types of materials is thus to be regarded as quite complex.

A network structure found in cast native starch films of intermediate amylose contents has been suggested to be built up by crystalline amylose or co-cristallised amylose

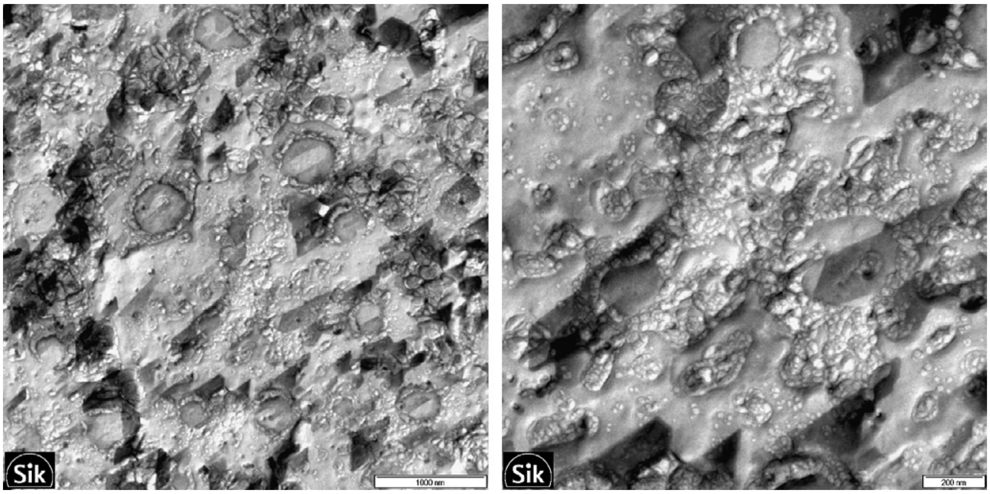

Fig. 6. TEM micrographs of film-blown HONPS with scale bars of 1000 nm (left) and 200 nm (right).

and amylopectin strands (Leloup, Colonna, Ring, Roberts, & Wells, 1992; Rindlav-Westling, 2002). The formation of such a network requires quite a high moisture content during the casting in order to provide sufficient molecular mobility. Although native potato starch was not used in the present work, it could be that a resembling type of network structure was formed in cast HONPS (Fig. 4, left). In case of the film-blown material, the lower moisture content, fairly low processing temperature ($T \leqslant 120$ °C) and the short residence time in the extruder would perhaps not provide sufficient mobility, thus suppressing the formation of such a network structure. The appearance of a more network-like structure in the compression-moulded films may then seem somewhat unexpected, but since the processing temperature was higher (140 °C) than with the film blowing and the melt was cooled fairly slow it may be that recrystallisation/forming of a network took place to some limited extent.

While the film blowing and compression moulding had a similar effect on the molecular structure, the conversion or disruption of the initial granular starch structure was different for the two. A substantially higher amount of residual granules was found in the compression-moulded material despite the somewhat higher temperature during the compression moulding. Locally, temperature in the melt of the extruder can of course reach higher temperatures due to shear-induced heating, which should be kept in mind. The higher shear rates in the extruder and more extensive mixing could explain the lower amount of granules found in the film-blown material. The existence of residual granules most likely has a negative effect on the film-blowing properties as they could be considered as weak spots in the material which could cause the failure of the bi-axially stretched bubble and therefore restrict the extent of stretching allowed.

4. Final remarks

The techniques used today for processing thermoplastics are well known, efficient and robust. It may be expected (and also quite reasonable) that any new type of polymeric materials that is introduced should be processable with such techniques if it is to gain a wide acceptance. Thermoplastic starch is not an exception in this respect. In this work, it has been shown that techniques like compression moulding and film blowing can lead to some degradation of the molecular structure. Furthermore, the choice of processing technique will affect the morphology of the formed product. The processing conditions as well as the detailed compositions of the thermoplastic starch will additionally affect the structural characteristics. The obvious influence of the processing on the molecular structure may be expected to be reflected also in the physical properties. Thus the processing operation must be carefully controlled in order to obtain an adequate structure and associated property profile of the final product. Clearly, the knowledge within this area needs to be improved, especially when modified starches are used.

