ELSEVIER

Preparation of cassava starch/montmorillonite composite film

Piyaporn Kampeerapappun, Duangdao Aht-ong, Duanghathai Pentrakoon,
Kawee Srikulkit *

Department of Materials Science, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

Abstract

Cassava starch/montmorillonite composite films were prepared by casting. This research was focused on the exploitation of chitosan as a compatibilising agent in order to homogeneously disperse the clay particles in a starch matrix. Mixtures of cassava starch, montmorillonite (MMT), chitosan, glycerol as a plasticizer, and distilled water adjusted to pH 3 by acetic acid addition was well mixed with a homogenizer and gelatinized by heating to temperatures of 70–80 °C. The obtained homogeneous starch solution was cast onto an acrylic mold and allowed to dry in open air.

X-ray diffraction of the dried film revealed that after treatment with chitosan the interlayer spacing of montmorillonite slightly increased from 14.78 Å to 15.80 Å, providing information that chitosan was too large to intercalate into clay the gallery in order to produce the nanocomposite. Despite the unachieved state of nanocomposite, the evidence from SEM showed that a finer size of clay particles was obtained in the case of the composite film containing chitosan. The results indicated that chitosan due to its hydrophilicity and capability of attaching to the clay surface played a role in compatabilising between starch matrix and montmorillonite. As a result, the starch/MMT composite film at low MMT content exhibited an improvement in tensile properties due to a reinforcement effect. It was also found that the surface hydrophobicity of the composite film increased with an increase in chitosan content. In association with film hydrophobicity, the water vapor transmission rate and moisture absorption were found to decrease with an increase in chitosan content.
© 2006 Elsevier Ltd. All rights reserved.

Keywords: Cassava starch/montmorillonite composite film; Chitosan; Mechanical and physical properties

1. Introduction

There has been a growing interest in the use of biodegradable polymers for packaging materials in order to reduce the environmental pollution caused by plastic wastes. Starch is known to be completely biodegradable in soil and water and inexpensive. Several studies have been carried out on starch-based films obtained by melt processing or casting from a solution or gel with addition of plasticizers. Even so, starch films have poor mechanical properties, brittleness, and sensitivity to water when compared to those of synthetic polymers due to their hydrophilic nature to control. In order to improve the mechanical properties and water resistance, starch can be modified by several methods such as blending with synthetic (Arvanitoyannis, Biliaderis, Ogawa, & Kawasaki, 1998; Bhattacharya, 1998; Wu & Zhang, 2001) or natural polymers (Coffin, Fishman, & Cooke, 1995; Xu, Kim, Hanna, & Nag, 2005), preparing in the composite form (Wilhelm, Sierakowski, Souza, & Wypych, 2003), and by crosslinking (Simkovic, Laszlo, & Thompson, 1996). Recently, special attention has been paid to montmorillonite minerals in the field of nanocomposites because of their small particle size, extremely large surface areas, and intercalation properties.

Montmorillonite is composed of silicate layers that are 1 nm thick in planar structure and 200–300 nm in the lateral dimension. The typical chemical structures of montmorillonite usually consist of two fused silica tetrahedral sheets sandwiching an edge-shared octahedral sheet of

* Corresponding author. Tel.: +66 22185544; fax: +66 22185561.
E-mail address: kawee@sc.chula.ac.th (K. Srikulkit).

either magnesium or aluminum hydroxide. The Na^+ and Ca^{2+} residing in the interlayer regions can be replaced by organic cations such as alkylammonium ions by a cationic-exchange reaction to render the hydrophilic layered silicate organophilic. The hydrophobic behavior and an increase in spacing between the layers of silicate are important factors which make organophilic montmorillonite compatible with most hydrophobic polymers (Hasebawa, Kawasumi, Kato, Usuki, & Okada, 1998; Wang et al., 2003). As a result, the ultrafine dispersion of the order of a few nanometers can be obtained. The unique properties of nanocomposite, not shared by conventional materials, include mechanical strength, thermal stability, fire retardant, molecular barrier, and corrosion protection properties. The preparation of starch/clay nanocomposites was investigated extensively. It was reported that better tensile strength and barrier properties to water vapor was achieved (McGlashan & Halley, 2003; Park, Lee, Park, Cho, & HA, 2003).

In this study, cassava starch/montmorillonite composite films were prepared by the casting process. In order to produce starch film with homogeneous dispersion of fine clay particles, chitosan, the naturally cationic polymer was used as a compatibilising agent for montmorillonite modification. The casting process was carried out by the thermal gelatinization of starch/modified montmorillonite dispersion on acrylic mold. The cast films were then subjected to characterisation analysis (X-ray diffraction and scanning electron microscopy), physical properties (transparency, contact angle, water absorption, and water vapor transmission rate), and mechanical properties (tensile test).

