

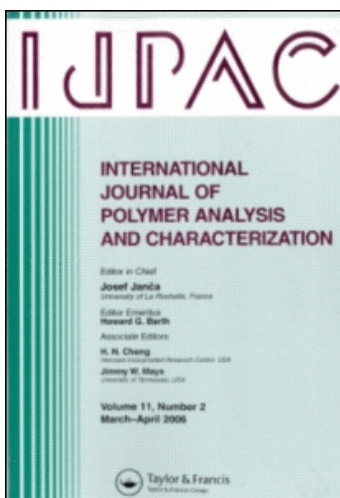
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Water Vapor Permeability and Mechanical Properties of Biodegradable Chitosan/Methoxy Poly(ethylene glycol)-*b*-Poly(ϵ -caprolactone) Nanocomposite Films

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Abstract: Nanocomposite films of chitosan/methoxy poly(ethylene glycol)-*b*-poly(ϵ -caprolactone) diblock copolymer were prepared by film casting of a diblock copolymer nanoparticle suspension-chitosan solution. The results obtained from thermogravimetric analysis confirmed that intermolecular bonds existed between the chitosan and the diblock copolymer. Percent moisture uptake and water vapor permeability of the chitosan films were decreased by incorporating diblock copolymer nanoparticles and decreased with increasing diblock copolymer content. The studies on tensile properties have shown that incorporation of nanoparticles into the chitosan film enhanced the tensile strength of the films in both dry and hydrated states.

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Keywords: Chitosan films; Mechanical properties; Nanocomposite films; Nanoparticles; Water vapor permeability

INTRODUCTION

Chitosan is a natural biopolymer derived by deacetylation of chitin, a major component of the shells of crustaceans such as crabs, shrimps, and crawfish. Several research works on the potential of chitosan for biodegradable food packaging applications, especially as edible films and coatings, have been published, e.g., in the storage of fruits^[1] and seafood products,^[2] because chitosan has good film-forming properties.^[3,4] A disadvantageous property of chitosan film, making it unpopular for packaging applications, is its high sensitivity to water as it has a large number of hydrogen bonds.^[5] The composite method used to mix some hydrophobic biodegradable polyesters such as poly(ϵ -caprolactone)^[5] and polylactide^[6,7] had been used in order to improve water-resistance properties of chitosan films. However, these composite films exhibit microphase separation, which may give rise to inconsistent properties such as nanocomposite films.

In our previous work,^[8] nanocomposite chitosan-based films containing methoxy poly(ethylene glycol)-*b*-poly(ϵ -caprolactone) (MPEG-*b*-PCL) diblock copolymer with chitosan/diblock copolymer ratios of 90/10, 80/20, and 70/30 (w/w) were prepared. The MPEG-*b*-PCL nanoparticles were formed in chitosan aqueous solution by the modified-spontaneous emulsification solvent diffusion method (modified-SESD method) before film casting. In this study, the moisture uptake, water vapor permeability, and mechanical properties of the nanocomposite films were investigated.

EXPERIMENTAL SECTION

Materials

Nanocomposite chitosan-based films containing nanoparticles of methoxy poly(ethylene glycol)-*b*-poly(ϵ -caprolactone) diblock copolymer were prepared by nanoparticle suspension-chitosan solution casting, as described in our previous work.^[8] The nanoparticles were formed in chitosan solution by the modified-SESD method. An acetone/ethanol (4/1 (v/v)) mixture was used as an organic solvent. The nanocomposite films with chitosan/diblock copolymer ratios of 90/10, 80/20, and 70/30 (w/w) were compared with the pure chitosan film.

Characterization of Chitosan and Nanocomposite Films

Thermal decomposition profiles of the films were determined by thermogravimetry (TG) using a TA-Instrument TG SDT Q600 thermogravimetric analyzer. For TG analysis, a 10–20 mg sample was heated from 50° to 1,000°C at the heating rate of 20°C/min under nitrogen atmosphere. Percent moisture uptake of the chitosan and nanocomposite films was determined by the method described by Suyatma et al.,^[9] modified as follows. The sample films, 20 × 20 mm in size, were dried in vacuo 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 being kept in the desiccator for two weeks. The percent moisture uptake was calculated from:

$$\% \text{ Moisture uptake} = [(M_f - M_i)/M_i] \times 100 \quad (1)$$

where M_i and M_f are the initial and final weight (g) of the films, respectively.

