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Effect of Antioxidants on Properties of Rice Flour/Cassava Starch Film Blends Plasticized with Sorbitol

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ABSTRACT

The effects of antioxidants (gallic acid (GA), propyl gallate (PG) and butyl hydroxyanisole (BHA)) on the mechanical properties, water solubility and melting point temperature (T_m) of rice flour/ cassava starch film blends with sorbitol were investigated. All films forming a solution were casted and dried at room temperature. Film blended with GA (400 mg) showed higher tensile strength and folding endurance, but lower %elongation than the control film blend. The tensile strength of film blended with PG and film blended with BHA were not significantly different ($p>0.05$) compared with the control film. Film blended with GA showed higher water solubility than the control film, film blended with PG and film blended with BHA, respectively, because GA had a higher polarity than PG and BHA, respectively. Differential scanning calorimeter (DSC) thermographs showed a single peak for all film blends with and without antioxidants, confirming their homogeneity. Changes in the T_m of film blends with antioxidants depended upon the T_m of the antioxidants.

Key words: blended rice/ cassava starch film, antioxidants, mechanical properties, water solubility, Tm

INTRODUCTION

Rice and cassava are economically crucial crops in Thailand. Rice and cassava flour are efficient thickeners and binding agents. They are used mainly and extensively in the production of soups, sauces and pastry filling amongst other products. In recent studies, cassava and rice flour and starch were used to produce edible films plasticized with glycerol and sorbitol (Laohakunjit and Noomhorm, 2004; Phan *et al*., 2005). Cassava starch-based film plasticized with glycerol showed interesting mechanical properties. It was transparent, clear, homogeneous, flexible, and easily handled, whereas rice starch-based films plasticized with glycerol were relatively brittle and had a low tension resistance (Phan *et al*., 2005). The tensile strength of glycerol-plasticized rice starch film was significantly lower than that of sorbitol-plasticized rice starch film, but its elongation was greater (Laohakunjit and Noomhorm, 2004).

Information on the effect of additives on the properties of rice flour and cassava starch films is not readily available at present (Rachtanapun and Tongdeesoontorn, 2008). Some research has been reported on using additives, such as antimicrobials (Flores *et al*., 2007), essential oils and antioxidants in biopolymer films to fortify other properties (Vermeiren *et al*., 1999). Antioxidants are widely used as food additives to improve the oxidation stability of lipids and to

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prolong shelf life, mainly for dried products and O_2-sensitive foods. Recently, antioxidants have been suggested for integration in polymer films to exert their antioxidative effect (Pascat, 1986). Hargens-Madsen *et al*. (1995) used tocopherols in an edible film to control the warmed-over flavor and improve precooked meat quality. Essential oils were mixed in a milk protein-based film (Oussalah *et al*., 2004).

However, few studies have been carried out on films made from rice flour and cassava starch (Laohakunjit and Noomhorm, 2004; Phan *et al*., 2005) Furthermore, there are only a few research studies reporting on the addition of antioxidants in blended film made from rice flour/ cassava starch. Rachtanapun *et al*. (2006) reported that rice flour/cassava starch film blends with PG, BHA and BHT gave no significantly different tensile strength, %elongation and folding endurance compared with film blends without antioxidant. The water vapor transmission rate (WVTR) and water permeability of rice flour/ cassava starch film blends decreased with the addition of antioxidants (PG, GA and BHA) (Rachtanapun and Tongdeesoontorn, 2008). There are no reported studies on the mechanical properties of rice flour/cassava starch film blends with gallic acid (GA), solubility and thermal properties of rice flour/cassava starch film blends with GA, PG and BHA. The current study added antioxidants (GA, PG and BHA) into rice flour/ cassava starch blended film to produce antioxidant films. Therefore, the aim of this study was to investigate the effect of the addition of antioxidant on the mechanical properties, solubility and thermal properties of rice flour/cassava starch film blends plasticized with sorbitol.

MATERIALS AND METHODS

Materials

Rice flour (Bangkok Inter Food Co., LTD., Thailand), cassava starch (Bangkok Inter Food Co., LTD., Thailand) and sorbitol (Northern Chemical, Thailand) were employed to obtain the film. Antioxidants (propyl gallate (PG), gallic acid (GA) and Butyl hydroxyanisole (BHA)) were purchased from Fluka (Sigma-Aldrich, USA).