2. Experimental

2.1. Materials

Cassava starch was purchased from E.T.C. International trading Ltd. (Thailand). Commercial grade montmorillonite clay under trade name of Mac-gel was supplied from Thai Nippon Chemical Industry Ltd. (Thailand). Clay was cleaned by immersing in concentrated HCl solution overnight to remove iron oxide. After washing, white clay was collected by filtration and dried at 60 °C. Commercial grade-chitosan flake (approximately 85% degree of deacetylation) with molecular weight of about 10^6 was purchased from Ebase Co., Ltd. (Thailand). Glycerol 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. Cassava/montmorillonite composite film preparation

Cassava starch/montmorillonite composite films were prepared by casting technique. The typical gelatinized starch solution containing well-dispersed particles of modified montmorillonite was prepared as follows: 5 g of oven dried cassava starch flour with chitosan powder (varied from 0 to 15 wt% of starch) and purified montmorillonite clay (varied from 0 to 15 wt% of starch) were physically mixed. Distilled water and glycerol were then added, respectively, to obtain 5 wt% of starch dispersion with 1 wt% glycerol as a plasticizer. Subsequently, the dispersion was mechanically stirred at 1000 rpm followed by the acetic acid acidification to 1% (v/v) in order to dissolve chitosan. The mixture was then heated to the gelatinization temperature of starch (70–80 °C) and continuously stirred at this temperature for 1 h. The starch solution was cast onto acrylic sheet mold with a wet thickness of 2–3 mm. The cast film was dried overnight at ambient temperature. After the water completely evaporated, films were removed and conditioned according to requirements the of the test method used.

2.3. Characterisation of the composite film

2.3.1. X-ray diffraction (XRD)

X-ray diffraction was performed using a PW 3710 Philips diffractometer with CuK_α radiation ($\lambda = 0.1542$ nm) in sealed tube operated at 40 kV and 30 mA. The diffraction patterns were obtained from 2° to 30° at a scanning rate $1° \text{ min}^{-1}$. The basal spacing of the silicate layer, d, was calculated using the Bragg's equation, $\lambda = 2d \sin\theta$ (where θ is the diffraction position and λ is the wavelength).

2.3.2. Scanning electron microscopy (SEM)

Film surface morphology was examined using scanning electron microscopy. The samples were mounted on stub with double-sided adhesive tape and coated with a thin layer of gold. Images were taken using a JEOL scanning electron microscope, JSM-5410LV, using an accelerating voltage of 15 kV, and a magnification 350 times of origin specimen size.

2.3.3. Tensile properties

The tensile strength, % elongation, and modulus values were investigated using Zwick Z010 universal testing machine according to ASTM D882 standard. Samples were cut to 200×15 mm in dimension, and conditioned at $50 \pm 5\%$ RH, 23 ± 2 °C for 24 h. The gauge length and crosshead speed were 100 mm and 10 mm/min, respectively. The tests were carried out at 23 ± 2 °C and $50 \pm 5\%$ RH. Each determination was taken from an average of five specimens.

2.3.4. Transparency

Transparency of cassava starch/montmorillonite composite film was obtained on an Instrument Color System (I.C.S.), Macbeth UV–Vis spectrophotometer, mode transmittance at wavelength from 360 to 750 nm.

2.3.5. Contact angle measurement

The contact angles of film samples were measured using a CAM-PLUS MICRO (Tantec, Inc.) according to Tantec's Half-Angle method. A contact angle of zero

results in wetting, while an angle between 0° and 90° results in spreading of the drop (due to molecular attraction). Angles greater than 90° indicate the liquid tends to bead or shrink away from the solid surface.

2.3.6. Moisture absorption

The moisture absorption of cassava starch/montmorillonite composite film was determined, and the test specimens were prepared in the dimension of 76.2×25.4 mm. The test specimens were dried in a 50 °C oven for 24 h, then cooled in a desiccator, and immediately weighed to obtain the initial weight. The specimens were conditioned in a container at 100% RH for 24 h. After 24 h, the specimens were removed from the container, dried by wiping with cloth, and then weighed immediately to obtain the final weight. The percentage of sample weight increase was calculated by using the formula below.

$$\text{Moisture absorption}(\%) = \frac{\text{final weight} - \text{initial weight} \times 100}{\text{initial weight}}$$

2.3.7. Water vapor transmission rate (WVTR)

The water vapor transmission rate of cassava starch/montmorillonite composite film was carried out according to the specification of ISO 2528-1995E. A minimum of three 90 mm diameter circular test specimens were prepared from each film sample. The test specimen was fastened to a deep dish containing 15 mm of distilled water using a condition B (temperature 38 ± 1 °C and relative humidity $90 \pm 2\%$). The dishes were weighed every hour. The total mass increase graphically as a function of time of exposure, the test being completed when three or four points lie on a straight line. The WVTR for each test piece was then calculated in grams per square meter per 24 h, from the equation.

$$\text{WVTR} = \frac{240 \times m_1}{S},$$

where m_1 is the rate of increase in mass, in mg h^{-1}, determined from the graph; S is the area of the tested surface of the test piece.

