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Properties of chitosan/poly(ethylene glycol)-*b*-poly(D,L-lactide) nanocomposite films: Water vapor permeability and mechanical properties

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ABSTRACT

Biodegradable chitosan nanocomposite films contained dispersed nanoparticles of methoxy poly(ethylene glycol)-*b*-poly(D,L-lactide) (MPEG-*b*-PDLL) diblock copolymer were prepared by film casting of MPEG-*b*-PDLL nanoparticle suspension-chitosan solution. The nanoparticles were formed in the chitosan solution by spontaneous emulsification solvent diffusion method. The nanoparticles with less than 500 nm in size distributed throughout the chitosan film matrices. They were nearly spherical in shape. The chitosan/MPEG-*b*-PDLL nanocomposite films had lower film transparency and water vapor permeability than the chitosan film. The tensile strength at break of the nanocomposite films increased and elongation at break decreased as the increasing of MPEG-*b*-PDLL ratio. The film transparency, water vapor permeability and mechanical properties of nanocomposite films can be controlled by adjusting the MPEG-*b*-PDLL ratio.

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KEYWORDS

Chitosan films;
Diblock copolymers;
Nanoparticles;
Nanocomposite;
Water vapor permeability;
Mechanical properties.

INTRODUCTION

Chitosan is a biopolymer that has received great attention in a variety of applications because of their biodegradability and biocompatibility^[1,2]. Because of its excellent film-forming property, chitosan can be used effectively as a film-forming material to carry active ingredients such as mineral or vitamin for food packaging applications^[3,4] and hydrophilic or hydrophobic drugs for drug delivery applications^[5,6]. Disadvantage property of chitosan film making it unpopular for packaging application is its high sensitive to water as it has large number of hydrogen bonds^[7]. Composite method used

to mix some hydrophobic biodegradable polyesters such as poly(ϵ -caprolactone)^[7] and polylactide^[8,9] had been tried out in order to improve water-resistance properties of chitosan films. However, these films are composite films containing microphase separation, which may be gave non-consistent properties as much as nanocomposite films.

In our previous work^[10], the chitosan/MPEG-*b*-PDLL nanocomposite films were prepared to compare with the chitosan/methoxy poly(ethylene glycol)-*b*-poly(ϵ -caprolactone) nanocomposite films in their morphology and thermal stability. The MPEG-*b*-PDLL nanoparticles were formed in chitosan aqueous solu-

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tion by the modified-spontaneous emulsification solvent diffusion method before film casting. In this research, the water vapor permeability and mechanical properties of these nanocomposite films were investigated.

EXPERIMENTAL

Materials

Chitosan (90% deacetylation and molecular weight of 80 kDa) was purchased from Seafresh Chitosan Lab Co., Ltd., (Thailand). Acetic acid (99.7%, Merck) was used without further purification. Methoxy poly(ethylene glycol)-*b*-poly(D, L-lactide) (MPEG-*b*-PDLL) diblock copolymer was synthesized by using MPEG with molecular weight of 5,000 g/mol and stannous octoate as the initiating system as described in our previous work^[11]. Molecular weight of the MPEG-*b*-PDLL obtained from curve of gel permeation chromatography was 73,600 g/mol.

Preparation of nanocomposite films

Nanoparticles of MPEG-*b*-PDLL diblock copolymer were prepared by the modified-SESD method in chitosan solution before film casting. The chitosan solution was prepared by using 1% (v/v) acetic acid aqueous solution as the solvent. The preparation of nanocomposite films was typically described as follows. The diblock copolymer was dissolved in 2 mL of 4/1 (v/v) acetone/ethanol mixture. The diblock copolymer solution was then added drop-wise into 20 mL of chitosan solutions with stirring at 600 rpm. The organic solvent was removed in fume hood for 5 hrs. The nanoparticles suspended in the chitosan solution were obtained. Then, the film casting was done on Petri dish, and subsequently dried at 30°C for 72 h. The nanocomposite films with chitosan/MPEG-*b*-PDLL ratios of 100/0, 90/10, 80/20 and 70/30 (w/w) were investigated. The chitosan nanocomposite film was kept in a vacuum at room temperature for a week before characterization.

Characterization of nanocomposite films

The chemical structures of chitosan, MPEG-*b*-PDLL and their nanocomposite films were determined by FTIR spectroscopy using a Perkin-Elmer Spectrum GX FTIR spectrometer with air as the reference. The

FTIR spectra of films were obtained with resolution of 4 cm⁻¹ and 32 scans.

