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学位論文全文に代わる要約
Extended Summary in Lieu of Dissertation

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学位論文題目：
Title of Dissertation
Effect of sugar on the physical properties of starch edible film
(可食性デンプンフィルムの物理的性質に対する糖の影響)

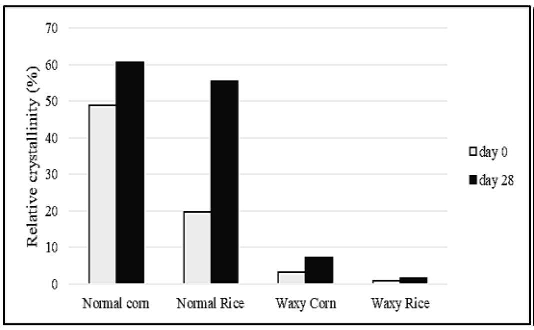
学位論文要約：
Dissertation Summary

Starch, a natural polysaccharide material composed of amylose and amylopectin, is a popular material using to produce a biodegradable and edible film (Dias et al., 2010; Thakur et al., 2017). Recently, many types of starch were researched to use as edible films such as corn starch, cassava starch, rice starch, potato starch, and wheat starch because starch could easily be extracted with high purity and the properties were white, tasteless and odorless powder (Abdou and Sorour, 2014; Menzel, 2014; Veena et al., 2015).

Properties of the film such as tensile strength, water solubility, and transparency from different base materials were important to selecting the film usage. Plasticization would happen in three theories, i.e. lubicity, gel and free volume (Saberi et al., 2016; Suyatma et al., 2005). For lubricity, plasticizer could perform as a lubricant and a reduced frictional force between polymer chains to lubricate the movement of a macromolecule. For gel, plasticizer could disturb the interaction between polymer bonds by hydrogen bonds and van der Waals or ionic force that effect to a three-dimensional structure of the polymer. And for free volume, plasticizer could increase free volume between a starch chain and decreased glass transition temperature (T_g) to lower temperature (Saberi et al., 2016; Suyatma et al., 2005). The plasticity of the polymer could depend on type and level of plasticizer that related to plasticizer chemical structure, chemical composition, molecular weight, and functional groups (Vieira et al., 2011). Thus, many researchers used a plasticizer to improve physical, mechanical and rheological properties of the film (Acosta et al., 2013; Ramos et al., 2013; Tongdeesoontorn et al., 2011; Veena et al., 2015). The selection of plasticizer would depend on component compatibility, amount of plasticizer, characteristic process, thermal, physical, and mechanical properties of the end product (Vieira et al., 2011).

The main purpose of this research is to study the properties of starch, sugar, and concentration that affectes the physical properties of edible film. Thus, the objectives are divided into two part as the effect of sugar type on different starch sources to produce the edible film and the effect of concentration of sugar, which is monosaccharides and disaccharides, on the physical properties of rice starch edible film.

At the first part, the effect of some sugar (maltose, sucrose, and D–allulose) on different starch (normal corn, normal rice, waxy corn, and waxy rice) to produce the edible film was studied (chapter 2). Samples were prepared using 3% (w/w) starch and 20% (w/w) sugar was added to the starch as a plasticizer. Different sources of starch films were prepared and the effect of sugars on the physical and mechanical properties of the films was investigated. The thickness of the starch films was increased by adding sugar. The thickness of the starch films with added sucrose and maltose increased more than the films with added D-allulose because of the higher molecular weight of the plasticizer (180.16, 342.30 and 360.31 g/mol for D-allulose, sucrose, and maltose, respectively). Crystallization was more pronounced by adding sugar and storage. Sugar could be homogeneous and miscible with the starch film. Added sugar decreased breaking stress during storage time when maltose, sucrose, and D–allulose were used as plasticizers. In particular, maltose and sucrose decreased breaking stress more than D-allulose because of the number of hydroxyl (OH) groups, which has the important role of hydration ability in sugar (Kawai et al., 1992). The number of OH groups and/or the size of the molecules of sucrose and maltose compared with that of D-allulose could affect the stabilization of water surrounding the sugar molecule and as a result retard the reorder of starch polymer chains during storage time (Chang et al., 2004; Souza et al., 2013). The results of flow behavior showed shear–thinning properties as determined by the Power law model, and flow behavior was clearly different during the drying process rather than after becoming gelatinized. The apparent viscosity of the waxy starch suspension tended to increase with added sugar in the sample in which sugar inhibited starch chain mobility in the amorphous region. Sugar addition had different effects on the crystallization, the thickness, the morphology of the film surface, the mechanical properties of the film and the flow behavior during drying. Both types of sugar and starch could interact and inhibit starch chain mobility due to the size, hydroxyl group, and hydrogen bond of sugar.



