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Modification of Cassava Starch by Esterification and Properties of Cassava Starch Ester Films

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ABSTRACT

Cassava starch, a naturally occurring biopolymer, is able to form films which are generally sensitive to moisture. Chemical modification by esterification can enhance the hydrophobicity of starch that depends on the nature of ester group and the degree of substitution (DS). The effects of the ester group chain-length and the DS on the properties of starch ester films were studied. Starch ester slurry containing starch ester 4% and sorbitol 30% w/w of starch as a plasticizer was cast into a film and its mechanical properties were determined. It was found that tensile strength and elongation were in the range of 2-3 kg/mm2 and 2-3%, respectively. The water absorptivity and water solubility of the starch ester films were reduced as the ester group chain-length and the DS of starch esters increased. The results indicate that starch esterification can improve the hydrophobicity of starch ester films and this relates directly to the ester group chain-length and the DS of starch esters.

Key words: cassava starch, modified starch, starch esters, starch film

INTRODUCTION

In recent years, many attempts have put emphasis on the search of naturally occurring polymers that can properly serve the needs of packaging industries and consumers. Starch is one of the most widely used biopolymers because of its low cost, abundant availability and renewability. However, the use of starch in packaging area has been limited due to its hydrophilic nature. Chemical modification by esterification, which changes the functional group of starch from highly hydrophilic hydroxyl groups to more hydrophobic ester groups, can produce more hydrophobic materials, depending on the nature of ester group and the DS (Fringant *et al.*, 1996). Thus, this research was aimed to investigate the effects of the ester group chain-length (C2 to C4) and the DS on the packaging properties of starch ester films.

MATERIALS AND METHODS

MATERIALS

Cassava starch was obtained from Sanguan Wong Co, Ltd, Thailand. All reagents (acetic anhydride (C2), propionic anhydride (C3), butyric anhydride (C4) and sorbitol) were analytical grade and used without further purification.

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METHODS

1. Preparation of starch esters

Cassava starch was esterified with various acid anhydrides following the method of Keowmaneechai (1995). Forty percent of starch suspension (w/w of water) was adjusted to pH 8.0-8.5 by adding 3% sodium hydroxide. Acid anhydride, the esterifying agent, of 10, 20 and 40% w/w of dried starch was then slowly added to the suspension, with continuous stirring and pH controlling at 8.0-8.5. After achieving the reaction time of 30, 40 and 60 minutes for acid anhydride of 10, 20 and 40% w/w of dried starch, respectively, the suspension was then neutralized to pH 6.5 by 0.5 N sulfuric acid and centrifuged to separate the esterified starch. The obtained starch ester was washed with distilled water to remove reagent residuals and dried at 50°C for 15 hours. The dried starch ester was ground to fine powder and then kept in a sealed plastic bag at a room temperature.

2. Determination of the degree of substitution (DS)

The DS of cassava starch ester was determined according to Sriroth (1987). Five grams of starch ester were mixed with 50 ml of distilled water and the mixture was saponified with 25 ml of a 0.5N sodium hydroxide solution, the excess of NaOH was then back titrated with 0.5 N sulfuric acid (V) using phenolphthalein as an indicator. The DS was calculated as follows:

$$\%\ \text{substitution} = (25 - \text{V}) \cdot \text{N of NaOH} \cdot \frac{\text{MW}}{1000} \cdot \frac{100}{\text{Ws}}$$

where MW = molecular weight of ester group
Ws = weight of sample, gram

$$\text{and} \quad \text{DS} = \frac{162 \times \%\text{substitution}}{100\text{MW} - ((\text{MW} - 1) \times \%\text{substitution}}$$

where 162 = molecular weight of anhydroglucose unit
MW = molecular weight of ester group

3. Preparation of starch ester films

A mixture of starch ester 4% (w/w of water) was heated until gelatinized and then sorbitol 30% (w/w of starch) was added to the mixture. After cooling to 45°C, the mixture was cast into a film on a glass plate covered by a hydrophobic film (Phuangkasem,1997) and dried at 60°C for 3-4 hours. The dried starch ester films were kept in a sealed plastic bag at a room temperature.

4. Determination of starch ester film properties

4.1 Mechanical properties

Mechanical properties of the films were determined according to ASTM D882-91 (1994) using universal testing instrument (LLOYD, LRX Plus). Before testing, samples of 25×150 mm were conditioned at 27°C, 65%RH for 24 hours. Tensile measurements were performed at cross-head speed of 20 mm/min and initial gauge length of 100 mm. Force and elongation at break were recorded for each sample with 5 replications.