3. Results and discussion

3.1. X-ray diffraction (XRD)

X-ray diffraction (XRD) is an effective method for the investigation of the intercalation existence of montmorillonite. In this study, the samples were conditioned at $50 \pm 5\%$ RH, 23 ± 2 °C for 24 h prior to the X-ray measurement. The wide angle X-ray diffraction patterns of montmorillonite (MMT) and chitosan treated montmorillonite in the region between $2\theta = 2°$ and $2\theta = 20°$ are shown in Figs. 1a and b, respectively. The X-ray diffraction curve of MMT shows a single peak at $2\theta = 5.975°$, corresponding to the 001 lattice spacing of silicate layer in montmorillonite as suggested by Usuki et al. (1992). Due
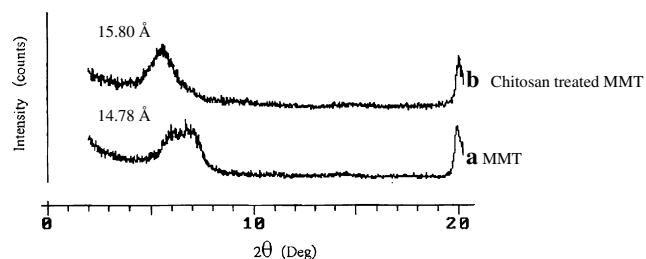

Fig. 1. XRD patterns of montmorillonite and chitosan treated montmorillonite.

to the polycationic characteristic of chitosan in acidic media, this polymer could easily be adsorbed onto the negative charge surface of montmorillonite when cationic-exchange between cationic chitosan and Na$^+$ and Ca^{2+} ions residing in interspacing layer can take place. As a consequence, the state of chitosan (polymer)-layer silicate nanocomposite (PLSN) could be achieved. Three types of PLSN can be described depending on the relative distribution/dispersion of the stacks of clay platelets (a) modified PLSN, where polymer chains are modified into the silicate layers (b) flocculated PLSN, where modified stacked silicate layers are sometime flocculated due to the hydroxylated edge–edge interaction and (c) exfoliated PLSN, where the silicate layers are completely homogenously dispersed in the polymer matrix (Wang et al., 2005). The interaction between chitosan and clay and clay dispersion in the composite film were characterized using XRD. The XRD pattern of chitosan treated MMT shows the diffraction peak of 001 lattice spacing of silicate layer slightly shifting from $2\theta = 5.975°$ to $2\theta = 5.590°$. According to Bragg's law, the interlayer spacing corresponding to these peaks increases from 14.78 Å ($2\theta = 5.975°$) to 15.80 Å ($2\theta = 5.590°$). The increase in interlayer distance is too small when compared to the molecular size of chitosan as the intercalating agent. The result indicates that the treatment of clay by chitosan alone without applying force could not achieve the intercalated state of the nanocomposite. From the previous report (Wang et al., 2005), to form the chitosan/montmorillonite nanocomposite required both the temperature treatment (60 °C) and prolonged stirring time (6 h).

Fig. 2a and b shows the XRD patterns of cassava starch film and its clay composite film containing 10 wt% MMT and 10 wt% chitosan. Both films display a broad band in the region between $2\theta = 15°$ and $2\theta = 30°$. The broad bands observed in this region reflect that the films exhibited a very low percentage of the degree of crystallinity. The XRD pattern of the composite film also shows a peak at $2\theta = 5.015°$ which corresponds to the interlayer spacing between silicate layers of montmorillonite. The interlayer spacing was calculated which slightly increased from 15.80 Å in the chitosan treated montmorillonite to 17.62 Å in the composite film. This phenomenon was likely to be due to the further expansion of layered silicate platelets occurring during the component blending. In the case of the composite films, glycerol was present. As the glycerol
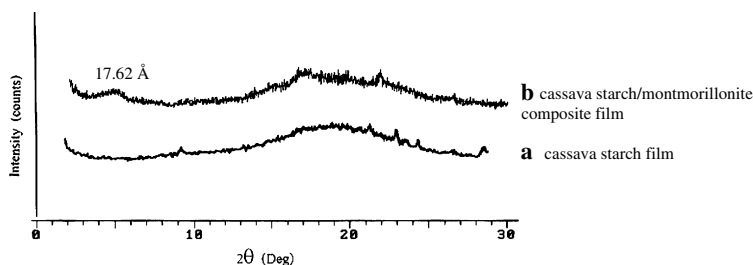
Fig. 2. XRD patterns of starch film samples.

is a very small hydrophilic molecule, it was likely that the further shift in the diffraction peak was due to the intercalation between glycerol molecules and the clay layers (Wilhelm et al., 2003). The XRD results of the composite film indicate that the state of nanocomposite could not be achieved using the method of film preparation described in the experiment since the formation of an exfoliated structure usually results in complete loss of registry between the clay layers. The phenomenon of exfoliation is desirable in terms of significant improvement in several properties of nanocomposites particularly mechanical properties. However, in practice, the problems of acid accelerated starch depolymerization as observed by a significant decrease in viscosity and excessive amount of air bubbles.

