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Preparation and properties evaluation of chitosan-coated cassava starch films

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Abstract

Chitosan-coated cassava starch films were prepared. In this study, chitosan coating solutions varying from 1 to 4 wt% were coated onto the free starch films containing 2, 3, 4, 5, and 6 wt% glycerol as a plasticizer. The X-ray patterns of the coated dry film showed that the reflection of B-type starch crystalline shifted to slightly higher degrees at about 17.2° (2θ) compared with the free starch film found at 17.0° (2θ). The shifting in starch diffraction peak was probably due to the change in its chain orientation caused by hydrogen-bonding interaction between chitosan and starch molecules, resulting in their good adhesion. Coating of chitosan solutions led to an improvement in several film properties including mechanical and physical properties. The results of mechanical properties evaluation showed that an increase in chitosan coating concentration resulted in a significant increase in tensile stress at maximum load and tensile modulus, and a decrease in percent elongation at break. Film strength along coating direction was higher than that of transverse direction as a result of force applied during coating process. Concerning physical properties, a remarkable decrease in water uptake was observed due to the contribution of hydrophobicity of chitosan coating layer. The hydrophobic acetyl groups of chitosan caused a notable reduction of wettability as well as water vapour permeability which are preferable for packaging film application.

Keywords: Chitosan-coated starch film; Biodegradable film; Water vapour transmission rate; Surface properties and mechanical properties

1. Introduction

Cassava (*Manihot esculenta* crantz) or tapioca is one of the economically important crops in Thailand and the cheapest raw material of starch production. Structurally, cassava starch consists of two types of molecules: amylose, a substantially linear polymer with a molecular weight of about 10^5; and amylopectin, a highly branched polymer with very high molecular weight of about 10^7. The approximate 17% of amylose content is responsible for strong film forming characteristics. Cassava starch can readily be cast into films. However, the cassava starch film is brittle and weak leading to inadequate mechanical properties. Overcoming the brittleness of the film can be accomplished by adding plasticizers. Common plasticizers used for starch films preparation are water, glycerol, sorbitol, and other low-molecular weight-polyhydroxy-compounds (Rindlav-Westling, Stading, Hermansson, & Gatenholm, 1998). Water is an excellent plasticizer, however, it has some disadvantages since water content varies with humidity. At low humidity there are problems with brittleness and at high humidity with softness. Glycerol and sorbitol are widely used as plasticizers because of their stability and edibility. Addition of plasticizers makes the brittle films more flexible, but also less strong. This problem has led to the development of mechanical properties of cassava starch film. Blending (Chandra & Rustgi, 1998) or laminating (Coffin & Fishman, 1993) with other materials could improve the disadvantages.

The scope of films made with starch combined with other polysaccharides was widened to include chitosan for several reasons. First, chitosan is a biopolymer, obtained by N-deacetylation of chitin, which is the second most abundant polysaccharide on the earth after cellulose (Arvanitoyannis, Nakayama, & Aiba, 1998). It is commercially available from a stable renewable source, that is, shellfish waste (shrimp and crab shells) of the sea-food industry. Second, chitosan forms good films and membranes.

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Chitosan films that were clean, tough, flexible, and good oxygen barriers were formed by solution casting (Jeon, Kamil, & Shahidi, 2002). Composited films from chitosan and cellulose have been made by casting dispersions on the steel or chrome plates at elevated temperatures from 70 to 100 °C (Nishiyama, 1993). Some of these films contained glycerol and had good tensile strength. They were readily biodegradable either in sea water or in soil. Third, the cationic properties of chitosan offer the film-maker an opportunity to take advantage of electrostatic interactions with other anionic polysaccharides. Coated films from chitosan and pectin, (Hoagland & Parris, 1996) were prepared by casting with either glycerol or lactic acid as plasticizers. The films were high modulus, flexible and self-supporting, and were advantageous in that all materials were derived from agricultural. In addition, chitosan possesses useful properties such as biodegradability, biocompatibility (Sashiwa, Fujishima, Yamano, Kawasaki, Nakayama and Muraki, 2003), and non-toxicity leading to extensively use over a wide range of applications. Chitosan film has a potential to be employed as packaging, particularly as an edible packaging. This is due to its excellent oxygen and carbon dioxide barrier properties and interesting antimicrobial properties. For example, biodegradable and edible chitosan films were produced to protect foods from fungal decay and modify the atmospheres of fresh fruits.

In this research, chitosan-coated starch film was prepared by coating chitosan solution on cassava starch film containing glycerol as a plasticizer. The combination of hydrogen bonding, opposite charge attraction between chitosan cations and negatively charged starch film surface, hydrophilicity, and compatible water activities provided a good adherence between a starch film and a chitosan film. The relatively more hydrophobicity of chitosan film could be expected to improve the moisture barrier properties and water resistance including dimensional stability of cassava starch film. To obtain the optimum condition for the coated film preparation, the effects of glycerol content and chitosan coating concentration on the physical and mechanical properties were investigated.

2. Experimental

2.1. Materials

Cassava starch or tapioca was purchased from ETC International Trading Co., Ltd (Thailand). The general specifications are as follows: 12.5–13.0% moisture content, 0.20% ash, 0.20% pulp, pH value of 5.00–7.00, and viscosity of 600 BU (Brabender unit). Cassava starch flour was dried in an oven at 50 °C for 24 h and kept in a desiccator prior to use. Commercial grade-chitosan flake (approx. 85% degree of deacetylation) with molecular weight of about 10^6 was purchased from Ebase Co., Ltd (Thailand). Glycerol (approx. 96%) used as a plasticizer in starch films was purchased from Merck KGaA, Darmstadt, Germany. Glacial acetic acid was purchased from BDH Laboratory Supplies (England).

2.2. Film preparation

General preparation procedure of chitosan-coated starch film was described in two steps as follows:

2.2.1. Step 1: Preparation of starch cast films

A mixture of cassava starch dispersion (6% w/v in water) and glycerol used as a plasticizer (varied from 2, 3, 4, 5, and 6% (w/v)) was heated at the starch gelatinization temperature of 70 °C under stirring until viscous and transparent solution was observed. After homogeneously mixing for 10 min this solution was poured into 5 mm thickness acrylic mold with removable edge strips (size: 0.5 cm (height) × 26 cm (width) × 36 cm (length)) and allowed to dry freely at room temperature. After air drying, the edges of the mold were removed and four sides of the film were sealed with adhesive tape to prevent the underneath of starch film from getting contact with chitosan coating solution in the next step.

