

Extrusion processing of high amylose potato starch materials

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Abstract

Thermoplastic starch was prepared by mixing native high amylose potato starch and normal potato starch in a Buss co-kneading extruder at starch to glycerol ratios of 100:45 and 100:30. The materials were also conditioned to different moisture contents at different relative humidities at 23 °C. After the mixing, the compounds were extruded into sheets with a Brabender laboratory extruder. The thermoplastic high amylose materials exhibited a higher melt viscosity than the normal potato starch materials when conditioned at 53% relative humidity. Increasing the moisture content in HAP from 27% to 30% (by weight) lowered the melt viscosity to the same level as that of normal potato starch with a moisture content of 28%. In general, the high amylose materials were more difficult to extrude than the thermoplastic material based on normal starch. The main extrusion problems encountered with the high amylose starch were unstable flow, insufficient melt tenacity and clogging of the die. By increasing the moisture content, increasing the compression ratio of the screw and increasing the rotation rate of the screw, the problems were reduced or eliminated. However, only with a starch to glycerol ratio of 100:45 was an acceptable extrusion result obtained. Extruded sheets of such high amylose materials had a stress at break of about 5 MPa at room temperature and 53% relative humidity, whereas the corresponding value for normal potato (thermoplastic) starch was 3 MPa. The elongation at break was also higher in the case of the high amylose material. The results are discussed in terms of residual crystallinity of the starch materials.

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1. Introduction

There is a great interest in using polymers based on renewable raw materials instead of synthetic polymers relying on fossil resources (Gällstedt, 2004). In many cases, such polymers also have the advantage of being truly biodegradable. An interesting group of materials in this context is those based on starch, since this material is available in large quantities with an established industrial structure for handling and modifying this material. Hitherto, however, materials such as starch have shown a limited mechanical performance and poor resistance to water or moisture. The need for more research and development has certainly been recognised, judging from the volume

of literature that has emanated within this area during the last years. However, in order to obtain useful products, appropriate process techniques and procedures must be used. This has apparently attracted less interest, judging from the available literature. Any development or modification of a raw material to improve its physical properties or application performance must be paralleled by an evaluation of its processing properties. In the present work, the effects of a modification of the starch material on both its processability and its mechanical properties were investigated. The modification considered here is mainly an increase in the amylose content of the starch material.

The most important processing method for thermoplastic materials is probably extrusion which is used to produce films, sheets and assigned profiles. The extrusion of high amylose starch can be more difficult than the processing of normal thermoplastic starches, partly due to the high die pressures required because of the high melt viscosity

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(Shogren & Jasberg, 1994). This has been attributed to the high melting temperatures of amylose at low moisture contents (Shogren, 1992). An increase in the amylose content relative to that of normal starch is however interesting, since higher strength and higher toughness is expected from high amylose materials (Van Soest & Borger, 1997). Most studies on the processing of high amylose starches have hitherto been carried out on corn starches (Van Soest & Essers, 1997; Willet, Jasberg, & Swanson, 1995). The present work deals with the extrusion of thermoplastic high amylose potato starch (HAP) materials and the necessary adaptation of the process to this material.

The compounding and extrusion of an HAP-material with an amylose content of 86% and the properties of the extrudate were compared with those of a normal potato starch (NPS) with an amylose content of 21%. The aim of the study was to improve, understand and give guidelines for the extrusion processing of thermoplastic high amylose materials from potatoes.

2. Experimental

2.1. Material

High amylose potato starch (HAP) with an amylose content of about 86% was supplied by Plant Science, Sweden and normal potato starch (NPS) with an amylose content of about 21% (Swinkels, 1985) was supplied by Lyckeby Stärkelsen, Kristianstad, Sweden. Rectapur glycerol from Prolabo, Sweden was used as plasticiser. The starch materials were mixed with glycerol in two different weight proportions; starch/glycerol 100:30 (on dry basis) and 100:45. A fluoro-elastomer lubricant, Viton® FF Z-100 from DuPont Dow Elastomers was added as process aid in order to reduce the tendency of the material to stick to the die and clogging it. Trials were also carried out with addition of a dextrin powder, White Dextrin HH from Lyckeby Industrial AB, Landskrona to lower the viscosity by adding a low molecular mass polymer. The different compositions used in this study are summarised in Table 1.