3.2. Scanning electron microscopy analysis (SEM)

Surface morphology of starch films under scanning electron microscopy (JEOL scanning electron microscope) was undertaken in order to investigate clay aggregation in the starch matrix. Fig. 3 compares between the microscopic surfaces of starch films containing 10 wt% MMT pristine montmorillonite (Fig. 3a) and those containing 10 wt% chitosan and 10 wt% montmorillonite (Fig. 3b). The bright spots on the image represent size and particle distribution of clay aggregates. It could be seen that, in starch film containing pristine montmorillonite the population of large aggregates around 10 μm in the diameter were commonly observed. In contrast, it is apparent that the clay particles with much smaller sizes are found scattered in the chitosan treated montmorillonite containing starch film. Typically, there is no attractive force between starch and clay, resulting in poor distribution of clay particles in starch matrix. The results show that the use of chitosan promoted the clay disaggregation as well as its better homogenous dispersion in starch matrix. In this system, the chitosan played the role of the compatibilising agent for the starch/clay composite. Since acidified chitosan easily adsorbed onto the clay surface, leading to chitosan modified clay. Also the nature of chitosan is hydrophilic and compatible with starch through hydrogen bonding attraction. Consequently, the chitosan modified montmorillonite aggregates under shear force during blending at the gelatinization temperature were easily dissociated into smaller particles which resulted in hybrids with better dispersion of the clay. It was
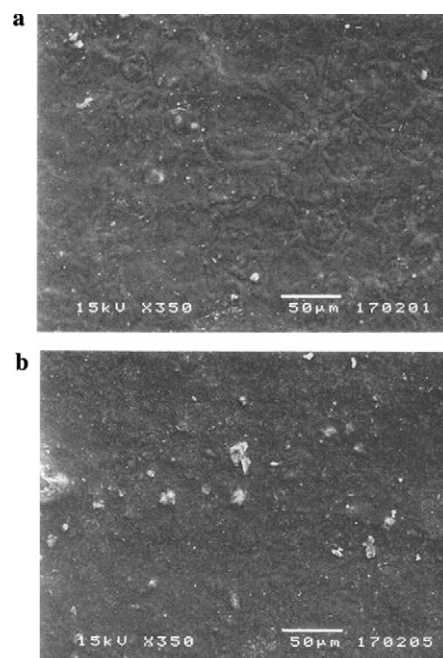

Fig. 3. SEM micrographs of (a) chitosan modified MMT/starch composite film (b) pristine MMT/starch composite film (a) SEM of chitosan modified MMT/starch composite film at 10 wt% MMT (b) SEM of pristine MMT/starch composite film.

expected that the finer clay dispersion, in the case of adding chitosan compatibiliser, in a starch matrix could act as an excellent reinforcement filler enhancing both the mechanical properties and physical properties of the hybrid starch film.

3.3. Tensile properties of starch/chitosan modified montmorillonite composite film

The mechanical properties of the composite films performed by Zwick universal testing machine were measured in terms of tensile strength, % elongation at break, Young's modulus according to ASTM D882. It was possible that varying amounts of clay might affect the film thickness and consequent the mechanical properties. Film thickness measurement was, therefore, carried out using Phynix digital micrometer. It was found that film thickness of films containing 5, 10, and 15 wt% MMT was 71.2, 71.3, and 71.4 μm, respectively. These results indicated that the dry film thickness was not significantly varied with different

amounts of added clay. The resulting mechanical properties of film therefore were reasonably comparable. Figs. 4 and 5 show tensile strength and Young's modulus of 1 wt% glycerol plasticized composite films containing various ratios of montmorillonite and chitosan. The results show that the preparation of starch/chitosan modified montmorillonite composite could improve the mechanical properties of the material. Both the addition of chitosan and montmorillonite increase the composite film strength and stiffness. However, the effect of the two components was quite different. For chitosan, an increase in the amount of chitosan brought about a gradual increase in both tensile strength and Young's modulus. For example, considering the fixed amount of montmorillonite at 5 wt%, the tensile strength values of starch films containing 5, 10, 15, and 20 wt% chitosan are about 21.02, 22.49, 23.14, and 24.64 MPa,

