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Extrusion processing and characterization of edible starch films with different amylose contents

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ABSTRACT

Various edible starch films were prepared via extrusion, with a particular focus on the effects of the amylose content of starches from the same resource (corn) on film processibility and performances. Four corn starches with different amylose contents (4.3–77.4%) were used as model materials. The effects of various extrusion processing conditions, such as temperature, screw speed, feeding rate, and water content were systematically investigated. It was found that, while a higher amylose content increased the difficulty of extrusion processing, this could be overcome by increasing the processing temperature, moisture content, and equilibration time. On the other hand, mechanical testing, differential scanning calorimetry, dynamic mechanical analysis, and microscopy showed that films based on higher amylose starch had better mechanical and thermal properties. The reasons include not only the easy entanglement of long linear amylose chains, but also the retained granular structure in high-amylose films, which may act as self-reinforcement.

1. Introduction

The use of edible films in the food industry has been constantly increasing (Arvanitoyannis et al., 1997, 1998; Beverlya et al., 2008; Carvalho et al., 2008; Chambi and Grosso, 2006; Cho et al., 2007), and starch-based films play a key role in this application, as starch is cheaper and more readily available worldwide than other natural resources. Although extrusion processing techniques for producing starch films have been developing for many years, there are few commercial products on the market, mainly because extrusion parameters such as barrel temperature, moisture content, screw speed, and feed rate have a significant influence on processibility. Furthermore, the extrusion of starch-based materials is much more complex than that of conventional polymers due to their multiphase transitions during processing, such as gelatinization, melting, decomposition, and recrystallization (Chen et al., 2007; Dean et al., 2007; Fishman et al., 2000; Ilo et al., 1999; Xue et al., 2008).

Starch is a polymeric carbohydrate consisting of anhydroglucose units linked together primarily through α-D-1,4 glucosidic bonds. Although the detailed microstructures of starch are still being elucidated, it has generally been established that starch is a heterogeneous material consisting of two microstructures – one linear (amylose), and the other branched (amylopectin). Amylose is essentially a linear structure of α-1,4-linked glucose units, making its behaviour more closely resemble that of conventional synthetic polymers. In addition, its molecular weight of about $\times 10^6$ is 10 times higher than that of conventional synthetic polymers. Amylopectin, on the other hand, has a highly branched structure of short α-1,4 chains linked by α-1,6 bonds, and its molecular weight is about $\times 10^8$, which is much greater than amylose. The high molecular weight and branched structure of amylopectin reduce the mobility of the polymer chains, and interfere with any tendency for them to orient closely enough to allow significant hydrogen bonding. Furthermore, most native starches are semi-crystalline, having a crystallinity of about 15–45% (Zobel, 1988).

In a starch, the amylose and the branching points of amylopectin form amorphous regions. As the short branching chains in the amylopectin are the main crystalline component in granular starch (Veregin et al., 1986), starches with different amylose/amylopectin ratios will behave differently during phase transition (Liu et al., 2006, 2007, 2009a; Xue et al., 2008) and have different rheological properties during extrusion (Chen et al., 2007; Della Valle et al., 2007; Xie et al., 2009).

Sheets and films based on high-amylose starch normally exhibit greater mechanical performance (Chaudhary et al., 2009; Van Soest and Borger, 1997). The extrusion of high-amylose starch, however,

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is more difficult than normal starches, because a higher die pressure is required due to the higher melt viscosity and unstable flow (Thuwall et al., 2006) under some conditions.

Starch cannot be thermally processed without a plasticizer or gelatinization agent, since its decomposition temperature is lower than its melting temperature before gelatinization (Liu et al., 2008). Various plasticizers and additives to gelatinize starch during thermal processing have been developed and evaluated. Water (Hulleman et al., 1998) and glycerol (Bergo et al., 2010; Fishman et al., 2000; Yu et al., 2005) are the most commonly used plasticizers in starch-based materials. Starch-based polymers partly plasticized using glycerol could be phase-separated biphasic systems, which are different from materials processed with only water during extrusion cooking (Chaudhary, 2010; Lourdin et al., 1997). In order to simplify the experimental system in this research, water was the only plasticizer used.

