



Thermal extrusion of starch film with alcohol



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ABSTRACT

A one-step thermal extrusion process has been investigated for the modification of starch with alcohol in order to improve the film properties. Unmodified starch/glycerol mixtures containing Methanol (MeOH), ethanol (EtOH) and their combinations (5, 10 and 15 wt%) were thermally extruded to produce thermoplastic. The final hot-pressed film showed increased stiffness and crystallinity, while having decreased moisture uptake due to oxidation and alcohol complexing molecular interactions. The Young's Modulus, tensile strength and elongation at break increased by 60%, 15% and 32% respectively, for 5 wt% MeOH derived film, compared to the control. The film moisture content was reduced by up to 15 wt% for 5 wt% EtOH-derived film. Generally the crystallinity increased in the alcohol-derived films due to an increased complexing of alcohol with starch forming the V_H polymorph. Fourier transform infra-red (FTIR) and proton nuclear magnetic resonance (¹HNMR) spectroscopic analysis were used to discuss the molecular interactions between the starch and alcohol molecules.

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1. Introduction

There are environmental concerns by the general public to reduce the carbon footprint and issues surrounding the disposal of fossil-based non-degradable plastics that pollute the environment. The current and continuing trend towards environmental sustainability along with increasingly stringent governmental legislation is driving manufacturers to increase investment and development in biodegradable plastics (Avérous and Pollet, 2012; Ho et al., 2012). Total consumption of biodegradable polymers is also expected to grow by nearly 15% annually from 2012 to 2017 in Asia, Europe and North America (Wright, 2015). Increasing prices and limited applications of biodegradable plastics have led many researchers to

focus on production of starch-based polymers to replace fossil-based plastics.

Thermal extrusion is one of the most widely used techniques to process starch-based polymers. It allows easier handling in the presence of small quantities of solvents, has a broad range of processing conditions and ensures good mixing that minimises phase separation. Starch can be processed into thermoplastic materials in the presence of plasticizers using heat and shear by extrusion (Liu et al., 2009). However, compared to synthetic plastics thermoplastic starch has a disadvantage since starch composites inherently absorb water that weakens the mechanical properties (Azeredo, 2009). One approach to help address these shortcomings is by incorporating through melt blending or reactive extrusion additives that will stiffen and cross-link the starch polymer (DeLeo et al., 2010; Liu et al., 2009; Miladinov and Hanna, 2001; Zhang et al., 2007). The advantages of the reactive extrusion process are: flexibility; low infrastructure cost; high throughput processing; and high conversion rates with few by-products (Moad, 2011).

Thermally extruded modified (oxidized) starch with alcohol has been shown to improve starch film properties. Starch oxidation

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improves moisture resistance with hydrophobic carbonyl groups replacing the hydrophilic hydroxyl groups in starch polymer film. Miladinov and Hanna (2001) thermally extruding acetylated starch with ethanol which produced a film with significantly improved spring indices while not adversely affecting compressibility or unit density. Miladinov and Hanna (2001) produced foam at 160 °C with 18 wt% (dry wt. basis) ethanol that gave the largest increase in springiness. Zhang et al. (2007) reacted ethanol and methanol with dialdehyde (oxidized) starch to form acetals that resulted in thermal plastic films with improved: mechanical/thermal properties and lower humidity absorption compared to the control film.

Our challenge has been to produce starch-based films that can be used in applications such as the production of sustainable biodegradable packaging materials. As a consequence of previously reported research, thermal reactive extrusion was chosen in this study to improve starch film properties. It was hypothesized that starch, glycerol and alcohols (MetOH and EtOH) will intimately react in one-step (oxidation/etherification or esterification) when processed at the temperatures, pressures and shearing rates present inside a twin-screw extruder. This study involved the use of methanol and ethanol and their mixtures that required special air ventilation of the laboratory to avoid any safety hazards. The properties of the films were examined by gravimetry, X-ray powder diffraction (XRD), thermogravimetric analysis (TGA), tensile testing and dynamic mechanical thermal analysis (DMTA). The microscopic structures of the films were examined by Fourier Transform Infra-red (FTIR) and proton nuclear magnetic resonance spectroscopy (¹HNMR) to provide further evidence on the differences in the mechanical properties.

2. Experimental

2.1. Materials

The high amylose maize starch (Gelose 80) (80 wt% amylose) used was generously supplied by National Starch Pty. Ltd. (Lane Cove, NSW, Australia). Glycerol, ethanol (EtOH) and methanol (MetOH) were purchased from (Merck Kilsyth, Vic, Australia).