respectively, whereas the tensile modulus values were about 1111, 1111, 1124, and 1225 MPa, respectively. The % elongation values (Fig. 6) also showed a similar trend. Structurally, chitosan is similar to cellulose but contains an NH_2 group in the position of the C_2 hydroxyl group. Due to its linearity high molecular weight chitosan generally possesses the higher mechanical properties when compared with starch which contains branching amylopectin. As a result, the incorporation of chitosan into the starch composite film led to an improvement in both tensile strength and Young's modulus due to the reinforcement effect. The obtained results are found in good agreement with previous report (Bangyekan, Aht-Ong, & Srikulkit, 2006). The effect of montmorillonite addition was found to enhance as well as impair the mechanical properties depending on the wt% addition of clay. At the low montmorillonite content (5–
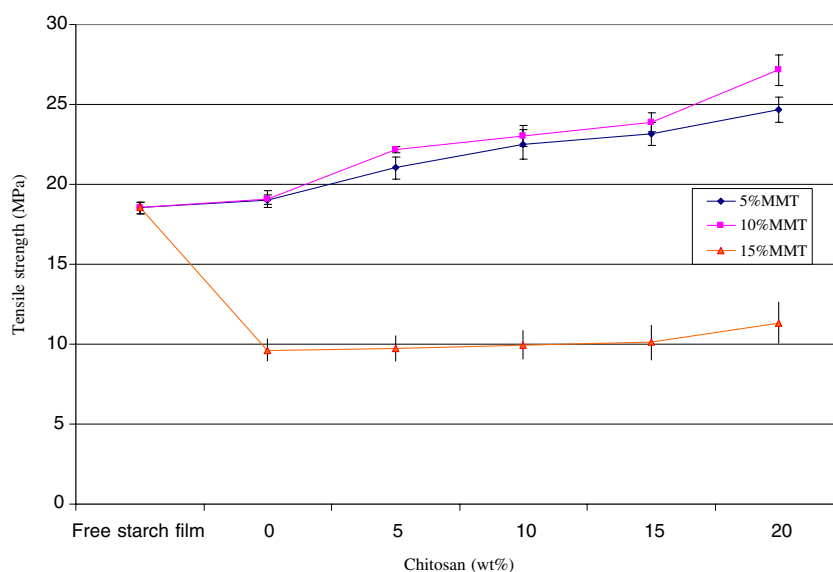

Fig. 4. Effect of MMT and chitosan contents on tensile strength.
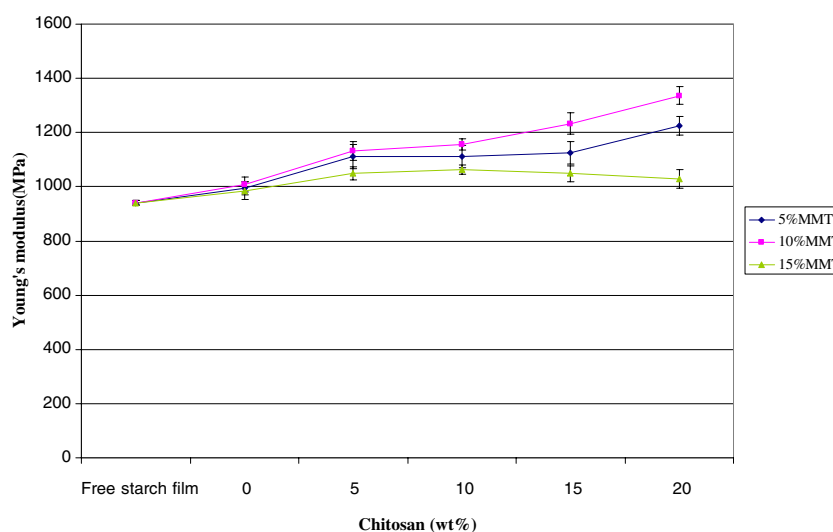

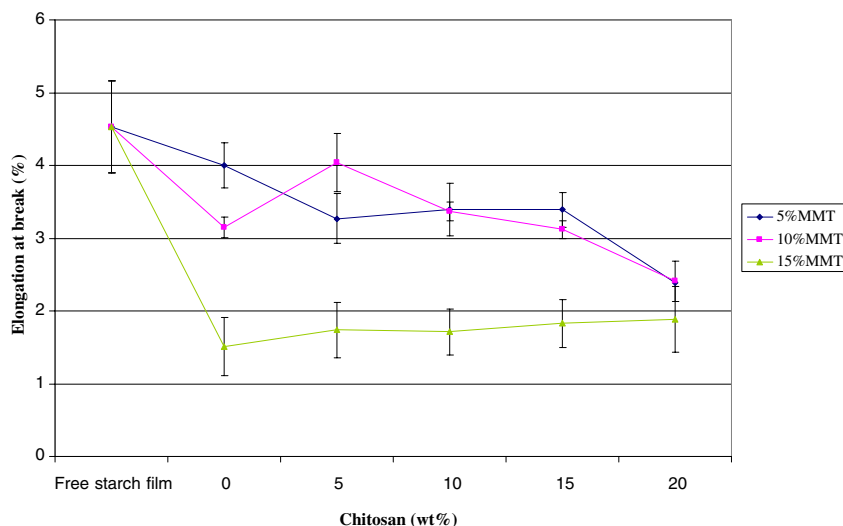Fig. 5. Effect of MMT and chitosan contents on Young's modulus.

