



American Journal of  
**Food Technology**

ISSN 1557-4571



Academic  
Journals Inc.

[www.academicjournals.com](http://www.academicjournals.com)

## Preparation and Characterization of Highly Flexible Chitosan Films for Use as Food Packaging

N. Niamsa and Y. Baimark

Center of Excellence for Innovation in Chemistry, Department of Chemistry,  
Faculty of Science, Maharakham University, Maharakham 44150, Thailand

---

**Abstract:** Highly flexible chitosan films were prepared by film casting of chitosan solutions by using lactic acid solutions as the solvents compare to acetic acid solution. Influences of chitosan molecular weights (100 and 740 kDa), lactic acid concentrations (1.0, 1.5 and 2.0% w/v) and lactic acid configurations (L- and DL-forms) on film characteristics were investigated. Fourier transform infrared (FTIR) spectra of the films showed that there were intermolecular bonds between chitosan film matrices and lactic acids. Tensile strengths at break of the films decreased and percent elongations increased when the lactic acid was used instead of acetic acid for dissolving chitosan. Flexibility of the chitosan films increased with the lactic acid ratio for the both L- and DL-lactic acids. The L-lactic acid showed higher plasticization effect than the DL-lactic acid. Film transparency did not change, whereas watability of the chitosan films increased as the lactic acid ratio increased.

**Key words:** Biodegradable films, lactic acids, plasticizers, mechanical properties

---

### INTRODUCTION

Chitosan is a natural polysaccharide that has received great attention in a variety of applications because of their biodegradability and biocompatibility (Ravi Kumar *et al.*, 2004; Muzzarelli and Muzzarelli, 2005). Because of its excellent film-forming property, chitosan can be used effectively as a film-forming material to use for food packaging (Park and Zhao, 2004; Rhim *et al.*, 2006), wound dressing (Yang *et al.*, 2008) and drug delivery applications (Senel *et al.*, 2000; Shu *et al.*, 2001). However, the broader applications of chitosan films were limited due to its film brittleness. Blending is a simple and convenient method to improve the film flexibility. Various plasticizers such as glycerol, sorbitol, erythritol, polyethylene glycol and fatty acids have been blended with chitosan (Rhim *et al.*, 2006; Kittur *et al.*, 2001; Jeon *et al.*, 2002; Cervera *et al.*, 2004; Srinivasa *et al.*, 2007; Ziani *et al.*, 2008). Different types and amounts of plasticizers used may affect the flexibility of the chitosan films. However, the other plasticizers for improving chitosan film flexibility are still interesting.

Although, the preparation of chitosan films by dissolving chitosan in lactic acid solution before film casting has been reported (Hoagland and Parris, 1996) but there are no reports in the systematic results on the effect of lactic acid with different concentrations and configurations on characteristics of chitosan films.

The objectives of this research were to prepare lower and higher molecular weights chitosan films with two dissolving agents (L- and DL-lactic acids) and to determine the intermolecular interactions between chitosan film matrices and these acids. Mechanical properties of chitosan films were measured to compare plasticizing effect with acetic acid. The morphology, transparency and water vapor sensitivity of the films were also investigated.

---

**Corresponding Author:** Yodthong Baimark, Center of Excellence for Innovation in Chemistry,  
Department of Chemistry, Faculty of Science, Maharakham University,  
Maharakham 44150, Thailand Tel/Fax: +66-43-754246

## MATERIALS AND METHODS

This research was conducted on November 2008-May 2009 at Mahasarakham University, Mahasarakham, Thailand.

### Materials

Chitosans (90% deacetylation) with molecular weights of 100 and 740 kDa were purchased from Sea fresh Chitosan Lab Co., Ltd., (Thailand). L- and DL-lactic acids (90%, Fluka, Switzerland) and acetic acid (99.7%, Lab Scan, Ireland) were used without further purification.

### Methods

#### Film Preparation

Lactic acid can protonate the chitosan molecules by changing  $-NH_2$  of the chitosan molecule to  $-NH_3^+$  in order to make the chitosan more soluble in water. The 1% (w/v) chitosan solutions were prepared by using lactic acid aqueous solution with different concentration as a solvent to obtain chitosan/lactic acid ratios of 1/1, 1/1.5 and 1/2 (w/w), respectively. Twenty milliliter of chitosan solution was poured onto glass Petri dish and dried at 40°C for 2 days before characterization. The film with chitosan/acetic acid ratio of 1/2 (w/w) was also prepared as control by using acetic acid aqueous solution as a solvent. All formulations of chitosan films were shown in Table 1.

