Hydroxypropylation improves film properties of high amylose corn starch

Hee-Young Kim^a, Jay-lin Jane^a, Buddhi Lamsal^a *

^a Department of Food Science and Human Nutrition, Iowa State University, Ames, IA
50011, USA

*Corresponding author. Tel: +1 515 294 8681; Fax: +1 515 294 8181.

E-mail address: lamsal@iastate.edu (B. Lamsal)

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.

Keywords

Cast-film; High amylose corn starch; Hydroxypropylation; Mechanical properties

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., 2005a).

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; Zdrahala, 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., 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. (2014b) 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⁻² day⁻¹ kPa⁻¹. 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⁻² day⁻¹ kPa⁻¹ (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 (Thunwall 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 (Thunwall et al., 2006; Chaudhary et al., 2009). Chemical modifications of starch may lend them amenable to film formation at lower temperatures and pressures.

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; Wootton and Manatsathit, 1984). The gelatinization temperatures (T_o , T_p , and T_c) and enthalpies (ΔH) 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 (Woggum 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., 2013 a, 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 1M 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 1M HCl. The recovered starch after centrifugation (1500 x g for 20 min) was washed with distilled water (3

X), and dried at 40°C for 24 h. The dried starch was passed through an ASTM E-11 standard sieve (aperture 300 µm) 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:

$$MS = 162W / 100M - (M-1) W$$

where, W is equivalent hydroxypropyl group in 100 mg of starch, M is molecular weight of propylene oxide (C₃H₆O).

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 µL 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×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 x g for 1 min to remove air bubbles. The solution (136 mL) was cast onto glass-plates (155 × 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 × 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 × 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 × 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/min, 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 break (Muscat et al., 2012). At least 5 specimens were tested for each film sample.

2.5.4. Fourier transform infrared (FT-IR)

FT-IR analysis of starch films was done for evaluating interactions between film components (starch and plasticizer). Absorbance spectra of the films were acquired using a Tension 37 FTIR spectrophotometer (Bruker Co., Ettlingen, Germany) in attenuated total reflectance (ATR) mode. Films conditioned at 25°C and 53% RH for 2 days were placed on the zinc selenide crystal (10×45×4 mm). The spectra were obtained in 400-4000 cm⁻¹ range by accumulation of 16 scans at 4 cm⁻¹ resolution. Area measurements and baseline corrections were carried out using OPUS 7.2.139 software (Bruker Co., Ettlingen, Germany).

2.5.5. Moisture content

Moisture content of films was determined by measuring the weight loss (20 × 20 mm) upon drying in a convection oven at 110°C until a constant dry weight was reached (Ghasemlou et al., 2013). At least duplicate samples for each film was used to measure the moisture content.

2.5.6. Water vapor permeability

Water vapor permeability (WVP) of starch films was determined gravimetrically using the dry cup method following ASTM D1653-13 guideline (2013). The test cup (Elcometer

5100, Payne permeability cup, Argenteau, Belgium) was filled with desiccant (calcium sulfate) to produce 0% RH and covered with film sample (diameter: 76.2 mm). The cup was fixed with four screws and placed in the chamber (ESPEC EPL-3H, Hudsonville, MI, USA) with 400 cubic feet per min airflow. The temperature and relative humidity of the chamber were 23°C and 50%, respectively. Water vapor transport into the cup was determined by the weight gained by desiccant in the cup. The cup was weighed to the nearest 0.1 mg periodically. Linear regression was used to fit the data, weight vs. time, to calculate the slope of the linear portion of the plot, which represents the steady state amount of water vapor diffusing through the film per unit time. The average time frame of the linear region was 50 h. The water vapor transmission rate (WVTR) was calculated from the slope of the linear portion, $\Delta W/\Delta t$, divided by the film area (A) as Eq. (1), ($\text{g day}^{-1} \text{m}^{-2}$).

$$\text{WVTR} = \Delta W / (\Delta t \cdot A), \quad (1)$$

Where, ΔW is the weight of water absorbed in the test cup (g), Δt is the time for weight change (day), A is the area exposed to moisture transfer (m^2). The water vapor permeability (WVP) was calculated as Eq. (2), ($\text{g mm day}^{-1} \text{kPa}^{-1}$)

$$\text{WVP} = (\text{WVTR} \times L) / \Delta p, \quad (2)$$

Where, L is the thickness of the film (mm) and Δp is the difference of partial water vapor pressure across the film ($\Delta p = p(\text{RH}_2 - \text{RH}_1)$, (kPa), where p is the saturation vapor pressure of water at 23°C, $\text{RH}_1 = 0\%$, $\text{RH}_2 = 50\%$. At least duplicate samples for each film was used to measure the water vapor permeability.

