The Journal of Applied Science
วารสารวิทยาศาสตร์ประยุกต์
ISSN 1513-7805 Printed in Thailand

Vol. 16 Special issue: 98-104 [2017]
doi: 10.14416/j.appsci.2017.10.S15

Research Article

Physical and mechanical properties of composite edible films from sago starch and bulk chitosan

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Abstract

The objective of this study was to investigate physical and mechanical properties, such as thickness, water vapor permeability, tensile strength, elongation at break, differential scanning calorimetry (DSC) and microstructure of composite edible films. The film was prepared by casting sago starch from sago palm (*Metroxylon sagu*) as film base with 10-50 %w/w glycerol as plasticizer and adding bulk chitosan as a reinforcing material (0.1, 0.3, and 0.5 %w/w). The continuous, homogenous and transparent films were obtained. With regard to mechanical properties, tensile strength decreased when the percentage of glycerol increased. Elongation at break (%E) improved with increasing percentage of glycerol from 10 %w/w to 50 %w/w. However, water vapor permeability properties diminished in all samples when the percentage of chitosan increased. The morphological study of the composite films exhibited rougher surfaces with increasing chitosan in the films. DSC thermograms showed that glycerol incorporated into composite films diminished the onset temperature (T_0) and degradation temperature (T_d). Having these physical and mechanical properties, this edible film has a potential to apply for food packaging purposes. Moreover, this edible film is proved to be more cost-effective and environmentally friendly.

Keywords: edible films, sago starch, bulk chitosan

Introduction

Nowadays, due to serious environmental problems together with the nonbiodegradability and nonedibility of synthetic packaging materials, there has been intensifying research attention regarding renewable resources for biodegradable edible films production. Potential meterial alternatives to synthetic polymer, which have been extensively researched, are biopolymers comprising polysaccharides, proteins, and lipids. The focus of the research in this area has been on studying the formation, diversity, availability, and unique characteristics of edible films from different sources, e.g. kefiran, starches of different sources, guar, alginate, chitosan, agar, and gelatin (Al-Hassan & Norziah, 2012; Galus & Lenart, 2013; Santacruz et al., 2015). Starch-based films are suitable for use as edible films. They have colorless, odorless, tasteless and good barrier properties (Santacruz et al., 2015). The addition of plasticizer is required to enhance the film elasticity. Glycerol is a well-known plasticizer in a film-forming process, as a result of its stability and compatibility with bioresources used in a packaging system. However, starch-based films are restricted by the water solubility and the water vapour permeability. To solve this drawback, chitosan combination to edible films provides good mechanical properties, no toxicity, biodegradability, higher water vapour barrier and water resistance (Antoniou et al., 2015; Silva-Pereira et al., 2015). Among the starch materials, sago starch obtained from a *Metroxylon sagu* palm tree is cheap and readily available in Southeast Asia. Moreover, sago palm is a local plant in Nakhon Si Thammarat province of Thailand. The physical and chemical properties of sago starch are absolutely similar to those of commercial starches but in-between to those of potato and cereal starches (Nafchi et al., 2012).

The aim of this study was to determine the effect of chitosan and glycerol on the physical and mechanical properties of composite edible films from sago starch-based, and a response morphology investigation for future use in food packaging.

Materials and methods

Materials

Sago starch was produced by Nakhon Si Thammarat Rajabhat University Nakhon Si Thammarat, Thailand. Food grade glycerol was purchased from Merck, Thailand. Chitosan was was purchased from BOI21 Co., Ltd., Thailand. Other reagents were all commercially available. Typically, distilled water was used for all sample preparation in experiments.

Film formation

Sago starch solution was mixed with glycerol as plasticizer at 10, 30, and 50 (%w/w, starch basis). In addition, chitosan was added into the mixing solution at 0.1, 0.3, and 0.5 (%w/w, starch basis). The mixed starch solution was heated at 70 °C for 30 min under continuous stirring and cooled to room temperature. The 35 g of solution was casted on plastic plates as film-forming area with a dimension of 14 × 14 cm^2. The edible films were dried in an oven at 60 °C for 4 h. Dried films were stored in a desiccator at room temperature until tested.

