S.S. VIER

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol



Amylose content and chemical modification effects on the extrusion of thermoplastic starch from maize

A.L. Chaudhary a,*, M. Miler b, P.J. Torley A, P.A. Sopade A, P.J. Halley

^a Centre of High Performance Polymers, Department of Chemical Engineering, School of Engineering, University of Queensland, St. Lucia 4072, Australia

ARTICLE INFO

Article history: Received 6 February 2008 Received in revised form 15 May 2008 Accepted 20 May 2008 Available online 27 May 2008

Keywords: Starch Amylose content Hydroxypropylation Extrusion Biodegradable thermoplastic

ABSTRACT

The effects of starch structural properties and starch modification on extruder operation were monitored via die pressure, motor torque, mean residence time and specific mechanical energy (SME). The structural properties studied involved variations in the ratios of amylose and amylopectin as well as the effect of a hydroxypropylated starch on the fore mentioned extruder properties. A full factorial design of experiments (DOE) was used to then determine the influence of starch type (unmodified starches with 0%, 28%, 50% and 80% amylose; 80% amylose hydroxypropylated starch) and screw speed (250, 300 and 350 rpm) on these processing parameters. The effects of starch type and screw speed on extrusion operation that were systematically investigated using the DOE and have provided valuable insight into the relationships between starch structure and processing. The design of experiments showed that starch type for both unmodified and modified maize had a statistically significant effect on parameters such as torque, die pressure and specific mechanical energy and that screw speed also significantly effected specific mechanical energy. Residence time distributions differed according to starch type (amylose content, hydroxypropylation) and screw speed. The additional study of residence time distribution also gave an indication of the degree of mixing in the extruder. Starch type variations were apparent at low screw speed however at higher screw speed the influence of starch type decreased significantly.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

The development of a fully biodegradable, natural, renewable thermoplastic is of increasing interest due to its low environmental impact when compared to current petroleum based products that contribute to litter and landfill problems (Swift, 1996). In response to these problems, research into the synthesis of materials from natural sources such as starch and cellulose is being undertaken with the aim of replacing their non-biodegradable counterparts.

Starch is a polymeric material that is biodegradable, renewable and also available worldwide at low cost, which makes it attractive as a substitute for petroleum based plastics (Trommsdorff & Tomka, 1995). However, simple extruded starches with water products are brittle and highly sensitive to water (Ollett, Parker, & Smith, 1991; Slade & Levine, 1993). As a result, development of practical thermoplastic starch resins includes the addition of processing aids and plasticisers to aid gelatinisation during processing thus producing suitable mechanical properties in the finished product (Doane, 1992; Shogren, Swanson, & Thompson, 1992). Recently, commercially biodegradable packaging has been developed to overcome these problems (Halley, Mcglashan, & Gralton, 2006 Pat-

ent No. 7094817), giving the opportunity to manufacture products from starch-based thermoplastic resins (Plantic Technologies Ltd YeBiodegradable Lethal Ovitrapar, 2007).

Prior to thermoplastic processing such as injection moulding, starch is extruded and gelatinised to form a thermoplastic material that can be subsequently processed into viable products (Wiedmann & Strobel, 1991). Different extrusion processing conditions will alter the transformation of the starch during the preparation of the thermoplastic starch resin (Wiedmann & Strobel, 1991), which ultimately affects the mechanical properties of the finished product (Van Soest, De Wit, & Vliegenthart, 1996). Screw speed is a particularly useful processing variable, since it is readily altered during extrusion operation, controls the amount of work done on the material during processing, affects the extent of degradation of starch and alters the rheology of starch melts (Tolstoguzov, 1993; Van Soest, Hulleman, De Wit, & Vliegenthart, 1996).

Just as there is a wide variety of synthetic thermoplastic polymers available which differ in their monomers, their structure (molecular weight of chains, extent of branching), particular processing characteristics, and desired products physical properties (e.g. mechanical properties, barrier properties, appearance), similarly, with thermoplastic starches, the type of starch, chemical modification of the starch and tailored processing conditions has

^b Ecole Europeenne de Chimie, Polymeres et Materiaux de Strasbourg, Louis Pasteur University, Strasbourg, France

^{*} Corresponding author. Tel.: +61 432 016 239. E-mail address: annalisach@gmail.com (A.L. Chaudhary).

been shown to be able to be optimised for particular of the finished product (Halley, et al. 2006).

When starch type and screw speed are considered together, they have been shown to have a major effect on extrusion and finished product properties. In a study of (Van Soest, De Wit, et al., 1996) it was shown that increasing the screw speed, increased single helical type crystallinity for higher amylose content starches, thus affecting the final product mechanical properties.

