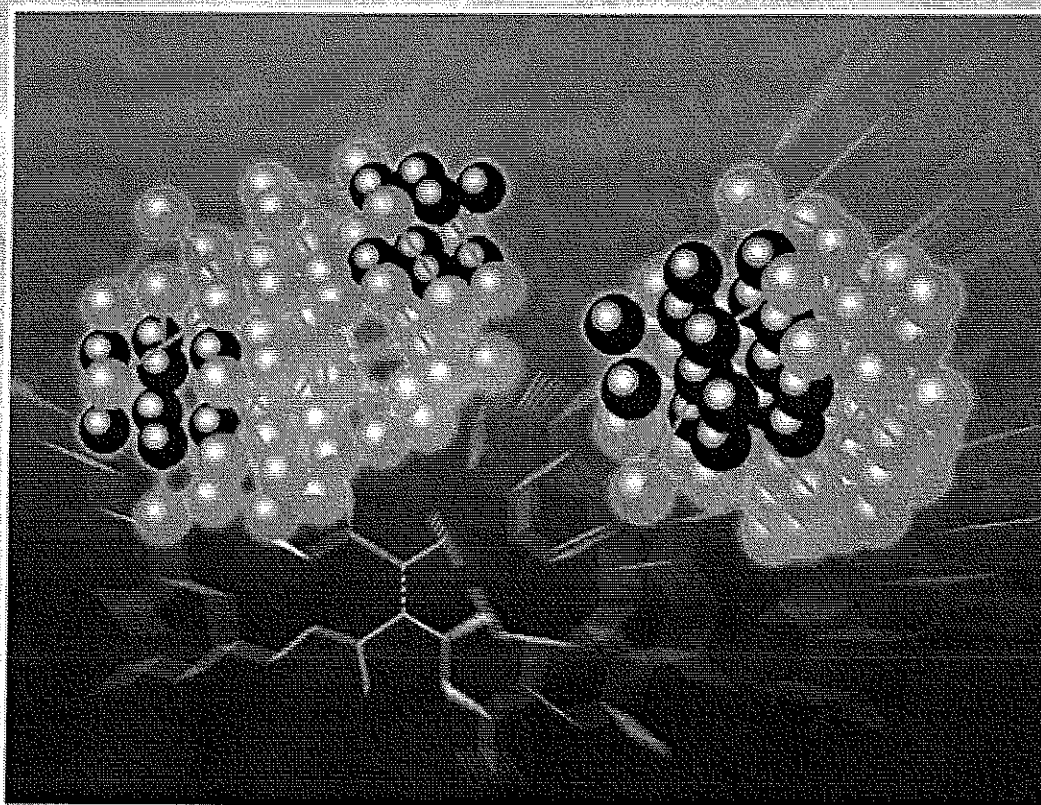


Suwabun Chirachanchai and Warayuth Sajomsang (Eds.)

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Biopolymer Films Based on Chitosan and Polyethylene Glycol with Pineapple Leaf Fiber for Food Packaging Applications

Padarat Ninjiaranai

Summary: Pineapple is a tropical plant native to South East Asia. Pineapple leaf fiber is rich in cellulose, relatively inexpensive and abundantly available. Furthermore, it has the potential for polymer reinforcement, and is more environmentally friendly than films that are reinforced with the artificial additives. The objectives of the present work were to compare the mechanical and water vapor barrier properties of biopolymer films, chitosan and polyethylene glycol 6000 (PEG 6000), with and without incorporating pineapple leaf fibers which had been chemically treated in an alkaline solution. The water vapor permeability (WVP), % soluble matter (SM), moisture index, tensile strength (TS) and % elongation (E) were investigated in these films. The composite yellow film exhibited an excellent water vapor permeability of 5.14 ± 1.87 g mm m⁻² day⁻¹ kPa⁻¹. The solubility was $65.00 \pm 0.97\%$ while the moisture index was in the range of 10.50–31.20%. The results suggested that biodegradable films could be advantageously used to replace polymer films in the packaging of freshly processed vegetables and thereby reduce the negative environmental impact of polymeric films.

Keywords: biopolymer; chitosan; mechanical properties; pineapple leaf fiber; reinforcement

Introduction

As a result of severe environmental pollution in the form of global warming, caused by the petroleum based polymer contained in plastic food packaging, there has been considerable interest in biodegradable films made from natural polymer.^[1] One possible solution to the problem is by finding an alternative material from which to make this packaging.^[2–3] Currently gaining interest and further research is active packaging due to its potential for providing protection against the permeation of gas, moisture and microbes, maintaining high food quality. Research into biodegradable packaging has focused on the use of natural fiber packaging material due to its ability to address the

consumer concerns over food-related health risks and environmental impact.^[4–6]