Film thickness

The thickness of each composite film was measured at five different positions with a micrometer (Mitutoyo, Tokyo, Japan).

Water vapor transmission rate (WVTR)

WVTR was evaluated by ASTM E 96-95 (ASTM, 1996) with some modification of the wet cup method. In this method, a Petri dish was filled with 30 mL of distilled water and the edible film was then placed on the Petri dish. The sample dish was placed in a convection oven at 70±0.5°C and 10%RH. The mass of water loss as a function of time was recorded. The slope of the water loss as a function of time normalized to the film area (A) was taken as the WVTR with units of $g.m^{-2}.hr^{-1}$.

$$\text{WVTR} = \frac{\text{mass } H_2O \text{ loss}}{\text{time x area}} = \frac{\text{slope}}{\text{area}} \qquad (1)$$

Tensile strength (TS) and elongation at break (%E)

A materials testing machine (LR150K, LLOYD instrument, USA) was used for TS and %E measurement in accordance with ASTM D882 (ASTM, 2012) with a few modifications. The films were conditioned at 27 °C and 60 ± 1% RH for 48 h prior cut into strips (2 × 6 cm^2). The initial grip separation was set at 50 mm with 10 mm/min of crosshead speed used. TS and %E were determined using parameters in accordance with the following equations (2) and (3):

$$TS = \frac{F}{L \times X} \tag{2}$$

$$\%E = \frac{l - l_1}{l_1} \times 100 \tag{3}$$

Where F is the force (N), L the width (mm), X the thickness (mm), l_1 is the initial length and l is the final length of the film at breaking point.

Differential scanning calorimetry (DSC)

Thermal properties of composite films were determined by using a differential scanning calorimeter (DSC822, Mettler-Toledo, Switzerland). The films were sealed tight in aluminum sample pans. The transition temperatures were achieved from thermograms detailed in the range of -50 to 400 °C at a rate of 10 °C/min in aluminium pans.

Microstructure of composite edible films

Scanning electron microscopy (SEM) was applied to evaluate the microstructure of the composite films. The films were immersed in liquid nitrogen, placed on bronze stubs and coated with a thin layer of gold for 35 s. The surface of each sample film was analyzed by a Merlin compact, Zeiss (Germany) scanning electron microscope.

Fourier Transform Infrared Spectrophotometer (FT-IR)

The FTIR Spectra of glycerol plasticized sago starch film were recorded on Perkin Elmer Spectrum One (USA) using attenuated total reflectance (ATR) accessories.

Results and discussion

The composite starch films were compatible, clear, transparent and uniform with the thickness of 0.04 mm. The physical and mechanical properties were investigated as described below. Figure 1 shows WVTR increased with increasing glycerol incorporation in the films (0.248 $g.m^{-2}.hr^{-1}$) compared to the film without glycerol (0.285 $g.m^{-2}.hr^{-1}$) used as a control. These results are compatible with a plasticizing role of glycerol that reduces intermolecular bonds between the starch chains leading to an increase in intermolecular spacing, which consequently accommodates water vapor transferring through the film (Al-Hassan & Norziah, 2012; Nafchi et al., 2012).

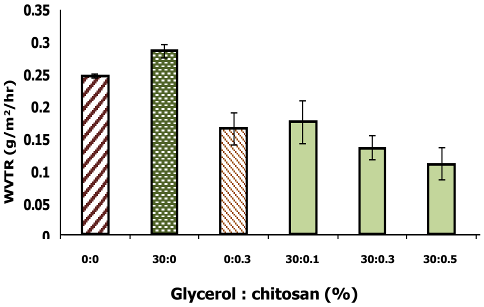

Figure 1. Effect of inclusion of glycerol and chitosan on water vapor transmission rate of composite sago starch films.

Addition of chitosan decreased WVTR of the films significantly. With increasing chitosan concentration and thus an increase in the amount of the amino groups, WVTR decreased indicating that the reduction of WVTR is according to the hydrogen bonding interaction between amino group of chitosan and hydroxyl group of starch and the insoluble in water of chitosan (Antoniou et al., 2015; Santacruz et al., 2015).