Fig. 6. Effect of MMT and chitosan contents on elongation at break.

10 wt%), an increase in clay content resulted in an increase in tensile strength and Young's modulus. A further increase in montmorillonite content such as 15 wt% brought about an adverse effect on the mechanical properties as evidenced by a significant decrease in tensile strength and Young's modulus. These show that clay size and the particle distribution are the crucial factors affecting the mechanical properties of typical composite materials. In this case, it is true to say that at low montmorillonite content chitosan could efficiently attach onto the silicate layer, producing a good chitosan/clay composite. Furthermore, due to its better compatibility with starch matrix, the in situ fine particles produced were easily dispersed, resulting in dispersions with good particle distribution. On the other hand, excess clay content was a likely cause of phase separation and poor particle distribution which led to poor mechanical properties as

proven by decreased tensile strength and Young's modulus. Therefore, the amount of clay addition is an important factor for preparing the composite starch film with desirable tensile properties.

3.4. Transparency

Film transparency provides information on the particle size of dispersed particle in starch matrix. The particle sizes larger than the visible wavelength would obstruct light, leading to translucent or opaque films. However, transparency may be affected by various factors including film thickness. In this study, fortunately, there was insignificant difference in average thickness among prepared films. The percent transmittance values of film samples are presented in Fig. 7.
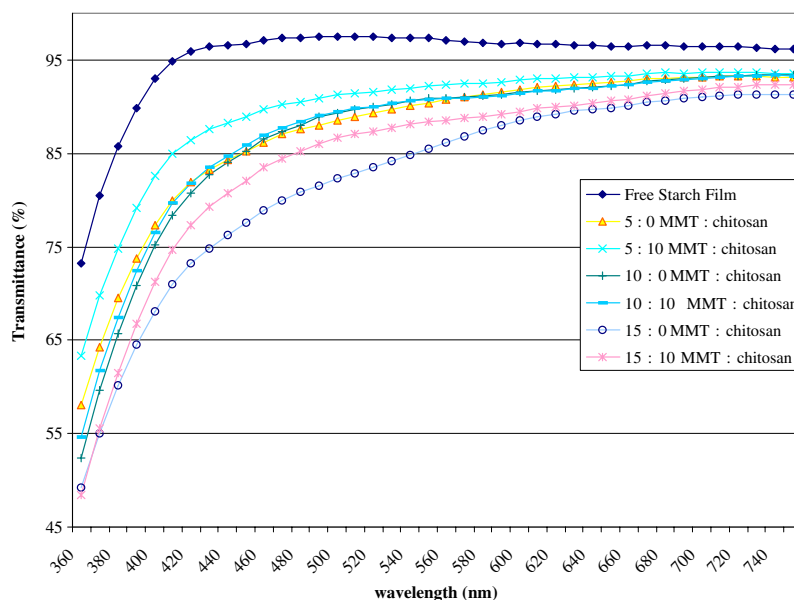

Fig. 7. The percent transmittance of starch/montmorillonite composite films.
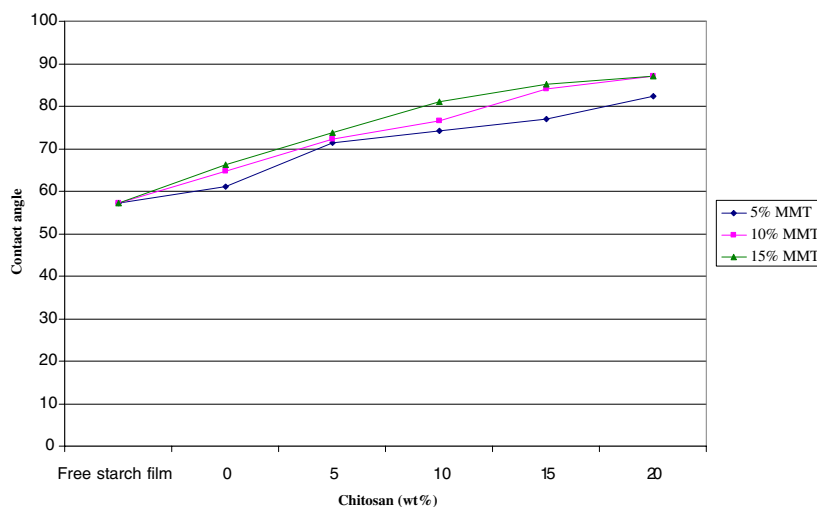
Fig. 8. Effect of chitosan and montmorillonite contents on contact angles of composite films.