#### Film Characterization

Fourier transform infrared (FTIR) spectroscopy was used to characterize functional groups of the films. The FT-IR spectra were obtained by FTIR spectroscopy using a Perkin-Elmer Spectrum GX FTIR spectrometer with air as the reference. The resolution of  $4\text{ cm}^{-1}$  and 32 scans were chosen.

Tensile strength and percentage of elongation at break of the films were measured by tensile tester using a Charra TA-XT2I Texture Analyzer Machine. The films were tested at the 40 mm of gauge length with speed of  $10\text{ mm min}^{-1}$  and 10 N load cell. The tensile strength and elongation at break are calculated from Eq. 1 and 2, respectively. The tensile strength and percentage of elongation at break are obtained from average values of at least three independent samples.

$$\text{Tensile strength at break (N mm}^{-2}\text{)} = \frac{\text{Break force(N)}}{\text{Cross - section area of the sample (mm}^2\text{)}} \quad (1)$$

$$\text{Elongation at break (\%)} = \frac{\text{The increase in length at breaking point (mm)}}{\text{Original length (mm)}} \times 100 \quad (2)$$

Table 1: Formulations, transparency and moisture uptakes of chitosan films

Film No.	M.W. of chitosan (kDa)	Acids	Chitosan/acid ratios (w/w)	$T_{660}^a$ (%)	Moisture uptake <sup>a</sup> (%)
1	100	Acetic acid	1/2	89.5	106
2		L-lactic acid	1/1	90.2	143
3			1/1.5	89.5	179
4			1/2	92.0	182
5	740	Acetic acid	1/2	89.3	104
6		L-lactic acid	1/1	89.5	164
7			1/1.5	90.5	206
8			1/2	90.2	240
9	740	DL-lactic acid	1/1	91.1	134
10			1/1.5	90.5	173
11			1/2	90.8	215

<sup>a</sup>SD were less than 5%

Morphology of film surface and cross-section were determined by Scanning Electron Microscopy (SEM) using a JEOL JSM-6460LV SEM. The film cross-section was obtained after cutting film with paper-scissors. Before SEM measurement, the films were sputter coated with gold for enhancing the surface conductivity.

Film transparency was measured by UV-Vis spectroscopy using a Perkin-Elmer Lambda 25 UV-Visible spectrophotometer at 660 nm as previously described by Rhim *et al.* (2006).

Moisture uptake of the films was determined by the method as earlier described by Khamhan *et al.* (2008). The typical procedure was explained as follows. The sample films with 20×20 mm in size were dried in vacuum at room temperature for a week. After weighing, they were kept in a desiccator with 90±5% Relative Humidity (RH) maintained with a saturated sodium chloride solution at 30±2°C. The sample films were weighed again after kept in the desiccator for a week. The percentage of moisture uptake was calculated from Eq. 3. The moisture uptakes are the average of three different measurements.

$$\text{Moisture uptake (\%)} = \frac{M_f - M_i}{M_i} \times 100 \quad (3)$$

where,  $M_i$  and  $M_f$  are the initial and final weights (g) of the films before and after moisture uptake, respectively.

#### **Statistical Analysis**

The data were expressed as means and SD. Statistical analysis was performed using a one-way analysis of variance (one-way ANOVA).

## **RESULTS**

#### **FTIR Analysis**

The FTIR spectra of chitosan films with M.W. of 100 and 740 kDa prepared by using acetic acid solution as a solvent are shown in Fig. 1a (film No. 1) and 2a (film No. 5), respectively that showed free amino absorption bands at 1547 and 1551  $\text{cm}^{-1}$ , respectively and polysaccharide structure broad bands in the range of 1200-1000  $\text{cm}^{-1}$ . The absorption bands at 1652-1648 and 1315-1310  $\text{cm}^{-1}$  were assigned to amide I and II of residue chitin fractions, respectively indicated that the chitosan used in present study was not fully deacetylated.