Table 1
Composition (wt.%) of the blends prior to compounding in the Buss co-kneading extruder

	HAP (%)	NPS (%)	Glycerol (%)	Water (%)	Dextrin (%)	Fluoro-elastomer lubricant (%)
NPS 100:30 (dry basis)		64	23	13		
NPS 100:45		57	31	12		
HAP 100:30	64		23	13		
HAP 100:45	57		31	12		
HAP 100:45 d5	54		29	11	5	
HAP 100:45 d10	51		28	11	10	
HAP 100:45 v	55		30	12		3

2.2. Compounding

The mix was compounded in a Buss PR 46 (screw diameter $D = 46$ mm, length $11D$) co-kneading extruder at 24 rpm with the cylinder and die temperatures set at 110 °C. No extra water was added. The material passed through the extruder once, except for the trials where the effect of repeated compounding extrusion with an intermediate conditioning was investigated. The resulting extrudate was cut into pellets and conditioned at 50% or 70% relative humidity (RH) and 23 °C.

2.3. Conditioning

A Firlabo SP-BVEHF climate controlled-chamber, Société Firlabo, Meyzieu, France, and closed chambers with saturated salt solutions were used to condition the pellets and the samples. The salts used were $MgCl_2$, $Mg(NO_3)_2$ and $SrCl_2$ giving 33%, 53% and 70% RH, respectively (Greenspan, 1977).

2.4. Moisture content

The equilibrium moisture of the conditioned samples content was determined gravimetrically by exposing them to 110 °C for 24 h in a Mettler M3 TG50 Thermobalance, thermo-gravimetric analyzer (TGA), Mettler Intrumente AG, Grefensee, Switzerland.

2.5. Capillary viscometry

The viscosity of the thermoplastic melts was measured with a Ceast 6742/00 Rheoscope 1000, Ceast SpA, Pianezza, Italy, conventional capillary viscometer. Capillaries with length/diameter ratios of 5/1 and 10/1 and an inlet angle of 120 ° were used, the diameter being 1 mm. All measurements were performed at 140 °C. The material was preconditioned at 50% or 70% RH before the measurement and the moisture content was determined with the TGA.

2.6. Extrusion

The pellets (see Table 2) were processed with a Brabender compact extruder, Brabender OHG, Duisburg, Germany, screw diameter $D = 19$ mm and screw length $25D$ with three individually controlled temperature zones and a temperature-controlled slit die with variable slit height and a fixed slit width of 100 mm. A Dynisco melt pressure transducer, model TPT463E-10M-6/18, Dynisco, Westwood, MA, USA, was positioned at the entrance of the die and connected to a Dynisco ER478 pressure indicator in order to measure the pressure loss over the die and the screw. Three different screws were used, one regular with a compression ratio of 4:1 and one with a special mixing section at the end of the screw. In the initial studies using the NPS material, a screw with a compression ratio of 2:1 was also used. The feed moisture content was 17%

Table 2

The moisture content of the different thermoplastic starch materials conditioned at 50% or 70% RH before extrusion and the capillary viscometric measurements (after compounding)

	HAP (%)	NPS (%)	Glycerol (%)	Water (%)	Dextrin (%)	Fluoro-elastomer lubricant (%)	Cond. (% RH)
NPS 100:30		62	19	19			50
NPS 100:45		50	22	28			50
NPS 100:45 re-run		54	24	22			50
HAP 100:30	64		19	17			50
HAP 100:45	50		23	27			50
HAP 100:30	58		18	24			70
HAP 100:45	48		21	31			70
HAP 100:45 d5	43		23	30	4		70
HAP 100:45 d10	40		22	30	8		70
HAP 100:45 v	44		24	30		2	70