2.2.2. Step 2: Coating process

Chitosan (varied from 1 to 4% (w/v)) was dissolved in 2% (v/v) acetic acid solution and stirred by a magnetic stirrer at about 700 rpm until the dissolution was completed, which typically taking about 2–3 h. The solution was then filtered prior to coating application. Coating chitosan solution (about 30 mL) onto the starch film was carried out by an automatic film coater with wire bar coating rod number 75(Tester Sangyo Co., Ltd (Japan)). After coating, the acrylic mold support containing chitosan-coated starch film was taken out from the automatic film coater and stored at room temperature, allowing the coated film to dry for at least 72 h. The coated film was peeled from the acrylic mold and measured thickness by micrometer. The dry coated film thickness was fallen within the range of 0.08–0.12 mm.

2.3. Structural analysis by X-ray diffraction

The crystalline structure of film samples was analysed by a Philips diffractometer (Model PW 3710). The Cu K_α radiation ($\lambda = 1.542$ Å) generated at 40 kV and 30 mA was monochromatized with a 15 μm Ni foil. The relative intensity was recorded in scattering range (2θ) of 3–40°.

2.4. Physical and Mechanical Properties Measurement

Film thickness was measured by a micrometer (Peacock, Model G, Japan). Five thickness values were taken along the length of the filmstrip and the mean value was used for tensile strength calculation. Micro-gloss 60° with standard holder of BYK-Gardner GmbH, Germany was employed to measure specular gloss of the film samples according to the ASTM D 523 standard method. Five positions of each film sample were tested and gloss values were averaged to obtain a mean value. The transparency of film samples was measured by Macbeth Color-Eye 7000 spectrophotometer. The percent transmittance of calibrated white standard and film samples was measured in the range of 400–750 nm. A contact angle meter model CAM-PLUS MICRO (Tantec Inc., USA) was used to evaluate the wettability of the film samples. Water Vapour Transmission Rate (WVTR) of films was determined by the gravimetric (dish) method according to ISO 2528 standard method (1995(E)). The determination of water absorption of films was carried out by twenty-four hour immersion method according to ASTM D 570 standard test (1995). Finally, tensile properties of the film samples were tested by universal testing machine LLOYD LR 100K according to the ASTM D 882.

3. Results and discussion

3.1. Physical structure analysis: X-ray diffraction (XRD)

The X-ray diffraction patterns of film samples including free chitosan film, free starch film and chitosan-coated starch film are displayed in Fig. 1.

The semicrystalline characters of free chitosan film and plasticized starch film are revealed from the diffractograms illustrated in Fig. 1(a) and (b), respectively. The diffractogram of chitosan film presented in Fig. 1(a) shows the crystalline peaks (2θ) at 15.3 and 21.1°, which are typical fingerprint for chitosan film and very similar to the work of Wan, Creber, Preppley, and Bui (2003). From previous report (Srinivasa, Ramesh, Kumar, & Tharanathan, 2004), the small peak at approximately 15° (2θ) was attributed to the anhydrous crystal of chitosan whereas the diffraction peak at around 21–22° (2θ) was observed in chitosan film prepared from dissolving chitosan in acetic acid solution (Ritthidej, Phaechamud, & Koizumi, 2002). In this study, however, the intensity of the crystal peak at about 21.1° (2θ) is very low, indicating low crystallinity. It is noted that the degree of deacetylation has obviously affected crystallinity of chitosan film. According to the previous research (Wan et al.), it was observed that the crystallinity of the chitosan film increased gradually with increasing degree of deacetylation ranging from 70 to 90%. This may be attributed to the fact that chains of chitosan with higher degree of deacetylation are more compact leading to facilitate the hydrogen-bonding formation and in turn crytallinity formation in the film. Furthermore, higher degree of deacetylation chitosan contains more glucosamine groups, which also facilitate the hydrogen-bonding formation. On the contrary, lower degree of deacetylation chitosan has more acetyl groups, which hinder the chitosan chain packing due to their rigidity and steric effect. Therefore, the chitosan films prepared from the high degree of deacetylation chitosan contain a large crystalline region. It is quite rare that the production of chitosan with 100% degree of deacetylation is achievable. Therefore, commercial chitosan with various degree of deacetylation in the range of 75–85% is commonly found.

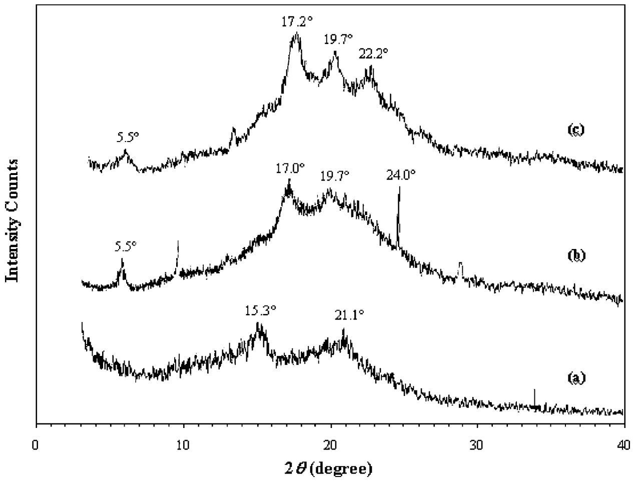


Fig. 1. X-ray diffractograms of: (a) free chitosan film, (b) glycerol-plasticized starch film, and (c) chitosan coated starch film.