The thermal properties of the samples were characterized by non-isothermal differential scanning calorimetry (DSC) using a Perkin-Elmer Pyris Diamond DSC. For DSC, the approximate 10 mg of sample was placed in a sealed aluminum pan and heated at the rate of 10°C/min under helium flow to measure the glass transition temperature (T_g).

Morphology of film surfaces and cross-sections was investigated 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 determined by UV-Vis spectroscopy using a Perkin-Elmer Lambda 25 UV-Vis spectrophotometer at $\lambda_{max} = 660 \text{ nm}$ ^[12].

Water vapor permeability of the films was measured following the method^[12]. The sample films were tightly adhered onto the top of glass vials with an approximate volume 24 cm³. Each vial was filled with pre-weighed anhydrous calcium chloride, whereas glass vials for control contained small glass beads of approximately identical weights to that of the sample vials. They were kept in a desiccator with 90 ± 5% relative humidity maintained with a saturated sodium chloride solution at 30 ± 2°C. The vials were weighed again after kept in the close desiccator for a week. Rate of water vapor permeability (WVP) was calculated by equation (1).

$$\text{Rate of water vapor permeability (g/day/L)} = [(T_f - T_i) - (C_f - C_i)] \times 1000 / (14v) \quad (1)$$

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

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

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

$$\% \text{Elongation at break (\%)} = \frac{\text{The increase in length at breaking point (mm)}}{\text{Original length (mm)}} \times 100 \quad (3)$$

RESULTS AND DISCUSSION

Chemical structures

The FTIR spectrum of chitosan film in Figure 1(a) showed the absorption bands at 1,654 and 1,587 cm^{-1} attributed to the amide carbonyl group (amide I) of residue chitin and the free amino groups of chitosan, respectively. The FTIR spectrum of MPEG-*b*-PDLL in figure 1(e) illustrated the strong carbonyl band at 1,735 cm^{-1} and CH stretching vibration band at 2865 cm^{-1} of PDLL and MPEG blocks, respectively. The FTIR spectra of chitosan/MPEG-*b*-PDLL nanocomposite films in figure 1(b)-1(d) demonstrated the both band characteristics of chitosan and MPEG-*b*-PDLL. As would be expected, the intensities of carbonyl bands increased as the increasing of MPEG-*b*-PDLL ratio.

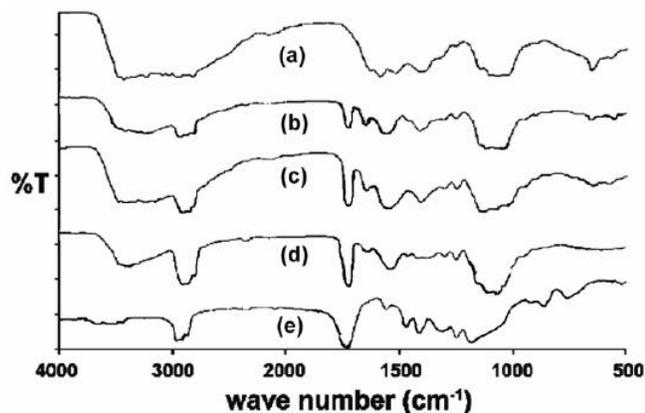


Figure 1 : FTIR spectra of (a) chitosan film and chitosan nanocomposite films prepared using chitosan/MPEG-*b*-PDLL ratios of (b) 90/10, (c) 80/20 and (d) 70/30 (w/w), and (e) MPEG-*b*-PDLL powder.

Film morphology

Figures 2 and 3 show SEM micrographs of film surfaces and cross-sections, respectively. The both surface and cross-section of chitosan film were smooth

appearance as shown in Figures 2(a) and 3(a), respectively. Surface roughness of chitosan films increased when the nanoparticles of MPEG-*b*-PDLL were incorporated. Dispersed nanoparticles in the chitosan films can observe on both film surface and cross-section. The higher MPEG-*b*-PDLL ratio film showed clearly nanoparticles as shown in Figures 2(d) and 3(d). The number of nanoparticles increased when the MPEG-*b*-PDLL ratio was increased. It can be seen that the nanoparticles distributed throughout the film matrix. The all nanoparticles were less than 500 nm.