Rice flour/ cassava starch blended film preparation

The film solution was prepared by dispersing 3.0 g rice flour and 7.0 g cassava starch in 100 ml distilled water (Rachtanapun and Tongdeesoontorn, 2008). The mixture was heated to 80°C with constant stirring to obtain starch gelatinization. Sorbitol (3.0 g) was added as plasticizer and the solution was stirred continuously for 5 min (Rachtanapun *et al*., 2006). Film-forming solution (30 g) was cast onto a flat 15 × 28.5 cm glass plate wrapped with a PVDC film. The films were dried at room temperature for 24 h. The thickness of the film samples was about 0.12-0.15 mm.

Where the films included antioxidant, 400 mg of propyl gallate (PG) or gallic acid (GA) or butyl hydroxyanisole (BHA) was added to the starch solution before heating at 80°C. Plasticizer and film casting were added using the same method as for the blended film without antioxidants.

Mechanical properties

Tensile strength and %elongation

Tensile strength and %elongation were analyzed according to ASTM 882-95 (2000), with some modification. Film strips (25 mm × 150 mm) were stretched at 25 mm/min (initial grip separation of 100 mm, load cell 1000 N) using Universal Testing Machine H1KS (Hounsfield, England). A minimum of ten strips were prepared for each film. Film specimens were equilibrated at 65% relative humidity and 27°C for 24 h before testing.

Tensile strength was calculated by dividing the maximum load by the original crosssectional area of the specimen. The percentage of elongation was calculated by dividing the elongation at the moment of rupture of the sample by the initial gauge length (100 mm) of the sample and multiplying by 100.

Folding endurance

Folding endurance was performed according to ASTM D2176-97a (2002). Film strips (15 mm × 140 mm) were equilibrated at 65%RH, 27°C for 24 h before folding (folding angle 135°, 175 times/min) using a folding endurance tester GT-6014-A (Gotech Testing Machine, Taiwan) with a 500 g load cell. Film strips were folded until they broke. The number of folds was recorded as the folding endurance value.

Water solubility

Film solubility in water was measured as the percentage of dry matter of the film solubilized in water during a period of 24 h (Phan *et al.*, 2005). The initial dry matter of each film was obtained after drying film samples at 65°C for 24 h and then placing in a desiccator for 2 d. Each dried film (0.50 g) was weighed and immersed in 50 ml of distilled water at 25°C, sealed in a bottle with parafilm and periodically agitated. Residual films were separated and dried to determine the weight of dry matter. Tests were performed in triplicate and the solubility was calculated using Equation 1:

$$\%\ solubility = \frac{(initial\ dried\ weight - final\ dried\ weight)}{initial\ dried\ weight} \times 100 \quad (1)$$

Thermal analysis by differential scanning calorimeter (DSC)

A DSC 823 Mettler Toledo Schwerzenbach instrument (Mettler Toledo, Switzerland) was used. Five to ten milligrams of sample each contained in an aluminum pan was heated in the range of -40°C to 270°C, at a scanning rate of 5°C/min. T_m was determinated from the thermogram. The average moisture content of the film samples was 11.61±0.62%.

RESULTS AND DISCUSSION

Effect of antioxidants on mechanical properties of rice flour/ cassava starch film blends

The tensile strength, % elongation and folding endurance of rice flour/cassava starch blended films without and with antioxidants are shown in Figures 1, 2 and 3, respectively. The thickness of film blends was about 0.12-0.15 mm. Film blended with GA gave the highest tensile strength and folding endurance, but lower % elongation than the control film blend, film blended with PG and film blended with BHA, respectively. There were no significant differences ($p>0.05$) between tensile strength, %elongation and folding endurance of the control film blend, film blended with PG and film blended with BHA. This result agreed with the mechanical properties of rice flour/cassava starch-film blends containing PG, BHA and BHT (Rachtanapun *et al.*, 2006). As GA has high polarity compared to PG and BHA, it had a higher interaction with the film blend than other antioxidants. This result corresponded to the results with oregano extract addition in soy protein film plasticized with sorbitol (Pruneda *et al.*, 2008) and the effect of the addition of BHT and α-tocopherol on elongation of fish skin gelatin films (Jongjareonrak *et al.*, 2008).