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References

Banks, W., & Greenwood, C. T. (1975). Fractionation of the starch molecule, and the fine structure of its components. In W. Banks & C. T. Greenwood (Eds.), *Starch and its components* (pp. 5–112). Edinburgh, UK: Edinburgh University Press.

Biliaderis, C., Page, C., Slade, L., & Sirett, R. (1985). Thermal behaviour of amylose–lipid complexes. *Carbohydrate Polymers, 5*(5), 367–389.

Brümmer, T., Meuser, F., van Lengerich, B., & Nieman, C. (2002). Effect of extrusion cooking on molecular parameters of corn starch. *Starch/Stärke, 54*(1), 1–8.

Forssell, P. M., Mikkilä, J. M., Moates, K. G., & Parker, R. (1997). Phase and glass transition behaviour of concentrated barley starch-glycerol-water mixtures, a model for thermoplastic starch. *Carbohydrate Polymers, 34*(4), 275–282.

Greenspan, L. (1977). Humidity fixed points of binary saturated aqueous solutions. *Journal of Research of the National Bureau of Standards – A. Physics and chemistry, 81A*(1), 89–96.

Hermansson, A.-M. (1995). The importance of biopolymers in structure engineering. In E. Dickenson & D. Lorient (Eds.), *Food macromolecules and colloids* (pp. 363–375). Cambridge, UK: Royal Society of Chemistry.

Jansson, A., & Järnström, L. (2005). Barrier and mechanical properties of modified starches. *Cellulose, 12*(4), 423–433.

Kalichevsky, M. T., & Ring, S. G. (1987). Incompatibility of amylose and amylopectin in aqueous solution. *Carbohydrate Research, 162*(2), 323–328.

Leloup, V. M., Colonna, P., Ring, S. G., Roberts, K., & Wells, B. (1992). Microstructure of amylose gels. *Carbohydrate Polymers, 18*(3), 189–197.

Lloyd, J. R., Hedley, C. L., Bull, V. J., & Ring, S. G. (1996). Determination of the effect of *r* and *rb* mutations on the structure of amylose and amylopectin in pea (Pisum sativum L.). *Carbohydrate Polymers, 29*(1), 45–49.

Lourdin, D., Della Valle, G., & Colonna, P. (1995). Influence of amylose content on starch films and foams. *Carbohydrate Polymers, 27*(4), 261–270.

Moates, G. K., Noel, T. R., Parker, R., & Ring, S. G. (2001). Dynamic mechanical and dielectric characterisation of amylose–glycerol films. *Carbohydrate Polymers, 44*(3), 247–253.

Morrison, W. R., & Laignelet, B. (1983). An improved colorimetric procedure for determining apparent and total amylose in cereal and other starches. *Journal of Cereal Science, 1*(1), 9–20.

Rindlav-Westling, Å., 2002. Crystallinity and morphology of starch polymers in films, Ph.D. Thesis, Chalmers University of Technology, Göteborg, Sweden 2002.

Rindlav-Westling, Å., Stading, M., & Gatenholm, P. (2002). Crystallinity and morphology in films of starch, amylose and amylopectin blends. *Biomacromolecules, 3*(1), 84–91.

Shogren, R. L. (1992). Effect of moisture content on the melting and subsequent physical aging of cornstarch. *Carbohydrate Polymers, 19*(2), 83–90.

Svegmark, K., Kidman, S., & Hermansson, A.-M. (1993). Molecular structures obtained from mixed amylose and potato starch dispersions and their rheological behaviour. *Carbohydrate Polymers, 22*(1), 19–29.

Thunwall, M., Boldizar, A., & Rigdahl, M. (2006). Compression moulding and tensile properties of thermoplastic starch materials. *Biomacromolecules, 7*(3), 981–986.

van den Einde, R. M., Bolsius, A., van Soest, J. J. G., Janssen, L. P. B. M., van der Goot, A. J., & Boom, R. M. (2004). The effect of thermomechanical treatment on starch breakdown and the consequences for process design. *Carbohydrate Polymers, 55*(1), 57–63.

Willet, J. L., Millard, M. M., & Jasberg, B. K. (1997). Extrusion of waxy maize starch: Melt rheology and molecular weight degradation of amylopectin. *Polymer, 38*(24), 5983–5989.