Preparation and Characterization of Biodegradable Chitosan and Methoxy Poly(ethylene glycol)-*b*-Poly(ε-caprolactone) Blend Homogeneous Films

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ABSTRACT: Blend homogeneous films of chitosan and water-soluble methoxy poly(ethylene glycol)-*b*-poly(ε-caprolactone) (MPEG-*b*-PCL) diblock copolymer with different blend ratios were prepared by aqueous solution blending method. The water-soluble MPEG-*b*-PCL was synthesized using MPEG with molecular weight of 5000 g/mol and stannous octoate as the initiating system. The molecular weight of MPEG-*b*-PCL obtained from ^{1}H-NMR was 5800 g/mol. FTIR spectra of the blend films showed that there were intermolecular bonds between chitosan and MPEG-*b*-PCL. Thermal properties of the blend films strongly depended on the blend ratios. Scanning electron micrographs indicated that the blend films were homogeneous films. However, roughness of the blend films increased whereas transparency and moisture uptake decreased upon increasing the MPEG-*b*-PCL blend ratios. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 418–423, 2008

Key words: chitosan films; MPEG-*b*-PCL; blend films; film morphology; thermal properties

INTRODUCTION

Chitosan produced by N-deacetylation of chitin. It is a biopolymer with biodegradability and biocompatibility leading to great attention in a variety of applications.[1,2] Several research works on potential of chitosan for biodegradable food packaging applications especially as edible films and coatings have been published, e.g., in the storage of fruits[3,4] and seafood products[5] because of chitosan having good film-forming properties.[6,7]

Disadvantage property of chitosan film which is unappropriate for packaging application is its high sensitivity to water because of its large number of hydrogen bonds.[8] Blending method was adopted to mix some hydrophobic biodegradable polyesters such as poly(3-hydroxybutyric acid),[9] poly(ε-caprolactone) (PCL),[8,10] and polylactide (PL)[11,12] to improve water-resistance properties of chitosan films. However, these films are microcomposite films, which may give nonconsistent properties. Chen et al.[13] have prepared chitosan/polylactide miscible blends by using acetic acid-DMSO as mixture solvent and found intermolecular bonds existing between chitosan and polylactide.

Poly(ethylene glycol) (PEG) and methoxy poly(ethylene glycol) (MPEG) are water-soluble biocompatible polymers with different molecular weights. PEG and MPEG have been copolymerized with linear aliphatic polyesters such as PL and PCL to form triblock and diblock copolymers, respectively.[14–17] These block copolymers are biocompatible and biodegradable polymers for potential use as drug delivery systems.[18–20]

In this study, water-soluble MPEG-*b*-PCL was synthesized. The series of blend homogeneous films with different chitosan/MPEG-*b*-PCL blend ratios were prepared by solution blending method and characterized. The intermolecular bonds between chitosan and MPEG-*b*-PCL of blend films were investigated and discussed as a function of blend ratios. The transparency and moisture uptake of the films were also determined.
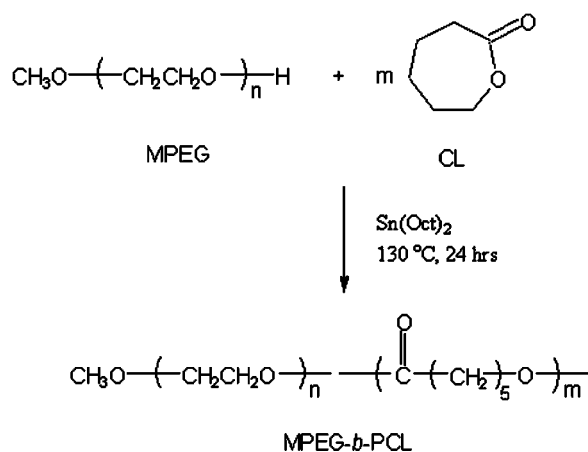
EXPERIMENTAL

