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Film blowing of thermoplastic starch

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Abstract

Thermoplastic starch materials are often based on a combination of starch, glycerol and water. In the present study, two potato starch grades were employed; a native (natural) grade and an oxidised and hydroxypropylated grade of the native material, in order to produce the thermoplastic material. The primary aim of the study was to identify possible routes for film blowing thermoplastic starch on a laboratory scale by a suitable choice of processing conditions, amount of glycerol and moisture content. With an appropriate combination of these parameters, the thermoplastic material based on the modified starch could be film blown in a satisfactory manner. Film blowing of material based on the natural starch was significantly more difficult. The difficulties encountered were mainly related to a sticky surface of the film, insufficient tenacity and foaming. The processing window for thermoplastic starch (related to film blowing) is briefly outlined and discussed.

Keywords: Film blowing; Mechanical properties; Plasticizer; Starch; Thermoplastic starch

1. Introduction

In order to convert starch materials into films or coatings in a feasible manner, techniques that are energy-efficient in combination with a high productivity are desired. Preferably such processes should be based on already existing converting technology.

Films of starch can be cast from aqueous solutions or suspensions, but significant amounts of water have to be evaporated in order to obtain the film. This can be relatively energy-consuming. When converting starch in the molten state, products with different shapes can, in principle, be attained, including films (using extrusion). The evaporation step is then avoided and is replaced by a cooling phase. In order to achieve thin films such as those obtained with laboratory scale solution casting, the melt has to be adjusted or shaped after the extruder die. This can be done simply by pulling and squeezing the melt through calendering nips or by stretching the melt in two directions, as in film blowing.

Film blowing is a commonly used method for producing self-supporting plastic films. A hollow tube is extruded and then expanded by increasing the pressure inside the tube. The tensile properties of the melt are of great importance for the final result in both melt calendering and film blowing. Poor melt tenacity has been identified as one of the potential limitations when extruding (or processing) thermoplastic starch, i.e. starch blended with plasticizer and water, at elevated temperatures (Thunwall, Boldizar, & Rigdahl, 2006a). Melt tenacity is here defined as the ability of the melt to deform without rupture. A high melt tenacity would make it possible to produce thinner films and also lead to higher production rates. A recent study identified factors influencing the melt tenacity of thermoplastic starch and indicated some ways of improving it (Thunwall, Kuthanová, Boldizar, & Rigdahl, 2006b). A high plasticizer content and a material system based on oxidised and hydroxypropylated starch seemed here to be favourable.

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In several studies on the film blowing of starch-containing materials, rather moderate quantities of starch have either been introduced in a synthetic polymeric system (Fishman, Coffin, Onwulata, & Willet, 2006; Jana & Maiti, 1999; Otey, Westhof, & Doane, 1987) or been used together with a biodegradable polymer, such as poly(vinyl alcohol), poly(caprolactone) or polyester (Halley et al., 2001; Matzinos, Tserki, Kontoyiannis, & Panayioto, 2002). It can be concluded that films based on such blends can be produced by film blowing.

In recent work on thermoplastic starch-containing plasticizers together with montmorillonite nanoclay, it was reported that film blowing was not possible due to flashing of part of the plasticizer at the die lip which led to holes and collapse of the blown bubble (McGlashan & Halley, 2003). The problem was eliminated by the addition of 30% polyester to the thermoplastic starch and it was also noted that the nanoclay appeared to reduce the migration of the plasticizer towards the surface of the film. Problems with the migration or build-up of deposits in the die region have also been reported elsewhere, not only causing failure of the blown bubble but also resulting in sticking problems after the nip roll (Otey et al., 1987). The latter problem can perhaps be one reason for using sorbitol and urea (Buehler, Schmid, & Schultze, 1994) as a complement to or replacement for glycerol, which is the most common plasticizer in thermoplastic starch. Water is also a plasticizer for starch and can be regarded as a process aid since the viscosity of the melt is lowered with increasing water content. However, water restricts the upper processing temperature because steam generation in the material leads to bubbles and foaming which is not desirable in film blowing (Thunwall et al., 2006a).