The objective of our research was to study the effects of varying amylose/amylopectin ratios of maize starches when processed using a twin screw extruder. Hydroxypropylated starch was used for two reasons. Firstly, starch modification is carried out to improve the functional and physicochemical parameters in various industries since native starch itself may not give optimal performance (Lawal, 2004) and it is high amylose hydroxypropylated starch that is commercially available in Australia to produce thermoplastic materials. The effects of starch type (0–80% amylose maize starch; hydroxypropylation of 80% amylose maize starch) and mechanical processing conditions (screw speed) on extruder operation (motor torque, SME, die pressure, mean residence time) were analysed.

2. Materials and methods

2.1. Materials

All of the maize starches (Table 1) were supplied by Penford Australia and New Zealand Limited (Lane Cove, Australia) and included four unmodified maize starches (Mazaca 3401X, Avon Maize Starch, Gelose 50, Gelose 80) that differ in their amylose content, and a hydroxypropylated high amylose starch (Gelose 939).

Plasticisers and emulsifiers were added [in accordance to US Patent No. 7094817 (Halley, et al. 2006) to the starch with an increased level of polyols to produce a thermoplastic starch (TPS) resin suitable for injection moulding applications. Three polyol plasticisers were used: sorbitol (Neosorb P60W, Roquette Freres, Lestrem, France), maltitol (Maltisorb, Roquette Freres, Lestrem, France) and glycerol (Glycerine USP, Consolidated Chemical Co., Arndell Park, Australia).

2.2. Feed material preparation

All dry ingredients were premixed in a Govan (Sydney, Australia) powder mixer for 3–5 min and stored in bulk containers prior

Table 1Starch type with amylose content and moisture content

Penford product	Starch type	Amylose content (%) ^a	Moisture content (%)*
Mazaca 3401X	Unmodified waxy	0	13.8
Avon maize starch	Unmodified regular	28	14.1
Gelose 50	Unmodified high amylose	50	14.6
Gelose 80	Unmodified high amylose	80	14.9
Gelose 939	Hydroxypropylated high amylose	80	14.9

^a Amylose content as specified by Penford, Australia.

to extrusion. Glycerol was dissolved in water and stored in 10 L plastic containers until required for extrusion. In order to keep the feed moisture content consistent between the different starches, moisture content of the raw starch was measured and water flow rates were adjusted accordingly.

2.3. Extruder and extrusion procedures

All thermoplastic starches (TPS) were made using an E-Max twin screw co-rotating intermeshing extruder (Entek Extruders, Oregon, USA). The diameter of the screw was 27 mm with a length to diameter (L/D) ratio of 40:1. The screw configuration is shown in Fig. 1 with a detailed description given in Table 2. The extruder was driven by a motor (14.9 kW, maximum torque 120 Nm, maximum speed of 1800 rpm; Marathon Y533, Oregon, USA) fitted to a twin shaft gearbox. The extruder had a maximum screw speed of 600 rpm.

The extruder was divided into twelve separately controlled zones: 10 barrel zones, the die adapter zone and the die block zone. Zone 1 had a dry feed port and zone 3 a liquid injection port. No vents were used in the extrusion system. The first barrel zone (dry feed port) was water cooled, but not electrically heated. The remaining nine extruder barrel zones were electrically heated by cartridge heaters, and cooled by refrigerated water flowing through channels in the barrel. The refrigerated water was cooled by an external cooling system (Hang Dong Industrial Chiller, Hong Kong). The combination of electrical heating and water cooling allowed accurate control of the barrel temperature profile. The die was connected to the extruder barrel using a die adapter plate. The die was attached to the adapter plate and consisted of three circular openings, each 3 mm in diameter. Thermocouples and pressure transducers were also inserted into the die plates to measure die pressure and temperature of the product.

The dry feed mixture was fed into the extruder at zone 1 using a single screw "loss in weight" feeder (Brabender Technologies, Canada), which was calibrated regularly according to the bulk density of the starch mixes. The glycerol/water feed was fed into the extruder at zone 3 using a diaphragm pump (Pulsatron Series M, Pulsafeeder, USA). The liquid injection system was calibrated manually for each glycerol/water mixture.