Materials

Chitosan (degree of deacetylation of 90% and molecular weight of 80,000) was purchased from Seafresh Chitosan Lab Co., Ltd., (Thailand) and used as received. MPEG with molecular weight of 5000 g/mol (Fluka, Germany) was dried at 120°C in vacuum

Scheme 1 Polymerization reaction of MPEG-*b*-PCL.

oven for 4 h before use. ε-Caprolactone (CL) monomer (99%, Acros, USA) was purified by drying with CaH_2 followed by distillation under reduced pressure before storage over the molecular sieves in a refrigerator. The stannous octoate ($Sn(Oct)_2$, 95%, Sigma, USA) and acetic acid (Merck, Germany) were used as received.

Synthesis of MPEG-*b*-PCL

MPEG-*b*-PCL was synthesized by ring-opening polymerization of CL monomer in bulk at 130°C for 24 h under nitrogen atmosphere. MPEG : CL feed mole ratio of 1 : 8 was used. $Sn(Oct)_2$ and MPEG were used as the initiating system. $Sn(Oct)_2$ concentration of 0.02 mol % was chosen. The polymerization reaction is illustrated in Scheme 1. The MPEG-*b*-PCL product was purified by drying at 120°C in vacuum oven to eliminate unreacted CL monomer followed by dissolving in distillated water before filtering to separate water-insoluble homoPCL and MPEG-*b*-PCL. The water-soluble MPEG-*b*-PCL solution was freeze-dried for overnight. According to this procedure, the purified water-soluble MPEG-*b*-PCL was obtained with ∼ 80% yield.

MPEG-*b*-PCL characterization

The structure of the MPEG and the obtained MPEG-*b*-PCL were studied by Fourier transform infrared (FTIR) spectroscopy using Perkin–Elmer Spectrum GX Series FTIR spectrophotometer with air as the reference. Resolutions of 4 cm^{-1} and 32 scans were chosen in this work. Copolymer composition and number-average molecular weight ($\overline{M}_n$) of the MPEG-*b*-PCL were determined by ^{1}H-NMR spectrometry using Bruker Advanced DPX 300 ^{1}H-NMR spectrometer. $CDCl_3$ was used as a solvent at room temperature. The thermal properties of the polymers

were characterized by nonisothermal differential scanning calorimetry (DSC) and thermogravimetry (TG). A Perkin-Elmer DSC Pyris Diamond differential scanning calorimeter and TA-Instrument TG SDT Q600 thermogravimetric analyzer were used to determine the copolymer transition temperatures and thermal decomposition profiles, respectively. For DSC analysis, sample (5–10 mg) was placed in a sealed aluminum pan and heated at the rate of 10°C min^{-1} under helium flow. For TG analysis, sample (10–20 mg) was heated from 50 to 1000°C at the rate of 20°C min^{-1} under nitrogen flow.

Chitosan and blend films preparation

The 1% (w/v) chitosan solution was prepared using 1% (v/v) acetic acid aqueous solution as the solvent. The chitosan/MPEG-*b*-PCL blend solutions with different blend ratios were prepared by dissolving 20, 40, and 60 mg MPEG-*b*-PCL in 18, 16, and 14 mL chitosan solutions for chitosan/MPEG-*b*-PCL blend ratios of 90/10, 80/20 and 70/30 (w/w), respectively. The blend solution was adjusted to 20 mL with distilled water and vigorous stirring for 6 h before film casting on Petri dishes. The chitosan and blend solutions were dried at 40°C for 48 h before dried in vacuum oven at room temperature for a week.