2.2. Film preparation method

2.2.1. Composite mixture proportions used in experiment

High amylose starch (Gelose 80) (100 g), glycerol (30 g) and water (35 g) were thoroughly mixed together before addition of 0, 5, 10 and 15 wt% alcohol (based on starch wt) combinations in the feed mixture. The starch mixture was stored overnight allowing diffusion of glycerol, water and alcohol into the starch granules. The mixture was fed into the thermal extruder at the rate of 35 g/min. Safety concerns for any flammable or toxic alcohol fumes present were addressed by keeping alcohol concentrations minimal and by continuously extracting the laboratory air. Specially designed purpose built strong air ventilation fans were used that continuously refreshed/replaced the lab atmosphere with clean fresh air.

2.2.2. Thermal reactive extrusion film preparation method

Thermoplastic starch was produced by thermal extrusion using a co-rotating twin screw extruder Prism (Eurolab, England), Fig. 1. Extensive experimentation was conducted before the desired operating conditions were established. The extruder barrel temperature profile was 35/70/100/130/130/120/110/80/80/90 °C from the feeder to the die end. This temperature profile readily volatilizes the alcohol used in the process.

The screw rotational speed was 110–120 r.p.m., which gave a residence time of 1.75–2.25 min and pressure that developed at the die end from 14 to 17 bar. The screws with a diameter of 16 mm and

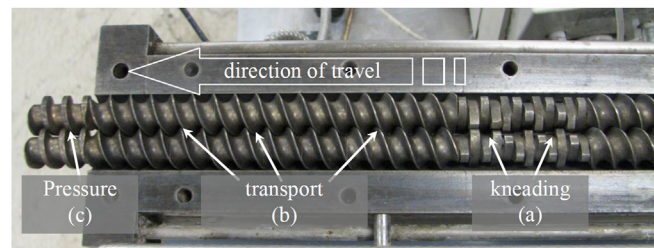


Fig. 1. Thermal extrusion machine with the top removed to expose part of the twin screws showing some of the: (a) kneading, (b) transport and (c) pressure element sections of the twin co-rotating screws.

L/D ratio of 40 were equipped with three kneading element sections (Fig. 1). The last section of the screw has thickened flutes developing the pressure required to extrude the plasticised starch through two 3 mm holes in the die (end section). Two 3 mm cylindrically extruded plastic strands were produced upon exiting the die, Fig. 2.

2.2.3. Hot pressing

Uniform films were prepared by pelletising (cutting into 4–5 mm lengths) the plastic strands prior to hot pressing. Hot pressing was conducted in a brass plate mould (90 mm × 60 mm × 1 mm) for 15 min at 130 °C between non-stick sheets. This ensured any residual alcohol was completely removed (EtOH boiling point (b.p.) 78.4 °C; MetOH b.p. 64.7 °C) as well as the complete melting/fusion of the plastic during film formation. A force of 7.5 t (m) was applied and maintained during the cooling period until 65 °C was reached to avoid foaming of the film by escaping steam bubbles. All films were conditioned at 58% RH (23 °C) before assessing film properties.

2.2.4. Moisture conditioning

All films were placed into a relative humidity (RH) chamber that contained a saturated aqueous salt solution of NaBr that created a 58% RH atmosphere at 23 °C (Greenspan, 1976). The films were left in the chamber until they reached moisture equilibration with the 58% RH (23 °C) atmosphere. Moisture uptake was determined gravimetrically based on the average of four sample measurements.

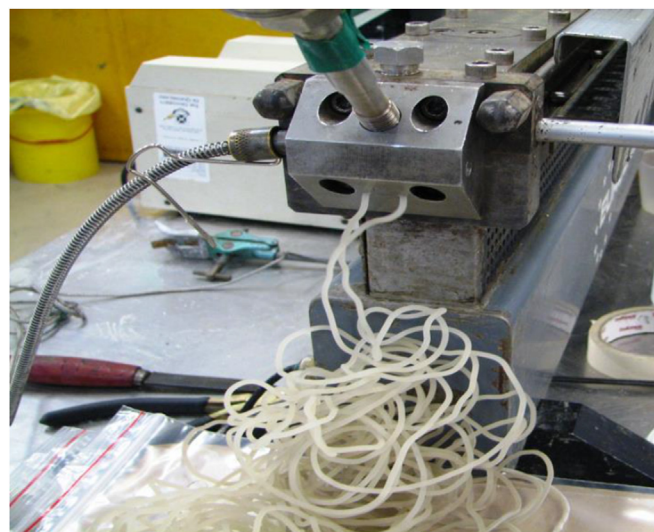


Fig. 2. The two strands of thermoplastic starch exiting the die section of the extruder.

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