Effect of antioxidants on water solubility of rice flour/ cassava starch film blends

The solubility in water of rice flour/ cassava starch-blended films without and with antioxidants (GA, PG, BHA) are shown in Table 1. The water solubility of rice flour/cassava starch-blended film without antioxidant (control film) was 24.27%, which was between the values for % solubility of rice flour film (0.84%) and cassava starch film (79.33%) (Phan *et al.*, 2005). The

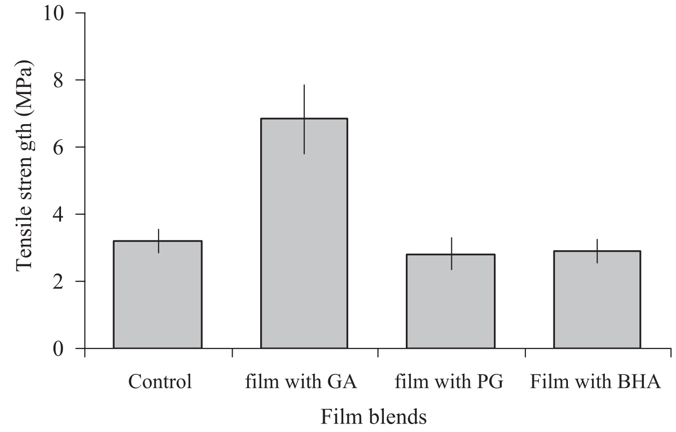

Figure 1 Effect of antioxidants on tensile strength of rice flour/cassava starch-blended films.

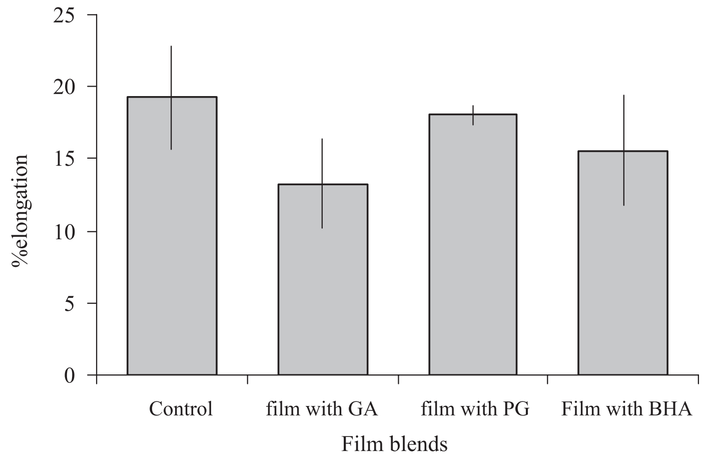

Figure 2 Effect of antioxidants on %elongation of rice flour/cassava starch-blended films.

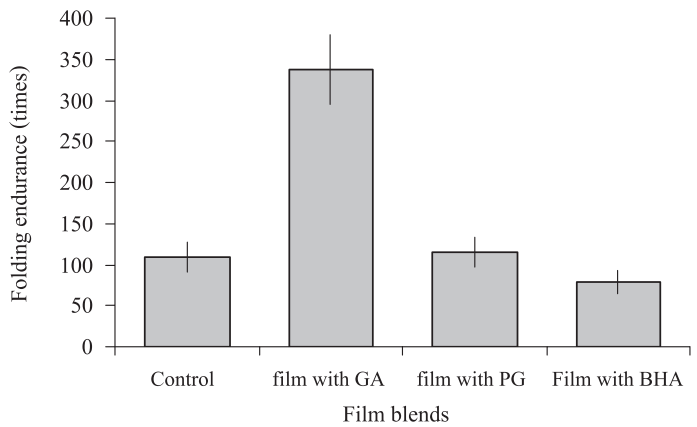

Figure 3 Effect of antioxidants on folding endurance of rice flour/cassava starch-blended films.

Table 1 Water solubility (%) of blended films and the control with antioxidants.

Film	% Solubility
Control film	24.27 ± 1.24[a]
Film +GA	30.15 ± 1.43[b]
Film +PG	22.56 ± 1.16[a]
Film +BHA	21.93 ± 0.92[a]

Note: a,b,c,d = values with different letters are significantly different ($p<0.05$).

solubility of film blended with GA was higher than the control, and film blended with PG and BHA because the polarity of GA was higher than PG and BHA, respectively (http://pubchem.ncbi.nlm.nih.gov). Therefore, GA addition increased the water solubility of the blended film. There were no significant differences ($p>0.05$) between the solubilities of the control film and film blended with PG and BHA. This result was related to the mechanical properties of the film blends.