Chitosan and blend films characterization

The FTIR spectroscopy was used to characterize both the functional groups of chitosan and MPEG-*b*-PCL in the chitosan and blend films. The FTIR spectra of the films were obtained with the resolution of 4 cm^{-1} and 32 scans. The thermal properties were measured by the DSC and TG techniques as described earlier. The film surface and cross section were studied by scanning electron microscopy (SEM) using 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 measuring the percent transmittance at 660 nm using a Perkin-Elmer Instrument Lamda UV–vis spectrophotometer as described by Rhim et al.[21] Percentages of moisture uptake of the films were determined following the method described by Suyatma et al.[11] with a slight modification. In brief, the films of 20 × 20 mm^2 in size were dried in a vacuum oven at room temperature for a week. After weighing, they were kept in a desiccator with 90 ± 5% relative humidity maintained with a saturated sodium chloride solution at 25 ± 5°C. The films were weighed again after storing in the close desiccator for 2 weeks. The %moisture uptake was calculated as follow: %mois-
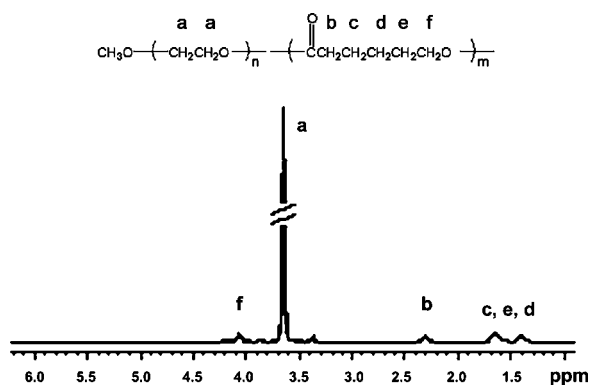
Figure 1 ^{1}H-NMR spectrum of MPEG-*b*-PCL.

ture uptake = $(M_f - M_i)/M_i \times 100$, where M_i and M_f are the masses of initial and final samples, respectively.

RESULTS AND DISCUSSION

MPEG-*b*-PCL characterization

The chemical composition of MPEG-*b*-PCL was determined from the ^{1}H-NMR spectrum by calculating the ratio of the integral peak areas corresponding to the ethylene oxide (EO, repeating units of MPEG) methylene protons at δ = 3.6–3.7 ppm and the CL ε-methylene protons at δ = 4.0–4.2 ppm. The ^{1}H-NMR spectrum of MPEG-*b*-PCL is shown in Figure 1. From the peak area integrations of the peaks a and f in Figure 1, the copolymer composition could be determined as MPEG : CL mole ratio of 1 : 7. As could be expected, this copolymer composition was similar to the MPEG : CL feed mole ratio (1 : 8). Therefore, the synthesized reaction was taken to near-quantitative conversion.

The $\overline{M}_n$ of MPEG-*b*-PCL was calculated from the MPEG : CL mole ratio from ^{1}H-NMR analysis on the basis of MPEG molecular weight and found to be
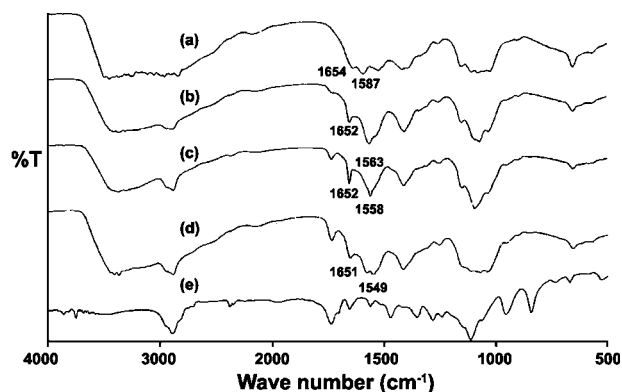

Figure 2 FTIR spectra of (a) chitosan film, (b) 90/10 blend film, (c) 80/20 blend film, (d) 70/30 blend film and (e) MPEG-*b*-PCL powder.
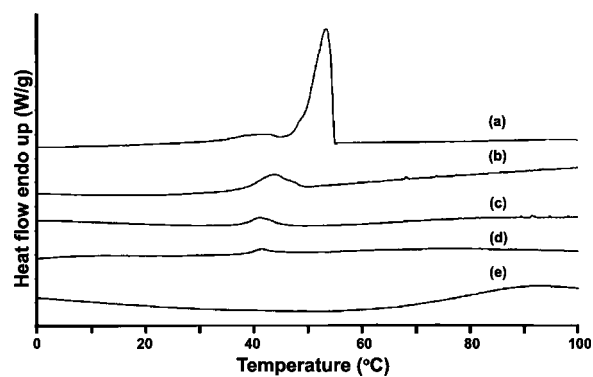

