



# Hydroxypropylation improves film properties of high amylose corn starch



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## ABSTRACT

Important characteristics of solvent-cast films prepared with modified high amylose corn starch were compared. The hydroxypropylation of high amylose corn starch with propylene oxide at 3–12% (w/w starch basis) and glycerol as plasticizer reduced film brittleness. Increasingly intact and transparent films with higher elongation at break ( $E$ ) were obtained with higher concentrations of propylene oxide-  $E$  increased from 37.55 to 63.37% for 3 and 12% propylene oxide, respectively. However, corresponding tensile strength (TS) of the films decreased from 15.98 MPa to 8.85 MPa. Plasticizer types (glycerol, sorbitol, xylitol, and mixtures of glycerol/sorbitol or glycerol/xylitol) and contents (10–25%, w/w of starch) strongly affected the film formation and characteristics of hydroxypropylated high amylose corn starch. The hydroxypropylation with 6% (w/w) propylene oxide (6HPHACS) and 20% (w/w) glycerol resulted in optimal cast-films, based on both appearance and mechanical properties. These films exhibited better flexibility with adequate tensile strength and water vapor permeability.

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## 1. Introduction

Utilizing renewable resources for industrial applications has become an important consideration due to economic and environmental concerns, for example, development of biodegradable plastics from renewable biopolymers. Starch is one such promising resource for biopolymer applications due to its abundance, renewability, low cost (0.25–0.6 dollar per kg), and thermoplasticity (Lai and Padua, 1997; Chiellini et al., 2009; Mali et al., 2005).

Granular starch has a semi-crystalline structure consisting of concentric alternating amorphous and semi-crystalline growth rings (French, 1984). The crystalline structure needs to be disrupted for starch to function as a film. This can be done in the presence of water and heat resulting in a homogeneous melt with thermoplastic properties (Shanks and Kong, 2012; Zdrachala, 1997). Conventional processing techniques, e.g., solvent-casting, extrusion-blowing, and injection or compression molding, have been adapted to obtain thermoplastic starch (TPS) (Van Soest et al., 1996).

Thermoplastic starches from various sources, e.g., rice, cassava, corn, and potato, etc. have been studied in the past for packaging applications; however, they exhibit several shortcomings such as

brittleness, lower mechanical properties and higher water sensitivity. Zhang et al. (2014) summarized properties of some TPS films made from unmodified starches. Tensile strength of films was typically less than 5 MPa with corresponding water vapor permeability up to 748.80 g mm m<sup>-2</sup> day<sup>-1</sup> kPa<sup>-1</sup>. Low-density polyethylene (LDPE), which is one of the most widely used synthetic polymers, was reported to have a tensile strength of 7.60–17.30 MPa and water vapor permeability of 0.08 g mm m<sup>-2</sup> day<sup>-1</sup> kPa<sup>-1</sup> (Briston, 1988).

Selecting starch sources with higher amylose content could be one way of overcoming said drawbacks in starch-based films. Several studies (Lopez and Garcia, 2012; Phan et al., 2005; Myllärinen et al., 2002; Muscat et al., 2012) have shown that starch films with higher apparent amylose content (up to 80%) were stronger and more water resistant than those with normal corn starch (apparent amylose content ca. 28%) (Van Soest et al., 1996). Nevertheless, the use of high amylose starch for film applications is rather limited, mostly due to its high melt viscosity (Thuwall et al., 2006), which is related to inherent high melting temperature of amylose (Shogren, 1992). There are a few studies on the use of native high amylose starches, and films have been mostly produced by extrusion under higher pressures and temperatures (Thuwall et al., 2006; Chaudhary et al., 2009). Chemical modifications of starch may lend them amenable to film formation at lower temperatures and pressures.

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The hydroxypropylation is one such chemical modification that results in starch ether when starch and propylene oxide are reacted (Tsuzuki, 1968). Hydroxypropyl group ( $-\text{CH}_2\text{CHOHCH}_3$ ) disrupts hydrogen bonds in the starch so that weakened starch can be more easily accessible to water (Wootton and Manatsathit, 1983, 1984). The gelatinization temperatures ( $T_0$ ,  $T_p$ , and  $T_c$ ) and enthalpies ( $\Delta H$ ) of hydroxypropylated starches are lower than those of native starch and is related to the degree of substitution. Peak gelatinization temperatures ( $T_p$ ) of normal maize starch were 68, 60, 54, and 50 °C after hydroxypropylation with 0, 4, 12, and 16 mL of propylene oxide (200 g dry starch basis), respectively (Wootton and Manatsathit, 1984). Lower gelatinization temperatures allow easy formation of hydroxypropylated high amylose starch films.

Rice (30% apparent amylose), potato (86% apparent amylose), and pea (34% apparent amylose) starches have been used for preparation of high amylose starch films (Wogugum et al., 2015; Jansson and Järnström, 2005; Lafargue et al., 2007). Use of high-amylose corn starch can also be found in the literature (Zhang et al., 2013a,b; Gilfillan et al., 2013; Dean et al., 2011; Isotton et al., 2015; Chaudhary et al., 2009; Bae and Lim, 1998). However, there is no information about properties of hydroxypropylated high amylose corn starch films as affected by propylene oxide levels. Thus, the aim of this study is to evaluate the effect of propylene oxide levels on solvent-cast films from high amylose corn starch (75% apparent amylose). The properties of optimally hydroxypropylated high amylose corn starch (HPHACS) were further investigated, e.g., optical, mechanical, and barrier properties with different plasticizers types and contents.