and 25% (by weight) for the HAP material with a dry starch-to-glycerol ratio of 100:30, and 27% and 30% for the HAP material with 45 parts glycerol per 100 parts of dry starch. The different moisture contents were achieved by conditioning the pellets at different relative humidities (50% and 70%) at 23 °C. The extrusion was carried out at different screw speeds, between 20 and 100 rpm. Blends containing 5% and 10% dextrin and 3% fluoro-elastomer lubricant were also processed. Trials with normal potato starch with dry starch-to-glycerol ratios of 100:30 (19% and 25% water) and 100:45 (22% and 28% water) were run as references. The extrudates were fed into a Univex take off unit from Brabender OHG, Duisburg, Germany.

2.7. Tensile tests

Tensile tests were performed with an Instron 1193, Instron Ltd, High Wycombe, UK, tensile tester according to ISO 527-1 using a strain rate of $6.6 \times 10^{-3} \text{ s}^{-1}$ (corresponding to a cross head speed of 10 mm/min). The tensile specimens were cut from the extrudate with a cutting die and were conditioned at a given humidity at least 5 days before the measurement. Some of the specimens were also tested 28 days after the processing (stored at 33%, 50% or 70% RH and 23 °C).

2.8. X-ray diffraction

X-ray diffraction was used in order to estimate the effect of the processing on the crystallinity of the starch materials. The measurements were carried out using a Siemens D8 Advance Theta X-ray diffractometer (XRD), with CrK_α radiation source equipped for low-angle XRD analysis. The samples were milled in a mortar together with liquid nitrogen before the measurement in order to produce a powder for the measurement.

3. Results and discussion

3.1. Water content

The samples conditioned at higher relative humidity had a higher equilibrium moisture content, and a higher

glycerol content also gave a higher equilibrium moisture content, Table 2. The moisture content decreased considerably after the extrusion and conditioning. For HAP materials with a starch to glycerol ratio of 100:45, at equilibrium in 50% RH, the moisture content was lowered from 27–28% to 21–22% by weight (see Tables 2 and 3). The values for the NPS-based materials were similar but slightly lower. Repeated compounding extrusion with an intermediate conditioning at 50% RH (23 °C) also led to a reduction in the equilibrium moisture content from 28% to 22% at 50% RH for NPS 100:45. The addition of dextrin and fluoro-elastomer lubricant did not have any major influence on the moisture content as shown in Tables 2 and 3.

3.2. XRD/crystallinity

The X-ray diffractograms exhibited distinct peaks indicating crystallinity in the case of the native HAP material, Fig. 1. The same has been found for native NPS in recent results not yet published. The intensity of these peaks was significantly lowered after the compounding and seemed to disappear after the extrusion, indicating a totally amorphous material, see Fig. 1. After the initial compounding, the material was opaque, whereas after the extrusion step or after repeated compounding steps, it was transparent. There seems to be a correlation between the crystallinity and the moisture content of the plasticised material. It has been suggested that the observed linear relation between the moisture content and the crystallinity is associated with a higher amount of incorporated water molecules in the B-type-crystalline phase (Rindlav, Hulleman, & Gatenholm, 1997). This crystalline structure is believed to form double-helices with a channel in which water molecules can be located although the material is

Table 3

The moisture content of the extruded films after 5 days of conditioning

	Conditioned at (% RH)	Moisture content (%)
HAP 100:45	33	17
HAP 100:45 d5	33	19
HAP 100:45	50	22
HAP 100:45 d5	50	21
HAP 100:45	70	30

