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Characteristics and properties of hydroxypropylated rice starch based biodegradable films

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ABSTRACT

The characteristics and properties of native rice starch (NRS) and hydroxypropylated rice starch (HPRS) in relation to HPRS films with 6–12% propylene oxide were investigated. The molar substitution of the resulting HPRS was in the range of 0.022–0.033. The results showed that gelatinization properties (To, Tp and Tc) and enthalpy (ΔH) of HPRS were lower than those of NRS, and these decreased with an increase in the propylene oxide. The pasting properties of the starch were determined by using a Rapid Visco Analyzer (RVA). The pasting temperature and peak viscosity was lower in the HPRS while the breakdown and setback viscosity was higher than in the NRS. In addition, the gel strength and paste clarity of HPRS demonstrated softer and clearer qualities than the NRS. The NRS and HPRS contained various concentrations of propylene oxide which were used for film preparation. The results showed that the elongation at break, water vapor permeability, film solubility and transparency of the HPRS films were higher than those of NRS film and increased with an increase in propylene oxide. In contrast, the tensile strength and yellowness (b*) of the HPRS films were lower than the NRS film and decreased with an increase in propylene oxide. The ether group band of the hydroxypropyl group in the FTIR spectrum was shifted from 990 cm^{-1} to 1015 cm^{-1} showing that the film was modified by propylene oxide. Moreover, the XRD analysis of the HPRS films showed a decrease crystallinity when the propylene oxide increased.

1. Introduction

The environmental pollution caused by using synthetic plastic produced by petroleum chemistry has been recently recognized as a serious problem. Moreover, synthetic plastic can protect food from contamination and spoilage but may also be the source of substances migrating into the food (Risch, 1988). The natural polymers have attracted interest and have been widely studied because they can be readily decomposed in the environment during their lifetime (Yoon et al., 1996).

Starch is one of the most studied and promising raw materials for the production of biodegradable plastics, by the reason of it being quite cheap, abundant, biodegradable and edible. Starch consists of two types of polysaccharides, namely amylose and amylopectin (Alves, Mali, Beleia, & Grossmann, 2006). Amylose is a linear molecule with few branches, while the amylopectin molecule has many branches. Therefore, the amylose content contributes to film strength and the branched structure of amylopectin generally leads to film with low mechanical properties (Mali, Grossmann, García, Martino, & Zaritzky, 2005). The relationship between the amylose content and film forming ability is quite good. This is because starches with a high amylose content (approximately 30% amylose) have excellent film forming properties compared to starches with low amylose content (Mali, Grossmann, García, Martino, & Zaritzky, 2002).

Based on this, rice starch (the high amylose group) can be used as a raw material in the manufacture of biodegradable films, because the amount of rice starch amylose is high enough. According to Khunae, Tran, and Sirivongpaisal (2007) who studied chemical compositions of glutinous rice, Jasmine rice and Chiang rice, the amylose content of them was found to be 6.09%, 18.87% and 30.40% respectively. The Chiang rice contained the highest amylose content, and was assumed to be suitable for use as the basis for good biodegradable films. Starch and starch derivative films have been widely studied due to their film forming properties, high oxygen barriers and good mechanical strength (Forssell, Lahtinen, Lahelin, & Myllärinen, 2002; Mali & Grossmann, 2003). However, the good mechanical strength results in brittle film which does not

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have desirable properties for application in packaging (Mali et al., 2005; Wu & Zhang, 2001). Modified starch was used to improve the properties of film. Examples include: hydroxypropylated starch; crosslinking starch; a blend of gelatin/hydroxypropyl starch/plasticizer (Arvanitoyannis, Psomiadou, & Nakayama, 1996) and acetylated starch (Larotonda, Matsui, Soldi, & Laurindo, 2004). Films formed from hydroxypropylated starch can be prepared more easily than from native starch because of the lower solubilization temperature. Advantageous properties for using these as packaging materials, especially the transparency and flexibility, have also been found (Lafargue, Lourdin, & Doublier, 2007; Lafargue, Pontoire, Buleon, Doublier, & Lourdin, 2007; Roth & Mehltretter, 1967; Vorwerg, Dijksterhuis, Borghuis, Radosta, & Kroger, 2004).

Hydroxypropylated starches are generally prepared by the etherification of native starch with propylene oxide under alkaline conditions. The hydroxypropyl groups present are of a hydrophilic nature and the effect after adding the propylene oxide in starch chains is for the internal bonds in the starch granules to be disrupted and weakened (Chun & Yoo, 2007). The gelatinization and paste temperature of hydroxypropylated starches decreased while the swelling power, viscosity, solubility freeze-thaw stability and clarity increased. In a preliminary study, the film from the hydroxypropyl-modified starches was formed and provided good properties. Currently there is very limited information on biodegradable film produced from hydroxypropyl-modified starches, their mechanical properties and their application. It is important to know about film preparation, and the effect of film forming parameters and film characteristics in order to undertake further research into their applications. Hence, the objective of this study was to prepare and investigate the properties of hydroxypropylated rice starch and hydroxypropylated rice starch film with varied amounts of propylene oxide.