Fig. 1(b) shows the diffraction peak of free starch film at approximately 17° (2θ), which resembles to the characteristic of B-type crystalline structure. From previous study (Myllärinen, Buleon, Lahtinen, & Forssell, 2002), amylose film showed the main peaks at about 5.5 and 17° (2θ) while amylopectin film showed broader reflection around 17–18° (2θ). The ordering of B-type structure with water uptake related to the peaks at about 5.5 and 24° (2θ) are the most sensitive to hydration. In addition, the diffraction peak at 19.7° (2θ) is similar to the B-type crystalline peak of amylopectin after storage seven days at 54% RH found in Myllärinen et al.'s work. The observation of the B-type crystalline in the free starch film should be attributed to the fact that crystallization of amylose was developed in the early stage of film formation, whereas that of amylopectin was varied upon the humidity during film formation. The final degree of crystallinity of starch film was dependent on the ability of chains to form crystals as well as the mobility of chains during the crystallization process. The linear amylose and branched amylopectin polymers exhibited different behavior with regard to gelation and development of crystallinity. Amylose and amylopectin are recrytallizable in B-type crystalline form from a dilute solution. In earlier study, X-ray diffraction of amylose solutions showed that the development of crystallinity though fast in the beginning was leveled off approximately 1 day after preparation. In amylopectin solutions, the development of crystallinity was much slower than in amylose solutions, and it had been shown to develop over a period of several days. The amylopectin film without glycerol was amorphous under all conditions because of insufficient time to crystallize before the water content reaching very low values during the drying process. When having glycerol as a plasticizer, however, B-type crystallinity was gradually produced with increasing humidity.

Compared to free chitosan film, the starch film exhibits higher crystallinity as indicated by sharper reflection with higher intensity. The result implies that the polymer chains of starch due to the absence of bulky side group exhibit more packing compact. The difference in molecular orientation is related to the physical appearance of starch and chitosan free films discussed in the next section.

The X-ray pattern of chitosan-coated starch film displayed in Fig. 1(c) shows reflection of B-type starch crystalline shifting to the slightly higher degrees at about 17.2° (2θ) while that of the chitosan appears as a smaller peak at about 22.2° (2θ). The shifting in starch diffraction peaks may be due to the change in its chain orientation caused by chitosan coating. It is likely that hydrogen-bonding interaction between chitosan and starch molecules is responsible for this phenomenon. For chitosan diffraction peak, force and pressure of an automatic film coater probably cause the higher molecular orientation compared to casting technique. In addition, the smaller peak at 5.5° (2θ) and disappearance of peak at 24° (2θ) observed in the diffraction indicate that the amount of water in the coated film was lower than that in the free starch film.

3.2. Surface properties

3.2.1. Physical appearance

Gloss is one of the aesthetic factors enhancing general appearance as well as consumer acceptance. The gloss values of chitosan-coated starch films including free starch film and free chitosan film are graphically shown in Fig. 2, respectively.

The gloss values of free chitosan films are found in the range of 132.5–145.6 units, indicating a highly glossy film probably due to a smooth surface. On the other hand, the gloss values of free starch films are between 52.4 and 60.1 units, reflecting the likelihood of uneven film surface. For the coated films, it can be seen that the gloss values increase with an increase in the chitosan coating solution content. From the results, only 1 wt% chitosan coating solution brings about a significant increase in gloss values of film compared with those of free starch film. The optimum gloss value is achieved when applying the 4 wt% chitosan coating solution. As seen from this figure, the gloss values of 1 wt% chitosan-coated films containing 2, 3, 4, 5, and 6 wt% glycerol are about 87.6, 68.7, 79.2, 80.5, and 83.5 units, respectively. Whereas 4 wt% chitosan-coated films reach the obviously higher gloss values of 107.3, 102.5, 99.3, 106.6, and 97.9 units, respectively, indicating the complete coverage by chitosan layer with an increase in chitosan coating concentration. It could be concluded that the smoother surface of chitosan film enhanced the regularity of coated film surface leading to increasing in the gloss value.

3.2.2. Transparency

The transparency may be affected by various factors including film thickness. In this study, however, there was insignificant difference in average thickness among prepared films. The percent transmittance values of coated films including starch and chitosan free films are presented in Fig. 3.

The percent transmittance of free starch films are found between 91.3 and 94.0% while those of free chitosan films are in the range of 95.3–95.7%. The transmittance of chitosan film is slightly higher than that of starch film. The smoother surface combined with relatively more amorphous structure of chitosan film (from X-ray evidence) may be responsible for transparency. By coating chitosan solutions on these starch films, the little more transparency of the coated films compared with the starch films are observed.

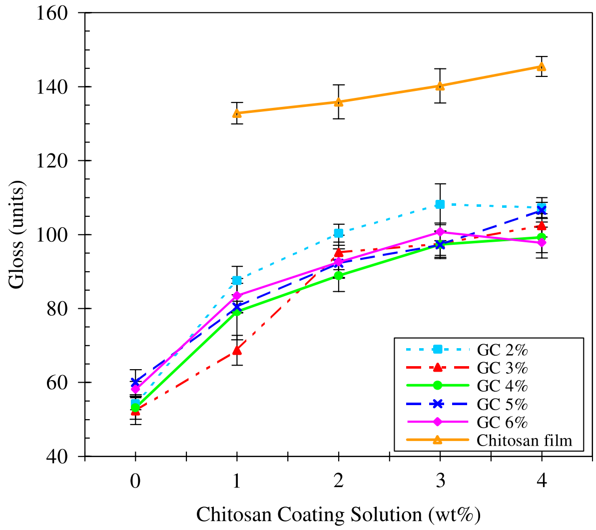


Fig. 2. The relationship between gloss and chitosan coating content of coated films containing 2, 3, 4, 5, and 6 wt% glycerol.

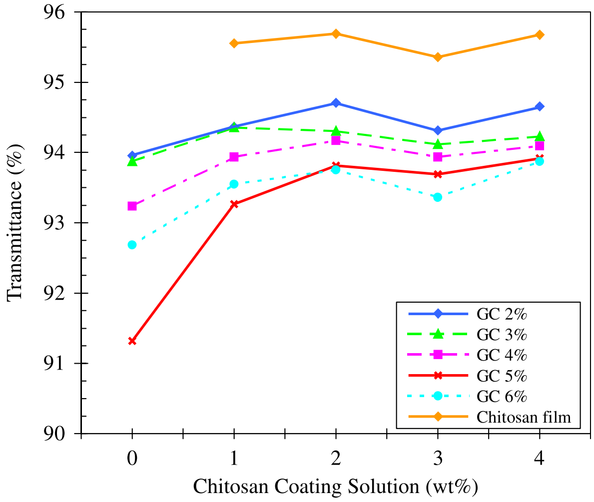


Fig. 3. The relationship between % transmittance and chitosan coating content of coated films containing 2, 3, 4, 5, and 6 wt% glycerol.

However, it can be said that chitosan-coated starch film exhibits higher transparent than the free starch film.