## 2. Materials and methods

### 2.1. Materials

Normal corn starch (NCS, PURE-DENT B700) was provided by Grain Processing Corporation (Muscatine, IA, USA). High amylose corn starch (HACS, AmyloGel™) containing 75% apparent amylose was provided by Cargill (Minneapolis, MN, USA). Glycerol, sorbitol, xylitol, propylene oxide, and magnesium nitrate ( $\text{Mg}(\text{NO}_3)_2$ ) were purchased from Fisher Scientific (Fair Lawn, NJ, USA). All other chemical reagents used were of analytical grade.

### 2.2. Hydroxypropylation (HP) of high amylose corn starch (HACS)

Hydroxypropylation reaction for high amylose corn starch (HPHACS) followed the procedures as described by Wootton and Manatsathit (1983) with some modifications. HACS (80 g, dry solids) was dispersed in distilled water (640 mL) containing anhydrous sodium sulfate (8%, w/w of starch), and pH adjusted to 11.5 using 1 M NaOH. Various amounts of propylene oxide (3, 6, and 12%, w/w of starch) were added dropwise to slurry with vigorous stirring at room temperature. The reaction bottle was sealed tightly and shaken in a water bath (150 rpm, 45 °C) for 20 h. Starch slurry was then neutralized to pH 5.5 by adding 1 M HCl. The recovered starch after centrifugation ( $1500 \times g$  for 20 min) was washed with distilled water (3 $\times$ ), and dried at 40 °C for 24 h. The dried starch was passed through an ASTM E-11 standard sieve (aperture 300  $\mu\text{m}$ ) and used for solvent casting of films.

The hydroxypropyl substitution (%) of starch was determined by using spectrophotometric method (Johnson, 1969). The moles of substituent per mole of anhydroglucose unit (MS) was calculated as:

$$\text{MS} = 162W/100M-(M-1)W$$

where, W is equivalent hydroxypropyl group in 100 mg of starch, M is molecular weight of propylene oxide ( $\text{C}_3\text{H}_6\text{O}$ ).

### 2.3. Thermal properties of HPHACS

Gelatinization properties of HPHACS were measured using differential scanning calorimeter (DSC 7, Perkin-Elmer, Norwalk, CT, USA). Starch (3 mg, dry solids) was weighted into an aluminum pan with 9  $\mu\text{L}$  of distilled water. The pan was sealed and equilibrated at room temperature for 2 h and then heated from 20 to 130 °C at a heating rate of 10 °C/min with an empty pan as reference. The analysis was done in duplicate.

### 2.4. Solvent casting of starch films

All starches used in this study were defatted first, as presence of lipid in the starch was reported to reduce the maximum elongations of films (Bader and Göritz, 1994). Native and hydroxypropylated starches (9 g, dry solids) dispersed in aqueous DMSO solution (90%, w/v, 300 mL) were heated in boiling water bath for 1 h, and continuously stirred overnight at room temperature. Precipitated starch was washed with absolute ethyl alcohol (250 mL  $\times$  2 times) (Klucinec and Thompson, 1998). No amylose-lipid complex peak was detected following this treatment. The purified wet starch was dispersed in hot water (60 °C, 20 mL/g of dry starch). Aliquot of hot water was added into calculated amount of plasticizers on starch weight basis (10, 15, 20, and 25% glycerol, sorbitol, xylitol, and 50:50 mixtures of glycerol/sorbitol or glycerol/xylitol) and stirred for 20 min for full dissolution of plasticizer in hot water. The plasticizer solution was added into starch solution and mixed in a water bath at 100 °C for 1 h with vigorous stirring. In the case of native high amylose corn starch, additional autoclaving at 130 °C was done for 20 min. The hot solution was centrifuged at  $1500 \times g$  for 1 min to remove air bubbles. The solution (136 mL) was cast onto glass-plates (155  $\times$  205 mm) placed on a level wood slab, and cooled down for 2 h followed by drying at 50 °C overnight. Dried films were peeled from the glass-plates and used for further analysis.

### 2.5. Characterization of cast films

#### 2.5.1. Thickness

The film thickness was determined using an electronic digital caliper (Marathon, Ontario, Canada) with an accuracy of 0.01 mm. The rectangular film specimens (20  $\times$  68 mm) were equilibrated at 25 °C for 2 days in a sealed chamber at 53% RH maintained with saturated solution of magnesium nitrate (Wexler and Hasegawa, 1954). Thickness of the equilibrated films was measured at 3 random positions and average values reported.

#### 2.5.2. Transparency

Starch film transparency was measured following method described by Li et al. (2015). A rectangular specimen (10  $\times$  3.5 mm) was placed in a spectrophotometer cell. The absorbance was measured at 600 nm using the UV-vis spectrophotometer (Shimadzu UV-160, Japan). Three replicates for each film specimen were done and the average values reported. Film transparency was calculated by dividing the absorbance with thickness (mm). The higher transparency value indicated lower transparency.

#### 2.5.3. Mechanical properties: tensile test

Mechanical properties of film were measured in tension using a universal testing machine (Instron 4500 series, USA) following the ASTM D882-02 guideline (2002). The rectangular specimens (20  $\times$  68 mm) were equilibrated at 25 °C and 53% RH for 2 days, prior to testing. Initial grip distance and crosshead speed were 50 mm and 50 mm/m in, respectively. Tensile strength (TS, MPa) was obtained by dividing the maximum load with specimen cross-sectional area. Elongation at break ( $E$ , %) was defined as the percent change in specimen length over the length between the grips at

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