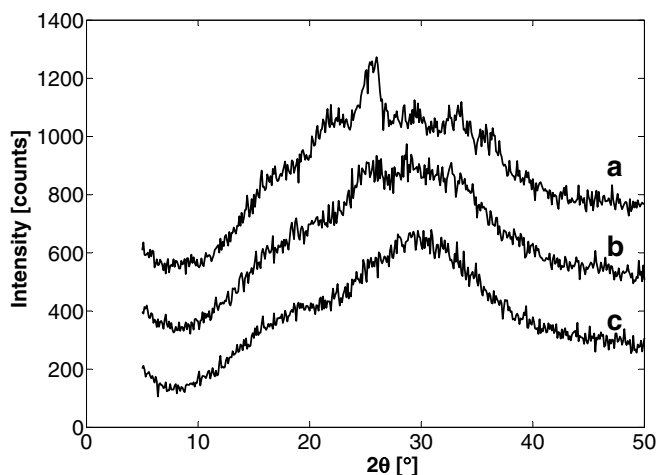


Fig. 1. X-ray diffractograms of (a) native high amylose starch (HAP), (b) plasticised HAP (100:45) after compounding and (c) an extruded HAP (100:45) film.

crystalline and the structure is assumed to be close-packed (Wu & Sarko, 1978).

3.3. Capillary viscometry

The HAP-materials had a higher melt viscosity than the corresponding NPS-compounds conditioned at the same relative humidity and containing the same amount of glycerol. Increasing the moisture content of the high amylose material by conditioning at 70% RH lowered the viscosity to a level similar to that of the NPS containing the same amount of glycerol conditioned at 50% RH (see Fig. 2). Note that the moisture content is not dramatically different for these two materials, Fig. 2 (HAP 100:45, 31% and NPS 100:45, 28%). A reduction in melt viscosity can also be achieved by increasing the temperature as shown in recent not yet published results.

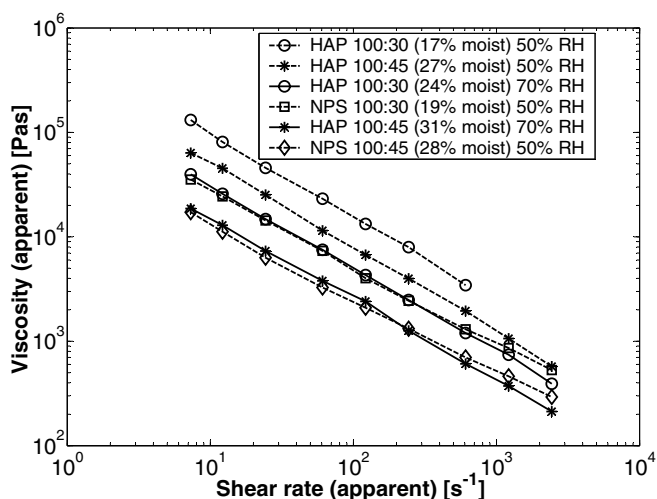


Fig. 2. Apparent melt viscosity at 140 °C versus apparent shear rate for NPS and HAP containing different amounts of glycerol and moisture. Different moisture contents were achieved by conditioning at 50% or 70% RH. The diameter of the capillary was 1 mm and the length was 10 mm.

Compounding the material twice in the co-kneading extruder reduced the viscosity somewhat as shown for NPS 100:45 in Fig. 3, despite the fact that the moisture content was also reduced. A possible reason for this may be a more complete melting or an elimination of the crystalline phase, the increased transparency of the material as indicated by the XRD-results, and the lower moisture content (Rindlav et al., 1997).

The addition of 3% fluoride elastomer lubricant to HAP 100:45 did not significantly change the melt viscosity. The addition of 5% dextrin to the same material reduced the viscosity at the lower shear rates, see Fig. 4. At a shear rate of about 200 s^{-1} , however, the viscosity shifted to a higher level. This change was paralleled by an increase in transparency of the material, implying an increase in homogeneity of the compound. At a higher dextrin content (10%) the extruded material was opaque over the whole shear rate range and there was no abrupt change in the viscosity when the flow rate was increased. In this series of experiments, the starch had been conditioned at 70% RH. In general, dextrin thus reduced the viscosity.