The FTIR spectra of chitosan films prepared by using lactic acid solution showed the absorption bands of the both chitosan and lactic acid characteristics as shown in Fig. 1b-d, 2b-d and 3b-d. The carbonyl bands of lactic acids were existed in the range of 1718-1729  $\text{cm}^{-1}$ . The position of amide I and II bands of the residue chitin were also slightly shifted when lactic acid solution was used as a solvent instead of acetic acid solution.

#### **Mechanical Properties**

The tensile strength and elongation at break of chitosan films increased with the M.W. of chitosan as shown in Fig. 4a and b. The chitosan films prepared by using lactic acid solution as a solvent showed more flexible than by using acetic acid solution. The tensile strengths at break of chitosan films decreased and the elongations increased as the lactic acid ratio increased for the all chitosan films prepared by using lactic acid solutions (Fig. 4).

The tensile strengths at break of chitosan films slightly increased and elongations slightly decreased when the DL-lactic acid solution was used instead of L-lactic acid solution as a solvent to prepare the chitosan films.

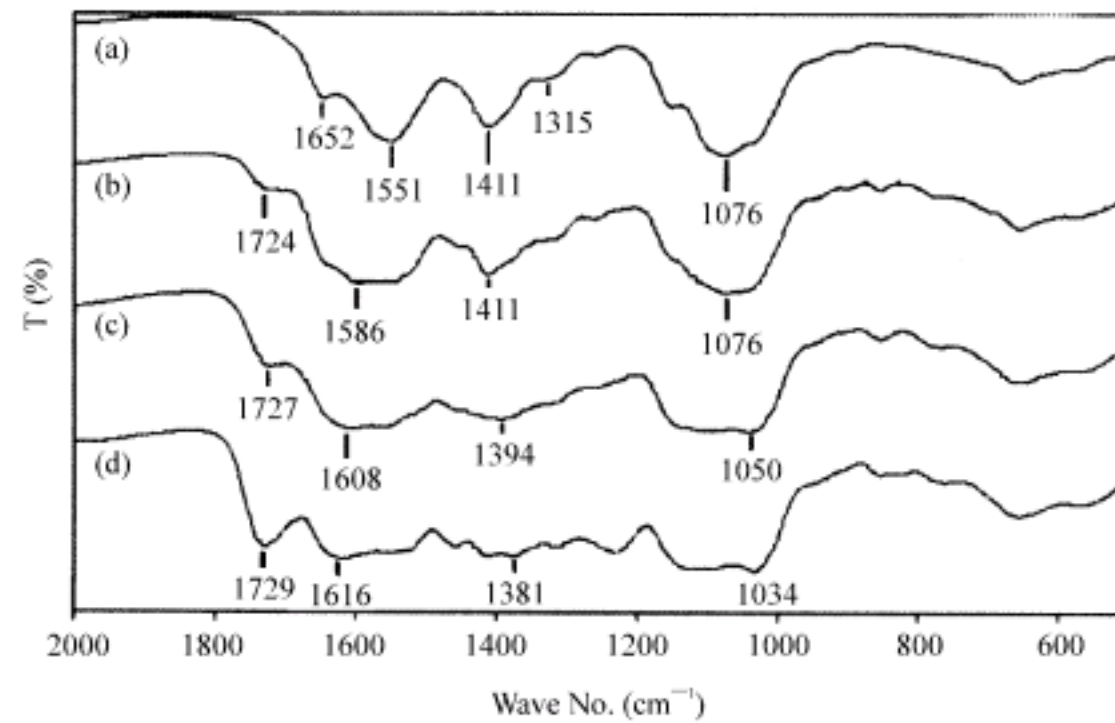


Fig. 1: FTIR spectra of chitosan films with molecular weights of 100 kDa obtained from (a) 2.0% acetic acid (film No. 1), (b) 1.0% L-lactic acid (film no. 2), (c) 1.5% L-lactic acid (film No. 3) and (d) 2.0% L-lactic acid (film No. 4)