Figure 3 DSC thermograms of (a) MPEG-*b*-PCL powder, (b) 70/30 blend film, (c) 80/20 blend film, (d) 90/10 blend film and (e) chitosan film.

5800 g/mol; similar value to the calculated $\overline{M}_n$ from feed ratio (∼ 5900 g/mol). The FTIR spectrum of MPEG-*b*-PCL appeared strong carbonyl band of CL units at 1736 cm^{-1} and CH stretching vibration band of MPEG units at 2887 cm^{-1}, as shown in Figure 2(e). From DSC thermogram, the MPEG-*b*-PCL had a melting temperature (T_m) and a heat of melting (ΔH_m) of 54°C and 142.0 J/g, respectively, as shown in Figure 3(a). As would be expected, the crystalline block of MPEG-*b*-PCL was a MPEG block because of the T_m and ΔH_m of MPEG with molecular weight of 5000 g/mol from DSC curve (did not shown) were 56°C and 176.5 J/g, respectively, whereas the T_m and ΔH_m of PCL (100% crystallinity) were 60°C and 139.5 J/g, respectively.[22] Thermogravimetric (TG) thermogram of the MPEG-*b*-PCL consisted a single step, in the range of 270–460°C with completely thermal decomposition at ∼ 500°C. Temperature of maximum decomposition rate ($T_{d, max}$) from differential thermal gravimetric (DTG) thermogram was 418°C, as shown in Figure 4. This is a decomposition of the MPEG block. However, from Figure 4, the decomposition temperature of PCL block was also observed at 360°C. The results suggested that the PCL block was decomposed before the MPEG block.
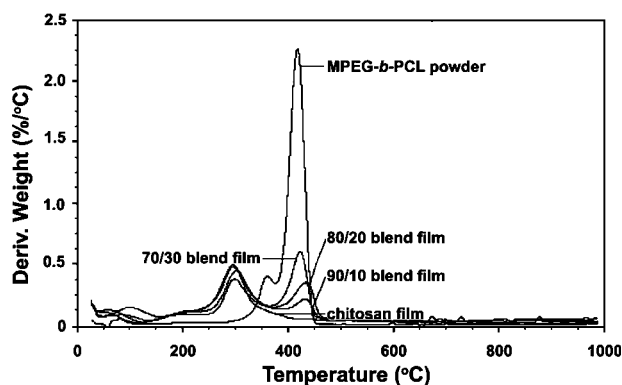

Figure 4 DTG thermograms of chitosan film, blend films and MPEG-*b*-PCL powder.

TABLE I
Thermal Properties of Chitosan Film, Blend Films, and MPEG-*b*-PCL Powder

Chitosan/MPEG-*b*-PCL blends	DSC		TG
	T_m (°C)	ΔH_m (J/g)	$T_{d,\,max}$ (°C)
100/0	–	–	296
90/10	41	5.3	296, 434
80/20	41	10.5	302, 435
70/30	44	21.5	297, 423
0/100	54	142.0	418