2.5.7. Oxygen permeability

Oxygen transmission rate of films was determined according to ASTM D3985-05 guideline (2010) using an Mocon OX-TRAN 2/20 (Minneapolis, MN, USA). The film sample equilibrated at 50% RH and 23°C for 2 days was placed on a stainless-steel mask with open

test area of 5 cm². Different gases passed on either side of the film- oxygen (100%) passed on one side of the film and nitrogen (98% N₂ and 2% H₂) on the other side. After leaving the sample chamber, nitrogen gas passed over to the coulometric oxygen sensor to measure oxygen concentration in nitrogen gas.

Oxygen permeability (OP) was calculated by dividing oxygen transmission rate by the difference in oxygen partial pressure between both sides of the film and multiplying by the average thickness of the film. Measurements were performed in duplicate at least and the unit for OP was cm³ μm m⁻² day⁻¹ kPa⁻¹.

2.6. Statistical analysis

Statistical analysis consisted of an analysis of variance (ANOVA) using SAS 9.4 software (SAS Institute, Cary, NC, USA). Duncan's multiple range test ($p < 0.05$) was done to identify statistical differences between mean values.

3. Results and Discussion

3-1. Film-forming ability of HACS

Fig. 1 presents the cast-films prepared from normal corn starches with apparent amylose content 25% or 75% (Fig 1a), and hydroxypropylated starches (Fig 1b). The normal corn starch (NCS) films plasticized with 20% (w/w) glycerol were structurally intact and had smooth surfaces (Fig 1(a)). On the other hand, high amylose corn starch (HACS) films with same amount of glycerol were brittle and cracked severely, thus, only a portion with the intact film could be used for testing.

One possible reason for severe cracking might be the different sensitivity of amylose and amylopectin to the plasticizers (Myllärinen et al., 2002), which is to decrease the inherent brittleness of starch by reducing the inter- or intra-molecular forces between starch chains, consequently, increase the flexibility of films (Souza and Andrade, 2002). Myllärinen et al. (2002) showed that amylose film was rather stronger (tensile strength of 10 MPa), whereas, the amylopectin film had lost its strength entirely when both films were plasticized with 30% glycerol. A similar trend was reported by Muscat et al. (2012). Elongation at break (E , %), which generally shows a trend opposite to the tensile strength, was higher for corn starch films with lower (25%) apparent amylose content compared to higher (80%). Lopez and Garcia (2012) observed that films made from ahipa starch with lower (11.6%) apparent amylose had higher E values at 21.8%, compared to 4.10% for starch films with higher (23.9%) apparent amylose content. To prevent or reduce cracking in the HACS films, more plasticizer may be required compared to NCS films. In the preliminary study, it was found that when 40% (w/w) glycerol was added with HACS, the films maintained flexibility, but were very sticky. While higher levels of plasticizers may help reduce brittleness, too much of it will produce sticky films.

3-2. Hydroxypropylation (HP) of HACS and films Properties

To produce less brittle HACS films with minimum plasticizer, hydroxypropylation (HP) of starch was carried out. Reacting propylene oxide with starch under alkaline conditions yields starch containing hydroxypropyl groups, that is, hydroxypropylated starch (Gray and BeMiller, 2005). Prior literature (Woggum et al., 2015) had shown that hydroxypropylated rice starch films had higher elongation to break than native ones. Also, HP reduced gelatinization temperature, thus, films could be produce at lower temperatures. This is advantageous if starch with higher and broader melting temperature range like HACS is used for film (Liu et al., 2006). Table 1 shows the hydroxypropyl group (%), molar substitutions (MS), and reaction efficiency (%) in hydroxypropylated HACS (HPHACS) when reacted with 3-12% (w/w) propylene oxide, to be referred to as 3HPHACS, 6HPHACS, and 12HPHACS, respectively. Both percent hydroxypropyl groups and corresponding MS increased with the level of propylene oxide, as reported in literature (Woggum et al., 2015; Gray and BeMiller, 2005). The concentration of propylene oxide used in this study did not exceed the maximum allowable level for food applications which is less than 25%, based on the dry starch weight; Food Chemicals Codex, 1972).