3.4. Extrusion of the thermoplastic starch materials

Extrusion of the HAP-materials was found to be more difficult processing than the NPS for several reasons, including the higher melt viscosity. The processing window for the starch materials, especially for the HAP, was quite narrow, and depended to a great extent on the moisture content which determines the viscosity of the material and its softening behaviour. At lower melt temperatures, any residual crystallinity may be detrimental to the processability, and the residual crystallinity associated with the amylose may be one reason for the processing problems encountered with HAP (Shogren & Jasberg, 1994). The

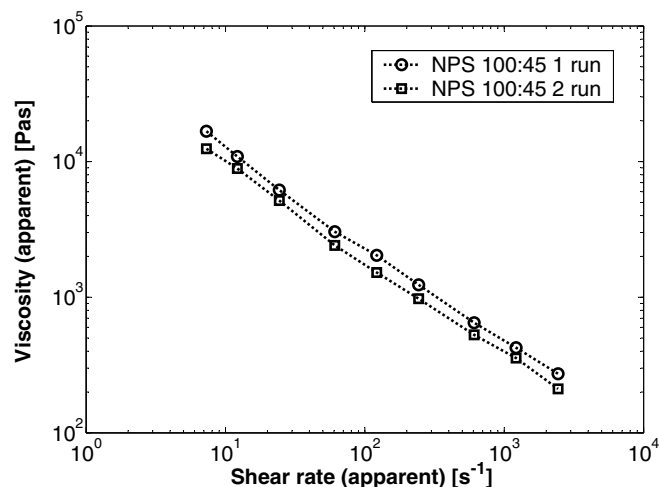


Fig. 3. The melt viscosity of NPS 100:45 as a function of the shear rate after the first and second passages through the Buss co-kneading extruder. The equilibrium moisture contents at 50% RH were different in the two cases, 29% after the first passage and 22% after the second passage through extruder. The diameter of the capillary was 1 mm and the length was 10 mm.

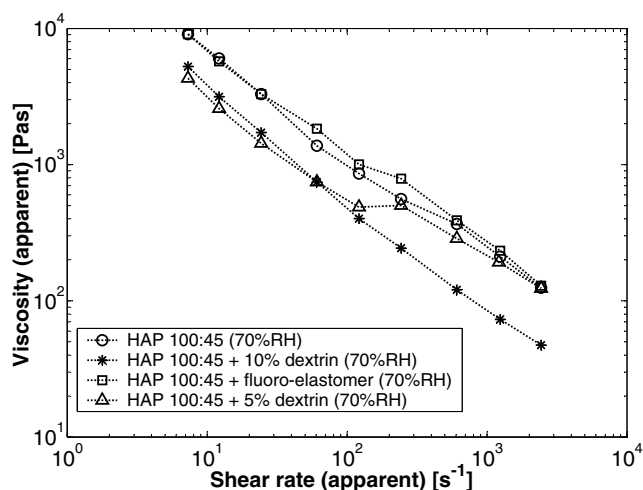


Fig. 4. The apparent melt viscosity versus the apparent shear rate for HAP 100:45 containing different additives. The material had been conditioned at 70% RH. The diameter of the capillary was 1 mm and the length was 10 mm.

upper extrusion temperature is set by the risk of degradation of the starch material and the generation of foam and bubbles.

A processing problem arising with both NPS and HAP was unstable flow and fluctuations in the pressure level. This was very obvious at the lower glycerol content (30 parts of glycerol per 100 parts of starch) where occasional pressures up to 20 MPa were noted in the case of NPS and 30 MPa with HAP. The processing torque was also close to the maximum allowable even at a moisture content as high as 25%. An increase in the glycerol content up to 45 parts by weight per 100 parts of starch was required in order to achieve a stable flow from the extruder. With this glycerol content, the upper moisture content limit, governed by the onset of bubble formation, in NPS was 17% (by weight) at 160 °C and 29% at 140 °C. For HAP, the corresponding moisture content was higher, 30%, at a processing temperature of 160 °C.