From the figure, the free starch film due to the absence of light blockage particles exhibits the highest percent transmittance followed by the starch/chitosan modified montmorillonite composite film and starch film containing pristine montmorillonite, respectively. The larger the particle size the lesser the light transmission, therefore; the results of light transmittance further prove that the particle size of chitosan modified montmorillonite is smaller than pristine montmorillonite.

3.5. Surface hydrophobicity

Another interesting property of the composite film is the surface hydrophobicity, which was evaluated by means of contact angle determination. The contact angles of film samples are shown in Fig. 8.

The results indicate that clay addition did not affect film surface hydrophobicity, however. When considering at a particular clay content, it can be clearly seen that an increase in chitosan content brought about a significant increase in contact angle values of the composite films. For example, at 5 wt% montmorillonite, the contact angles of composite films increase from 62° to 72°, 75°, 78°, and 83° with an increase in the chitosan content from 0, 5, 10, 15, and 20 wt%, respectively. These results indicate that

the wettability of the composite films decreased with an increase in the chitosan content. This phenomenon was attributed to the higher hydrophobicity of chitosan which was associated with the hydrophobic acetyl groups present in chitosan chain. This finding suggests that chitosan is more hydrophobic than starch.

3.6. Water vapor transmission rate (WVTR)

The water vapor transmission rate (WVTR), often erroneously called water vapor permeability (WVP), is a mass of water vapor transmitted through a unit area in a unit time under specified condition of temperature and humidity. The relationship between the WVTR and montmorillonite and chitosan content is presented in Table 1.

The results show that the WVTR values of the composite film are between about 2000 and 1082 $g\,m^{-2}\,day^{-1}$. From the table, it is clearly observed that the WVTR value of the composite film decreases significantly as the chitosan

Table 1
The relationship between WVTR and MMT:chitosan ratio

MMT:chitosan ratio	WVTR ($g\,m^{-2}\,day^{-1}$)
0:0	2000
10:0	1880
10:5	1790
10:10	1669
10:15	1507
10:20	1082
5:10	1583
15:10	1173
20:10	1284

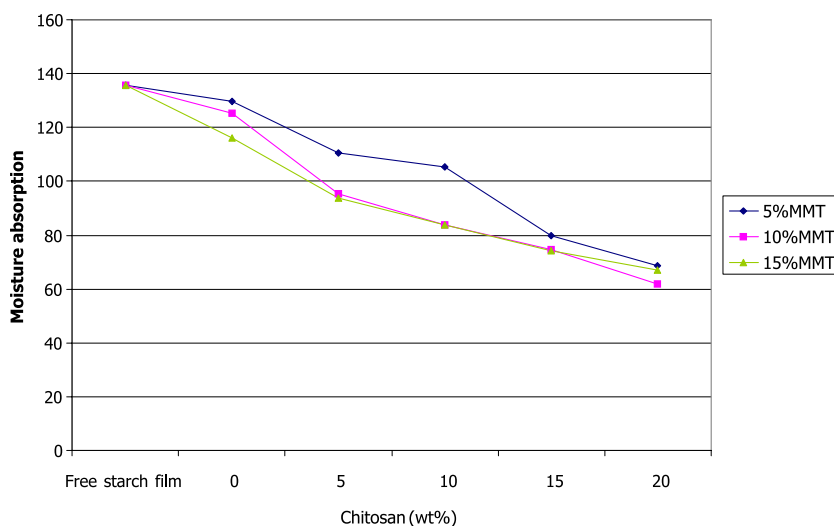Fig. 9. Demonstration of starch/MMT composite film holding water.

Fig. 10. Effect of chitosan and montmorillonite contents on moisture absorption of composite films.

and MMT contents increase. However, the effect of MMT seems to produce an erratic trend. In the case of chitosan, it could be said that an improvement in water vapor barrier was attributable to the film surface hydrophobicity due to the hydrophobic acetyl groups present in the structure of incompletely deacetylated chitosan. This indicates that the residual acetyl groups played an important role in hindering the transport of water vapor, as they increase the hydrophobic characteristic to the composite film. As a result, the composite film showed lower WVTR compared to the plain starch film (see Fig. 9).

3.7. Moisture absorption

The effects of chitosan contents and montmorillonite on moisture absorption values of composite films are graphically shown in Fig. 10.

This result is in good agreement with the result from WVTR measurement described earlier in that the chitosan contents had great effect on the % moisture absorption values of composite films when compared with montmorillonite. For example, at a fixed amount of MMT at 10 wt%, the moisture absorption values decrease significantly from 125% to 95%, 83%, 74%, and 61% with respect to the chitosan contents of 0, 5, 10, 15, and 20 wt%, respectively. The remarkable reduction in moisture uptake is seen with the composite film containing 20 wt% chitosan content. The reason for these results is similar to that discussed in the previous section. The hydrophobic acetyl groups in the chitosan molecules would result in the lowered moisture absorption values, surface contact angle as well as WVTR.