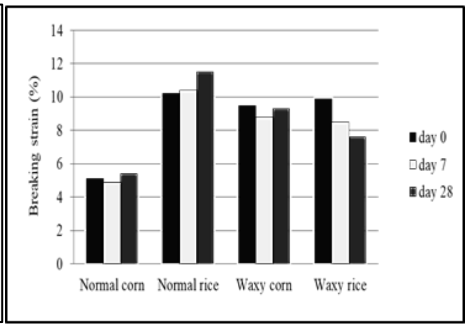


Figure 1 Relative crystallinity and breaking strain of starch film without sugar

The comparison properties between types of starch showed that relative crystallinity of rice starch film was less than that of corn starch film, and breaking strain of rice starch film was more than that of corn starch film (Fig. 1). The effect of sugars as plasticizers on the properties of the starch films was related to both the type of starch and type of sugar. The results of this experiment indicated that rice starch film showed better trend than corn starch film, since rice starch film was less in relative crystallinity and higher in breaking strain than corn starch film on the preparation day and after 28 days storage. Moreover, the mechanical properties of rice starch film were obviously changed by sugar addition.

At the second part, the effect of concentration of sugar on the physical properties of rice starch edible film was described into two experiments as the effect of monosaccharide (chapter3) and the effect of disaccharide (chapter4).

Monosaccharides were studied to use as plasticizer related to hydroxyl groups of sugar and hydrogen bonds formation as similar to glycerol such as sorbitol. Sorbitol was usually used as plasticizer because numerous OH groups of sorbitol could interact with starch (Laohakunjit and Noomhorm, 2004; Saberi et al., 2017; Teixeira et al., 2007). Rare sugar, that is hard to find in nature, has advantage on health to decrease blood glucose level, is lower calories, inhibit body fat accumulation, inhibits cell cancer proliferation, has anti-oxidation, and improves characteristics of food during the food processing (Ikeda et al., 2014; Ishihara et al., 2011; O'Charoen et al., 2014). D–allose, that is a rare sugar also reported to use in health, has a different conformation at C–3 primer from glucose (Bhuiyan et al., 1998; Ishihara et al., 201). Allitol, a rare polyol, resides at the center of the changing way between D–psicose to L–psicose in Izumoring (Hassanin et al., 2017; Izumori, 2006).　The allitol characteristics are sweet and colorless. Allitol was used as a low calories' sweetener, and as a saturation enhancer for a vacuum lyophilization in freeze–dry process (Hassanin et al., 2017). In this part, the characteristics of rice starch film with and without monosaccharide of the different structure (Fig. 2) were investigated.