Each barrel section had a type J thermocouple installed to monitor temperature and Gefran (USA), M and W series melt pressure transducers were fitted in zones 2, 4, 5, 6, 7, 8 and 9. Both dry and

Detailed description of the screw profile (Fig. 1) used for TPS resin extrusion

Description	Length (mm)
Twin flight feed screw (40 mm pitch)	270
Twin flight feed screw (30 mm pitch)	90
30° Forward kneading blocks (10 lobes)	60
Twin flight feed screw (30 mm pitch)	120
30° Forward kneading blocks (5 lobes)	30
60° Forward kneading blocks (5 lobes)	30
30° Reverse kneading blocks (5 lobes)	30
Twin flight feed screw (20 mm pitch)	135
30° Forward kneading blocks (5 lobes)	30
60° Forward kneading blocks (5 lobes)	30
30° Reverse kneading blocks (5 lobes)	30
Twin flight feed screw (40 mm pitch)	150
Twin flight feed screw (20 mm pitch)	60



^{*} Moisture content determined using Sartorius Moisture Content Analyser with an error of ±0.0002.

liquid feed streams entered the extruder and the process was allowed to run until it had stabilised (generally 10–15 min) before material was collected. Data from the extruder such as temperatures, pressures, screw speed and dry feed rate was relayed to a computer and manually recorded at 1-min intervals for a total collection time of 20 min after steady state in the extruder.

The same barrel and die temperature profile was used in all extrusion trials (Table 3). A maximum barrel temperature of 150 °C was used to ensure starch gelatinisation due to the limited water content (Cameron & Donald, 1993) and high level of polyols in the formulation (Perry & Donald, 2002; Tan, Wee, Sopade, & Halley, 2004), both of which tend to increase the gelatinisation temperature.

The dry feed rate was kept constant at 5 kg/h and the liquid feed rate adjusted according to the starch moisture content so that the total water content was consistent.

The extrudate was collected onto reels, pelletised then stored in sealed bags at room temperature (23 $^{\circ}$ C) until required for testing and analysis.

3. Extruder operating characteristics

3.1. Extruder torque and die pressure

Motor torque in the extruder, barrel pressures and die pressure were monitored and recorded during the extrusion process using a configured spreadsheet with process status displayed in real time (RSLinx software, version 3.12, Entek Extruders, Oregon, USA).

3.2. Residence time distribution

A tracer (allura red dye) was dropped into the feed port of the extruder and this was labelled as time zero. Changes in time interval collection (listed below) were based on colour concentration, the more concentrated the colour the more frequent the sample collection

Samples were then collected at the following time intervals:

- 1st sample collected after the first 30 s for 15 s
- 2nd to 16th samples, every 5 s for the next 75 s
- 17th to 22nd samples, every 10 s for the next 60 s
- 23rd and subsequent samples, every 30 s until the red colour in the extrudate disappeared.

Typically, samples were collected for a total of 240 s after the tracer was added, with a total of about 24 samples per trial. Samples collected for residence time distribution analysis were dried in an incubator oven at 60 °C for 24 h. The samples were then

Table 3 Extruder barrel and die set point and operating temperatures

Zone	Set temperatures (°C)	Operating temperatures (°C)
1 (dry feed port) a	45	47
2	75	75
3 (liquid feed port)	95	95
4	120	120
5	140	140
6	150	150
7	150	150
8	130	132
9	110	110
10	90	90
Die adapter	90	90
Die block	80	80

^a Zone 1 has no heater bands, so heating is by conduction only.

quenched with liquid nitrogen and then ground to pass through a 710 um sieve.

The concentration (*C*) of tracer (allura red) in the ground extrudate was measured with a Minolta Chroma Meter (Konica Minolta Sensory, Japan) using the Hunter Lab colour space setting. The Hunter Lab method for determining colour is commonly used in the food industry (Ibanoglu, 2001; Yuliani, Torley, D'Arcy, Nicholson, & Bhandari, 2006). The tracer concentration was determined from the Hunter *a* value an indication of the sample's redness.

The exit age distribution function, E(t), accumulated tracer quantity, F(t), mean residence time (MRT) and variance, σ^2 , and vessel dispersion number, D/uL, (where D is the diffusivity, u is the flow rate and L is the length of vessel) were calculated (Yeh, Hwang, & Guo, 1992).

3.3. Specific mechanical energy

Specific mechanical energy (SME) was calculated using:

$$\psi = \frac{\textit{N}_{(run)}}{\textit{N}_{(rated)}} \cdot \frac{\Phi}{\Phi_{max}} \cdot \frac{\textit{K}_{w}}{Q}$$

where:

 ψ = specific mechanical energy (kW h/kg)

 $N_{(\text{run})}$ = actual screw speed (rpm)

 $N_{\text{(rated)}}$ = maximum extruder screw speed (rpm)

 Φ = actual torque during operation (Nm)

 Φ_{max} = maximum torque (Nm)

 $K_{\rm w}$ = maximum motor power (kW)

Q = mass flow rate (kg/h) (production capacity).