3.2.3. Surface hydrophobicity

Another interesting property of the chitosan-coated starch film is the surface hydrophilicity, which was evaluated by means of contact angle determination. The contact angles of coated films including starch and chitosan free films are shown in Fig. 4.

The contact angles of the free starch films containing 2, 3, 4, 5, and 6 wt% glycerol are 64.4, 59.8, 49.2, 37.8, and 29.8°, respectively. An increase in the amount of glycerol as a plasticizer led to a gradually decreasing contact angle value of starch films due to hydrophilicity of glycerol. The important role of glycerol was to impart the thermoplasticity to the starch film. However, the addition of excess amount of glycerol caused the substantial increase in moisture absorption, which reflected in the decreased contact angle, bringing about the deteriorating mechanical properties of the film (discussed later). Coating of chitosan layer onto the starch film resulted in the change in surface properties including contact angle.

When considering at the particular glycerol content, the free starch film exhibits the smallest contact angle. It can be clearly seen that an increase in concentration of chitosan coating solution brought about a significant increase in contact angle values of the coated films. For example, at 6 wt% glycerol, the contact angle of starch film is 29.8°, whereas that of 1, 2, 3, and 4 wt% chitosan-coated starch film are 40.6, 48.2, 55.8, and 68.6°, respectively, which increase significantly. These results indicate that the wettability of the coated films decreased with an increase in the chitosan coating concentration. This phenomenon was attributed to the higher hydrophobicity of chitosan surface layer, which was associated to the role of available hydrophobic acetyl groups present in chitosan chain. This finding evidence suggests that chitosan film was more hydrophobic than starch film.

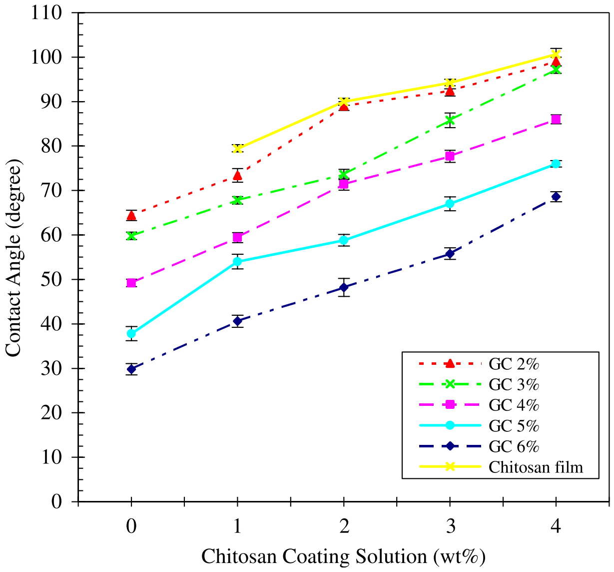


Fig. 4. Effect of chitosan coating contents on contact angles of coated films ccontaining 2, 3, 4, 5, and 6 wt% glycerol.

3.3. Water vapour transmission rate (WVTR)

The water vapour transmission rate (WVTR), often erroneously called water vapour permeability (WVP), is a mass of water vapour transmitted through a unit area in a unit time under specified condition of temperature and humidity. Previous reports stated that the WVTR of polysaccharide films were related to their thickness (Myllärinen et al., 2002). In this study, it was expected to experience the difficulty of minimizing the film thickness variation, which was commonly found from casting technique. In fact, the results of thickness measurement revealed that there was no significant change in thickness among the chitosan-coated films despite the variation of plasticizer concentration and chitosan coating content in each recipe. In this work, factors affecting the WVTR are discussed as follows:

3.3.1. Effect of glycerol contents

Coating of 1 wt% chitosan solution onto the series of foundation starch films containing varying glycerol concentrations was carried out in order to investigate the effect of the plasticizer. The relationship between WVTR and glycerol content is displayed in Fig. 5.

The results show that the WVTR values of the coated films are between about 2290 and 3134 g m^{-2} day^{-1}. As can be seen, an increase in WVTR values depends upon the increasing amount of glycerol. The finding results are found in good agreement with the work of Arvanitoyannis and Biliaderis (1999). Similarly, due to its hydrophilic nature,

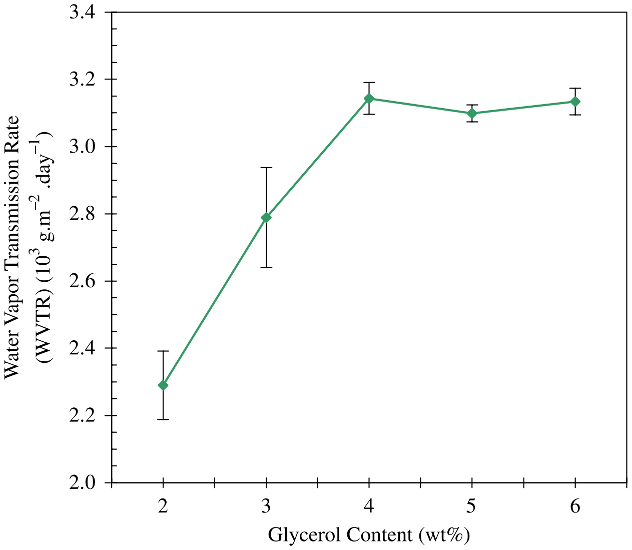


Fig. 5. Water vapor transmission rate values of coated films with respect to glycerol content.

the presence of glycerol seemed to reduce the water vapour barrier properties of the chitosan-coated film. It is known that the role of glycerol is to reduce the polymer packing density, hence increasing the starch film permeable to water vapour. As a result of an increase in free volume, the water vapour diffusion ability rises. Therefore, it is common to observe the high WVTR value of the typical edible film with the addition of hygroscopic plasticizer like glycerol. High water vapour permeability of the edible film is not desirable with respect to its usage performance. The amount of added glycerol, hence, is important in order to balance the thermoplastic property and good barrier properties of the film.

The further results provide information that the WVTR value of the chitosan-coated film reaches its maximum value at 4 wt% glycerol. As seen, there is a sharp increase in the WVTR values of the coated films containing 3 and 4 wt% glycerol before the WVTR values begin to level off afterwards. Hence, it should be recommended that the most suitable glycerol concentration added to starch base film is in the range of 2–4 wt%.