Water vapor permeability of the films was measured following the method described by Rutnakornpituk and Ngamdee.^[10] The sample films were tightly adhered onto the top of glass vials with an approximate volume of 24 cm³. Each vial was filled with pre-weighed anhydrous calcium chloride; glass vials for control contained small glass beads of approximately identical weights to those of the sample vials. They were kept in a desiccator with 90 ± 5% RH maintained with a saturated sodium chloride solution at 30° ± 2°C. The vials were weighed again after being kept in the close desiccator for two weeks. Rate of water vapor permeability (WVP) was calculated from:

$$\text{Rate of water vapor permeability (g/day/L)} = [(T_f - T_i) - (C_f - C_i)] \times 1000/(14v) \quad (2)$$

where T_i and T_f are the initial and final weights (g) of the sample vials, respectively, C_i and C_f are the initial and final weights (g) of the control vials, respectively, and v is the volume (cm³) of each vial. The % moisture uptake and water vapor permeability values are the average of three different measurements.

Tensile strength and elongation at break of the films were measured by a Texture Analyzer Machine using a Charra TA-XT2I Texture Analyzer. The films were prepared at 25 mm of gauge length with a speed of 20 mm/min and 10 N load cell. Tensile strength and % elongation at break were calculated using Equations (3) and (4), respectively. The film with hydrated state was prepared by immersion in distilled water for 2 h.

The water on the film surface was wiped with filter paper before immediate tensile testing.

$$\text{Tensile strength (N/mm}^2\text{)} = \frac{\text{Breaking force (N)}}{\text{Cross-section area of the sample (mm)}^2} \tag{3}$$

$$\begin{aligned} \text{Elongation at break (\%)} \\ = \frac{\text{The increase in length at breaking point (mm)} \times 100}{\text{Original length (mm)}} \end{aligned} \tag{4}$$

RESULTS AND DISCUSSION

Thermal Decomposition Behaviors of Nanocomposite Films

Thermal decomposition of chitosan and nanocomposite films was studied by TG analysis, as shown in Figure 1. The thermal decomposition profile of the chitosan film consisted of two stages, representing the moisture evaporation and complex decomposition processes^[4]; the remaining weight was approximately 30% at 1,000°C. The diblock copolymer showed a single stage of thermal decomposition in the range of 400°–450°C. As expected, the nanocomposite films showed three stages representing the moisture evaporation, complex chitosan decomposition, and diblock copolymer decomposition processes. However, the nanocomposite films exhibited slower decomposition in the stages of complex chitosan and diblock copolymer decomposition than the pure materials.

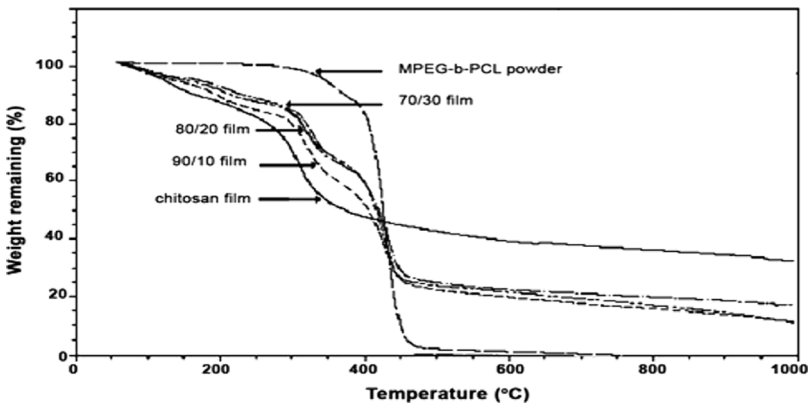


Figure 1. TG thermograms of chitosan, MPEG-*b*-PCL powder, and chitosan/diblock copolymer (w/w) nanocomposite films.