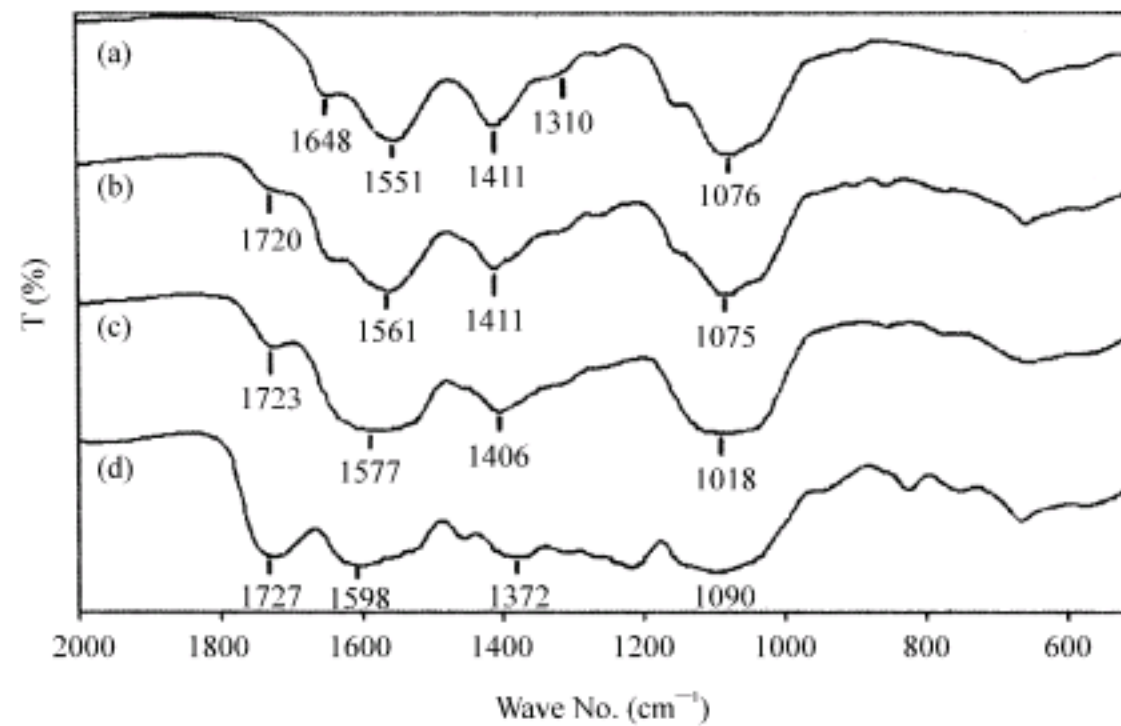


Fig. 2: FTIR spectra of chitosan films with molecular weights of 740 kDa obtained from (a) 2.0% acetic acid (film No. 5), (b) 1.0% L-lactic acid (film No. 6), (c) 1.5% L-lactic acid (film No. 7) and (d) 2.0% L-lactic acid (film No. 8)

#### Film Morphology

All chitosan film thicknesses determined from several SEM images were in the range of 30-40  $\mu\text{m}$  and slightly increased with the lactic acid ratio. The all chitosan films showed homogeneous and continuous phase as example of which is shown in Fig. 5 for the chitosan film with 1/2 (w/w) chitosan/L-lactic acid ratio (film No. 8). The phase separation did not found.

#### Film Transparency

The all chitosan films were transparent and slight yellowish. The transmittance (%) at  $\lambda_{\text{max}}$  660 nm ( $T_{660}\%$ ) was used for studying the film transparency. The  $T_{660}$  (%) values of chitosan films are shown in Table 1. It was found that the  $T_{660}$  (%) values of all chitosan films were similar.