3.4. Experimental design and statistical analysis

The experiment was designed to determine the effect of starch type and screw speed on extruder responses (motor torque, SME, die pressure, RTD, MRT).

A multivariable random block design was devised to analyse the relationships of input variables to outputs and to quantify the significance of each. Two factors were studied: starch types (five levels: 0% amylose, 28% amylose, 50% amylose, 80% amylose and hydroxypropylated 80% amylose; Table 1) and screw speeds (three levels: 250, 300 and 350 rpm). The design was done in triplicate giving a total of 45 trials. SAS for Windows (version 9.1, SAS Institute, Cary, North Carolina, USA) and JMP6 (SAS Institute, Cary, North Carolina, USA) software were used to perform statistical analysis on the data. To determine how significantly effective each of the inputs were on the outputs, *t*-tests were performed where the mean and least significant difference values were determined.

4. Results and discussion

4.1. Extruder operation

Extrusion stability and quality were be monitored by observing the flow rate, melt temperature, motor torque, and barrel and die pressures (Stevens & Covas, 1995). After start-up, it took approximately 15 min for the process to stabilise (constant barrel and die pressures, flow of extrudate out of the die, and motor torque). The process did not experience any surging (i.e. variation in die pressure, motor torque, or flow of extrudate out of the die), and the melt exiting die was uniform and consistent.

4.2. Statistical analysis

The analysis of variance for the experimental design is presented in Table 4. These results show that starch type significantly

Table 4Probability of a significant effect from starch type, screw speed, or their interaction on extruder operating parameters

	Torque	SME	Die pressure	MRT
Starch type	<0.0001	<0.0001	<0.0001	0.20
Screw speed	0.42	< 0.0001	0.3	0.07
Replicate	0.0004	0.04	0.9	0.46
Starch type × screw speed	0.23	0.54	0.63	0.61

affected torque, die pressure and SME, but did not significantly affect the MRT. Screw speed only had a significant effect on SME. There were no significant interactions between starch type and screw speed. These results are further discussed in subsequent sections.

4.3. Extruder torque and specific mechanical energy (SME)

Starch type had a significant effect on extruder torque (p < 0.0001) and SME (p < 0.0001). Both torque and SME increased with increasing amylose content in the unmodified starches (Fig. 2a and c), while the torque and SME of the hydroxypropylated 80% amylose starch was significantly less than for unmodified 80% amylose starch. Screw speed had no significant effect on torque (p = 0.42) (Fig. 2b), although there was a linear decrease in torque with an increase in screw speed. By contrast, there was a highly significant effect of screw speed on SME (p < 0.0001) (Fig. 2d), with SME increasing with increasing screw speed. There was no signifi-

cant interaction between starch type and screw speed for extruder torque (p = 0.23) or SME (p = 0.54).

For the starches investigated here, extruder torque was predominantly controlled by the starch type. The increase in motor torque with increasing amylose content is due to an increase in melt viscosity similar to a recent finding showing that high amylose materials such as potato starch, 86% amylose (Thuwall, Boldizar, & Rigdahl, 2006). Further, the incorporation of hydroxypropyl groups in the starch chains primarily in the amorphous region changes its granular and molecular structure allowing easier water absorption (Pal, Singhal, & Kulkarni, 2002). When hydroxypropylated and unmodified starches are compared at the same water content, the modified starch undergoes gelatinisation more easily (Morikawa & Nishinari, 2000) thus resulting in a lower melt viscosity (Liu, Ramsden, & Corke, 1999).

The decrease in screw speed relates to a decrease in the amount of shear exerted on the polymer melt therefore lowering the viscosity of the melt (Della Valle, Tayeb, & Melcion, 1987). The decrease in toque with an increase in screw speed shown in this study (Fig. 2b), was also observed in a study of a rice starch extrusion system (Akdogan, 1996).

Specific mechanical energy is an important factor in the extrusion of thermoplastic starch, as SME is related to the structural and functional properties of starch (Van Lengerich & Meuser, 1985). SME is also dependent on extrusion parameters such as screw speed, moisture content of the feed, die temperature and mass flow rate (Akdogan, 1996).