The mechanical properties of the composite films with different concentrations of glycerol and chitosan are displayed in Figure 2. As anticipated, by increasing the percentage of glycerol from 0 to 30 %w/w, the TS of the films decreased obviously from 9.77 to 3.01 MPa (Figure 2(a)), while the %E increased from 12% to 23% (Figure 2(b)). The influence of plasticizers on mechanical properties of composite films was caused by hydrogen bonding interaction between the plasticizer and the starch chain causing a disordered stretch with increased chain flexibility (Antoniou et al., 2015). By increasing the amount of chitosan from 0.1 to 0.5 %w/w, the TS of the composite films increased from 3.89 ± 0.03 to 6.02 ± 0.23 MPa (Figure 2(a)), while the %E decreased from 17.12% to 14.05% (Figure 2(b)). Combination of chitosan improved the film's rigidity confirming the reinforcing effect of chitosan on the composite starch films. It could be assumed that the high competency of polar interaction between the amino groups of chitosan and the hydroxyl groups of starch molecule contributes to the film's stiffness (Kelnar et al., 2013).

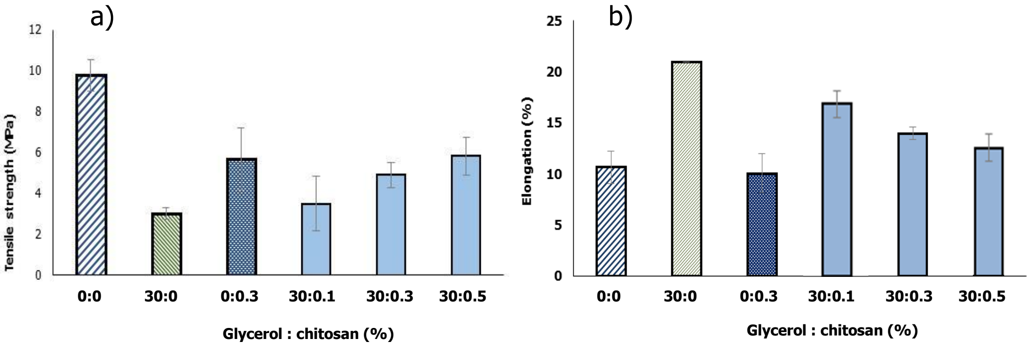

Figure 2. TS and %E of the composite sago starch films with different concentrations of glycerol and chitosan.

DSC was used to investigate the thermal characteristics of the composite films. Figure 3(a) shows DSC thermograms of the composite sago starch-chitosan films with the gelatinization temperature for the sago starch film ranged from 69 to 75 °C which corresponds to the melting temperature of starch (t_m). The transition temperature of the sago starch film exhibited a sharp endothermic peak at 238 °C indicating film degradation temperature due to the chitosan portion (t_d). The characteristic temperature of the starches depends on the morphology and degree of crystallinity within the starch molecule (Ahmad et al., 1999). With the glycerol incorporation into the sago starch-chitosan films, the DSC thermograms illustrated a broad endothermic peak at 165 to 280 °C corresponding to the degradation temperature of 182.2 °C of the glycerol. It causes starch-chitosan-glycerol degradation temperature lies between starch and chitosan film degradation point. Figure 3(a-c) shows increasing of the glycerol concentration decreased onset temperature (T_0) of the films from 38 °C to 30 °C and the T_d from 240 °C to 230 °C. The influences of glycerol on the thermal characteristics are very complicated as a result of the interaction of water on the plasticization process (Mohammadi Nafchi et al., 2011).

The microstructure of the films was studied by scanning electron microscopy (SEM). Figure 4 shows that the incorporation of chitosan into the films interrupted the smooth surface. The composite films presented a rough and non-uniform structure, which was probably due to the aggregated chains of chitosan (Antoniou et al., 2015).

