



## Properties and characteristics of dual-modified rice starch based biodegradable films



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### ABSTRACT

In this study, the dual-modified rice starch was hydroxypropylated with 6–12% of propylene oxide followed by crosslinking with 2% sodium trimetaphosphate (STMP) and a mixture of 2% STMP and 5% sodium tripolyphosphate (STPP). Increasing the propylene oxide concentrations in the DMRS yielded an increase in the molar substitution (MS) and degree of substitution (DS). However, the gelatinization parameters, paste properties, gel strength and paste clarity showed an inverse trend. The biodegradable films from the DMRS showed an increase the tensile strength, elongation at break and film solubility, while the transparency value decreased when the concentration of propylene oxide increased. However the water vapor permeability of the films did not significantly change with an increase in the concentration of propylene oxide. In addition, it was found that DMRS films crosslinked with 2% STMP demonstrated higher tensile strength, transparency value and lower water vapor permeability than the DMRS films crosslinked with a mixture of 2% STMP and 5% STPP. The XRD analysis of the DMRS films showed a decrease in crystallinity when the propylene oxide concentrations increased and the crystallinity of DMRS films with 2% STMP were higher than the DMRS films with a mixture of 2% STMP and 5% STPP.

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## 1. Introduction

Biodegradable packaging, such as edible film, biodegradable film and coatings, is increasing because it uses natural materials and renewable resources, which do not contribute to environmental pollution [1,2]. Among all biopolymers, starch is being investigated as a potential material for biodegradable films [3]. Starch is a natural carbohydrate based polymer that is globally available from various natural sources including wheat, rice, corn and potato. Starch consists of two molecules: the essentially linear polysaccharide amylose; and the highly branched polysaccharide amylopectin. The amylose content in starch contributes to film strength and the branched structure of amylopectin generally leads to film with low mechanical properties [4]. Biodegradable films from starches with high-amylose content exhibit excellent oxygen barrier properties, lower water solubility, lower retrogradation temperature, and more stable mechanical properties at high RHs compared with those of native starch [5–7]. In addition, Muscat et al. [8] found that, the films with high amylose content showed higher tensile

strength and modulus of elasticity values but lower elongation values than those of low amylose starch films. Based on this, the rice starch (Chiang rice) has a higher amylose content of 30.40% in its composition [9]. This is assumed to be suitable for use as the basis for good biodegradable films which exhibit high oxygen barriers and good mechanical strength [10]. However, the strength, flexibility and film transparency of high amylose film are still poor and these undesirable properties limited its application in packaging. Modified starch has to be used to improve the properties of the film.

Chemical modification is usually undertaken to improve film properties. Hydroxypropylation and crosslinking are methods widely used to produce modified starch. Starches that are etherified with propylene oxide (hydroxypropylated starches) exhibit lower gelatinization temperature, increased granule swelling, higher paste viscosity and greater paste clarity than native starches. This is because the incorporation of a hydroxypropyl group is capable of disrupting inter- and intra-molecular hydrogen bonds in the starch chains, thus weakening the granular structure of starch and increasing the accessibility of the starch granules to water [10]. Crosslinking reinforce the hydrogen bonds in the granules with chemical bonds that act as a bridge between the starch molecules [11]. Crosslinking provides paste viscosity and temperatures, and

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acid and shear stability [12]. Reagents such as phosphorus oxychloride, sodium trimetaphosphate, and epichlorohydrin were reported to be generally used as crosslinking reagents [13]. Lim and Seib [14] investigated the preparation of starch phosphates and found that a mixture of phosphate salts (sodium trimetaphosphate (STMP) and sodium tripolyphosphate (STPP)) gave better results than using STMP alone to prepare distarch phosphate (crosslinked starch). This combination of STMP and STPP showed that the starch paste was more stable with heating and shearing and gave a high consistency after cooling [14]. In a previous study, the film from hydroxypropylation modified starches was formed and provided a higher flexibility and film transparency obtained, while the tensile strength value was low [10,15]. Meanwhile Kim and Lee [16] reported that the mechanical properties of starch films prepared with crosslinked corn starch show higher values than native corn starch. Detduangchan et al. [17] also reported that the tensile strength and water barrier of the rice starch films were improved by using crosslinking agents while the flexibility and film transparency were poor. When starch is modified by both hydroxypropylation and crosslinking or dual modification, the functional benefits from each individual modification are realized. The obtained films from dual modification would promise and has good potential in many food applications. Hence the objective of this study was to prepare and investigate the properties of dual-modified rice starch and dual-modified rice starch films from Chiang rice starch with various levels of propylene oxide and different crosslinking reagents compared with native starch.