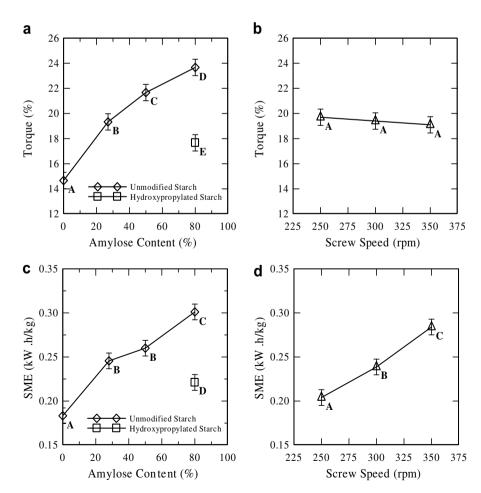


Fig. 2. The effect of starch type (a), (c) and screw speed (b), (d) on torque (a), (b) and specific mechanical energy (SME), (c), (d). A, B, C, D, E – Means with the same letters are not significantly different (*p* > 0.05). Error bars represent the least significant difference.

For the unmodified starches, the increasing SME with increasing amylose content reflects the higher viscosity of high amylose material (Thuwall et al., 2006). While the relatively low SME of the hydroxypropylated 80% amylose starch translates into a decrease in the strength of the associative bonding forces within the micellar network (Perera, Hoover, & Martin, 1997) thus reducing viscosity and SME. The progressive increase in SME with increasing screw speed is expected as these parameters are directly proportional to each other, provided torque is constant. This reflects a larger amount of mechanical work being performed on the material in the extruder. An increase in SME with increasing screw speed is typically observed in starch extrusion (Akdogan, 1996; Della Valle, Boche, Colonna, & Vergnes, 1995).

4.4. Die pressure

Die block pressure was significantly affected by starch type (p < 0.0001). For the unmodified starches, the die block pressure progressively increasing with increasing amylose content (Fig. 3a), while the die pressure for the hydroxypropylated 80% amylose starch was significantly less than for unmodified 80% amylose starch. Screw speed had no significant effect on die pressure (p = 0.30), however, similar to torque results, there was a slight decrease in die pressure with an increase in screw speed (Fig. 3b). For the die pressure results there was no significant interaction between starch type and screw speed (p = 0.63).

The trends seen with die pressure are similar to that of extruder torque. As mentioned earlier, melt viscosity changes with both amylose content and starch modification (Perera et al., 1997; Thuwall et al., 2006). The differences in melt viscosity can also account for the changes in die pressure; increasing amylose content increases melt viscosity thus affecting the die pressure. Modification in starch compared to unmodified starch also results in a lower die pressure.

Similar to the observations made with the extruder torque results, an increase in screw speed resulted in a decrease in die pressure. This is consistent with other literature studies (Akdogan, 1996; Ollett, Li, Parker, & Smith, 1989) where the relationship between die pressure and screw speed was understood as a change of melt viscosity.

4.5. Residence time distribution (RTD)

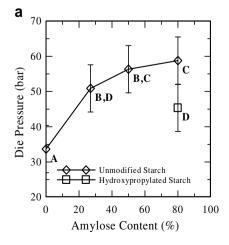
Residence time distribution and mean residence time gives information about how long a material spends in the extruder, how uniformly the material is processed in the extruder, and the degree of mixing (Seker, 2005).

The tracer concentration RTD curves resulting from varying screw speeds for the five different starches are shown in Fig. 4A and B. (Note that the data for 300 rpm is not presented; it lies intermediate between 250 and 350 rpm curves.) The location and general shape of the RTD curves are similar irrespective of the screw speed, as has been previously shown (Altomare & Ghossi, 1986; Yeh et al., 1992). It is interesting to note the effect of starch type on the tracer concentration and cumulative plots.

At normalised RTD curves (Fig. 4) give an indication of the flow behaviour within the extruder. Plug flow (where *D/uL* approaches 0) indicate a flow situation where all fluid elements move at the same velocity (Rauwendaal, 1990), that is flow without shear, Mixed flow (where D/uL approaches infinity) occurs when there is mixing of material that entered the extruder at different times, which is the flow pattern observed in this study (Fig. 4C and D). The extent of mixing increased with increasing screw speed; at 250 rpm the D/uL had a high value of 0.077 and decreased to 0.049 at 350 rpm. This agrees with a study by Yeh et al. who showed that there is more axial dispersion at higher screw speeds (Yeh et al., 1992). At 250 rpm, starch type also affected the extent of mixing, with the low (0% and 28%) amylose samples diverging more from plug flow at D/uL values of 0.092 and 0.071, respectively. Higher amylose samples (50% and 80%) showed mixing behaviour closer to plug flow (D/uL = 0.036 and 0.042, respectively). The hydroxypropylated 80% starch lay intermediate between the low and high amylose samples with a dispersion number of 0.056. Starch type had a small effect on flow patterns at 300 rpm, and no effect at 350 rpm.