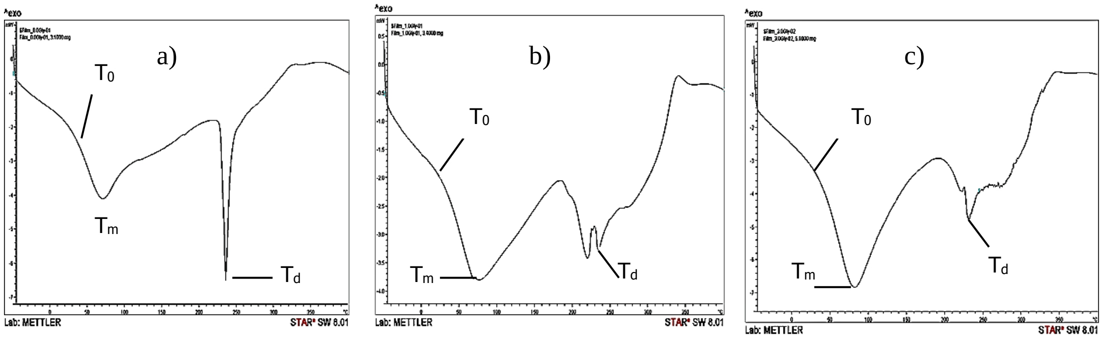

Figure 3. DSC thermograms of the composite sago starch with chitosan films contained different concentration of glycerol: a) 0 %w/w, b) 30 %w/w and c) 50 %w/w.

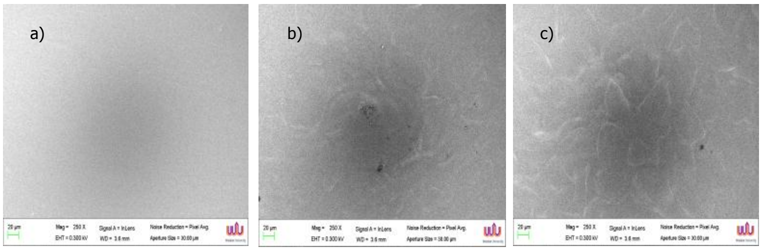

Figure 4. SEM images (100×) of the composite films: a) sago starch film, b) sago starch film with 30%w/w glycerol and c) sago starch film with 30%w/w glycerol and 0.5% chitosan.

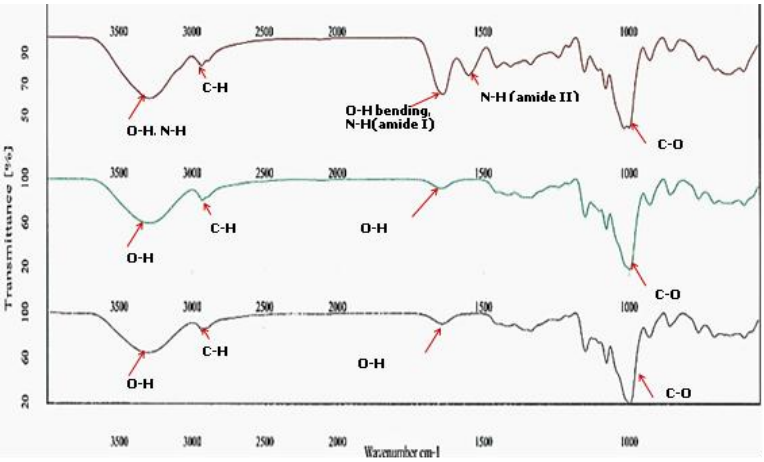

Figure 5. FTIR Spectra of of the composite sago starch films: a) sago starch film, b) sago starch film with 30% glycerol and c) sago starch film with 30% glycerol and 0.5% chitosan.