In the present work, the film blowing of materials containing only starch, glycerol and water was investigated. The main objective was to establish that film blowing is possible with such materials and to estimate the processing window, i.e. the conditions which limit the processability. A high blow-up ratio (BUR), i.e. the ratio of the diameter of the die to that of the blown bubble, was here desirable and was interpreted as being an indication of good processing behaviour. A normal grade of potato starch with an amylose content of about 21% (Swinkels, 1985) and the same starch material but oxidised and hydroxypropylated were used.

2. Experimental

2.1. Materials

Normal (native) potato starch (NPS) and hydroxypropylated and oxidised potato starch (HONPS) were supplied by Lyckeby Stärkelsen, Kristianstad, Sweden. According to (Jansson & Järnström, 2005), the latter 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. Compounding

Starch and glycerol were premixed by hand and then fed into a Buss co-kneading single screw extruder (Buss PR 46, Switzerland, diameter $D = 46$ mm and length $L = 11D$). In this type of extruder the compounding is facilitated by an oscillatory axially screw movement and kneading pins the reorients the flow and folds the material. The screw speed was 24 rpm and the barrel and die temperatures were both set to 90 °C. No extra water was added, but the initial moisture content of the starch gave a moisture content of 11–13 weight-% in the starch–glycerol mixtures, depending on the glycerol content. HONPS was mixed with glycerol in ratios of dry starch to glycerol of 100:15, 100:22, 100:30 and 100:45 (by weight) and NPS was mixed with the glycerol in a ratio of 100:30. Extruded strands were cut into pellets and conditioned prior to further processing. Table 1 summarises the formulations used and the moisture contents after conditioning at 53% relative humidity (RH) and 23 °C.

2.3. Conditioning

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). The materials were conditioned for at least 3 days prior to any measurement or processing. The equilibrium moisture contents of the specimens were determined gravimetrically by exposing the samples to a temperature of 105 °C in a ventilated oven.

2.4. Rheological measurements

A Rheoscope 1000 CEAST 6742/000 (Ceast SpA, Italy) capillary viscometer was used to determine the melt viscosity as a function of the shear rate for some selected materials of special interest. Three different capillaries were used, all having the same diameter (1 mm) but different length-to-diameter ratios (L/D); 5, 10 and 40, respectively. The measurements were carried out at 120 °C and corrections according to Rabinowitz and Bagley were applied. The results were fitted to a power-law relation between the shear stress (τ) and the shear rate ($\dot{\gamma}$); i.e.

Table 1
The starch–glycerol formulations used and the moisture contents of the mixtures after conditioning at 53% RH and 23 °C

Material	Parts dry starch (by weight)	Parts glycerol (by weight)	Water content (weight-%)
NPS 30	100	30	13
HONPS 15	100	15	7
HONPS 22	100	22	9
HONPS 30	100	30	10
HONPS 45	100	45	13

$$\tau = K \cdot \dot{\gamma}^n \quad (1)$$

The parameters K (consistency constant) and n (flow index) were evaluated from the dependence of the viscosity ($\eta = \tau/\dot{\gamma}$) on the shear rate.

2.5. Film blowing

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. 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. The extruder was equipped with a conventional temperature-controlled film-blowing die having a diameter of 24 mm and a film-blowing tower, Brabender OHG, Duisburg, Germany, with a calendering nip and take-off rolls. The velocity of the take-off rolls and the pressure inside the film "bubble" were adjusted in order to achieve as good a result as possible, i.e. a stable process with a blow-up ratio greater than two.

2.6. Mechanical properties

Tensile specimens having a width of 4 mm, a thickness of about 0.15 mm and gauge length of 20 mm were cut from the films, both in the flow direction of the extruder and in the perpendicular direction. The tensile tests were carried out at 23 ± 2 °C and 40 ± 5% RH with an Instron 1122, Instron Ltd., High Wycombe, UK, tensile tester according to ISO 527-2 using a strain rate of 6.6×10^{-3} s^{-1} (corresponding to a cross-head speed of 10 mm/min). The specimens were conditioned at 53% RH (23 °C) before the measurements.