At the lower screw speed of 250 rpm, the differences in variance (σ^2) of the different starch types were calculated. As the amylose content increases for the unmodified starch, the curve shifts to the left and the variance decreases from 2840 to 760. The modified starch shows a broader variance $(\sigma^2=1100)$ when compared to the unmodified counterpart $(\sigma^2=760)$. This suggests that at low screw speeds, the RTD variance is greater between starches possibly due to the differences in gelatinisation behaviour (Liu, Yu, Xie, & Chen, 2006). As the screw speed increases this variance becomes less apparent with variance values of 2300, 1020 and 850, respectively for 250, 300 and 350 rpm. Further, at 350 rpm the RTD curves begin to overlap indicating that the effect of starch type in the extruder is decreased at higher speeds.

The MRT was marginally significantly affected by the screw speed (p = 0.07), with the MRT progressively decreasing with increasing screw speed (Fig. 5). The decrease in MRT with increasing screw speed was also seen by Valle et al. where a comprehensive model of starch in a co-rotating twin extruder was developed (Valle, Barres, Plewa, Tayeb, & Vergnes, 1993). Valle et al. con-



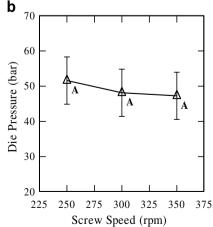


Fig. 3. The effect of (a) starch type and (b) screw speed on die pressure. A, B, C, D – Means with the same letters are not significantly different (p > 0.05). Error bars represent the least significant difference.

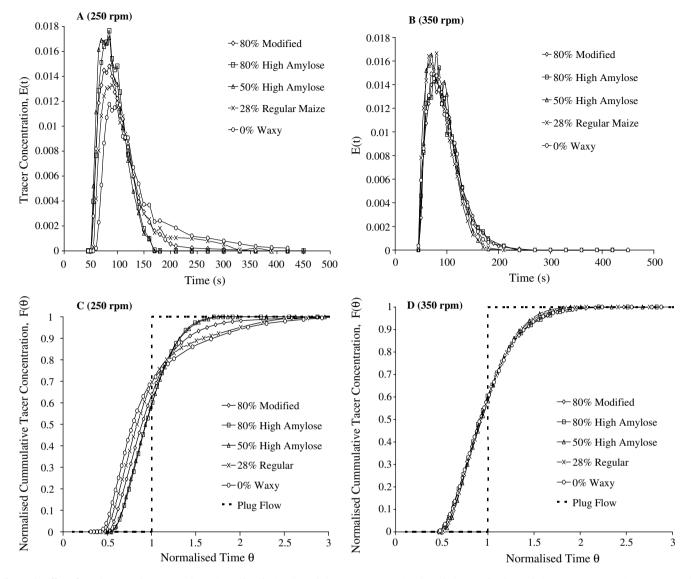


Fig. 4. The effect of starch type and screw speed on exit age distribution. (A and B), tracer concentration; (C and D), normalised cumulative tracer concentration. Screw speed: (A and C) are 250 rpm; (B and D) are at 350 rpm.

cluded that at constant dry feed rate, increasing screw speed decreased the fraction filled in the screw, thus reducing the MRT. The MRT was not significantly affected by starch type (p = 0.20). Again, there was no significant interaction between starch type and screw speed (p = 0.61).

5. Overall discussion

The processing behaviour of the five starch types showed that starch structure (amylose and amylopectin) have an individual effects on extrusion processing parameters. The results show that from a processing point of view, the amylose content and the modification of starch greatly affect the behaviour of the material; however, screw speed influence does to a lesser degree and is primarily due to the viscosity changes during gelatinisation transitions and the interactions between the amylose and amylopectin molecules.

Starch containing only amylopectin (0% amylose) had the lowest values of torque and energy while high amylose starch (80% amylose) had the highest torque and energy values. The behaviour of 0% amylose agreed with a previous study (Yu & Christie, 2005)

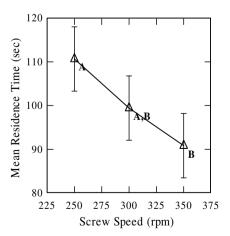


Fig. 5. The effect of screw speed on MRT. A and B – Means with the same letters are not significantly different (p > 0.05). Error bars represent the least significant difference.

that showed that during gelatinisation, the short chained branches of amylopectin separate to form 'gel-balls' and these 'gel-balls' require less energy to process than that of long linear chains (amylose chains) as the former lubricate more efficiently with water, thus lowering viscosity. Similarly, hydroxypropylated starch, behaved very differently to its unmodified counterpart in all aspects of extrusion processing. This was due to its ability to absorb moisture more efficiently (Liu et al., 1999; Perera et al., 1997) hence lowering viscosity and in turn resulted in lower torque, die pressure and energy.