The FTIR spectra of composite films were recorded on Perkin Elmer Spectrum One using attenuated total reflectance (ATR) accessories. The FTIR spectra of the films are presented in Figure 5. The broad band at 3200-3400 cm^{-1} is a result of O-H stretching of hydroxyl groups and the peak in the region of 2927 cm^{-1} is a result of C-H stretching. The small peak at 1630-1650 cm^{-1} is O−H bending. In the starch-chitosan film spectrum (Figure 5(c)), the characteristic band at 1598 cm^{-1} was related to the stretching vibration of NH_2 groups (primary amine) of chitosan which is covered by O−H stretching peak since both of them lie in the same wavenumber. The N-H bending peak (secondary amide) is observed at 1563 cm^{-1}. The result indicates the interaction between O-H group in starch and N-H group in chitosan. The band located between 1102 and 980 cm^{-1} are attributed to the stretching vibrations of alcoholic C-O in C-O-H bonds corresponds to the hydrogen bonding of the hydroxyl groups of both the starch and glycerol structures (Antoniou et al., 2015).

Conclusion

Edible films were successfully prepared via a casting process of mixing sago starch, chitosan and glycerol composites. The film preparation was produced by mixing sago starch as film base with 10-50 %w/w glycerol as plasticizer. For mechanical improvement, chitosan was added to reinforce the composite edible films with 0.1-0.5 %w/w. The films obtained were uniform and translucent. Increasing of the percentage of glycerol led to decreasing of TS, whereas %E enhanced with increasing percentage of glycerol. The addition of chitosan into the film was achieved. WVTR properties reduced in all sample films when the proportion of the chitosan increased. The microstructure of the films was studied using a SEM. By increasing chitosan in the samples with glycerol plasticizer, the composite films showed a rough and uniform structure. DSC scans displayed that the increase of glycerol content incorporated into the composite films diminished the onset temperature (T_0) and degradation temperature (T_d). The obtained cost-effective and environmentally friendly edible films showed proper physical and mechanical properties and thus have a potential to be used for food packaging purposes.

References

Ahmad, F. B., Williams, P. A., Doublier, J. L., Durand, S. & Buleon, A. (1999). Physico-chemical characterisation of sago starch. *Carbohydrate polymers*, *38*(4), 361-370.

Al-Hassan, A. A. & Norziah, M. H. (2012). Starch–gelatin edible films: Water vapor permeability and mechanical properties as affected by plasticizers. *Food Hydrocolloids*, *26*(1), 108-117.

Antoniou, J., Liu, F., Majeed, H. & Zhong, F. (2015). Characterization of tara gum edible films incorporated with bulk chitosan and chitosan nanoparticles: A comparative study. *Food Hydrocolloids*, *44*, 309-319.

ASTM E 96-90 (1996). Standard test methods for water vapor transmission of materials.

ASTM D882-12 (2012). Standard Test Method for Tensile Properties of Thin Plastic Sheeting.

Galus, S. & Lenart, A. (2013). Development and characterization of composite edible films based on sodium alginate and pectin. *Journal of Food Engineering*, *115*(4), 459-465.

Kelnar, I., Kaprálková, L., Brožová, L., Hromádková, J. & Kotek, J. (2013). Effect of chitosan on the behaviour of the wheat B-starch nanocomposite. *Industrial crops and products*, *46*, 186-190.

Abdorreza, M. N., Cheng, L. H. & Karim, A. A. (2011). Effects of plasticizers on thermal properties and heat sealability of sago starch films. *Food Hydrocolloids*, *25*(1), 56-60.

Nafchi, A. M., Alias, A. K., Mahmud, S. & Robal, M. (2012). Antimicrobial, rheological, and physicochemical properties of sago starch films filled with nanorod-rich zinc oxide. *Journal of food engineering*, *113*(4), 511-519.

Santacruz, S., Rivadeneira, C. & Castro, M. (2015). Edible films based on starch and chitosan. Effect of starch source and concentration, plasticizer, surfactant's hydrophobic tail and mechanical treatment. *Food Hydrocolloids*, *49*, 89-94.

Silva-Pereira, M. C., Teixeira, J. A., Pereira-Júnior, V. A. & Stefani, R. (2015). Chitosan/corn starch blend films with extract from Brassica oleraceae (red cabbage) as a visual indicator of fish deterioration. *LWT-Food Science and Technology*, *61*(1), 258-262.