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

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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.

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 Patent 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

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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 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

Table 1
Starch 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.
[*] Moisture content determined using Sartorius Moisture Content Analyser with an error of ±0.0002.

Table 2
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

Fig. 1. Schematic of screw configuration from twin screw extruder (not to scale).