3.3.2. Effect of chitosan coating contents

The chitosan-coated films containing 4 wt% glycerol were selected to study the effect of chitosan coating contents on WVTR. The results of the test are presented in Fig. 6.

It can be clearly observed that effect of chitosan coating on WVTR is opposite to that of glycerol. The WVTR value of the coated film decreases gradually as the concentration of chitosan coating solution increased from 1 to 4 wt%. The decreasing WVTR value of the coated film may be related to the hydrophobicity of chitosan due to the presence of hydrophobic acetyl groups of incompletely deacetylated chitosan. The residual acetyl groups played its part in hindering the transportation of water vapour. In other words, chitosan coating rendered the hydrophobic characteristic to the coated film surface. As a result, the chitosan-coated film exhibited lower WVTR compared to the plain starch film. The chitosan-coated starch film as packaging film therefore offers preferable performance.

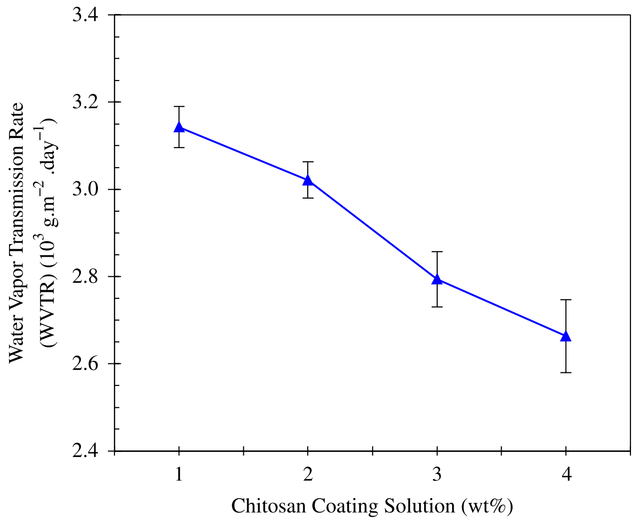


Fig. 6. Effect of chitosan coating contents on water vapor transmission rate of coated films containing 4 wt% glycerol.

3.4. Water absorption

The effects of chitosan coating contents and glycerol on water absorption values of starch and chitosan free films coated films are graphically shown in Fig. 7.

The results reveal that the plasticizer contents had great effect on the % water absorption values of free starch films and coated films. The % water absorption values of 2, 3, 4, 5, and 6 wt% glycerol plasticized starch films are about 84.5, 92.5, 113.0, 125.1, and 172.4%, respectively. The similar trend can be observed in the chitosan-coated films, albeit lower % water uptake compared to the free starch film.

It is quite certain that the relatively lower water uptake of the coated film resulted from the presence of chitosan coating since the ability of the water uptake of the coated film decreased with an increase in chitosan coating content. The remarkable reduction in water uptake is seen with the coated film containing 4 wt% chitosan coating. For example, at 2, 3, 4, 5, and 6 wt% glycerol, the water absorption values of 1 wt% chitosn-coated films are about 71.8, 78.4, 92.2, 113.8, and 125.4%, respectively, whereas those of 4 wt% chitosan-coated films rapidly decrease to 35.7, 49.0, 49.6, 73.7, and 74.8%, respectively. This result is in good agreement with the result from WVTR measurement described earlier. The reason for these results is similar to that discussed in the previous section. Conclusively, the hydrophobic acetyl groups in the chitosan molecules would

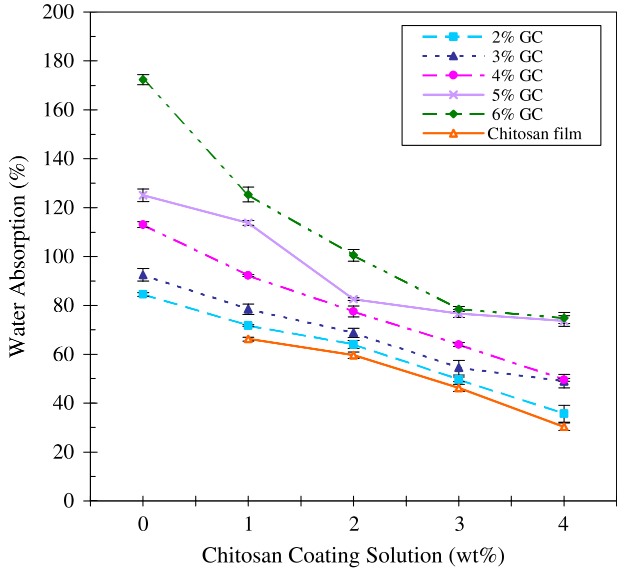


Fig. 7. Effect of chitosan coating contents on water absorption of laminated films containing 2, 3, 4, 5, and 6 wt% glycerol.

result in the lowered water absorption values as well as WVTR.

It should be noted that, however, coating chitosan solution onto starch film containing above 5 wt% glycerol brought about a little drop in percent water uptake. It is likely that the high amount of glycerol in starch film would interfere the surface hydrophobic property of the coated film due to the significant increase in water absorption of the starch base film.

3.5. Mechanical properties evaluation

3.5.1. Effect of glycerol contents

Fig. 8 presents the effect of glycerol content on tensile properties of the free starch films. It is obvious that the tensile strength, tensile modulus, and % elongation at break are strongly influenced by concentration of glycerol.