2.7. Dynamic-mechanical measurements

The dynamic-mechanical properties of the films were evaluated as a function of temperature using a strain-controlled rheometer, RSA II analyzer, Rheometrics Inc., Piscataway, NJ, USA. The frequency was 1 Hz, the strain amplitude 0.01% (in the tensile mode) and the temperature range scanned was 30–95 °C. The thickness of the specimens was about 0.1 mm and the heating rate used was 5 °C/min. All the samples were covered with silicone grease in order to reduce the moisture loss during the measurement (Stading, 1998). The specimens were conditioned at 23 °C and 33%, 53% or 70% RH for 3–5 days before the measurements.

2.8. X-ray diffraction (XRD)

X-ray diffraction was used to estimate possible effects of the processing on the crystallinity of the starch materials. The measurements were carried out using a Siemens D8 Advance Theta X-ray diffractometer, with a CrK_α radiation source ($\lambda = 2.2897$ Å) equipped for low-angle XRD analysis. The samples were milled in a mortar together with liquid nitrogen before the measurements in order to produce a powder.

3. Results and discussion

3.1. Rheological measurements

As shown in Fig. 1, both HONPS 22 and 30 had a significantly lower melt viscosity and exhibited a less pronounced shear-thinning behaviour than NPS 30, even at with lower plasticizer content, as in the case of HONPS 22. Similar results have been reported earlier and indicate that the thermoplastic materials based on the modified starch grade are easier to process (Thunwall et al., 2006b). The lower viscosity and less pronounced shear-thinning behaviour of the HONPS materials is most likely an effect of the lower molecular weight obtained when oxidising the starch.

3.2. Film blowing

It was possible, without any significant problems, to blow high glycerol content materials based on HONPS with 45 parts glycerol per 100 parts dry starch and a moderate moisture content of 13 weight-% to a blow-up ratio of 2–3. However, due to the sticky surface of the extruded material, a double-walled film impossible to separate was obtained after passage through the calendering nip. Reducing the moisture content by drying the pellets prior to the film blowing reduced the problem but not to a sufficient extent. Simultaneously, the torque required from the extruder and the die pressure increased significantly due to the lower moisture content (giving a higher viscosity).

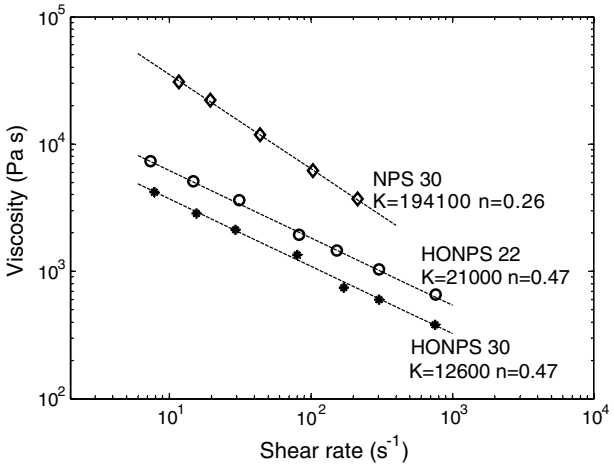

Fig. 1. Melt viscosity as a function of shear rate at 120 °C (corrected according to Bagley and Rabinowitz). The material parameters K (unit Pa s^n) and n in the power law, Eq. (1), are included in the graph.

HONPS containing 30 parts of glycerol gave also a sticky extrudate which made it difficult to separate the folded film after the calendering nip. Reducing the moisture content from 10 to 5 weight-% by drying reduced this undesired effect but, upon folding, the blown-up tube cracked at the crease. A very low glycerol content (15 parts) and a lower moisture content eliminated the blocking problem due to the sticky extrudate but, on the other hand, the material was too stiff to expand during the blowing and the material failed in a brittle manner at the nip. The lower glycerol content also led to a significant increase in the torque required from the extruder. The unmodified NPS with 30 parts glycerol had insufficient tenacity to be satisfactorily expanded.