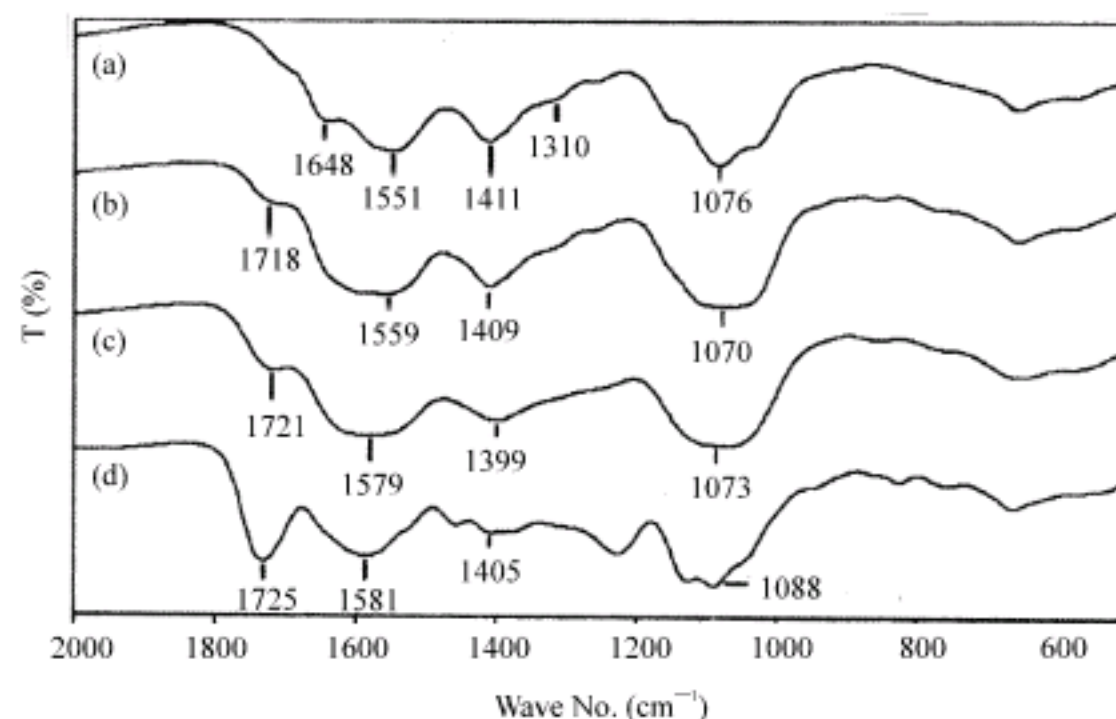


Fig. 3: FTIR spectra of chitosan films with molecular weights of 740 kDa obtained from (a) 2.0% acetic acid (film No. 5), (b) 1.0% DL-lactic acid (film No. 9), (c) 1.5% DL-lactic acid (film No. 10) and (d) 2.0% DL-lactic acid (film No. 11)