2. Materials and methods

2.1. Raw materials

Chiang rice grain was purchased from a local rice mill in Phattalung, Thailand. The rice grain was stored in an ambient temperature until used.

2.2. Preparation of rice starch

Rice starch was isolated by the alkaline method following the procedures of Ju, Hettiarachchy, and Rath (2001), Sawai and Morita (1968), and Sugimoto, Tanaka, and Kasai (1986). The rice grain was soaked in 4 volumes of distilled water for 24 h, followed by wet grinding with a rice grinder machine. The slurry was isolated by centrifuging at 3000 × *g* for 30 min and was called rice flour. Then the flour was extracted with 4 volumes of 5% NaCl for 2 h (globulin extract) and centrifuged at 3000 × g for 30 min. The flour was then extracted for the prolamin with 4 volumes of 70% ethanol for 2 h and followed by glutelin extraction with 4 volumes of 0.35% NaOH with continuous stirring. After 16 h, the starch was adjusted to pH 7 with 1 M HCl and isolated by centrifuging (3,000 × *g*, 30 min), and washed with 4 volumes of distilled water 3 times(with albumin extract and other chemical reagents). The starch was dried at 50 °C overnight to ensure 10–12% moisture content.

2.3. Preparation of hydroxypropylated rice starch (HPRS)

The rice starch was modified by its reacting with propylene oxide following the procedures modified from Hung and Morita (2005), Suwanliwong (1998), and Wattanachant, Muhammad, Hashim, and Rahman (2003). Fifteen grammes of sodium sulphate (15% based on dry wt. of starch) were added to 300 ml of distilled water and stirred. When the salt was dissolved, 100 g of rice starch (dbs, equivalent to 30% starch solid in slurry) were added and the mixture stirred to make up a uniform slurry. Then a 5% sodium hydroxide solution was added with vigorous stirring to prevent starch gelatinization and to adjust the slurry to pH 11.5. Then 6–12% propylene oxide (vol. by weight of starch solid) was added and the slurry, which was at room temperature, was stirred for half an hour. The slurry was then transferred to centrifugal bottles and placed in a 40 °C water bath with continuous shaking. After 24 h, the slurry was adjusted to pH 5.5–6.0 with 10% hydrochloric acid solution to terminate the reaction. The hydroxypropylated starch was isolated by centrifuging (3,000 × *g*, 5 min), washed with 1 volumes of distilled water for 4 times and air-dried overnight.

2.4. Determination of hydroxypropyl group and molar substitution

The hydroxypropyl group in the modified starches was determined according to the procedure as described by the Joint FAO/WHO Expert Committee on Food Additives (2001). A sample (50–100 mg) was weighed into a 100-ml volumetric flask and 25 ml of 0.5 M sulfuric acid was added. Native starch was prepared in the same manner. The flasks were placed in a boiling water bath and heated until the solution became clear. The samples were cooled and the contents diluted to 100 ml with distilled water. One milliliter of the solution was placed by pipette into 25 ml graduated test tubes with glass stoppers. The tubes were immersed in an ice bath and then 8 ml of concentrated sulfuric acid were added in drops to each tube. The solution was mixed well and the tubes were placed in a boiling water bath for exactly 3 min. The tubes were immediately transferred to an ice bath until the solution was chilled. An aliquot (0.6 ml) of ninhydrin reagent was added, and the reagent was carefully allowed to run down the walls of the test tubes. The tubes were immediately shaken well and placed in room temperature for 100 min. The volume in each tube was adjusted to 25 ml with the concentrated sulfuric acid and mixed by inverting the tubes several times. Portions of the solution were immediately transferred to 1-cm cells, and, after exactly 5 min, the absorbance was measured at 590 nm, using the starch blank as a reference. A calibration curve was prepared with an aliquot (1 ml) of standard aqueous solutions, containing 10, 20, 30, 40 and 50 mg of propylene glycol per ml. The hydroxypropyl groups (by %) were calculated by the following equation:

$$\text{Hydroxypropyl groups}(\%) = \frac{C \times 0.7763 \times 10 \times F}{W}$$

where, C is amount of propylene glycol in the sample solution read from the calibration curve (mg/ml), F is the dilution factor and W is weight of the sample (mg).

The molar substitution (MS) of the modified starch was calculated in the normal fashion (Rutenberg & Solarek, 1984; Suwanliwong, 1998).

$$\text{MS}(\text{Hydroxypropylated starch}) = \frac{\text{moles of substituent}}{\text{mole of anhydro} - \text{glucose unit}}$$

$$\text{MS} = \frac{\%\text{HP} \times 162}{59.08 \times (100 - \%\text{HP})}$$

2.5. Functional properties of hydroxypropylated rice starch (HPRS)

2.5.1. Gelatinization properties (DSC)

Gelatinization and dissociation parameters were measured using differential scanning calorimetry (DSC-7, Perkin Elmer Inc., Norwalk, CT, USA). A starch: distilled water slurry of 1:4 weight