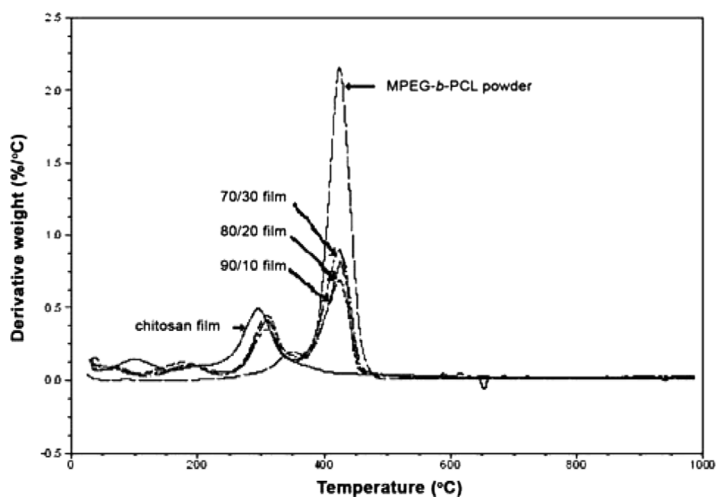


Figure 2. DTG thermograms of chitosan, MPEG-*b*-PCL powder, and chitosan/diblock copolymer (w/w) nanocomposite films.

Consequently, it can be suggested that the thermal stability of the chitosan film is improved by compositing diblock copolymer nanoparticles. The thermal decomposition can be clearly observed from differential TG (DTG) thermograms, as shown in Figure 2. From DTG thermograms, the temperature of maximum decomposition rate ($T_{d, max}$) was determined and is reported in Table I. It was found that the chitosan film and the MPEG-*b*-PCL powder had a single $T_{d, max}$ at 296° and 418°C, respectively. The DTG thermograms of nanocomposite films consisted of $T_{d, max}$ of both the chitosan and the diblock copolymer. The $T_{d, max}$ of each component of nanocomposite films slightly shifts toward higher temperature than those of chitosan film and MPEG-*b*-PCL powder,

Table I. Thermal decomposition, moisture uptake, and water vapor permeability of chitosan nanocomposite films

Chitosan/diblock copolymer (w/w) nanocomposite films	$T_{d, max}$ (°C)	Moisture uptake (%)	Rate of water vapor permeability (g/day/L)
100/0	296	79.5 ± 0.3	6.6 ± 0.3
90/10	308, 429	79.0 ± 0.1	6.0 ± 0.4
80/20	309, 425	78.5 ± 0.3	5.6 ± 0.5
70/30	311, 423	78.0 ± 0.4	5.2 ± 0.3
0/100	418	—	—

supporting the existence of intermolecular bonds between chitosan and diblock copolymer. The result indicated that the thermal stability of chitosan composites can be influenced by its diblock copolymer components.

Moisture Uptake and Water Vapor Permeability of Nanocomposite Films

The % moisture uptakes of chitosan and nanocomposite films were measured instead of water uptake (immersion in water) because of the partial dissolution of chitosan. The % moisture uptakes of films were calculated from Equation (1) and are summarized in Table I. The % moisture uptake of the chitosan films slightly decreased when the nanoparticles were formed into the chitosan film, which indicates that the nanoparticles enhanced the moisture resistance of the chitosan film. The % moisture uptake slightly decreased as the diblock copolymer ratios increased. The rate of WVP of the chitosan and nanocomposite films is also presented in Table I. It illustrates the influence of the diblock copolymer nanoparticles with different composite ratios on the rate of WVP of chitosan films. It was found that the rate of WVP of chitosan film decreased when the nanoparticles were incorporated into the chitosan films, corresponding to % moisture uptake results. This suggests that the hydrophobic characteristics of the diblock copolymer exhibit resistant properties to water vapor.^[5,6] The rates of WVP of nanocomposite films significantly decreased when the diblock copolymer ratios were increased.