A material based on 100 parts dry HONPS with 22 parts of glycerol and a moisture content of about 10% was found to be a reasonable compromise when trying to avoid a double-walled glued film while still maintaining a sufficient expansion potential. A stable bubble with a BUR (blow-up ratio) of about three could be achieved, resulting in a film with a thickness of 0.10–0.15 mm. An extruder temperature profile of 90, 120, 115 and 95 °C was favourable in order to avoid foaming while keeping a melt with good extensibility. With these processing conditions, the pressure loss over the die was stable at about 10^6 Pa, but the extruder torque was rather high; between 60 and 90 Nm.

Problems related to bridging in the hopper of the extruder were overcome by drying the pellets at 105 °C for 2 min prior to extrusion. Bridging led to an uneven feed of the material and thus instabilities in the flow through the die leading to a collapse of the blown bubble. Table 2 summarises some of the processing conditions used in the trials together with comments on the extrusion result.

Figs. 2 and 3 provide some illustrations of the film blowing of HONPS 22.

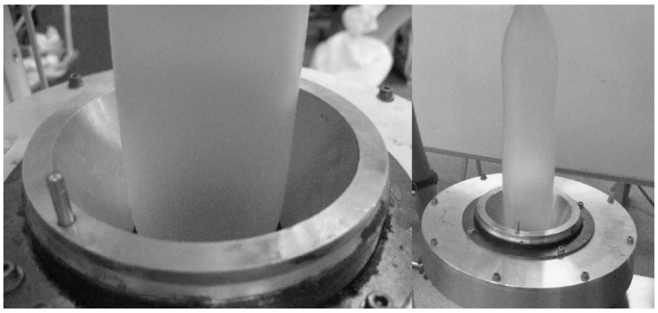

Fig. 2. Film blowing of HONPS 22 illustrated with a close up of the die (left) and of how the bubble begins to rise (right).

Fig. 3. Film blowing of HONPS 22, at the start of blowing (left) and after some time when the bubble is stable (right).

3.3. X-ray diffraction (XRD)

The unprocessed HONPS material exhibited a peak in the X-ray diffractograms at about $2\theta = 26°$ as shown in Fig. 4. This corresponds to a diffraction angle (2θ) of 17° if a CuK_α radiation source, and is probably to be associated with the B-type of crystallinity (Rindlav, Hulleman, & Gatenholm, 1997). The corresponding diffractogram for the HONPS 22 film is also included in the figure. The processing obvious reduced the intensity of the peak significantly, indicating a more or less amorphous material. Similar effects of the processing of the thermoplastic starch on the degree of crystallinity have been reported earlier (Thun-

Table 2
Processing parameters for a number of selected trials in which the screw speed was held constant at 30 rpm, together with visual observations

Material	Condition. (% RH)	Moist. (wt-%)	Temperature profile zones 1/2/3/die (°C)	Torque (Nm)	Pressure (MPa)	Notes
HONPS 45	53	13	100/120/130/130			Sticky
HONPS 45	53 + D30	5	120/140/140/130	25–50	2–5	Somewhat less sticky
HONPS 30	53	10	100/120/130/130	–	–	Foam and sticky
HONPS 30	53 + D30	5	120/140/150/140	50	–	Brittle/broke when folded
HONPS 15	30	7	100/120/130/130	–	–	No expansion
HONPS 15	30	7	100/120/130/160	100	–	Foam/high torque
NPS 30	53	8	100/120/130/130	–	–	No expansion
NPS 30	53	13	100/120/130/130	–	–	No expansion
HONPS 22	53	10	110/120/120/110	–	–	Possible to blow
HONPS 22	53	10	110/120/110/95	30	1	Feeding problem, BUR ≈ 1.5
HONPS 22	53 + D2	9	90/120/115/95	60–90	1	Easy feed, no stick, BUR ≈ 2.9

D30 = Dried 30 min at 105 °C before extrusion, D2 = Dried 2 min at 105 °C before extrusion.