4. Conclusions

Starch/montmorillonite composite films were prepared by casting technique. In order to obtain well-dispersed

MMT particles in the starch matrix, chitosan was employed as a compatibiliser by modifying clay surface through cationic-exchange reaction between acid cationised chitosan and Na^+ or Ca^{2+} ions presented the interlayer region of the aminosilicate layers. As a result, the chitosan modified MMT was in situ produced. Surface morphology examined by SEM and percent transmittance measurement suggested that the average particle size of chitosan treated MMT was notably smaller than those of pristine MMT. Tensile properties of the composite film could be improved by the addition of both chitosan and MMT. Chitosan reinforced the tensile strength and Young's modulus due to the structural similarity to starch, high molecular weight and linearity. In the case of MMT, its size and size distribution played a role in controlling the mechanical properties. At low MMT content, MMT existed in finer particle with chitosan, resulting in an improvement in the tensile properties. On the other hand, an excess in clay content was a likely cause of phase separation and poor particle distribution, leading to poor mechanical properties.

The preparation of starch/montmorillonite composite film also achieved an improvement in the physical properties including reduced surface wettability, a decrease in water vapor transmission rate and moisture absorption. All of these properties were found to be related to the presence of chitosan. It was suggested that the contribution of chitosan to hydrophobicity was associated with the role of available hydrophobic acetyl groups present in chitosan chain. This suggested that chitosan is generally more hydrophobic than starch.

Acknowledgement

References

Arvanitoyannis, I., Biliaderis, C. G., Ogawa, H., & Kawasaki, N. (1998). Biodegradable films made from low density polyethylene (LDPE), rice starch, and potato starch for food packaging applications: Part 1. *Carbohydrate Polymers, 36*, 89–104.

Bangyekan, C., Aht-Ong, D., & Srikulkit, K. (2006). Preparation and properties evaluation of chitosan-coated cassava starch films. *Carbohydrate Polymers, 63*, 61–71.

Bhattacharya, M. (1998). Stress relaxation of starch/synthetic polymer blends. *Journal of Materials Science, 33*, 4131–4139.

Coffin, D. R., Fishman, M. L., & Cooke, P. H. (1995). Mechanical and microstructural properties of pectin starch films. *Journal of Applied Polymer Science, 57*(6), 663–670.

Hasebawa, N., Kawasumi, M., Kato, M., Usuki, A., & Okada, A. (1998). Preparation and mechanical properties of polypropylene-clay hybrids using a maleic anhydride-modified polypropylene oligomer. *Journal of Applied Polymer Science, 67*(1), 87–92.

McGlashan, S. A., & Halley, P. J. (2003). Preparation and characterization of biodegradable starch-based nanocomposite materials. *Polymer International, 52*, 1767–1773.

Park, H. W., Lee, W. K., Park, C. Y., Cho, W. J., & HA, C. S. (2003). Environmentally friendly polymer hybrids Part I Mechanical, thermal, and barrier properties of thermoplastic starch/clay nanocomposites. *Journal of Materials Science, 38*, 909–915.

Simkovic, N., Laszlo, J. A., & Thompson, A. R. (1996). Preparation of a weakly basic ion exchange by crosslinking starch with epichlorohydrin in the presence of NH_4OH. *Carbohydrate Polymers, 30*(1), 25–30.

Usuki, A., Kawasumi, M., Kojima, Y., Okada, A., Kurauchi, T., & Kamigaito, O. (1992). Swelling behavior of montmorillonite cation exchanged for ω-amino acids by ε-caprolactam. *Journal of Materials Research, 8*(5), 1174–1180.

Wang, S. F., Shen, L., Tong, Y. J., Chen, L., Phang, I. Y., Lim, P. Q., et al. (2005). Biopolymer chitosan/montmorillonite nanocomposites: preparation and characterization. *Polymer Degradation and Stability., 90*, 123–131.

Wang, S., Hu, Y., Tang, U., Wang, Z., Chen, Z., & Fan, W. (2003). Preparation of polyethylene-clay nanocomposites directly from Na^+ montmorillonite by a melt intercalation method. *Journal of Applied Polymer Science, 89*, 2583–2585.

Wilhelm, H. M., Sierakowski, M. R., Souza, G. P., & Wypych, F. (2003). Starch films reinforced with mineral clay. *Carbohydrate Polymers, 52*(2), 101–110.

Wu, Q. X., & Zhang, L. N. (2001). Structure and properties of casting films blended with starch and waterborne polyurethane. *Journal of Applied Polymer Science, 79*(11), 2006–2013.

Xu, Y. X., Kim, K. M., Hanna, M. A., & Nag, D. (2005). Chitosan-starch composite film: preparation and characterization. *Industrial Crops and Products, 21*(2), 185–192.