As reported earlier, amylose content and starch granule size have been reported to be factors which influence starch gelatinisation and extrusion behaviour. High amylose contents are responsible for strong associative forces in the granules which prevent penetration of water inside the granules, thus delaying gelatinisation and increasing viscosity (Pal et al., 2002; Yu & Christie, 2005), hence the increased values for torque, SME and RTD. Hydroxypropylated starch, on the other hand, behaved very differently to its unmodified counterpart in all aspects of extrusion processing. This was due to its ability to absorb moisture more efficiently (Liu et al., 1999; Perera et al., 1997) hence lowering viscosity and in turn resulted in lower torque, die pressure and energy.

5. Conclusion

Starch with low amylose content gave lower torque values, die pressure values and was subjected to a reduced amount of mechanical work, which resulted in a reduced axial mixing at slower screw speeds. However, these effects were less apparent as screw speed increased.

The results showed that processing hydroxypropylated 80% amylose starch was substantially different to unmodified 80% amylose starch. Modification due to hydroxypropylation of the starch affects its gelatinisation behaviour (increased interactions with water molecules) which in turn can result in a lower viscosity. This was evident with a reduction in torque, die pressure and SME when compared to the unmodified 80% amylose starch.

Effects of starch type on RTD were apparent at low screw speed however at higher screw speed the influence of starch type decreased significantly. At higher screw speeds, axial mixing differences between starch types were negligible. Residence time distributions were assessed and differed according to starch type (amylose content, starch modification) and screw speed. As reported earlier, as amylose content increased motor torque, die pressure and SME also increased. Also, an increase in screw speed only significantly affected SME and no other extrusion variables.

The findings showed that both amylose content and the hydroxypropylated starch have a significant impact on extrusion processing. This knowledge can be developed further and used to optimise the process to form a suitable commercial thermoplastic resin to replace existing non-environmentally friendly plastics. A subsequent paper will examine the mechanical and structural properties of samples moulded from these thermoplastic starch resins.

Acknowledgements

The authors thank Dr. Kishan Khemani, Mr. Nick McCaffery (Plantic Technologies) and Dr. Deeptangshu Chaudhary (Curtin University) for their valuable advice and insight given during this study.

References

Akdogan, H. (1996). Pressure, torque, and energy responses of a twin screw extruder at high moisture contents. *Food Research International*, 29, 423–429. Altomare, R. E., & Ghossi, P. (1986). Analysis of residence time distribution patterns in a twin screw cooking extruder. *Biotechnology Progress*, 2, 157–163.