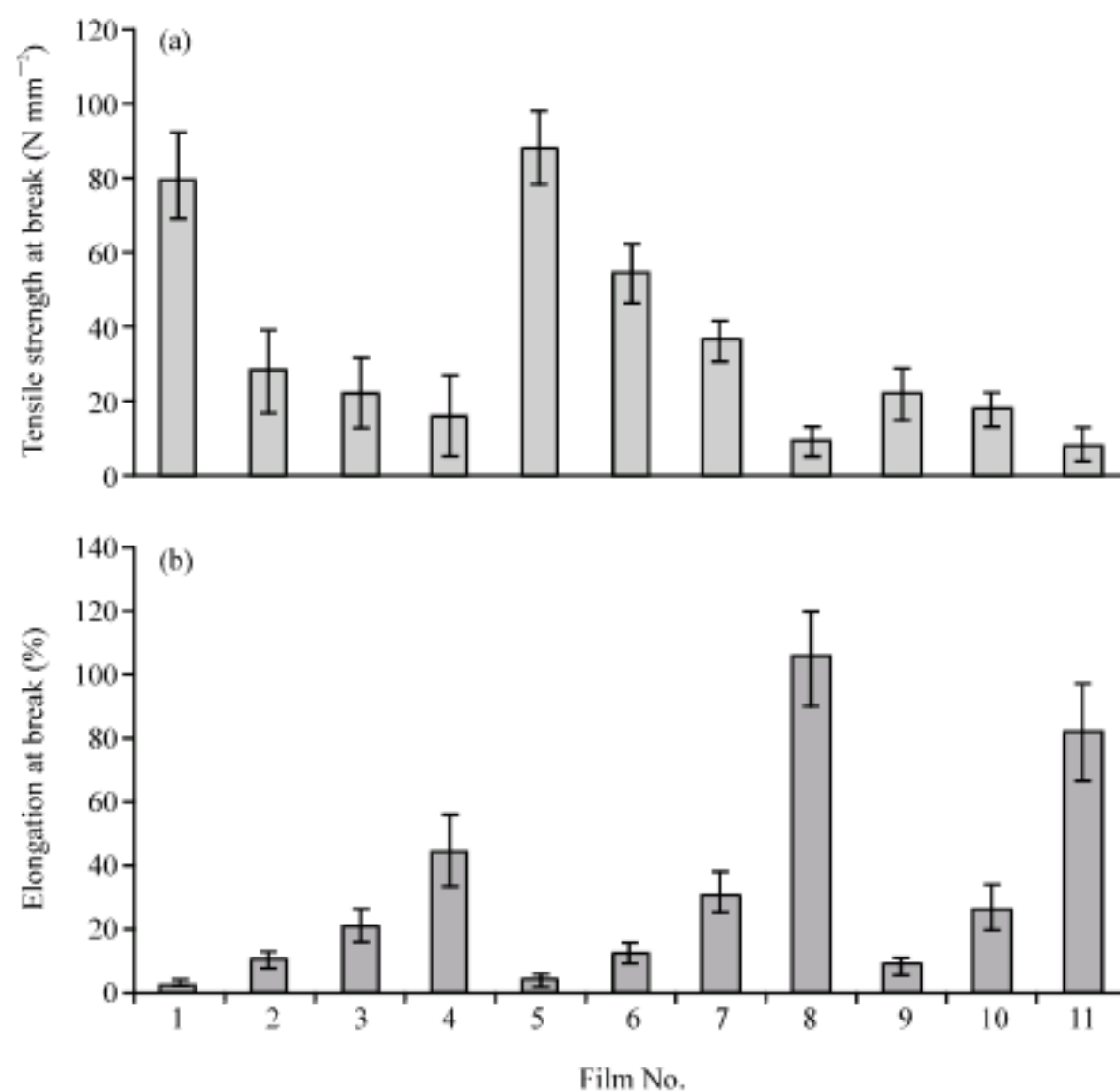


Fig. 4: (a) Tensile strength and (b) elongation at break of chitosan films of various film No. in Table 1

#### Moisture Uptakes of the Films

The moisture uptakes of chitosan films were measured instead of water uptake (immersion in water) because of the partial dissolution of chitosan. The moisture (%) uptakes were calculated from Eq. 3 and also shown in Table 1. The moisture uptakes of chitosan films were increased as the lactic acid ratio increased.