Fig.1(b) shows the films made with up to 12% hydroxypropylated corn starches. The cracks observed in HACS film noticeably reduced after adding 3% (w/w of starch) propylene oxide; more propylene oxide (e.g., 6 and 12%, w/w of starch) led to intact HACS films, with hydroxypropyl groups also likely acting as plasticizer. Plasticizer inserted among and between starch chains increases film flexibility by weakening inter- and intra-molecular hydrogen bonding between starch chains by favorably forming hydrogen bonds between hydroxyl groups (-OH) of plasticizer and starch chains (Muscat et al., 2012). Similarly, during the hydroxypropyl groups (-CH₂CHOHCH₃), during hydroxypropylation, interacted with starch

chains, disrupting inter-and intra-molecular hydrogen bonds of the native starch. The extent of the disruption of hydrogen bonds between starch chains may be greater with more hydroxypropyl groups.

These observations of more flexible starches films with higher levels of HP could be related to their thermal properties. As shown in Fig. 2., both gelatinization temperatures (T_o , T_{p1} , T_{p2} , and T_c) and enthalpies (ΔH) of HPHACS decreased gradually with increasing levels of propylene oxide. Hydrophilic hydroxypropyl groups would facilitate water sorption into the starch, leading to lowering of gelatinization temperatures (Seow and Thevamalar, 1993). Also, hydroxypropyl groups would disrupt the double helices within the amorphous region in starch granules, owing to the rotation of flexible hydroxypropyl groups (Perera et al., 1997). As a result, enthalpies indicating loss of double helical order (Cooke and Gidely, 1992) were lower in HPHACS than in native HACS.

Mechanical properties of HPHACS films with 3-12% (w/w of starch) propylene oxide are presented in Table 2. All films tested were in the same thickness range (0.10 to 0.12 mm), and not significantly different. Films without propylene oxide, that is, native HACS films, showed TS of 18.90 MPa and E of 28.17%, respectively. The increase in propylene oxide levels (3-12%, w/w) led to decrease in film TS (from 15.98 to 8.85 MPa) and increase in the E values (from 37.55 to 63.37%). This result can also be explained by the role of hydroxypropyl groups in weakening the strong molecular attraction between starch chains, resulting in decreased TS of HPHACS films. The disruption of starch chains reduced rigidity and enhanced flexibility of HPHACS films by allowing increased chain mobility. Similar result was also reported for rice starch containing 30.4% apparent amylose and hydroxypropylated with propylene oxide at 6-12% (w/w of starch). The TS and E values of the films ranged from 5.53 to 3.88 MPa and from 79.58 to 132.59%, respectively, at the level of 6 and 12% of propylene oxide (w/w of starch)

(Woggum et al., 2015).

It is noteworthy that 6HPHACS films were intact without any cracks compared to 3HPHACS films (Fig. 1b). The difference in hydroxypropyl groups (%) influenced this morphological difference. Based on our results, the minimum level of hydroxypropyl groups required to obtain intact HACS film may be between 1.4 to 2.5%. Excessive hydroxypropyl groups rather led to sharply decreased TS in films. Along with mechanical properties, transparency of HACS films was also affected by the degree of hydroxypropylation (Fig. 1(b) and Table 2). Increasing the level of propylene oxide increased film transparency, as shown by higher transmission of light across the films. It is assumed that bulky and hydrophilic hydroxypropyl groups would restrict reassociation of amylose chains (Choi and Kerr, 2004), thus, improving transparency.

3-3. Effect of plasticizers on 6HPHACS films

3-3-1. Mechanical properties

The 6HPHACS starch films were further prepared with various plasticizers and their properties were compared for effect of plasticizers. These 6HPHACS films plasticized with glycerol, sorbitol, xylitol and mixtures of glycerol/sorbitol or glycerol/xylitol at 10-25% (w/w) levels are shown in Fig. 3. Films plasticized with 10G, 15S, 15X, 20S, 20X, and 25S cracked to varying degrees upon drying. However, films plasticized with glycerol (15G, 20G), xylitol (25X), and 50:50 mixtures glycerol/sorbitol (15GS), and glycerol/xylitol (15GX) remained almost or completely intact. This indicates the superior plasticizing ability of glycerol compared to others, as also reported in many studies (Zhang and Han, 2006b; Bertuzzi et al., 2007; Jangehud and Chinnan, 1999; Müller et al., 2008). Zhang and Han (2006a) reported efficient plasticizing ability of glycerol by comparing glass transition temperatures (T_g) for pea