One of the most interesting of these biopolymers is Chitosan which is obtained from the shells of crab, shrimp and other shell fish.^[7] It is found to be nontoxic, biodegradable and containing antioxidant characteristics as it is a linear polysaccharide produced by the deacetylation of chitin. This leads it to be considered as an environmentally friendly packaging material.^[8] A major component of bio-based film is the plasticizer, polyethylene glycol 6000 (PEG 6000), the film forming polymer. The water vapor transmission rate (WVTR) can be reduced slightly by adding a plasticizer.^[9] Moreover, the various natural fibers such as rice husks, kenaf, pineapple leaf and sugarcane act as reinforcements for the polymer composites.^[10] Also these bio-based, natural fibers have not caused allergic reactions in the human body.^[11] Pineapple leaf fibers (PALF) can be easily and inexpensively obtained for industrial purposes as they are at present a waste product of

Department of Chemistry, Faculty of Science and Technology, Pibulsongkram Rajabhat University, Phitsanuloke 65000, Thailand
E-mail: padaratt@gmail.com

pineapple cultivation. PALF has a higher cellulose content and a lower microfibrillar angle than other natural fibers making its mechanical properties more attractive, it also has the potential for polymer reinforcement. Therefore low cost, biodegradable materials with superior mechanical properties could be produced by incorporating the waste pineapple leaves into chitosan and PEG 6000 film.^[12–13]

The objective of this study is to produce chitosan and PEG 6000 blended film with and without PALF to determine the mechanical and barrier properties and sorption characteristics.

Materials and Methods

Materials

Chitosan (deacetylated degree: 75–85%, viscosity: 200–800 cps) and polyethylene glycol 6000 (PEG 6000) (C_2H_4O)_n were purchased from the Sigma-Aldrich. Pineapple leaves were collected from cultivation area in Nakhon Thai District, Phitsanulok Province, Thailand.

Alkaline Treatment

The efficient cleaning of the natural fiber is very important for clarifying the origin of positively charged groups present in functionalized fibers. In this research, the conventional cleaning procedure commonly used was an alkaline pre-treatment process. Firstly, fresh pineapple leaves were weighted and recorded before they were cut to the length of 5 mm. Secondly, pineapple leaves were immersed in 5% w/v NaOH solution for 3 hrs at 80 °C. Thirdly, the fibers were poured from the beaker and filtered through filter paper to remove remaining small particles from the fibers. Finally, the natural fibers were washed with 1% v/v acetic acid solution for neutralization, and then the fibers were dried at 80 °C for 4 hrs in an oven.

Film Production

1 g of chitosan was dissolved in 2% v/v 100 ml of acetic acid solution. Then a

known amount of 0.3 g PEG 6000 was added into the chitosan solution and stirred for 2 hrs. The solution was then filtered through filter paper to remove remaining small particles from the solution. After that, chitosan and PEG 6000 synthesized with PALF were obtained by adding 0.1 g PALF into the chitosan mixture solution, while stirring for 10 min at room temperature. Chitosan film with and without PALF had an average thickness 0.1 ± 0.01 mm. The dry films had the following composition:

- i Film without pineapple leaf fiber: chitosan and PEG 6000.
- ii Film with pineapple leaf fiber: chitosan, PEG 6000 and PALF.
- iii Chitosan film (Control)

Film Thickness

The thicknesses of the films were measured with a vernier micrometer at 5 random positions on the film. The mean values were used to calculate the water vapor transmission (WVT) and the tensile strength (TS).

Film Solubility

The solubility test was performed in boiling water. The film was cut into 1.5×1.5 cm pieces and weighted. Then, samples were placed into beakers with 50 ml deionized water and heated for 4 min at 100 °C on a hot plate. After that, the samples were filtrated to keep the undissolved films that were dried in the oven at 70 °C for 24 hrs to constant weight. The final films are then weighted again. The percentage solubility (%S) test was calculated from 3 replicated tests. The water solubility of the film was calculated according to the equation (1).

% Solubility =

$$\left[\frac{(\text{Initial dry weight} - \text{Final dry weight})}{\text{Initial dry weight}} \times 100 \right] \quad (1)$$

Equilibrium Moisture Content

Water content of the films was determined by measuring the weight loss of the films, after drying in an oven at 110 °C until a

constant weight (dry sample weight) was achieved. Samples were analyzed in triplicate. Equilibrium moisture content (%) was calculated according to the equation (2)

$$\text{Equilibrium moisture content\%} = \left[\frac{\text{Initial sample weight} - 1}{\text{Dry sample weight}} \right] \times 100 \quad (2)$$

Water Vapor Permeability

Water vapor transmission rate (WVTR) was determined according to the ASTM E96 method.^[14–16] The test cup was filled with 15 ml of distilled water and was sealed with film, and then placed in a desiccator at 25 °C and 60% RH. Triplicate samples were tested for each sample. Weight loss of the test cup was weighed at intervals of 2 h for 2 days until the change in weight became constant. WVTR was determined from the slope which plotted the weight changes and time divided by the absorption surface area. The water vapor permeability (WVP) was then calculated from the following equation (3):

$$\text{WVP} = (\text{WVTR} \times L) / \Delta P \quad (3)$$

where WVP is the water vapor permeability ($\text{g mm m}^{-2} \text{ day}^{-1} \text{ kPa}^{-1}$), WVTR is the measured water vapor transmission rate through a film ($\text{g m}^{-2} \text{ day}^{-1}$), *L* is the mean film thickness (mm) and ΔP is the water vapor partial pressure difference between the two sides of the film (kPa).