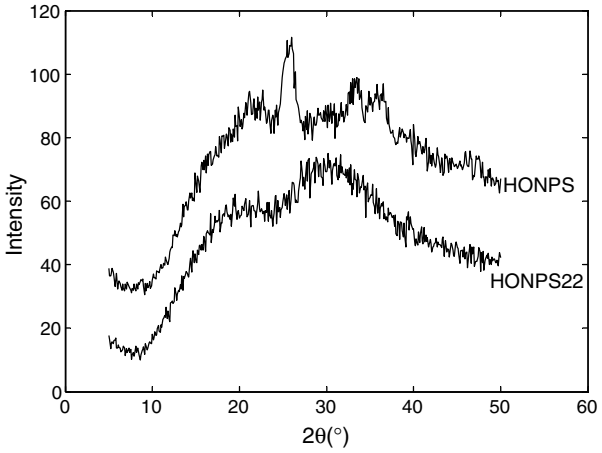

Fig. 4. X-ray diffractograms of non-processed HONPS starch and of film-blown HONPS 22.

wall et al., 2006a). The films were not however totally transparent, which means that some residual crystallinity cannot be excluded. The compounded (pelletised) materials were not investigated by XRD in this work, however, in a previous work (Thunwall et al., 2006a) it was indicated that some crystallinity might be present after the compounding step. This is further supported by the opaque appearance of the pellets. However, the film blowing was carried out at higher processing temperatures which should yield a further reduction in crystallinity. It can however not be completely ruled out that some minor residual crystallinity was present also after the film blowing, cf. Thunwall et al. (2006b).

3.4. Dynamic-mechanical properties of HONPS 22 films

Fig. 5 shows that the storage modulus decreased drastically at about 40 °C for the films of HONPS 22 when initially conditioned at 53% RH. This is probably associated with the glass transition of the thermoplastic starch. The softening temperature of the material increased when it was conditioned at 33% RH as shown in the figure where the curve is shifted towards higher temperatures whereas, after conditioning at 70% RH, the film was in a soft rubbery state from room temperature and upwards.

A comparison between three of the HONPS-compounds conditioned at 33% RH showed that the glycerol content influenced the softening temperature significantly. An increase in the amount of glycerol shifted the curves towards lower temperatures, as shown in Fig. 6. The moisture content increased with increasing glycerol content (at a given relative humidity), so that a plasticizing effect of the "extra" water is thus expected. When comparing the curves it should be kept in mind that, at a temperature of ca. 60 °C, the water holding ability provided by the silicone grease will be less efficient and that a loss of water will probably lead to an increase in the stiffness of the samples (Stading, 1998).

Obviously, it is not easy to find a relationship between the curves shown in Figs. 5 and 6 and the processability of the thermoplastic starches. It is however obvious that the material, during the extrusion and the blowing phases, should change from a rather rubbery state (allowing expansion) to a more glassy material (avoiding stickiness) as the material cools down. This change should match the chosen extrusion speed (and other conditions) and the behaviour illustrated by the storage modulus for HONPS 22 provided, in a sense, this matching in the present case. If the processing conditions were changed, another material formulation might however be more suitable.

3.5. Mechanical properties

There was a clear difference between the mechanical properties parallel to and perpendicular to the flow direction for the HONPS 22 film, as shown in Fig. 7. The tensile

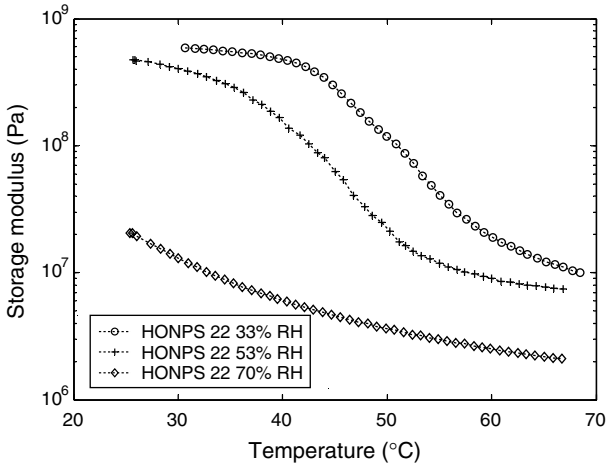

Fig. 5. The storage modulus at 1 Hz as a function of temperature for HONPS 22-based material conditioned at 33%, 53% and 70% RH (resulting in moisture contents of 9, 11 and 20 weight-%, respectively).