starch films upon added plasticizers. The glass transition temperature (T_g) of a material reflects the transition from solid to rubber to viscous liquid; at temperatures below the T_g , the material is in glassy state, and at temperatures above the T_g in rubbery state (Gibson and Ashby, 1988). The glycerol-plasticized films were reported to have lower T_g value (-66.1°C) than those of sorbitol or monosaccharides-plasticized films ($-3.62 \sim -32.6^\circ\text{C}$) (Zhang and Han, 2006a). This indicates the rubbery state of glycerol-plasticized films compared to other films in our study, most likely to result in more flexible films. Plasticizing effect of glycerol was almost minimal when its concentration was relatively lower (i.e. 10G) requiring extra care to minimize cracking prior to testing.

Fig. 4 presents the effects of plasticizer types and contents on mechanical properties of 6HPHACS films. An intact specimen from the highly cracked 10G film exhibited the highest TS (33.81 MPa), but very low E value (16.69%) among tested samples. This could be explained by relatively lower amount of plasticizer (Muscat et al., 2012), which causes the rigidity, rather than flexibility of starch films, consequently, films become stiffer than without plasticizer (Chang et al., 2006).

At 15% (w/w) plasticizer level, all films exhibited similar E values (16.66-16.68%), even though the extent of the cracking was different (Fig. 3). When the plasticizer concentration increased to 20% (w/w), E values between films showed significant differences. The E values followed the order: 20G (39.64%) > 20X (36.51%) > 20S (17.87%). E values for 20G and 20X films increased more than 2 times, compared to E for 15G and 15X films. In contrast, E values for sorbitol-plasticized films almost did not change- 16.67% for 15S film and 17.87% for 20S film- when the concentration increased from 15% to 20% (w/w) respectively. Further increase in sorbitol content to 25% (w/w), led to increased E values up to 48.01%, however, it was still lower than E value of 54.31% for xylitol-plasticized films at the same concentration level.

Sorbitol was consequently considered as less efficient plasticizer than glycerol and xylitol to achieve the same degree of *E*.

The difference in plasticizing effect between sorbitol and glycerol may be attributed to their differing abilities to associate with water (Gontard et al., 1993). Sorbitol is 71% water soluble with medium to low hygroscopicity, whereas, glycerol is infinitely soluble in water at 25°C with a medium to high hygroscopicity (Griffin and Lynch, 1980). However, greater plasticizing effect of xylitol than sorbitol is hard to explain because they have similar solubility, even with xylitol having lower hygroscopic properties (Bär, 1991; Griffin and Lynch, 1980). One possible reason may be slightly greater xylitol molar ratio per g of starch than sorbitol (1.313 vs. 1.097 mmol/ g of starch).

The TS values of the films with plasticizer were inversely related to the *E* values, as reported by many other studies (Myllärinen et al., 2002; Zhang and Han, 2006a, b; Alves et al., 2007). Films with higher *E* values over 35% (i.e. 20G, 20X, 25S, and 25X) showed lower TS values of less than 20.00 MPa. Whereas, films with lower *E* values of 16-17% (i.e. 10G, 15G, 15S, 20S, 15X, 15GS and 15GX) exhibited higher TS values ranging from 24.95 to 33.81 MPa. It is notable that the tensile properties of the films with combination of plasticizers was slightly improved, compared to glycerol alone. However, the cracks on the edges of these films were still present as some brittleness remained, but the extent was not severe. For example, 15GS and 15GX films exhibited higher TS values of 30.09 and 32.00 MPa, respectively, compared to 28.46 MPa for 15G films. Muscat et al. (2012) also observed similar results for high amylose corn starch films plasticized with the mixture of glycerol and xylitol (50:50, by weight). They were slightly stronger than the corresponding films plasticized with glycerol only (37.29 vs. 30.65 MPa). Overall, the 6HPHACS films plasticized with 15% (w/w) glycerol provided reasonable tensile strength and flexibility.