As increasing the amount of glycerol, the tensile strength and tensile modulus were decreased. The tensile strength values of starch films containing 2, 3, 4, 5, and 6 wt% glycerol were about 4.3, 2.2, 1.0, 0.54, and 0.36 MPa, respectively, whereas the tensile modulus values were about 146.2, 25.1, 5.2, 3.4, and 2.8 MPa, respectively. Considering the % elongation at break, it is found that the % elongation values also decrease sharply with an increase of glycerol content. The % elongation at break of starch films containing 2, 3, 4, 5, and 6 wt% glycerol were 38.9, 33.9, 29.3, 18.3, and 8.3, respectively. It may be argued that the starch films are fairly ductile, especially at 2, 3, and 4 wt% glycerol, since the % elongation at break exceeds 20%. However, as increasing glycerol content, the lower % elongation at break observed in this research did not mean that the starch films showed more brittle character. In contrast, the starch films were more ductile resulting in easy breakage. As seen from the result, addition of 5 and 6 wt% glycerol, the starch films had lost their strength clearly. The tensile strength was decreased to about 0.54 and 0.36 MPa, respectively. Referred to previous reports (Arvanitoyannis, 1999; Arvanitoyannis, Kolokuris, Nakaya, Yamamoto, & Aiba, 1997; Arvanitoyannis, Nakayama, & Aiba, 1998) the strength of plasticized biopolymer films was strongly influenced by the plasticizer. The high plasticizer contents were related to lower crystallinity of biopolymer films, leading to a significant decrease in the mechanical properties. In the study of Rindlav-Westling et al. (1998), it was found that amylopectin was more sensitive than amylose to plasticization caused by glycerol. At 10% glycerol, the mechanical properties measurement of amylopectin film was extremely difficult to perform, whereas stronger amylose film yielded higher mechanical properties. Nevertheless, the effect of glycerol on overall behavior of both amylose and amylopectin films was similar. It was revealed that under low glycerol contents both tensile strength and percentage elongation decreased.

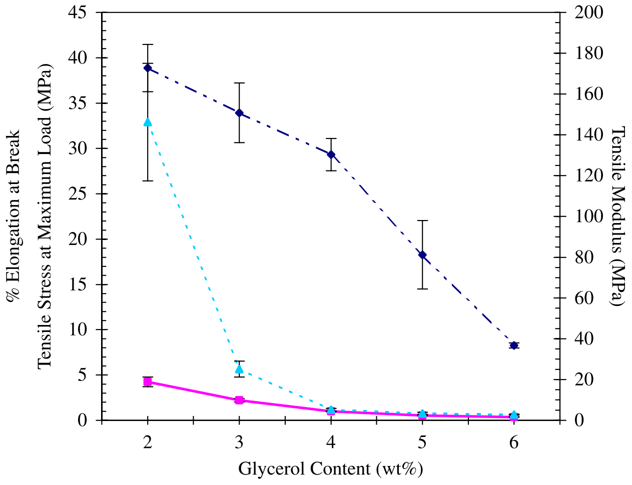


Fig. 8. Effect of glycerol contents on tensile stress at maximum load, tensile modulus, and % elongation at break of free starch films.

3.5.2. Effect of chitosan coating contents

The effect of chitosan coating contents on tensile properties in both machine direction (MD) and transverse direction (TD) of chitosan-coated starch films are shown in Table 1 and 2, respectively.

It can be clearly seen that at individual glycerol content in the coated film there is a significant change on the tensile stress at maximum load and tensile modulus in both of MD and TD upon increasing the amount of chitosan coating. It was found that the tensile stress and tensile modulus values in MD were higher than those values in TD. This is probably because polymer chain of chitosan aligned along the MD of automatic film applicator during applying force to wire bar coater. Regarding to percentage elongation at break, the % elongation at break values in both directions tended to be lower than that of uncoated or free starch films. In addition, % elongation at break in MD was found to be lower than in TD. These results indicate that by coating chitosan onto starch film the tensile properties, in particular tensile stress at maximum load and tensile modulus, of coated film could be improved due to the strength reinforcement of chitosan to the coated film. However, it should be noted that concentration of glycerol in foundation starch film results in a change in anisotropic properties. Anisotropic properties of one-side coated film in the present study can be clearly explained from the coated film containing 2 wt% glycerol. Upon increasing chitosan coating contents, the tensile stress at maximum load and tensile modulus in both directions tend to increase, whereas % elongation at break tends to decrease. For example, in MD, tensile stress at maximum load, tensile modulus, and % elongation at break of 1 wt% chitosan-coated film are about 8.27, 506.29 MPa, and 14.48%, respectively. When chitosan coating solution reaches to 4 wt%, these values are found to be 14.47, 751.34 MPa, and 9.8%, respectively. In TD, tensile stress at maximum load, tensile modulus, and % elongation at break of 1 wt% chitosan-coated film are about 5.08, 267.84 MPa,

Table 1
Tensile properties in machine direction and average thickness of starch and chitosan free films and chitosan coated starch films

	Glycerol (wt%)	Chitosan coating solution (wt%)	Thickness (mm)	Tensile stress at maximum load (MPa)	Modulus of elasticity (MPa)	Elongation at break (%)
Chitosan films	–	1	0.10	10.71 ± 1.61	859.77 ± 71.29	3.16 ± 0.80
	–	2	0.10	14.47 ± 0.41	996.20 ± 97.5	3.45 ± 0.62
	–	3	0.10	17.17 ± 0.73	1133.06 ± 192.24	4.08 ± 1.11
	–	4	0.10	21.02 ± 2.01	1265.53 ± 59.75	4.42 ± 0.27
Starch films	2	–	0.10	4.25 ± 0.53	146.23 ± 28.83	38.87 ± 2.61
	3	–	0.11	2.21 ± 0.17	25.08 ± 3.90	33.93 ± 3.29
	4	–	0.10	0.98 ± 0.05	5.19 ± 0.72	29.33 ± 1.78
	5	–	0.11	0.54 ± 0.03	3.44 ± 0.49	18.28 ± 3.77
	6	–	0.11	0.36 ± 0.04	2.79 ± 0.24	8.27 ± 0.28
Chitosan coated films	2	1	0.10	8.27 ± 1.38	506.29 ± 64.42	14.48 ± 3.57
		2	0.10	7.05 ± 0.56	336.96 ± 121.44	21.32 ± 3.22
		3	0.10	8.02 ± 0.63	453.30 ± 36.35	17.00 ± 1.83
		4	0.10	14.47 ± 1.25	751.34 ± 67.93	9.80 ± 1.06
	3	1	0.10	2.73 ± 0.30	35.36 ± 7.57	27.55 ± 3.73
		2	0.11	3.23 ± 0.19	52.50 ± 6.31	23.58 ± 1.43
		3	0.10	3.44 ± 0.43	80.44 ± 10.27	24.55 ± 4.81
		4	0.11	4.38 ± 0.26	128.32 ± 19.52	20.17 ± 3.22
	4	1	0.11	1.21 ± 0.06	8.29 ± 0.64	17.71 ± 1.26
		2	0.11	1.62 ± 0.11	12.69 ± 0.66	16.60 ± 1.69
		3	0.10	2.38 ± 0.28	22.79 ± 1.11	17.56 ± 2.47
		4	0.10	2.75 ± 0.13	37.70 ± 1.42	17.75 ± 0.73
	5	1	0.11	1.18 ± 0.12	8.82 ± 0.75	15.03 ± 0.86
		2	0.12	1.34 ± 0.01	10.85 ± 0.64	14.55 ± 1.98
		3	0.12	1.48 ± 0.10	12.54 ± 1.52	15.24 ± 1.95
		4	0.11	1.66 ± 0.04	12.94 ± 1.89	17.91 ± 1.04
	6	1	0.11	0.51 ± 0.06	3.71 ± 0.80	15.89 ± 1.33
		2	0.11	0.77 ± 0.03	5.54 ± 0.50	12.51 ± 1.08
		3	0.11	0.81 ± 0.04	5.85 ± 1.18	12.93 ± 1.67
		4	0.10	1.24 ± 0.15	11.71 ± 2.60	13.76 ± 1.01