Tensile Strength and Elongation at Break

The ASTM standard method D 882 is used to measure the mechanical properties of the film sample specifically the tensile strength (TS) and the percentage of elongation at break (%E). Films are cut

into $1 \times 1.5 \text{ cm}^2$ pieces, the initial gauge separation and crosshead speed are fixed at 50 mm and 50 mm/min, respectively. The percentage of elongation at break is calculated from the ratio of increase in length while the tensile strength is calculated by dividing the maximum force by the area of the cross section.^[17]

Results and Discussion

Film Characterization

The results show that chitosan film both with and without PALF are transparent. However, the addition of PEG 6000 as a plasticizer produces more flexible films. The thickness of the film is shown in Table 1.

Table 1 shows that the moisture content of chitosan film with the PALF was $31.20 \pm 1.33\%$, which compared to the moisture content without PALF at $16.64 \pm 2.13\%$ was far greater because PALF is naturally hydrophilic. For that reason the biological performance of a composite made from natural fibers is affected greater by the moisture content at a given relative humidity.^[18]

Solubility is an important characteristic of chitosan films especially when considered for packaging considering food protection in areas with high water activity and frequently contact with water.^[16] Chitosan film without PALF has a higher percentage of water solubility ($70.00 \pm 1.91\%$) than chitosan film with PALF content ($65.00 \pm 0.97\%$). Amino groups of chitosan create bonds with hydroxyl groups of PALF (table 1) which could explain the slight decrease in solubility of the chitosan film.^[19]

Table 1.
Thickness, moisture and solubility of various films.

Film type	Thickness (mm)	Moisture content (%)	Solubility (%)
Control	0.11 ± 0.02	10.50 ± 1.66	15.40 ± 1.35
Chitosan/PEG6000	0.11 ± 0.04	16.64 ± 2.13	70.00 ± 1.91
Chitosan/PEG6000 and PALF	0.12 ± 0.01	31.20 ± 1.33	65.00 ± 0.97

Table 2.

Tensile strength (TS), elongation at break (E) and water vapor permeability (WVP) of various films.

Film type	Tensile strength (MPa)	Elongation at break (%)	WVP ($\text{g} \cdot \text{mm} \cdot \text{m}^{-2} \cdot \text{day}^{-1} \cdot \text{kPa}^{-1}$)
Control	16.20 ± 0.52	22.20 ± 0.81	3.81 ± 0.13
Chitosan/PEG6000	27.00 ± 0.66	33.33 ± 1.10	6.84 ± 0.02
Chitosan/PEG6000 and PALF	38.10 ± 1.01	13.05 ± 0.80	5.14 ± 1.87

Water Vapor Permeability

Water transfer between internal products and its exterior surroundings is a major reason packaged food deteriorates. Consequently the permeability levels of packaging is very important.^[13] Low water vapor permeability of the film surrounding the food is a major advantage for food packaging material.^[20–21]

The results of WVP in the present study are shown in Table 2. The control film exhibited the lowest value of WVP at $3.81 \pm 0.13 \text{ g mm m}^{-2} \text{ day}^{-1} \text{ kPa}^{-1}$, compared to the chitosan-based film with and without PALF which were 5.14 ± 1.87 and $6.84 \pm 0.02 \text{ g mm m}^{-2} \text{ day}^{-1} \text{ kPa}^{-1}$, respectively. The WVP of the chitosan-based film decreased slightly when PALF was added to the film. This result may be attributed to hydrogen bond interactions between amino groups present in chitosan and hydroxyl groups of PALF. These interactions decreased the availability of the hydrophilic groups and destroyed the hydrogen bonding of the chitosan-water in the matrix.^[22–25]

Tensile Strength and Elongation

The mechanical properties, including the tensile strength (TS) and the percent of elongation at break (%E), are important parameters for polymer film used as food packaging material. The values of all the composite films are summarized in table 2. It can be seen that the chitosan-based film with PALF had the highest TS and the lowest %E values. Because of the intermolecular hydrogen bonding between the amino groups of chitosan and the hydroxyl groups of the fibers a good film was produced.^[2–3]

Conclusion

This study demonstrated that a high quality bio-based film made from chitosan/PEG6000 could be achieved by incorporating with PALF as a reinforcement. The addition of PALF lead to an improvement in the mechanical properties of the resulting film. The tensile strength of this film increased significantly compared with other films. It was attributed to the intermolecular hydrogen bonding between the amino groups present in the chitosan and the hydroxyl groups in the fiber. On the other hand, it slightly decreased the WVP, solubility and %E. The results suggest that these film have potential for use in food packaging.

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