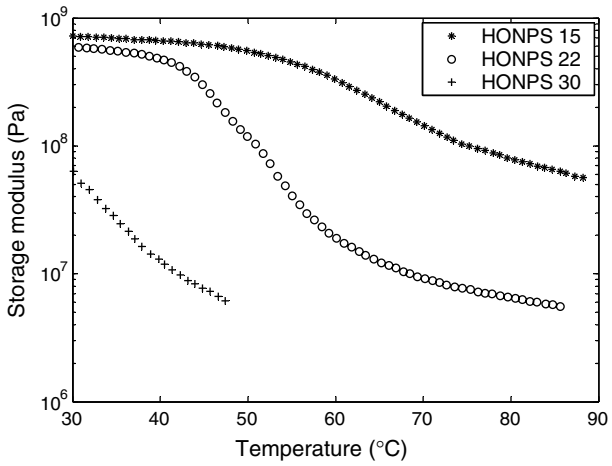

Fig. 6. Storage modulus at 1 Hz versus temperature for HONPS-films containing 15, 22 and 30 parts glycerol and conditioned at 33% RH (resulting in moisture contents of 7, 9 and 10 weight-%, respectively).

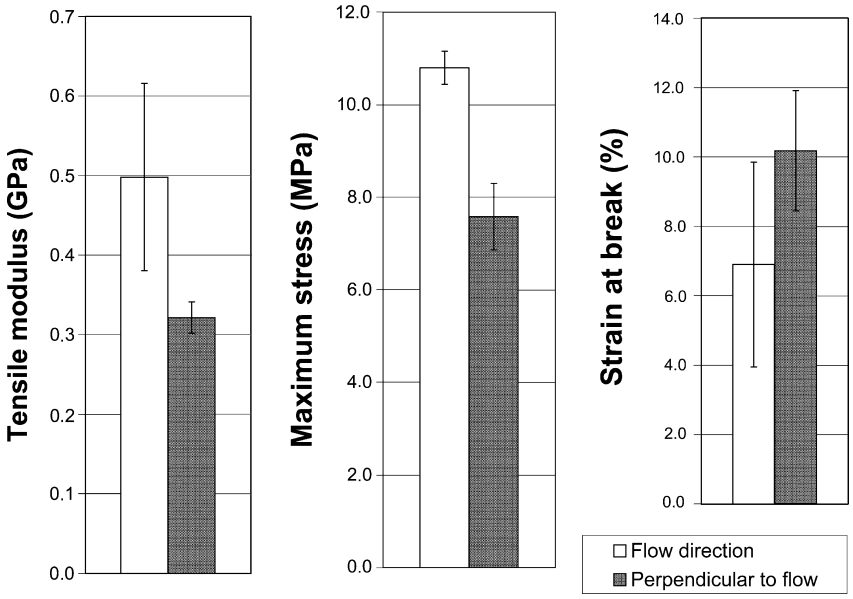

Fig. 7. Tensile modulus, tensile strength (maximum nominal stress) and strain at break for the HONPS 22 film in the flow direction and perpendicular to the flow direction.

strength and modulus were higher in the flow direction whereas the strain at break was lower, indicating that the films were anisotropic. This kind of anisotropy is well-known in the case of film-blown synthetic polymers (Dealy & Wissbrun, 1990) and is thus not unexpected. The anisotropy is also reflected in the shrinkage behaviour of the starch-based films. When the HONPS 22-films were stored for a month at room temperature at 53% RH, they shrunk on average 26 % in the flow direction and about 17% in the perpendicular direction. At the same time, the thickness increased from around 0.15 to 0.24 mm, which indicates that the volume remained constant. The dimensional changes could partly be due to some change in the moisture content during the ageing, but it is not unlikely that they were associated with relaxation of oriented molecules. The softening temperature of the films was not too different from room temperature, which promote such a relaxation. Further studies are however required to assess the mechanisms involved in more detail. From a more practical point of view, the dimensional changes encountered have to be taken into consideration (or reduced by some suitable measures) when films of this type are to be used in practical situations.