Effect of antioxidants on thermal analysis of rice flour/ cassava starch film blends

Thermographs of the control film and films with antioxidants (GA, PG, BHA) (Figure 4) showed a single peak indicating homogeneity of films. The melting temperature of the antioxidants (GA, PG, BHA) and rice flour/ cassava starch blended film without (control) and with antioxidant from DSC are shown in Table 2. The T_m of rice flour/cassava starch film blends (control sample) was 101.00 ±1.21°C and for GA, PG and BHA was 118.17, 71.00 and 65.17°C, respectively. The T_m of films blended with antioxidants was the average of the T_m of the control film and antioxidants. It indicated that the T_m of films with antioxidants was affected by the T_m of the antioxidants, which was related to the polarity of the antioxidant. Film containing a high polar antioxidant (GA), which had a T_m higher than the control film, would cause the T_m of film to increase, but film containing a low polar antioxidant (PG and BHA), which had a T_m lower than the control film, would cause the T_m of film to decrease. This was due to the highly polar group of antioxidants (GA) increasing intermolecular binding in the polymer chain, but the low polar group of antioxidants decreased the intermolecular force (Selke *et al.*, 2004). These results were in general agreement with the DSC thermograph of potato starch-chitosan-blended films with ferulic acid (Mathew and Emilia Abraham, 2008).

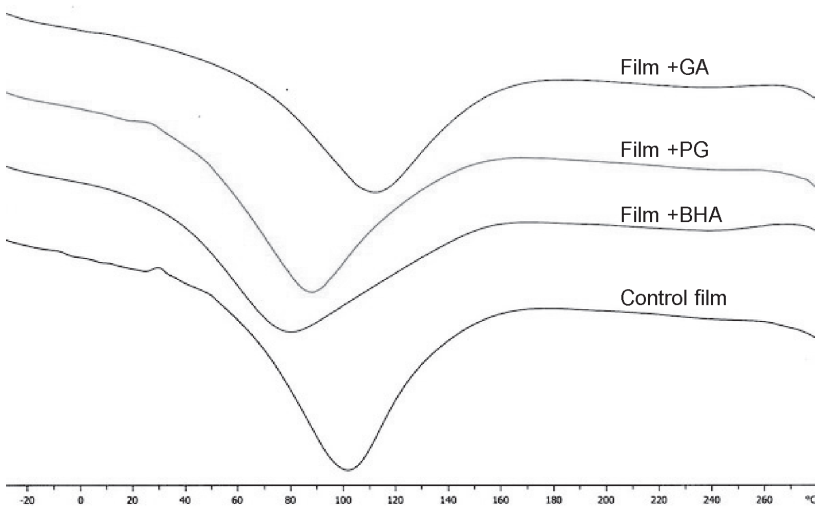

Figure 4 DSC thermographs of control film and films with antioxidants (GA, PG and BHA).

Table 2 Melting temperature (T_m) of antioxidants (GA, PG, BHA) and rice flour/cassava starch blended film without (control) and with antioxidant (GA, PG, BHA).

Samples	Tm (°C)
Rice flour/cassava starch film blends	
(Control)	101.00 ± 1.21a
GA	118.17*
PG	71.00*
BHA	65.17*
Film blend +GA	111.83 ± 8.73b
Film blend +PG	87.83 ± 6.66c
Film blend +BHA	79.50 ± 14.26d

Note: * = Tm values of antioxidants from Sigma-Aldrich®.
a,b,c,d = values with different letters are significantly different ($p<0.05$).

CONCLUSION

The effect of antioxidants on the mechanical properties, water solubility and melting temperature of rice flour/cassava starch-film blends plasticized with sorbitol was investigated. The tensile strength and folding endurance increased, but %elongation decreased in films blended with GA, whereas the mechanical properties of the control film and films blended with PG and BHA were not significantly different. The water solubility of film blends with antioxidants increased with antioxidant polarity. Film blended with GA had the highest water solubility. The T_m of film blends with antioxidants increased or decreased depending on the T_m of the antioxidants. The DSC results confirmed the homogeneity of all film blends.

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