



# The physicochemical characteristics and hydrophobicity of high amylose starch–glycerol films in the presence of three natural waxes



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## ABSTRACT

The film forming behaviour and hydrophobicity of high amylose (HA) starch in the presence of three different natural waxes (beeswax, candelilla wax and carnauba wax) were studied in the presence and absence of Tween-80. The HA starch:glycerol (G) ratio was maintained at 80:20 (on dry solid basis) and the concentration of wax was varied from 5% and 10% (w/w). The melted wax samples were homogenized with HAG dispersion with or without Tween-80 and the films were prepared by solution casting. The hydrophobicity and water-barrier properties in these films were determined by using contact angle (CA), water vapour permeability ( $K_w$ ) tests, and water sorption isotherm at 0.529 RH and 20 °C. The  $K_w$  values of the HAG films decreased significantly ( $p < 0.05$ ) with the addition of 5% concentration of these waxes. Then the addition of Tween-80 to the HAG + wax films increased the  $K_w$  values significantly ( $p < 0.05$ ). The presence of these waxes in the presence and absence of Tween-80 resulted into different sorption isotherms and the water adsorptivity and moisture diffusion coefficient values were also affected. The presence of Tween-80 increased the CA in HAG + carnauba wax films while the CA was found to decrease in the case of other two waxes. The highest hydrophobicity was observed in HAG + carnauba wax + Tween-80 films in which the CA was  $>80.0^\circ$  both at 5% and 10% (w/w) wax concentration. These higher CA values in HAG + carnauba wax + Tween-80 films were found to be related to the higher surface roughness in these films.

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## 1. Introduction

Over the years a number of renewable biopolymers derived especially from natural resources have been extensively studied as possible biodegradable packaging materials (Rhim and Ng, 2007). These biopolymers include polysaccharides (e.g. starch), lipids (e.g. wax) and their composites (Bourlieu et al., 2008). These natural biopolymers have an advantage over synthetic polymers as they are biodegradable, have renewable source and they are even edible (Rhim and Shellhammer, 2005; Zhang and Han, 2006).

Starch is one of the most commonly used natural biopolymers to develop environment-friendly packaging materials. However, much broader applications of starch-based products in packaging have not been realised due to its hydrophilic nature and weaker water barrier properties. The packaging films derived from starch suffer from water sensibility, brittleness and relatively poor flexibility owing to the hydrophilic nature of starch. When starch has a greater portion of amylose ( $>70\%$ , w/w) the mechanical

properties of the starch-based films are improved in terms of tensile strength and elongation. To improve the overall flexibility and extensibility of starch films plasticizers are commonly added. Many studies have emphasized that the nature, composition and the plasticizer to starch ratio in the film are important parameters in developing starch-based films (Muscat et al., 2012; Myllarinen et al., 2002). When the plasticizer content becomes higher than 20% (w/w), the flexibility and elongation properties of starch-based films improve due to reduction in intramolecular hydrogen bonding amongst starch molecular chains and increase in intermolecular spacing (Janjarasskul and Krochta, 2010). The most commonly used plasticizers in starch-based packaging are hydrophilic polyols such as glycerol, xylitol and sorbitol (Zhang and Han, 2006; Lao-hakunjit and Noomhorm, 2004; Pareta and Edirisinghe, 2005).

Lipids, particularly waxes are hydrophobic and exhibit high water barrier characteristics when formed into films. However, they have limited oxygen barrier properties due to their relatively low polarity. Moreover, the molecular nature of lipids is such that their ability to form enduring and functioning films is quite limited. In addition, although waxes have the highest hydrophobicity of the lipid compounds (Cha and Chinnan, 2004) they are in solid

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phase at room temperature and require to be melted at elevated temperature causing difficulties in film formation and casting.

By combining starch and natural wax (i.e. beeswax, candelilla wax, carnauba wax) into a composite film, it is possible to develop a biodegradable stand-alone starch-based packaging where each component will aid in improving the film functionality. That is, the starch-plasticizer matrix will act as a support matrix for the wax, while the presence of wax will enhance the water barrier properties of the film (Perez-Gago and Krochta, 2005; Baldwin et al., 1997).

A number of methods of blending starch and wax together have been practised over the years including oil-in-water (*o/w*) emulsion. The emulsion technique is a one-step technique in which melted wax droplets are dispersed in gelatinized starch suspension prior to film casting (Tadros, 2009). During drying, the cast solution containing the melted wax and gelatinized starch can give rise to the following two scenarios. A bilayer film will be formed when the continuous phase (i.e. starch solution) cannot stabilize the emulsion therefore phase separation occurs causing the lipid to migrate to the top of the film (Perez-Gago and Krochta, 2005). If there is no phase separation, the lipid will be evenly distributed within the dried film creating an emulsion film. Emulsions are thermodynamically unstable systems and hence their stability is limited unless proper emulsifiers (surfactants) are added to reduce the interfacial tension (Friebreg et al., 2004). The addition of emulsifier reduces the oil or wax droplet aggregation by occupying the oil–water interface (Ruzette and Leibler, 2005). The polyoxyethylene 20 sorbitan monooleate (Tween-80) with hydrophilic/lipophilic balance (HLB) value of 15 is commonly used to stabilise oil-in-water (*o/w*) emulsions. This non-ionic emulsifier is condensation product of long chain alcohol with ethylene oxide, where the ethylene oxide is hydrophilic while the hydrocarbon chain is hydrophobic. Organic substances including waxes have been assigned with a HLB number which indicates the optimum emulsifier to be used for optimum emulsification. The HLB numbers for beeswax, candelilla wax and carnauba wax are 9, 14.15 and 12, respectively (Holmberg et al., 2002). Emulsifiers with higher HLB value allow a greater association of their hydrophilic fraction with the hydrophilic film matrix which, in turn, may reduce the amount of water binding sites while the hydrophobic fraction may act as a water vapour permeability barrier (Brandelero et al., 2010). Hence, the choice of the emulsifier is critical aspect in creating lipid-starch films (Debeaufort and Voilley, 1995).