4. Final remarks

A sticky extrudate, resulting in a double-walled film, was in this case identified as the main difficulty when extruding the thermoplastic starches, and it is believed that this is mainly due to the presence of glycerol or to the amount of glycerol. Explanations, observations and speculations regarding the possible migration of plasticizer seem to be relevant in this context (McGlashan & Halley, 2003). It appears that the maximum amount of glycerol that can be accumulated in a starch melt is probably somewhat higher than 22 parts (per 100 parts of dry starch) or about 16 weight-% in a blend that contains 75 weight-% starch and 9 weight-% water. This conclusion is of course valid only for the system and the processing conditions used in this study. Indications of phase separation have previously been reported at high contents of glycerol in amylose–glycerol and amylopectin–glycerol systems, cf. (Lôpez-Rubio et al., in press; Lourdin, Ring, & Colonna, 1998), and again, such a phase separation is likely to lead to or contribute to stickiness in the extrudate. It could be that the stickiness also could yield problems when using the produced films at high humidities. This warrants however a separate study and is outside the scope of the present work.

It is nevertheless clear together with the melt tenacity results (Thunwall et al., 2006b) that glycerol or some other suitable plasticizer is required in order to achieve an extrudate that can be expanded satisfactorily. As mentioned, sorbitol and urea have been used as alternative plasticizers for starch (Buehler et al., 1994), and nanoclay has been suggested to block the migration of plasticizer (McGlashan & Halley, 2003). This type of approach might provide a potential route for reducing the sticky character of the extrudate and thus widening the processing window. The use of hydroxypropylated starch seems more favourable in the context of film blowing, and it may be that its somewhat less hydrophilic character, compared to the NPS-based materials, cf. (Thunwall et al., 2006b), reduces the stickiness. A lower melting temperature of the modified starch, resulting in a more homogenous material, might also explain why HONPS was easier to film blow.

An attempt to illustrate the complexity of film blowing with thermoplastic starch and to describe the processing window or volume is shown in Fig. 8. The glycerol content seems to be a major factor but the combination of temper-

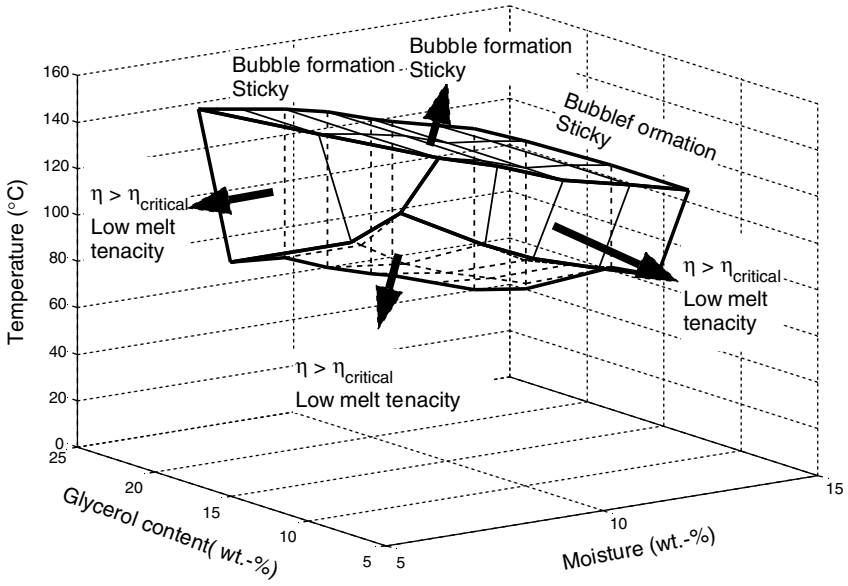

Fig. 8. Illustration of the limiting process parameters as identified in this investigation.

ature and moisture is also important in order to avoid foaming of the extrudate. Initial speculations or expectations that a good result might be obtained since a high melt tenacity could be achieved with a rather high moisture content were not supported by the experiments. The tendency towards bubble formation in the extrudate, and the subsequent rupture of the stretched melt is here probably a counteracting factor. Not only does a high temperatures promote the formation of water vapour, but at temperatures higher than 140 °C the glycerol may also start to evaporate (Lôpez-Rubio et al., in press) and this can lead to processing disturbances.