Mechanical Properties of Nanocomposite Films

The tensile strength and % elongation at break of the films were tested in both dry and hydrated states. Figures 3 and 4 show the results. It was found that the tensile strength at break of the dry chitosan film increased but not % elongation at break when the nanoparticles were incorporated into the chitosan film. The tensile strengths of the films increased with increasing diblock copolymer ratios. Suyatma et al. investigated mechanical properties of biodegradable chitosan and poly(L-lactic acid) microcomposite films.^[6] They have found that the mechanical resistance of the microcomposite films decreased because there was no specific interaction and no compatibility between two components. Our results proved that the diblock copolymer nanoparticles could act as reinforcing fillers of the chitosan matrix to improve the tensile strength of chitosan film. The interactions between chitosan and nanoparticles were indicated by TG and DTG results. Finally, the tensile strengths at break of the films significantly decreased in the hydrated state. However, the tensile

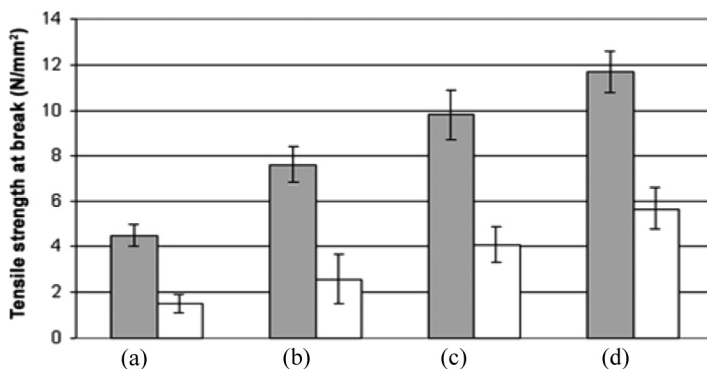


Figure 3. Tensile strength in dry (■) and hydrated (□) states of (a) chitosan, (b) 90/10, (c) 80/20, and (d) 70/30 (w/w) chitosan/diblock copolymer nano-composite films.

strengths at break of the hydrated nanocomposite films were higher than that of the hydrated chitosan film corresponding to the dry state. It indicated that the nanocomposite films had higher tensile strength than the chitosan film in both dry and hydrated states.

CONCLUSIONS

Chitosan films containing diblock copolymer nanoparticles, called nanocomposite films, with different chitosan/diblock copolymer ratios

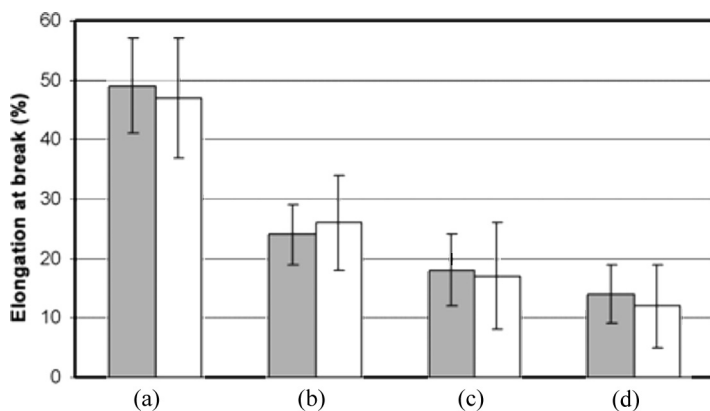


Figure 4. % Elongation at break in dry (■) and hydrated (□) states of (a) chitosan, (b) 90/10, (c) 80/20, and (d) 70/30 (w/w) chitosan/diblock copolymer nano-composite films.

of 90/10, 80/20, and 70/30 (w/w) were prepared. The nanoparticles incorporated into the chitosan film improved thermal stability of the chitosan film. The moisture uptake and water vapor permeability of the chitosan film can be decreased with the hydrophobic characteristic of the diblock copolymer nanoparticles. The diblock copolymer nanoparticles acted as reinforcing fillers to improve the tensile strength of the chitosan film in both dry and hydrated states. These nanocomposite films can be used as packaging and drug-loaded controlled release films with higher water vapor resistance and tensile strength than the pure chitosan film.

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