4.2 Water absorptivity

According to the method of Vimolvan *et al.* (2001), samples were cut into 50x50 mm and were placed in a silica gel desiccator until constant weight before weighing (W_0). The samples were then conditioned at 27°C, 65%RH for 24 hours and weighed (W_1) again. The water absorptivity was calculated as follows:

$$\text{Water absorptivity} = \frac{(W_1 - W_0)}{W_0} \times 100$$

4.3 Water solubility

The test method was adopted following the procedure of Aicello water solubility test (2003). Test samples were cut into 23x34 mm and gripped on a glass plate of 25x35 mm. Water 800 ml was poured into a 1L beaker and the test sample was placed and spun in water at the level of 600 ml. The water solubility was expressed as the time required for swelling the sample in water.

5. Statistical analysis

Factorial in CRD (Completely Randomized Design) was used as an experimental design. The SPSS for Windows program, version 11.0, was employed for analyzing the results obtained from three replications. The analysis of variance (ANOVA) and duncan multiple range test (DMRT) were used for comparing differences of the mean values at the 0.05 level (Vanitbuncha, 2000)

RESULTS AND DISCUSSION

The DS of starch esters and properties of starch ester films were investigated. The results are summarized in Table 1. It shows that the DS of starch esters increased when the amount of esterifying agents increased.

Mechanical properties of the starch ester films were determined as the tensile strength and elongation. It is obvious that the mechanical properties of the films depend significantly on the amount of acid anhydride. With the increased amount of the acid anhydrides, the tensile strength increases while the elongation slightly decreases. It reveals that the starch esters films with the higher DS are slightly harder and more brittle than those of lower DS. However, plasticization can be applied to improve their flexibility.

Hydrophobicity of the starch ester films were investigated in terms of the water absorptivity and water solubility. It has been found that the water absorptivity and water solubility of starch ester films with the long ester group chain-length as starch propionate (C3) and starch butyrate (C4) significantly decreased when the amount of esterifying agents increased. This is due to the fact that the long ester group chain-length makes starch esters more hydrophobic.

Interestingly, it can also imply that the water absorptivity and water solubility of starch ester films decreases when the DS of starch esters increases resulting from the substitution of hydrophilic hydroxyl groups with hydrophobic ester groups except the starch acetate film. Fringant *et al.* (1996) explained that starch acetate with DS ranging from 0 to 1.3 has insufficient acetyl groups to change the hydrophilic nature of hydroxyl groups. Moreover, the acetyl group is slightly more hydrophilic than the hydroxyl group owing to the polarity of carbonyl group. The DS of starch acetate to behave more hydrophobic is higher than 1.7.

Table 1 The DS of starch esters and properties of starch ester films.[1]

Type of starch	Amount of esterifying agent (%w/w dried starch)	DS	Tensile strength (kg/mm^2)	Elongation (%)	Water absorptivity (%)	Water solubility (min.)
Native starch	-	-	3.07a	3.02b	7.11a	12.62d
Starch acetate	10	0.273e	2.26f	2.67d	5.83e	7.07i
	20	0.314c	2.29f	2.49e	5.96d	7.36gh
	40	0.369a	2.37e	2.23f	7.07a	7.54g
Starch propionate	10	0.275e	2.52d	3.28a	6.91b	7.17hi
	20	0.295d	2.88b	2.93c	6.65c	8.26f
	40	0.325b	3.12a	2.42e	5.46f	9.07e
Starch butyrate	10	0.260g	2.64c	2.98bc	3.68g	20.26c
	20	0.266f	2.93b	2.68d	3.32h	21.11b
	40	0.276e	3.14a	2.48e	3.28h	22.49a

[1] Results are expressed as an average of three replications. Mean in a column not sharing a common superscript are significantly different at the 0.05 level by ANOVA and DMRT.

CONCLUSION

The cassava starch was chemically modified via esterification by using esterifying agents as acetic anhydride (C2), propionic anhydride (C3) and butyric anhydride (C4) at 10, 20 and 40% w/w of dried starch. The amount of the esterifying agents significantly affected the DS of starch esters and their film properties, mainly mechanical properties, water absorptivity and water solubility. The results indicate that starch esterification can enhance the hydrophobicity of starch ester films.

SUGGESTION

For further study on the effects of esterifying agents, it would be more interested to vary the mole ratio of esterifying agents to anhydroglucose units, rather than the weight ratio. This is due to the difference in molecular weight of esterifying agents that could play an important role in the obtained starch esters.

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