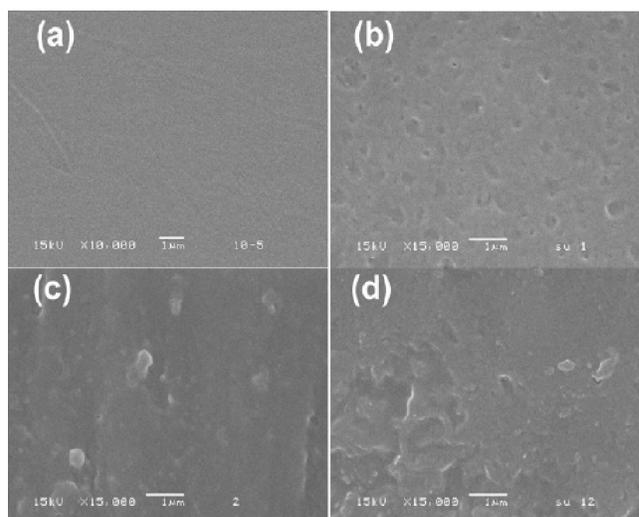


Figure 2 : SEM micrographs of film surfaces of (a) chitosan and chitosan nanocomposite films prepared using chitosan/MPEG-*b*-PDLL ratios of (b) 90/10, (c) 80/20 and (d) 70/30 (w/w). All bars = 1 μm .

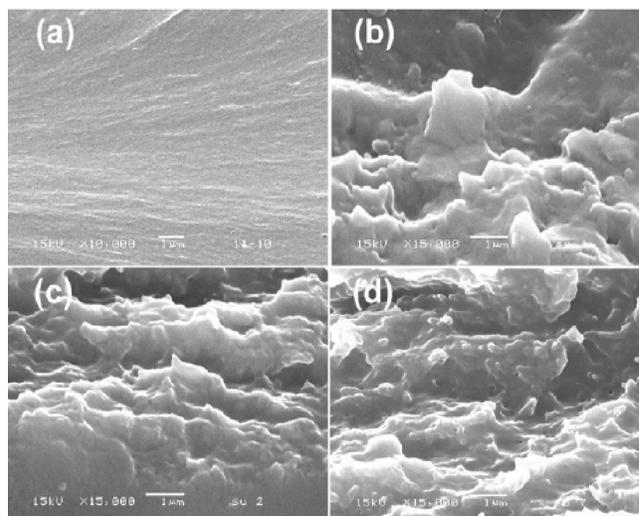


Figure 3 : SEM micrographs of film cross-sections of (a) chitosan and chitosan nanocomposite films prepared using chitosan/MPEG-*b*-PDLL ratios of (b) 90/10, (c) 80/20 and (d) 70/30 (w/w). All bars = 1 μm .

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Thermal properties

The DSC thermograms of chitosan film, nanocomposite films and MPEG-*b*-PDLL are shown in figure 4. It was found that the T_g of the nanocomposite film decreased as the chitosan ratios increased. The T_g results may indicate the interaction between chitosan and the MPEG-*b*-PDLL. This suggests that the T_g of MPEG-*b*-PDLL in nanocomposite films were controlled by the composite ratio.

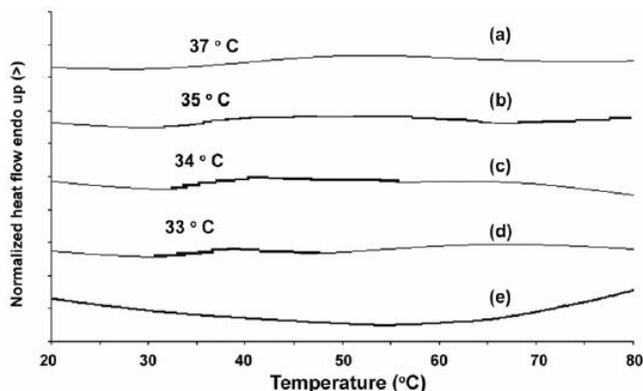


Figure 4 : DSC thermograms of (a) MPEG-*b*-PDLL powder and chitosan nanocomposite films prepared using chitosan/MPEG-*b*-PDLL ratios of (b) 70/30, (c) 80/20 and (d) 90/10 (w/w), and (e) chitosan film.

Film transparency

The film transparency was designed as %transmittances at 660 nm (T_{660}) from UV-Vis spectrophotometry. The T_{660} values of films were reported in TABLE 1. The transparency of chitosan film slightly decreased when the nanoparticles were incorporated into the film and the MPEG-*b*-PDLL ratio was increased. However, the chitosan/MPEG-*b*-PDLL nanocomposite films showed higher film transparency than that of the chitosan/MPEG-*b*-PCL nanocomposite films in the same chitosan/diblock copolymer ratio^[10]. The film transparency is an important factor for food packaging applications. This can be explained that the MPEG-*b*-PDLL and the MPEG-*b*-PCL are amorphous and semi-crystalline polymers, respectively.