In NPS that had been compounded twice, the possible residual crystallinity would probably have been further reduced and this material showed less flow instability, and the pressure drop over the extruder die was also reduced. With twice compounded material, the extrusion could be performed in a satisfactory manner at a moisture content of 22%, whereas NPS compounded only once, possibly containing a larger amount of residual crystallinity, was more difficult to extrude even at a higher moisture content of about 28%. For the HAP-material (100:45), repeated compounding did not give the same positive results. A rather high moisture content around 30 wt%, was required in order to avoid flow instability and reduce the pressure level. This is probably coupled to a required decrease in the residual crystallinity.

In some cases, problems with insufficient melt tenacity were encountered when the extrudate was stretched after leaving the die. This is probably associated with an incom-

plete melting/softening of the material and some residual crystallinity, since the low melt tenacity often was observed in conjunction with opaque regions of the extrudate. An increase in the extrusion (screw) speed improved the melt strength as well as the stability of the flow. The accompanying increase in transparency indicated a more complete melting/softening and a greater homogenisation of the material due to a more intense shearing. Similar observations have also been reported by others (Jasberg & Willet, 1996). A decrease in the die gap from 0.95 to 0.35 mm also had a positive effect on the homogenisation of the material, and furthermore, problems with clogging of the die were reduced as a result of the higher pressure drop over the die and the higher shear rates.

Using the screw with the higher compression ratio, 4:1, gave a more stable flow than the compression ratio 2:1, and the former configuration was used throughout this work. The screw with the attached mixing element did not provide any advantage since a more extensive clogging of the die was the result.

The additives used did not improve the processability of materials. On the contrary, addition of 10% dextrin had a detrimental effect on the melt tenacity of the extrudate.

3.5. Mechanical properties of the extrudates

No satisfactory specimens could be produced with the composition 100:30 and the results of the mechanical tests are thus reported only for extruded samples containing 45 parts by weight of glycerol per 100 parts starch after conditioning at 23 °C and 53% RH, see Table 4. Both the NPS and the HAP had a tensile modulus of about 40 MPa, but the stress and strain at break were significantly higher for the latter material. The better mechanical performance of HAP is in agreement with earlier results (Van Soest & Borger, 1997; Van Soest & Essers, 1997; Myllärinen, Partanen, Seppälä, & Forssell, 2003) and recent unpublished results. The screw speed had no significant influence on the mechanical properties and nor did conditioning for 28 days at 23 °C and 50% RH.

The addition of 5% dextrin increased the tensile modulus, but it had no significant effect on the ultimate mechanical properties of the HAP.

4. Final remarks

Thermoplastic HAP is quite suitable for extrusion although it is more difficult to process than thermoplastic

Table 4
Mechanical properties of the extruded starch materials

	Tensile modulus (MPa)	Strain at break (%)	Stress at break (MPa)
NPS 100:45	45 (3.8)	47 (2.5)	3 (0.0)
HAP 100:45	36 (6.6)	80 (10.8)	4.9 (0.3)
HAP 100:45 + 5% dextrin	68 (16.5)	67 (8.2)	5 (0.3)

starch based on normal potato starch. This is however compensated for by a better mechanical property profile. Compared to NPS, a higher moisture content and a higher extrusion temperature is required with HAP. This is due to the higher melting temperature as, discussed previously (Shogren, 1992), which can lead to problems with high melt pressures and high melt viscosities (González, Torres, De Greef, & Guadalupe, 2006; Shogren & Jasberg, 1994). Even though the XRD-measurements do not indicate a crystalline phase of the HAP-extrudate, it can not be ruled out that residual crystallinity exists, both after and in the extrusion process since the detection threshold can be rather high for such measurements (Lourdin, Della Valle, & Colonna, 1995).

The higher melt viscosities might also be a result of a more entangled structure in the amylose (Van Soest & Borger, 1997) which then partly would account for the higher tensile strength of the HAP-material. Highly entangled structures are often more prone to a shear thinning behaviour, something that was not observed in the capillary measurements though.

Here it was found that the high amylose material could be successfully extruded at a temperature of 160 °C if the starch contained 45 parts of glycerol per 100 parts of starch and the moisture content was 30%. The extrusion was facilitated by a higher compression ratio of the screw, increased flow rate and smaller die gap.

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