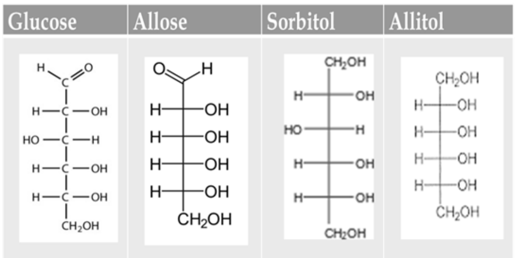


Figure2 Monosaccharides structure

The thickness, moisture content, and water solubility of the film increased, while transparency decreased with increasing concentration of all monosaccharide in this study. Allitol addition showed the highest in moisture content and the lowest in transparency. The breaking stress decreased with an increase in concentration of monosaccharide and storage time. On the day of preparation, breaking strain increased with increasing monosaccharide concentration except for 30% allitol addition. However, breaking strain of all samples decreased after 28 days storage. The high concentration of monosaccharide addition decreased recrystallization of starch film on the day of preparation. However, the recrystallization of starch film obviously increased with 20% and 30% allitol after storage. These results might be due to both anti–plasticization effect and hygroscopic nature or crystal characteristic of allitol according to crystal growth and phase separation by SEM observation. This phase separation might be the resulting of polymer weakness since the function group of plasticizer at a high concentration of allitol was excessive to interact with starch (Ajiya et al., 2017; Sanyang et al., 2016). The anti-plasticization at high allitol concentration was indicated with high relative crystallinity and low mechanical properties of the film, and the results were explained by crystal growth in film morphology. The different characteristic of monosaccharide added rice starch film related to hydrogen bonding interaction for OH of starch with the OH group in sugar alcohol and C-3 primer in rare sugar. The interaction was determined by the chemical shift in NMR. Not only the concentration of sugar but also the structure of sugar was an important factor to the physical properties of rice starch film.

Table 1 Disaccharides properties

Sugar	Sucrose	Maltose	Trehalose
Monomers	Glucose-Fructose	Glucose- Glucose	Glucose-Glucose
OH group	8	8	8
equatorial OH group	6.3	7.6	8
Hydration number	5	5.9	6.6

(Kawai et al., 1992; Ikeda et al., 2011; Saberi et al., 2017)

The effect of concentration of disaccharides on the physical properties of rice starch edible film was studied with varying in number of equatorial OH group as Table 1. The properties of rice starch film with disaccharide (sucrose, maltose, and trehalose) were investigated for thickness, transparency, moisture content, and water solubility. The mechanical properties and relative crystallization were determined on the day of preparation and after storage for 7 days and 28 days. The morphology and NMR analysis were examined on the day of preparation and after storage for 28 days. The results of the experiments showed the film thickness increased with increasing concentration of all three disaccharides, and transparency had a negative relationship with thickness. Moisture content increased with added disaccharide, and water solubility increased with increasing concentration of disaccharide. Water solubility for each concentration increased with increasing both the number of equatorial OH groups and hydration number of disaccharide. Both the number of equatorial OH groups and the hydration number were presented in the order of trehalose > maltose > sucrose. The higher water holding capacity might be a result of higher hydration number and bigger hydrate shell due to the stronger interaction with water structure at higher equatorial OH per molecule of sugar (Russ et al., 2014). In the mechanical properties of the film, the breaking stress of the rice starch film without disaccharide increased with increasing storage time, while the breaking strain decreased with increasing storage time. Adding disaccharide decreased the breaking stress of the rice starch film on the day of preparation and after storage. On the day of preparation, adding 10% disaccharide increased the breaking strain, which was caused by the hydrophilic nature and the number of OH groups of sugar. However, in the case of storage, all concentrations of added disaccharide decreased the breaking strain during storage because of the anti-plasticizing effect of the interaction between plasticizer and starch. The intensity and relative crystallinity increased with the increasing concentration of all three disaccharides. The increasing trend of changing for relative crystallinity (ΔRC) after 28 days storage was inhibited by low concentration of maltose and trehalose addition. The relation of sugar and starch crystalline region might relate to stabilization of starch-sugar interaction associated to the degree of modification of water structure due to steric compatibility of sugar with the pattern of hydrogen bond of the water molecule, that is, the effectiveness of different sugar depended on the matching of an equatorial hydroxyl group in sugar and the “lattice” structure of liquid water (Evageliou et al., 2000). In this situation, the sugar would induce modification of water structure (Chang et al., 2004). Thus, the film with different disaccharide addition had different ΔRC in this study. Pearson bivariate correlation showed a high correlation between the concentration of the disaccharides, thickness, transparency, moisture content, water solubility, and mechanical properties. The rice starch film with 30% disaccharide addition showed homogeneous matrix by SEM and lower frequency chemical shift of proton OH group by NMR than that of the film without disaccharide on the day of preparation. However, the film with 30% maltose addition cracked after 28 days storage. Adding disaccharide as a plasticizer affected the crystallization and the physical and mechanical properties of the rice starch film based on the type and concentration of disaccharide because of the number of OH groups in the disaccharide.

Thus, effect of sugar on the physical properties of starch edible film was depended on many factors such as source of starch, sugar types and concentration of sugar. The effect of sugar was related to the comfortable structure of sugar for interaction with the starch polymer.

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