Water vapor permeability

The rate of water vapor permeability (WVP) of the chitosan and nanocomposite films was also summarized in TABLE 1. It indicates influence of the dispersed nanoparticles on the rate of WVP of chitosan films. It was found that the rate of WVP of chitosan film de-

creased when the nanoparticles were incorporated in the chitosan films and the MPEG-*b*-PDLL ratio was increased. This can be explained that the hydrophobic characteristics of MPEG-*b*-PDLL exhibited resistant property to water vapor. The water vapor barrier is the most important property for considering food packaging material. The food freshness depends on the water vapor permeability. The results suggest that the water vapor permeability of chitosan film can be controlled by adjusting the MPEG-*b*-PDLL ratio.

TABLE 1 : Film transparency and water vapor permeability of chitosan and chitosan/MPEG-*b*-PDLL nanocomposite films.

| Film (chitosan/MPEG- <i>b</i> -PDLL ratio, w/w) | Film transparency (% T_{660}) | Rate of water vapor permeability (g/day/L) |
|---|----------------------------------|--|
| 100/0 | 78.7 ± 0.4 | 6.6 ± 0.3 |
| 90/10 | 72.5 ± 0.3 | 6.5 ± 0.2 |
| 80/20 | 71.3 ± 0.2 | 6.1 ± 0.4 |
| 70/30 | 70.6 ± 0.4 | 5.6 ± 0.3 |

Mechanical properties

The tensile strength and %elongation at break of the films were determined in both dry and hydrated states. Figures 5 and 6 exhibit the tensile strength and the %elongation at break of films, respectively. The tensile strengths at break of the dry chitosan film increased and %elongations at break decreased when the nanoparticles were incorporated into the chitosan film and the MPEG-*b*-PDLL ratio increased. This suggests that the MPEG-*b*-PDLL nanoparticles could act as reinforcing fillers to improve the tensile strength of chitosan film. The tensile strengths at break of the films were significantly decreased for the hydrated state. The elongations at break of films in dry and hydrated states are similar. However, it should be noted that the

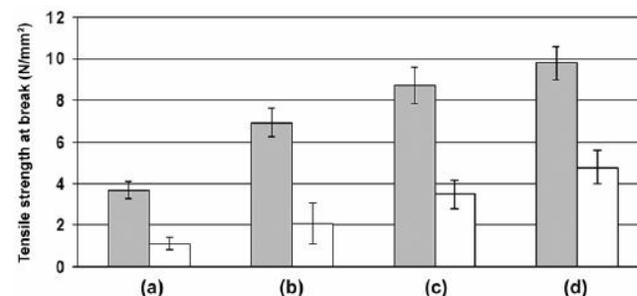


Figure 5 : Tensile strengths at break in dry (■) and hydrated (□) states of (a) chitosan film and chitosan nanocomposite films prepared using chitosan/MPEG-*b*-PDLL ratios of (b) 90/10, (c) 80/20 and (d) 70/30 (w/w).

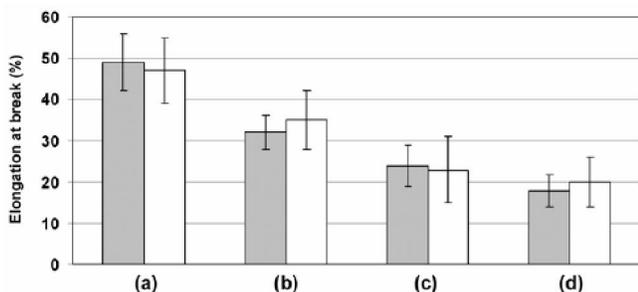


Figure 6 : Elongations at break in dry (■) and hydrated (□) states of (a) chitosan film and chitosan nanocomposite films prepared using chitosan/MPEG-*b*-PDLL ratios of (b) 90/10, (c) 80/20 and (d) 70/30 (w/w).

nanocomposite films had higher tensile strength than the chitosan film in both dry and hydrated states for the all chitosan/MPEG-*b*-PDLL ratio.

CONCLUSIONS

The chitosan/MPEG-*b*-PDLL nanocomposite films with different composite ratios were prepared via a film casting of MPEG-*b*-PDLL nanoparticle suspension-chitosan solution. Distribution of nanoparticles throughout the chitosan film matrices can be observed from SEM micrographs. The water vapor permeability of the chitosan film decreased with hydrophobic characteristic of the MPEG-*b*-PDLL nanoparticles. The MPEG-*b*-PDLL nanoparticles also acted as reinforcing fillers to improve the tensile strength of the chitosan film in both dry and hydrated states. These nanocomposite films might be of interesting for packaging and drug-loaded controlled release films.

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