and 33.1%, respectively, whereas those of 4 wt% chitosan-coated film are 9.6, 657.0 MPa, and 20.26%, respectively.

A significant difference in tensile properties between MD and TD results from the coating process performing on an automatic film applicator. The higher % elongation value found in TD is probably due to less molecular alignment of chitosan film in this direction due to lack of applying force compared to MD as mentioned earlier. In addition, with increasing chitosan coating concentration, a remarkable decrease in % elongation at break compared to coated films containing 3, 4, 5, and 6 wt% glycerol may be attributed to the less plasticizing effect due to the minimized concentration of plasticizer in starch base film, including the effect of brittleness of chitosan film.

As stated earlier, high glycerol contents added to the starch base film result in lowered strength. This effect remains in the coated films. As increasing chitosan coating concentration, an increase in tensile stress at maximum load and tensile modulus in MD and TD of coated films is observed. An increasing trend of coated films containing higher glycerol content is inferior to that of coated film containing 2 wt% glycerol. This is probably because the plasticization in starch base film is more influence than reinforcement of chitosan film. Moreover, it seems that an increase in glycerol content brings about changing properties of the coated films from anisotropy to isotropy. It is observed that there is a little effect on tensile strength of the coated film containing 5 and 6 wt% glycerol upon increasing chitosan coating concentration. Fig. 9 presents the effect of chitosan coating contents on tensile properties of coated film containing 5 wt% glycerol in both directions.

With high glycerol content, especially 5 and 6 wt% glycerol, tensile properties of the coated films in MD and TD are not much difference. Focused on MD of 1 and 4 wt% chitosan-coated films containing 5 wt% glycerol as shown in Fig. 9, tensile stress at maximum load and tensile modulus of the former are about 1.2 and 8.8 MPa, respectively, whereas those of the latter slightly increase to 1.7 and 12.9 MPa, respectively. At 6 wt% glycerol (Fig. 10), although the improved tensile properties of coated films in MD and TD are attributed to an increase in chitosan coating concentration, the greatest tensile strength values obtained from 4 wt% chitosan coating are relatively low, i.e., in MD, the tensile stress at maximum load and tensile modulus are about 1.2 and 11.7 MPa, respectively. Considering overall % elongation at break of coated films containing high glycerol content, the % elongation at break in both directions, especially in TD, tended to increase with increasing the amount of chitosan coating. For example, in TD, the % elongation at break of 1, 2, 3, and 4 wt% chitosan-coated films containing 5 wt% glycerol are about 13.6, 13.7, 15.8, and 18.2, respectively. For 6 wt% glycerol,

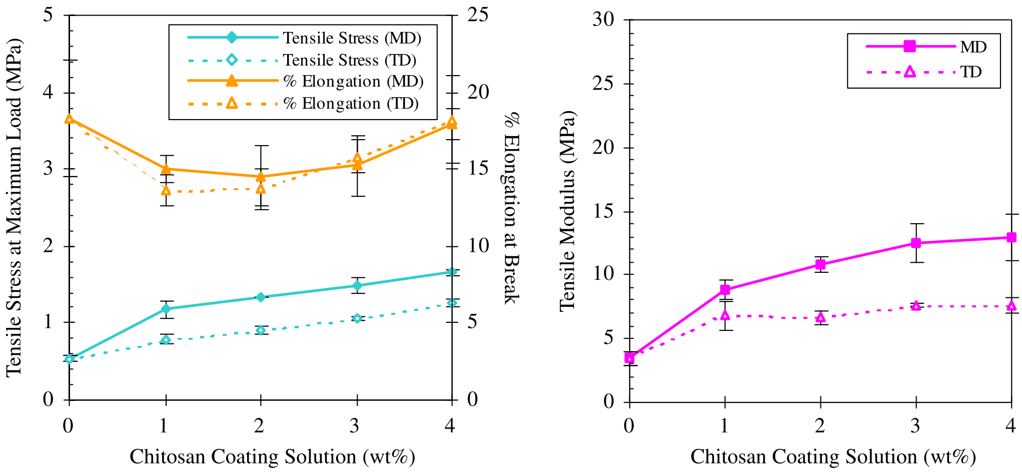
Table 2
Tensile properties in transverse direction and average thickness of starch and chitosan free films and chitosan coated starch films