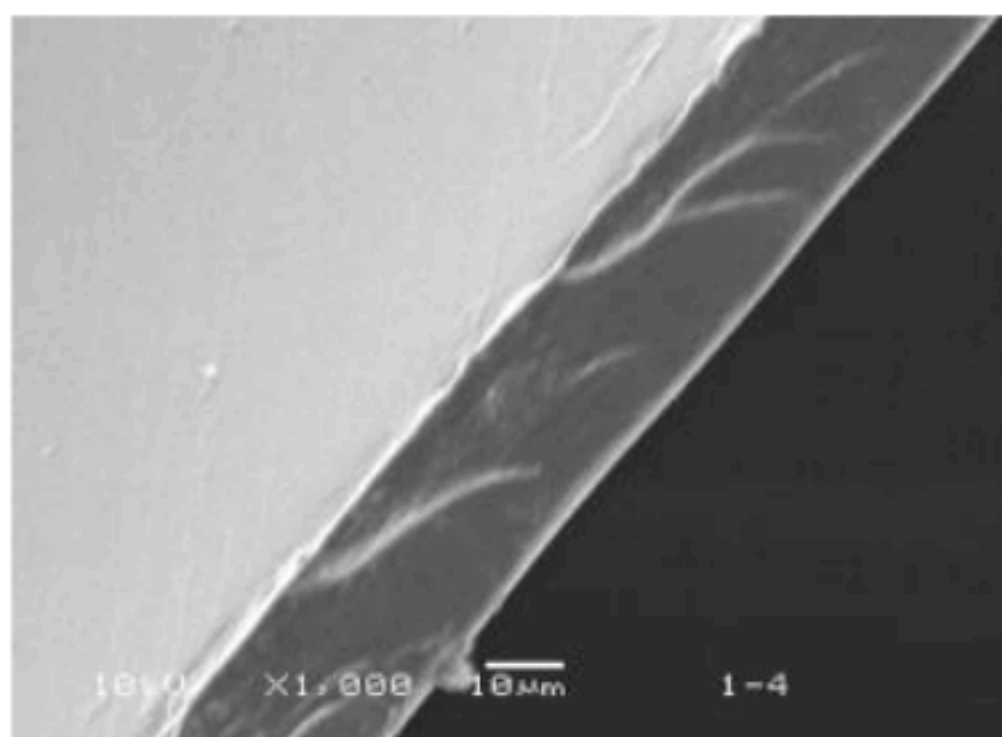


Fig. 5: SEM micrograph of film No. 8

## DISCUSSION

### FTIR Analysis

As would be expected, the intensities of carbonyl bands in the FTIR spectra (Fig. 1-3) increased as the increasing lactic acid ratio. It was found that the free amino bands of chitosan were shifted to higher wave number when the lactic acid was used instead of acetic acid. The existence of intermolecular bonds between free amino groups of chitosan and carbonyl groups of polylactide in the chitosan/polylactide blends has been determined from their FTIR spectra as previously reported by Chen *et al.* (2005). Thus, the shifting of free amino bands of chitosan in our research could be explained by the fact that the intermolecular hydrogen bonds between free amino groups of chitosan and carbonyl groups of lactic acid had occurred. The intermolecular interactions between chitosan film matrix and lactic acid were also confirmed by shifting of the carbonyl bands of lactic acid to higher wave number. In addition, the interactions between residue chitin and lactic acid were detected by shifting of their amide I and II bands.

The carbonyl bands of lactic acid in low M.W. Chitosan films (Fig. 1a-d) shifted to higher wave number than the high M.W. films (Fig. 2a-d) for the same chitosan/lactic acid ratio suggested that the shorter chitosan molecules can interact with lactic acid more than another one. In addition, the carbonyl bands of L-lactic acid in the films (Fig. 2) shifted to higher wave number than the DL-lactic acid in the films (Fig. 3a-d) for the same chitosan/lactic acid ratio. The results indicated that the lactic acid in L-form can interact with chitosan better than the DL-form.

### Mechanical Properties

All high M.W. Chitosan films showed higher tensile strength and elongation at break than the lower M.W. films for all chitosan/acid ratios proposed that an entanglement network forming of high M.W. chitosan molecules during film formation. The L-lactic acid solution has been used to dissolve chitosan for film preparation as previously reported by Hoagland and Parris (1996). However, they did not compare the mechanical properties of chitosan films prepared by using different lactic acid configurations (L- and DL-forms) and ratios. In this study, we add more results of mechanical properties on chitosan film analysis data.

The results of mechanical properties indicated that the both lactic acids act as better plasticizers for the chitosan films than the acetic acid. It is important to note that the chitosan films changed from rigid to highly flexible films when the lactic acid blend ratio was increased for the both chitosan molecular weights (100 and 740 kDa) and lactic acid configurations (L- and DL-forms). In addition, the L-lactic acid showed greater plasticization effect than the DL-lactic acid for the all chitosan/lactic acid ratios. This may be indicated that the D-lactic acid contained in DL-lactic acid should be worse than the L-lactic acid for chitosan film plasticization.

#### **Film Morphology**

From the morphological results, the adding lactic acids did not effect to film morphology suggested that the film properties were consistent throughout the film matrices.

#### **Film Transparency**

The  $T_{660}$  (%) values of all chitosan films did not different suggested that their film transparencies were similar. The results showed that the lactic acid loading did not effect to chitosan film transparency. This can be explained that the lactic acids are well homogeneous blended through the chitosan film matrix. These clear chitosan films can be used as edible invisible films for food packaging.

#### **Moisture Uptakes of the Films**

The moisture uptakes of chitosan films were decreased when the methoxy poly (ethylene glycol)-b-poly( $\epsilon$ -caprolactone) contained hydrophobic character was nano-composited (Khamhan *et al.*, 2008). In our study, increasing of moisture uptakes of chitosan films with the lactic acid ratio may be due to the lactic acid had higher moisture adsorption than the acetic acid. Then, lactic acids enhanced watability of the chitosan films.

### **CONCLUSION**

The L- and DL-lactic acid solutions can be used as the solvents instead of acetic acid solution to prepare the chitosan films. The intermolecular interactions between chitosan film matrix and lactic acids were determined from the FTIR analysis. The carbonyl groups of lactic acids can interact with the free amino and amide groups of chitosan and residue chitin, respectively. The both L- and DL-lactic acids showed potential for using as good plasticizers to improve film flexibility (increasing elongations at break of the films) of the both low and high chitosan molecular weights. The plasticization effect of L-lactic acid showed greater than the DL-lactic acid. Then, it may be expected that the lactic acid in L- and DL-forms can act as better plasticizers than in D-form. The using lactic acid instead of acetic acid for chitosan film preparation did not effect to film transparency but increasing the moisture uptakes.