- Cameron, R. E., & Donald, A. M. (1993). Small-angle X-ray scattering study of starch gelatinization in excess and limiting water. *Journal of Polymer Science, Part B: Polymer Physics*, 31, 1197–1203.
- Della Valle, G., Boche, Y., Colonna, P., & Vergnes, B. (1995). Extrusion behaviour of potato starch. *Carbohydrate Polymers*, 28, 255–264.
- Della Valle, G., Tayeb, J., & Melcion, J. P. (1987). Relationship of extrusion variables with pressure and temperature during twin screw extrusion cooking of starch. *Journal of Food Engineering*, 6, 423–444.
- Doane, W. M. (1992). USDA research on starch-based biodegradable plastics. Starch-Stärke, 44, 293-295.
- Halley, P., Mcglashan, S., & Gralton, J. (2006). YeBiodegradable polymerar. USA: Plantic Technologies Ltd.
- lbanoglu, S. (2001). Influence of tempering with ozonated water on the selected properties of wheat flour. *Journal of Food Engineering*, 48, 345–350.
- Lawal, O. S. (2004). Succinyl and acetyl starch derivatives of a hybrid maize: Physicochemical characteristics and retrogradation properties monitored by differential scanning calorimetry. Carbohydrate Research, 339, 2673–2682.
- Liu, H., Ramsden, L., & Corke, H. (1999). Physical properties and enzymatic digestibility of hydroxypropylated ae, wx, and normal maize starch. Carbohydrate Polymers, 40, 175–182.
- Liu, H. S., Yu, L., Xie, F. W., & Chen, L. (2006). Gelatinization of cornstarch with different amylose/amylopectin content. *Carbohydrate Polymers*, 65, 357–363.
- Morikawa, K., & Nishinari, K. (2000). Rheological and DSC studies of gelatinization of chemically modified starch heated at various temperatures. *Carbohydrate Polymers*, 43, 241–247.
- Ollett, A.-L., Li, Y., Parker, R., & Smith, A. C. (1989). Comparative study of the conveying performance of screws in a twin-screw co-rotating extrusion-cooker. *Journal of Food Engineering*, 10, 165–181.
- Ollett, A. L., Parker, R., & Smith, A. C. (1991). Deformation and fracture behavior of wheat-starch plasticized with glucose and water. *Journal of Materials Science*, 26, 1351–1356.
- Pal, J., Singhal, R. S., & Kulkarni, P. R. (2002). Physicochemical properties of hydroxypropyl derivative from corn and amaranth starch. *Carbohydrate Polymers*, 48, 49–53.
- Perera, C., Hoover, R., & Martin, A. M. (1997). The effect of hydroxypropylation on the structure and physicochemical properties of native, defatted and heatmoisture treated potato starches. *Food Research International*, 30, 235–247.
- Perry, P. A., & Donald, A. M. (2002). The effect of sugars on the gelatinisation of starch. *Carbohydrate Polymers*, 49, 155–165.
- Plantic Technologies Ltd. (2007) YeBiodegradable lethal ovitrapar (Vol. 2007) Melbourne.
- Rauwendaal, C. (1990). Polymer Extrusion. Munich: Hanser Publishers.
- Seker, M. (2005). Residence time distributions of starch with high moisture content in a single screw extruder. *Journal of Food Engineering*, 67, 317–324.
- Shogren, R. L., Swanson, C. L., & Thompson, A. R. (1992). Extrudates of cornstarch with urea and glycols – structure mechanical property relations. Starch-Stärke, 44, 335–338.
- Slade, L., & Levine, H. (1993). Water relationships in starch transitions. Carbohydrate Polymers, 21, 105–131.
- Stevens, M. J., & Covas, J. A. (1995). Extruder principles and operation. London: Chapman & Hall.
- Swift, G. (1996). YePolymers, environmentally degradablear. In Kirk-Othmer encyclopedia of chemical technology (Vol. 2000). John Wiley & Sons, Inc.
- Tan, I., Wee, C. C., Sopade, P. A., & Halley, P. J. (2004). Estimating the specific heat capacity of starch-water-glycerol systems as a function of temperature and compositions. Starch-Stärke. 56, 6–12.
- Thuwall, M., Boldizar, A., & Rigdahl, M. (2006). Compression molding and tensile properties of thermoplastic potato starch materials. *Biomacromolecules*, 7, 981–986.
- Tolstoguzov, V. B. (1993). Thermoplastic extrusion the mechanism of the formation of extrudate structure and properties. *Journal of the American Oil Chemists Society*, 70, 417–424.
- Trommsdorff, U., & Tomka, I. (1995). Structure of amorphous starch 1. An atomistic model and X-ray scattering study. *Macromolecules*, 28, 6128–6137.
- Valle, G. D., Barres, C., Plewa, J., Tayeb, J., & Vergnes, B. (1993). Computer simulation of starchy products' transformation by twin-screw extrusion. *Journal of Food Engineering*, 19, 1–31.
- Van Lengerich, B. & Meuser, F. (1985). YeQuality optimization and scale-up possibilities of extruded cereal products through system analysis and RSMar. In 1985 Annual meeting American institute of chemical engineers. AIChE, New York, NY, USA, Chicago, IL, USA, pp. 29.
- Van Soest, J. J. G., De Wit, D., & Vliegenthart, J. F. G. (1996). Mechanical properties of thermoplastic waxy maize starch. *Journal of Applied Polymer Science*, 61, 1927–1937.
- Van Soest, J. J. G., Hulleman, S. H. D., De Wit, D., & Vliegenthart, J. F. G. (1996). Crystallinity in starch bioplastics. *Industrial Crops and Products*, 5, 11–22.
- Wiedmann, W., & Strobel, E. (1991). Compounding of thermoplastic starch with twin-screw extruders. *Starch–Stärke*, 43, 138–145.
- Yeh, A.-I., Hwang, S.-J., & Guo, J.-J. (1992). Effects of screw speed and feed rate on residence time distribution and axial mixing of wheat flour in a twin-screw extruder. *Journal of Food Engineering*, 17, 1–13.
- Yu, L., & Christie, G. (2005). Microstructure and mechanical properties of orientated thermoplastic starches. *Journal of Materials Science*, 40, 111–116.
- Yuliani, S., Torley, P. J., D'Arcy, B., Nicholson, T., & Bhandari, B. (2006). Extrusion of mixtures of starch and d-limonene encapsulated with β-cyclodextrin: Flavour retention and physical properties. Food Research International, 39, 318–331.