The main purpose of the present work was to investigate whether it is possible to use film blowing to produce a film of thermoplastic starch based only on starch and glycerol, at least on a laboratory scale. Another purpose was to identify processing limitations and indicate possible routes to reduce the associated problems, in the first place the sticking behaviour. An obvious continuation of this study would be to consider scaling-up the process.

No effort was here made to optimise the properties of the final film by manipulation of the processing operation. Future studies can include optimisation of the BUR by increasing the melt tenacity while maintaining control over the migration of the plasticizer. It is obviously interesting to test other plasticizing systems and other modified starches. Not only the mechanical performance of the films but also their shrinkage behaviour needs to be addressed in more detail.

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References

Buehler, F. S., Schmid, E., & Schultze, H. -J. (1994). Starch/polymer mixture, process for the preparation thereof, and products obtainable therefrom. US Patent 5,346,936.

Dealy, J. M., & Wissbrun, K. F. (1990). *Melt rheology and its role in polymer processing*. New York: Van Nostrand Reinhold , pp. 531–534.

Fishman, M. L., Coffin, D. R., Onwulata, C. I., & Willet, J. L. (2006). Two stage extrusion of plasticized pectin/poly(vinyl alcohol) blends. *Carbohydrate Polymers, 65*(4), 421–429.

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.

Halley, P., Rutgers, R., Coombs, S., Kettels, J., Gralton, J., Christie, G., et al. (2001). Developing biodegradable mulch films from starch-based polymers. *Starch/Stärke, 53*(8), 362–367.

Jana, T., & Maiti, S. (1999). A biodegradable film,1. *Die angewandte makromolekulare Chemie, 267*(1), 16–19.

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

Lôpez-Rubio, A., Lagaron, J. M., Ankerfors, M., Lindstöm, T., Nordqvist, D., Mattozzi, A., & Hedenqvist, M. S. (in press). Enhanced film forming and film properties of amylopectin using micro-fibrillated cellulose. *Carbohydrate Polymers*.

Lourdin, D., Ring, S. G., & Colonna, P. (1998). Study of plasticizer-oligomer and plasticizer-polymer interactions by dielectric analysis: maltose–glycerol and amylose–glycerol–water systems. *Carbohydrate Research, 306*(4), 551–558.

Matzinos, P., Tserki, V., Kontoyiannis, A., & Panayioto, C. (2002). Processing and characterization of starch/polycaprolactone products. *Polymer Degradation and Stability, 77*(1), 17–24.

McGlashan, S. A., & Halley, P. J. (2003). Preparation and characterisation of biodegradable starch-based nanocomposite materials. *Polymer International, 52*(11), 1767–1773.

Otey, F. H., Westhof, R. P., & Doane, W. M. (1987). Starch-based blown films. 2. *Industrial and Engineering Research, 26*(8), 1659–1663.

Rindlav, Å., Hulleman, S. H. D., & Gatenholm, P. (1997). Formation of starch films with varying crystallinity. *Carbohydrate Polymers, 34*(1), 25–30.

Stading, M. (1998). Dynamic mechanical analysis of biopolymer films. *Annual Transactions of the Nordic Rheology Society, 6*, 147–150.

Swinkels, J. J. M. (1985). Composition and properties of commercial native starches. *Starch/Stärke, 37*(1), 1–5.

Thunwall, M., Boldizar, A., & Rigdahl, M. (2006a). Extrusion processing of high amylose potato starch materials. *Carbohydrate Polymers, 65*(4), 441–446.

Thunwall, M., Kuthanová, V., Boldizar, A., & Rigdahl, M. (2006b). On the stress–strain behaviour of thermoplastic starch melts. *International Journal of Polymer Analysis and Characterisation, 11*(6), 419–428.