These highly flexible edible chitosan films may possibly have potential for use as the invisible food coating and the drug delivery applications. The film flexibility can be adjusted by varying the chitosan/lactic acid ratio and lactic acid configuration.

### **ACKNOWLEDGMENTS**

The authors gratefully acknowledge the Research Development and Support Unit, Maharakham University and the Center of Excellence for Innovation in Chemistry (PERCH-CIC), Commission on Higher Education, Ministry of Education, Thailand for financial supports.



## REFERENCES

- Cervera, M.F., J. Heinamaki, K. Krogars, A.C. Jorgensen, M. Karjalainen, A.I. Colarte and J. Yliruusi, 2004. Solid-state and mechanical properties of aqueous chitosan-amylose starch films plasticized with polyols. *AAPS Pharm. Sci. Technol.*, 5: E15-E15.
- Chen, C., L. Dong and M.K. Cheung, 2005. Preparation and characterization of biodegradable poly (L-lactide)/chitosan blends. *Eur. Polym. J.*, 41: 958-966.
- Hoagland, P.D. and N. Parris, 1996. Chitosan/pectin laminated films. *J. Agric. Food Chem.*, 44: 1915-1919.
- Jeon, Y.J., J.Y.V.A. Kamil and F. Shahidi, 2002. Chitosan as an edible invisible film for quality preservation of herring and atlantic cod. *J. Agric. Food Chem.*, 50: 5167-5178.
- Khamhan, S., Y. Baimark, S. Chaichanadee, P. Phinyocheep and S. Kittipoom, 2008. Water vapor permeability and mechanical properties of biodegradable chitosan/methoxy poly (ethylene glycol)-*b*-poly(*ε*-caprolactone) nanocomposite films. *Int. J. Polym. Anal. Cha.*, 13: 224-231.
- Kittur, F.S., N. Saroja and H.R.N. Tharanathan, 2001. Polysaccharide-based composite coating formulations for shelf-life extension of fresh banana and mango. *Eur. Food Res. Technol.*, 213: 306-311.
- Muzzarelli, R.A.A. and C. Muzzarelli, 2005. Chitosan chemistry: Relevance to the biomedical sciences. *Adv. Polym. Sci.*, 186: 151-209.
- Park, S.I. and Y. Zhao, 2004. Incorporation of a high concentration of mineral or vitamin into chitosan-based films. *J. Agric. Food Chem.*, 52: 1933-1939.
- Ravi Kumar, M.N.V., R.A.A. Muzzarelli, C. Muzzarelli, H. Sashiwa and A.J. Domb, 2004. Chitosan chemistry and pharmaceutical perspectives. *Chem. Rev.*, 104: 6017-6084.
- Rhim, J.W., S.I. Hong, H.M. Park and P.K.W. Ng, 2006. Preparation and characterization of chitosan-based nanocomposite films with antimicrobial activity. *J. Agric. Food Chem.*, 54: 5814-5822.
- Senel, S., G. Ikinici, S. Kas, A. Yousefi-Rad, M. F. Sargon and A.A. Hincal, 2000. Chitosan films and hydrogel of chlorhexidine gluconate for oral mucosal delivery. *Int. J. Pharm.*, 193: 197-203.
- Shu, X.Z., K.J. Zhu and W. Song, 2001. Novel pH-sensitive citrate cross-linked chitosan film for drug controlled release. *Int. J. Pharm.*, 212: 19-28.
- Srinivasa, P.C., M.N. Ramesh and R.N. Tharanathan, 2007. Effect of plasticizers and fatty acids on mechanical and permeability characteristics of chitosan films. *Food Hydrocolloids*, 21: 1113-1122.
- Yang, J.M., S.J. Yang, H.T. Lin, T.H. Wu and H.J. Chen, 2008. Chitosan containing PU/Poly(NIPAAm) thermosensitive membrane for wound dressing. *Mater. Sci. Eng. C*, 28: 150-156.
- Ziani, K., J. Oses, V. Coma and J.I. Mate, 2008. Effect of the presence of glycerol and Tween 20 on the chemical and physical properties of films based on chitosan with different degree of deacetylation. *LWT. Food Sci. Technol.*, 41: 2159-2164.