3-3-2. FTIR spectroscopy

FT-IR spectroscopy was used to elucidate possible molecular interactions between starch and plasticizer in films (Fig. 5). Although all films appeared to have the quite similar profiles, there were some differences in peak areas. The broad peak at 3600-3000 cm^{-1} (Zone 1), corresponding to stretching mode of hydroxyl groups due to water and carbohydrates (Piermaria et al., 2011), followed the order 20G HPHACS (20.29) > 20S HPHACS (5.09) > 20G HACS (2.90) > 15G HPHACS (0.61). The peak areas at 1700-1580 cm^{-1} (Zone 2) assigned to another water molecule (specifically, bending mode of hydroxyl groups in water molecules) (Piermaria et al., 2011), were relatively lower compared to that at 3600-3000 cm^{-1} . The peak areas at around 1000 cm^{-1} (Zone 3), also recognized as water sensitive (Van Soest et al., 1995), exhibited the same trend as Zone 1 peaks. The 20G HPHACS films contained larger amount of water molecules than the 20S HPHACS films. This might be attributed to the higher hygroscopic character of glycerol than sorbitol, which strongly interacts with water (Laohakunjit and Noomhorm, 2004). This is in agreement with the moisture content data presented in Fig. 6, indicating sorbitol-plasticized films containing less moisture.

The increase of glycerol content from 15 to 20% (w/w of starch) made more water molecules available for HPHACS films than native HACS films, indicating increased hydrophilicity due to hydroxypropylation. Moisture content of HPHACS films was higher than that of HACS films (12.00 vs. 7.51%, Fig. 6), which gradually increased with increase in hydroxypropyl groups. The moisture contents of 3, 6 and 12 HPHACS films with 20% glycerol (w/w of starch) were 11.59%, 12.00% and 14.13%, respectively (data not shown).

The FTIR results discussed above suggest intermolecular interaction between starch and plasticizer through the hydroxyl groups. Possibly, the most extensive interaction may occur for

the 20G 6HPHACS films containing more water molecules among tested samples. This interaction reduced the free volume for starch mobility, resulting in rigid films. As seen in Fig. 4, the 20G 6HPHACS films had the lowest TS (15.66 MPa), whereas, the strongest TS (28.45 MPa) for 15G 6HPHACS film could be attributed to the lack of water molecules in films.

3-3-3. Barrier properties

Barrier properties of 6HPHACS films against water and oxygen are presented in Fig. 7. Water vapor permeability (WVP) for 20G 6HPHACS films was higher than for 15G 6HPHACS films- 0.04 and 0.03 g mm m⁻² day⁻¹ kPa⁻¹- respectively. This suggests that more glycerol in film contributed to higher water vapor permeability, perhaps due to the hydrophilic nature of glycerol for the presence of hydroxyl groups (-OH). The existence of 3 hydroxyl groups (-OH) in glycerol influences the solubility and hygroscopic characteristics of the film (Isotton et al., 2015).

Oxygen permeability of films showed the similar pattern. The 20G 6HPHACS film had higher oxygen permeability (OP) than 15G 6HPHACS film (267.52 vs. 230.59 cm³ μm m⁻² day⁻¹ kPa⁻¹). Similar to the results reported in literatures increasing glycerol content increased oxygen permeability as well (Mali et al., 2004; Banker, 1966; McHugh and Krochta, 1994). The water barrier properties of 6HPHACS films can be considered ‘superior’ (less than 0.1 g mm m⁻² day⁻¹ KPa⁻¹) based on classification suggested by Han (2014), which is comparable to commercial plastics. However, its oxygen barrier properties were marginal (100-1000 cm³ μm m⁻² day⁻¹ KPa⁻¹). Superior oxygen permeability was less than 10 cm³ μm m⁻² day⁻¹ KPa⁻¹. The oxygen permeability of the 6HPHACS films was within high density polyethylene (HDPE, 100-1000 cm³ μm m⁻² day⁻¹ KPa⁻¹) range but much higher than ethylene vinyl alcohol (EVOH, <10 cm³ μm m⁻² day⁻¹ KPa⁻¹).

4. Conclusions

Low degree of hydroxypropylation could effectively reduce the brittleness in high-amylose corn starch films with minimal plasticizer required. The hydroxypropylation played an important role in decreasing the intermolecular interactions between starch chains like an internal plasticizer, thereby, effectively increasing flexibility of the films. After the hydroxypropylation, only the minimal amount of plasticizer (approximately 20% by weight) was required for obtaining the HACs film with good flexibility. Based on our results, hydroxypropylation with 6% propylene oxide (w/w of starch) and 20% glycerol (w/w of starch) was the optimal condition for solvent casting of starch films with better mechanical properties.