	Glycerol (wt%)	Chitosan coating solution (wt%)	Thickness (mm)	Tensile stress at maximum load (MPa)	Modulus of elasticity (MPa)	Elongation at break (%)
Chitosan films	–	1	0.10	10.71±1.61	859.77±71.29	3.16±0.80
	–	2	0.10	14.47±0.41	996.20±97.5	3.45±0.62
	–	3	0.10	17.17±0.73	1133.06±192.24	4.08±1.11
	–	4	0.10	21.02±2.01	1265.53±59.75	4.42±0.27
Starch films	2	–	0.10	4.25±0.53	146.23±28.83	38.87±2.61
	3	–	0.11	2.21±0.17	25.08±3.90	33.93±3.29
	4	–	0.10	0.98±0.05	5.19±0.72	29.33±1.78
	5	–	0.11	0.54±0.03	3.44±0.49	18.28±3.77
	6	–	0.11	0.36±0.04	2.79±0.24	8.27±0.28
Chitosan coated films	2	1	0.10	5.08±0.40	267.84±55.93	33.10±4.88
		2	0.11	5.47±0.34	149.17±14.92	31.52±2.15
		3	0.10	6.78±0.70	271.67±11.21	22.54±1.87
		4	0.10	9.6±1.01	657.01±53.98	20.26±2.45
	3	1	0.11	1.67±0.07	7.68±0.84	33.28±3.00
		2	0.10	2.46±0.16	22.63±0.85	35.95±2.81
		3	0.11	2.82±0.07	39.06±4.05	39.70±2.48
		4	0.10	4.17±0.19	53.84±4.69	39.86±1.87
	4	1	0.11	1.17±0.04	6.47±0.49	22.06±1.19
		2	0.10	1.35±0.01	7.23±1.01	23.32±3.37
		3	0.11	1.87±0.08	14.41±2.06	19.72±1.11
		4	0.10	2.40±0.34	18.28±2.38	23.80±2.13
	5	1	0.12	0.79±0.07	6.80±1.14	13.60±1.00
		2	0.11	0.90±0.05	6.68±0.52	13.74±1.34
		3	0.12	1.06±0.02	7.67±0.15	15.79±1.08
		4	0.12	1.26±0.06	7.60±0.66	18.23±2.82
	6	1	0.11	0.38±0.03	4.11±0.95	7.14±1.54
		2	0.11	0.50±0.04	9.05±1.48	7.42±1.08
		3	0.12	0.62±0.05	5.96±0.80	9.92±0.53
		4	0.11	0.88±0.21	7.35±1.68	12.17±1.97

these values are found to be 7.1, 7.4, 9.9, and 12.2, respectively.

High concentration of chitosan coating causes a simultaneously little increase in tensile properties of these coated films. However, the influence of chitosan coating concentration is less than that of glycerol content resulting in a relatively low strength of the films.

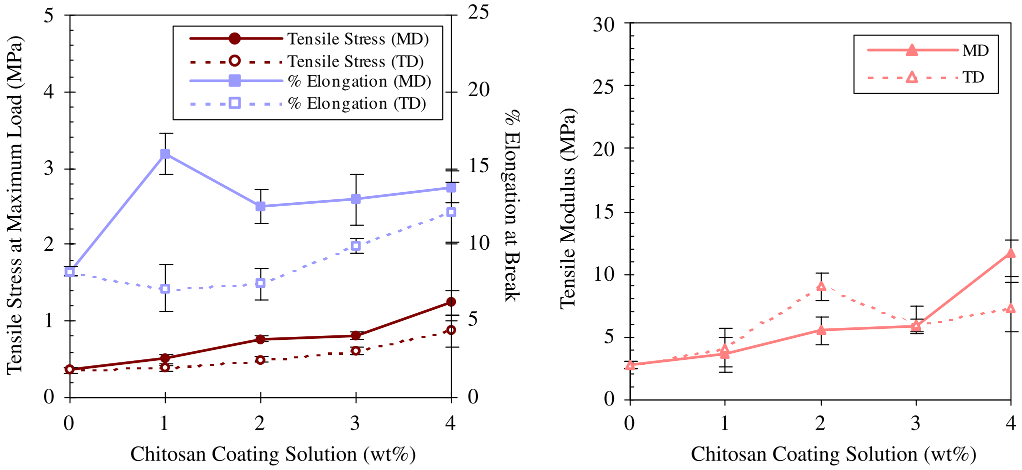
It could be concluded that the tensile strength and modulus values of the coated films are significantly larger than those of free starch films, but overall the elongation at



(a) Tensile stress at maximum load and % elongation at break

(b) Tensile modulus

Fig. 9. Effect of chitosan coating contents on tensile properties of coated films containing 5 wt% glycerol. (a) Tensile stress at maximum load and % elongation at break. (b) Tensile modulus.



(a) Tensile stress at maximum load and % elongation at break

(b) Tensile modulus

Fig. 10. Effect of chitosan coating contents on tensile properties of coated film containing 6 wt% glycerol in MD and TD.

break values are smaller. The higher the chitosan coating concentration, the higher the film strength. The brittle characteristic of chitosan film may be responsible for an increment of tensile strength and tensile modulus of the coated films in both directions. However, the amount of glycerol in foundation film affects the anisotropic properties and characteristic of the coated films. At higher glycerol content, tensile properties of the coated films in MD is similar to that in TD. The coated film is more ductility. The % elongation at break of the film is not still low while the tensile stress at maximum load and tensile modulus of these coated films is close to be zero. The relationship between glycerol content added in foundation starch film and concentration of chitosan coating solution is a very important factor for preparing the coated film with desired tensile properties.

3.6. Conclusions

Coating of chitosan onto starch film by automatic film coater produced the chitosan-coated film with improving performance including surface properties, water vapour barrier capability and mechanical properties. The X-ray diffractogram of the coated film showed the change in reflection characteristics of starch crystalline, indicating the chitosan-starch interaction occurring at the molecular level which led to the strong adhesion between starch base film and chitosan coating layer. This fact was attributed to the hydrogen-bonding interaction between chitosan and starch molecules, leading to structural reorientation and subsequent starch crystallinity.

Glycerol content in foundation starch film was found to adversely affect the water vapour permeability and water absorption. This was because of hygroscopic character of glycerol leading to an increase in free volume of the system, consequently increasing the mass transfer through the film. Fortunately, this disadvantage was compensated by chitosan coating. The chitosan coating resulted in a decrease in water vapour transmission rate as well as the percent water uptake. This may be attributed to the presence of the hydrophobic acetyl group in chitosan, hence rendering the more hydrophobicity to the coated film surface. Furthermore, a significant decrease in wettability of the coated film was obtained as indicated by a sharp increase in water contact angle. The higher the chitosan coating content, the higher the degree of contact angle. This is due to the likelihood of the complete coverage of the chitosan with an increase in chitosan coating concentration.

The results on mechanical properties showed that the tensile properties of the coated films were superior to the free starch films. At low glycerol content, an increase in chitosan coating concentration contributed to a significant increment of tensile strength and tensile modulus in MD and TD while % elongation at break decreased. The coating process caused the improvement in film strength in MD. For coated films containing high glycerol content, the tensile properties were slightly increased as increasing the concentration of chitosan coating solution. However, the film strength was interfered by plasticizing effect. This results provided information that the concentration of a plasticizer was an important factor for preparing the chitosan coated starch film.

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