A specific focus of this work was the effects of different amylose/amylopectin ratios in starches from the same source (corn) on processibility and film performance. Corn starches with different amylose contents (waxy, 4.3%; regular corn, 29.0%; Gelose 50, 61.5%; Gelose 80, 77.4%) were used as modal materials, and their processibility was evaluated using a twin-screw extruder with a film die, taking into account the torque and die pressure as major practical parameters. Furthermore, the effects on processing of the method used to add the water in starch were also investigated. In previous studies (Berzin et al., 2007; Bindzus et al., 2002; Brummer et al., 2002; Chuang and Yeh, 2004), the specific mechanical energy (SME) has frequently been used to measure the energy input and thus the degradation and decrease in viscosity during processing. The three key factors influencing SME are screw speed, torque, and mass flow rate, which also have an interactive influence on each other. In this work, these factors will be separately studied to give a better understanding of their effects. The extruded starch films with different amylose contents were characterized by tensile and impact testing, microscopy, differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA) to gain a better understanding of their performance.

2. Experimental

2.1. Materials

Four commercially available corn starches with different amylose/amylopectin ratios were used as modal materials in this work:

- Waxy (4.3% amylose content), supplied by Shanxi Jinli Industry Group Co., Ltd.
- Regular (29.0% amylose content), supplied by Huanglong Food Industry Co., Ltd.
- Gelose 50 and Gelose 80 (61.5 and 77.4% amylose content, respectively), supplied by Penford Australia.

The amylose content of the starches was ascertained by the iodine-binding method (Morrison and Laignelet, 1983), and an infrared heating balance (Model DHS-20) was used to measure the moisture contents of starch samples heated to 110 °C for 20 min. The moisture contents of the four corn starches prior to extrusion were 15.2%, 15.5%, 15.0% and 14.9%, respectively.

2.2. Film extrusion

As mentioned previously, water was the only plasticizer used for extrusion, and it was added to the starch in either of two ways:

- Separately feeding the water via a liquid feeder and the starch via a powder gravimetric feeder (GBL SS ST) during extrusion.
- Premixing the starch and water in a high-speed mixer (SRL-Z) at 1500 rpm for 5 min. This premixing evenly distributed low water contents (25–40% in this work) into the native starch powder, and the resultant mixture retained a powdery state. The premixed samples were then stored overnight in hermetically sealed polyethylene bags before extrusion.

Starch films were extruded using a Haake twin-screw extruder (Rheomex PTW 24/40p, Ø30, screw diameter $D = 24$ mm, screw length $L = 28D$) with a 150 mm wide film die. There are eight temperature controlling zones along the barrel of the extruder. A haul-off device was used for collecting the extruded films. Fig. 1 shows a schematic representation of the extrusion system. The effect of extrusion temperature on the processibility of starch was studied by varying the temperature in zones 4, 5 and 6 between 115 and 180 °C, while keeping temperatures in the other zones constant. Based on the starch type and moisture content used, the temperature of the die was accordingly adjusted to between 90 and 100 °C to avoid bubbling but to ensure a smooth flow through the die. A feeding rate of 1.2–2.4 kg/h was used and the extruder screw speed was varied between 30 and 120 rpm.

After extrusion, starch films were conditioned for a week in an environment chamber at about 75% relative humidity (RH) and room temperature prior to characterizations. The RH was maintained by saturated solution of sodium chloride in the chamber. The final moisture contents of the starch films was 17.0 ± 0.5%, which was calculated by the weight loss after drying in a vacuum oven at 120 °C for 24 h.

2.3. Mechanical testing

The tensile properties of samples were determined using an Instron Universal Testing Machine (5566). The films were cut parallel to the extrusion direction into dumbbell-shaped strips, according to ASTM D882-10. The waxy starch-based film was tested performed using a low cross-head speed (1.0 cm/min) due to its relatively brittle nature. Impact properties were evaluated using an Instron Impact Testing Machine (9250G) according to ASTM D1709-09. All data was recorded and processed using Instron computer software, and the results presented here are the averages of 10 replicate tests.

2.4. Microscopy

A microscope (Axioskop 40 Pol/40 A Pol, Zeiss) with both normal and polarized light was used to investigate the microstructure of extruded starch films. Films were cut into small squares (about 15 × 15 mm and about 0.23 mm thick) and each specimen was clipped between two microscopic glass slides, and photographs were taken under both lights at a magnification of 500 (50 × 10). For comparison purposes, the native starches were dispersed in distilled water at a concentration of about 0.5% and were also studied. At least five replicates were performed for each sample to ensure consistency of results.

2.5. Differential scanning calorimetry (DSC)

A PerkinElmer Diamond DSC with an internal coolant (Intercooler 1P) and nitrogen purge gas was used to investigate the endothermic behaviours of the native starches and extruded starch films. For each experiment, an approximately 2 mg sample was sealed in an aluminum pan (PE No. 0219-0041) and heated from 30 to 200 °C at a rate of 10 °C/min. For comparison purposes, native starches conditioned in the environment chamber under the same