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Figure captions

Fig. 1. Appearance of cast-films made from native (a), and hydroxypropylated (b) corn starches.

In (b), high amylose corn starch was hydroxypropylated with propylene oxide (PO) at 3-12% (starch weight basis, [s.w.b.]). All films were plasticized with 20% glycerol (s.w.b.).

Fig. 2. Thermal properties of HPHACS with PO of 3-12% (s.w.b.).

Fig. 3. Appearance of 6HPHACS films with various plasticizing conditions. G, glycerol; S, sorbitol; X, xylitol; GS, glycerol and sorbitol (50:50); GX, glycerol and xylitol (50:50).

Fig. 4. Thickness and mechanical properties (TS and E) of 6HPHACS films depending on the plasticizing conditions. The data sharing the same alphabet are not significantly different, $p < 0.05$.

Fig. 5. ATR-FTIR spectra of HACS and 6HPHACS films. The numbers in parentheses represent the total relative absorption intensity of the bands assigned to water molecules (Zone 1, 2, and 3).

Fig. 6. Moisture contents of HACS and 6HPHACS films. The data sharing the same alphabet are not significantly different, $p < 0.05$.

Fig. 7. Water vapor permeability and oxygen permeability of 6HPHACS films. The data sharing the same alphabet are not significantly different, $p < 0.05$.

Table lists

- Table 1.** Hydroxypropyl group levels (%), molar substitution (MS), and reaction efficiency (%) for hydroxypropylation of high amylose corn starches (HPHACS).^A
- Table 2.** Thickness, transparency, and mechanical properties of cast-films made from HPHACS with PO of 3-12% (s.w.b.).^A

(a) Native starches

(b) Hydroxypropylated starches

Fig. 1.

Fig. 2.

Plasticizer concentration

10% (w/w)

15% (w/w)

20% (w/w)

25% (w/w)

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Table 1. Hydroxypropyl group (%), molar substitution (MS), and reaction efficiency (%) of hydroxypropylated high amylose corn starches (HPHACS).^A

Starch	Propylene oxide concentration (% , starch weight basis)	Hydroxypropyl group (%)	Molar substitution (MS)	Reaction efficiency (%) ^B
HACS	0	0.31 ± 0.14 ^d	0.01 ± 0.00 ^d	-
3HPHACS	3	1.38 ± 0.05 ^c	0.04 ± 0.00 ^c	49.38
6HPHACS	6	2.50 ± 0.04 ^b	0.07 ± 0.00 ^b	43.20
12HPHACS	12	5.08 ± 0.07 ^a	0.15 ± 0.00 ^a	46.29

^A Values followed by the same superscripts in the same column are not significantly different ($p < 0.05$).

^B Reaction efficiency (%)=(MS×starch weight (g)×100)/ (moles of added propylene oxide×162) (Choi et al., 1997)

Table 2. Thickness, transparency, and mechanical properties of cast-films made from HPHACS with propylene oxide of 3-12% (w/w).^A

Film composition	Thickness (mm)	Mechanical properties		Transparency (A ₆₀₀ /mm)
		TS (MPa)	<i>E</i> (%)	
20G HACS	0.12 ± 0.01 ^{aa}	18.90 ± 1.05 ^a	28.17 ± 7.97 ^c	2.04 ± 0.04 ^{aa}
20G 3HPHACS	0.11 ± 0.01 ^{aa}	15.98 ± 0.61 ^{bb}	37.55 ± 3.90 ^b	1.88 ± 0.05 ^a
20G 6HPHACS	0.11 ± 0.00 ^{aa}	15.66 ± 0.50 ^b	39.64 ± 6.02 ^{bb}	1.29 ± 0.11 ^{bb}
20G 12HPHACS	0.10 ± 0.02 ^a	8.85 ± 0.90 ^c	63.37 ± 4.22 ^a	1.26 ± 0.19 ^b

20G, 20% glycerol (w/w, dry starch basis); TS, tensile strength; *E*, elongation at break.

^A Values followed by the same superscripts in the same column are not significantly different ($p < 0.05$).