## 2. Materials and methods

### 2.1. Raw material

Chiang rice grain was purchased from a local rice mill in Phattalung, Thailand. The Chiang rice starch was isolated in our laboratory by the alkaline method following the procedures of Sawai and Morita [18], Sugimoto et al. [19] and Ju et al. [20].

### 2.2. Preparation of dual-modified rice starch (DMRS)

The rice starch was modified by its reacting with propylene oxide following modified procedures from Hung and Morita [21], Suwanliwong [22], and Wattanachant et al. [13]. 15 g 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 suspension) were added and stirred to make up a uniform suspension. Then a 5% sodium hydroxide solution was added with vigorous stirring to prevent starch gelatinization and to adjust the suspension to pH 11.5. Then 6–12% propylene oxide (vol. by weight of starch solid) was added and stirred at room temperature for 30 min. The suspension was then transferred to centrifugal bottles and placed in a 40 °C water bath with continuous shaking for 24 h. The starch suspension was transferred into a mixing container at room temperature. Then it was cross-linked by using 2% STMP (w/wt. of dry starch, HPC1) and a mixture of 2% STMP and 5% STPP (w/wt. of dry starch, HPC2) based on the methods of Hung and Morita [21], Suwanliwong [22], Wattanachant et al. [13] and Woo and Seib [23]. The suspension was held in a 40 °C water bath for 3 h with continuous stirring. Then the suspension was adjusted to pH 5.5–6.0 with 10% hydrochloric acid solution to terminate the reaction. The starch suspension was washed with 1 time the volume of distilled water four times and isolated by centrifuging (3000 × g, 5 min); thereafter the starch was dried at 50 °C for 24 h.

### 2.3. Determination of hydroxypropyl group and molar substitution (MS)

The hydroxypropyl group in the modified starches was determined according to the procedure described by the Joint FAO/WHO Expert [24]. A sample (50–100 mg) was weighed into a 100-ml volumetric flask and 25 ml of 0.5 M sulfuric acid was added. The flasks were placed in a boiling water bath and heated until the solution became clear. The samples were cooled and diluted to 100 ml with distilled water. One milliliter of the solution was placed by pipette into 25 ml test tubes with glass stoppers. The test tubes were immersed in an ice bath and then 8 ml of concentrated sulfuric acid were dropped into 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 test 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 solution, containing 10, 20, 30, 40 and 50 mg of propylene glycol per ml. The hydroxypropyl groups (by %) were calculated by the following equation:

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

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 the weight of the sample (mg).

The molar substitution (MS) of the modified starch was calculated in the normal fashion [12,22].

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

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

### 2.4. Determination of phosphorus content and degree of substitution (DS)

The content of the phosphorus in modified starches was determined according to a modified procedure as described by the A.O.A.C. [25]. A sample (2 g) was burned in a muffle furnace at 600 °C for 4 h. This was then cooled to room temperature and 10 ml of 5 M hydrochloric acid was added in the ash. NRS was prepared in the same manner. The contents were diluted to 100 ml with distilled water and 50 ml of the solution were then diluted again to 100 ml with distilled water. The vanadate molybdate (25 ml) was added to the solution and then the absorbance of the sample was measured at 470 nm. A calibration curve was prepared from 0, 2.5, 5, 10, 20, 30, 40 and 50 ml of potassium dihydrogen phosphate (KH<sub>2</sub>PO<sub>4</sub>), using the 0 ml of KH<sub>2</sub>PO<sub>4</sub> as a reference. The phosphorous content was calculated from the absorbance curve which was obtained by using a standard phosphorous solution.

$$\begin{aligned} \text{Phosphorous (\%)} \\ = \frac{P \times \text{dilution volume in ml} \times 100}{(\text{aliquot volume in ml} \times \text{sample weight in g} \times 1000)} \end{aligned}$$

where  $P$  is the phosphorous content (mg/100 ml) from the calibration curve.

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