In this context, the objectives of this work were to study the film forming behaviour and hydrophobicity of high amylose corn starch-based films where natural waxes are added as the hydrophobic phase. The (starch + glycerol) + wax films were developed using emulsification followed by film casting method. The mechanical properties (tensile strength, modulus of elasticity and flexibility), hydrophobicity, interaction between starch and wax components, colour, water vapour permeability and water sorption isotherms of these films were measured and compared with those of the starch + glycerol films.

## 2. Materials and methods

### 2.1. Materials

High amylose (HA) starch (Gelose 80) containing 70–80% (w/w) amylose and moisture content of 12.60% (w/w) was purchased through Penfolds (Australia) and constituted the continuous matrix of films. Glycerol (G) was used as a plasticizer and was purchased from Consolidated Chemical Company (Melbourne, Australia). It contained 2% (w/w) moisture at the time of its use. Tween-80 was used as an emulsifier and was purchased from

Sigma Adrich (Australia). The natural waxes, i.e. beeswax (BW), candelilla wax (CL) and carnauba wax (CB), were purchased from New Directions Aromatics Inc. (Australia). The Certificate of Analysis of these waxes was provided by this company. All the materials were used as received and the moisture content of the raw materials was compensated for while preparing the slurry mixture for gelatinization.

### 2.2. Methods

#### 2.2.1. Suspension preparation

High amylose corn starch and glycerol were added to distilled water maintaining a total solid concentration of 5% (w/w). The (HA) starch:glycerol dry solid ratio of (80:20) was maintained in all the cases. This starch:glycerol ratio is above the anti-plasticizing threshold of glycerol and produced good flexible films as reported in our previous study (Muscat et al., 2012).

The gelatinisation of starch–glycerol (HAG) suspension was carried out using a high temperature–high pressure laboratory autoclave (Amar Equipment Company, Mumbai, India). The starch–glycerol suspension was gelatinised at 140 °C using 500 rpm agitator speed. The suspension was held for 30 min at 140 °C before cooling down to below 100 °C. While maintaining a temperature above 85 °C by a hot plate (Framo Geratechnik, Germany) the Tween-80 (20% w/w) was added, as described by Soaza et al. (2011), to the fully gelatinized HAG dispersion and thoroughly stirred. It is reported that the Tween-80 remains chemically stable up to 160 °C (Bruno and Svoronos, 2011). Hence, the Tween-80 remains chemically intact within the fully gelatinized HAG dispersion and the addition of wax does not affect its chemical stability.

In producing an emulsion film, this dispersion was kept heated above 85 °C before the molten waxes were added. The beeswax (BW), candelilla wax (CL) and carnauba wax (CB) were added individually at two different concentrations of 5% (w/w) and 10% (w/w) with and without Tween-80. To ensure a thorough mixing of molten wax droplets within the HAG dispersion, coarse homogenisation with a high-shear mixer (Ultra-Turrax, Model T25, IKA-Works, USA) was performed at 15,000 rpm for 3 min followed by 22,000 rpm for 5 min.

#### 2.2.2. Film casting and conditioning

Films were prepared by syringing 10 mL of the suspension into plastic polystyrene dishes with a 90 mm diameter. Films were dried overnight at  $20 \pm 1$  °C, in air conditioned room. These films were stored in a desiccator containing magnesium nitrate (52.9% RH ( $a_w = 0.529$ ) at  $20 \pm 1$  °C) for at least 48 h for conditioning before analysis. The films which had no physical defects such as cracking and visual wax separation were used for further analysis. Triplicate experiments were carried out regarding the film preparation.

#### 2.2.3. Mechanical properties

The mechanical properties such as tensile strength (TS, in MPa), modulus of elasticity (EM, in MPa) and elongation at break ( $E$ , in %) of the films were evaluated. The mechanical properties of the films were determined in tension mode using a texture analyser (TA-XT Plus™, Stable Micro Systems, UK) in accordance with ASTM method D 882 (ASTM, 2000). A manual micrometer (Kincrome,  $0.01 \pm 0.004$  mm) was used to measure the thickness of the films. The average value of the 10 readings was used as the film thickness and the averaged values were subsequently used to calculate the mechanical and water vapour barrier properties. The modulus of elasticity (EM, in MPa) of the each film was calculated from the slope of the initial linear portion of the stress–strain curve as given by the following equation:

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