Chitosan and blend films characterization

FTIR analysis

The intermolecular bonds existing in chitosan and polylactide have been studied by FTIR.[13] The amine, residual amide, and hydroxyl groups of chitosan could form the intermolecular hydrogen bonds with the carbonyl groups in polylactide. Figure 2 shows the FTIR spectra of chitosan film, blend films and MPEG-*b*-PCL powder. The FTIR spectrum of chitosan film in Figure 2(a) shows the absorption bands at 1654 and 1587 cm^{-1}. These bands correspond to the amide carbonyl group (amide I) and the free amino groups, respectively.[23] It should be noted that amide carbonyl and ammonium groups of ammonium acetate derivatives from acetic acid residue reacting with amino groups of chitosan should be occurred due to the films, which were not be neutralized. The amide carbonyl group of ammonium acetate derivatives showed at 1646 cm^{-1}, which overlapped with the amide I of the chitosan and blend films. Whereas, the ammonium group of ammonium acetate derivatives showed as shoulder band at 1522 cm^{-1}. The FTIR spectra of blend films in Figure 2(b–d) show absorption bands of both chitosan and MPEG-*b*-PCL characteristics. The intensities of carbonyl and CH stretching bands were at 1730 and 2887 cm^{-1}, respectively, which were increased according to the increasing of MPEG-*b*-PCL ratios. In addition, the free amino band of chitosan was shifted to lower wave number as blended the MPEG-*b*-PCL. The lower wave number shift of the free amino band of chitosan can be attributed to its interaction with the MPEG-*b*-PCL.[23] This could be explained by the fact that the hydrogen bonds between ether groups of MPEG and hydroxyl group of chitosan occurred.

Thermal properties

The DSC thermograms of chitosan film, blend films and MPEG-*b*-PCL powder are shown in Figure 3 and thermal properties from DSC curves are summarized in Table I. It was found that the T_m and ΔH_m of the blend films decreased as the chitosan ratios increased. This could be attributed to crystalli-zation disturbance of chitosan in the blend state. The DSC results confirmed that the chitosan and the MPEG-*b*-PCL have some interactions indicated by FTIR result. The results also suggested that chitosan and MPEG-*b*-PCL could be miscible blended in amorphous phase.[24]

Thermal decomposition behaviors of chitosan film, blend films, and MPEG-*b*-PCL powder were studied by TG analysis. From TG thermogram, thermal decomposition profile of the chitosan film consisted of two stages representing the moisture evaporation and complex degradation processes, respectively,[7] and the remaining weight was approximately 40% at 1000°C. The blend films had %remaining weights in the range of 50–400°C higher and in the range of 400–1000°C lower than the chitosan film. The change of thermal decomposition behavior of the chitosan film occurred when blended with MPEG-*b*-PCL. From DTG thermograms of the blend films shown in Figure 4, the $T_{d,\,max}$ were determined and reported in Table I. It was found that the chitosan film and the MPEG-*b*-PCL powder had a main $T_{d,\,max}$ at 298 and 413°C, respectively. The DTG thermograms of blend films consisted of both $T_{d,\,max}$ of the chitosan and the MPEG-*b*-PCL. The both $T_{d,\,max}$ of each fraction of blend films were higher than those of chitosan film and MPEG-*b*-PCL powder supporting intermolecular bonds existed between chitosan and MPEG-*b*-PCL. In addition, the ammonium acetate derivatives in chitosan and blend films also showed the small $T_{d,\,max}$ at 160°C, which this peak decreased as decreasing the chitosan ratio. The results confirmed that the ammonium acetate derivatives were occurred in the chitosan and the blend films corresponding to FTIR results. The result indicated that chitosan and MPEG-*b*-PCL can be influenced on the thermal stability of its blend components.[22]

Surface morphology

Average thicknesses of the chitosan and the blend films obtained from SEM micrographs were in the range of 20–40 μm. SEM micrographs of the surfaces and fracture surfaces of the chitosan and the blend films are showed in Figure 5. The surface and fracture surface of the chitosan film were smooth surface [Fig. 5(a)], whereas the blend films were rough surfaces [Fig. 5(b–d)]. The film surface roughness increased when the MPEG-*b*-PCL ratios were increased, as shown more clearly in higher magnification in Figure 6. This could be hypothesized that the hydrophobic component of MPEG-*b*-PCL was assembled and microscopically phase separated from hydrophilic chitosan during the drying process.[25,26] The results may be discussed from the FTIR spectra in Figure 2. The free amino band of the chitosan film
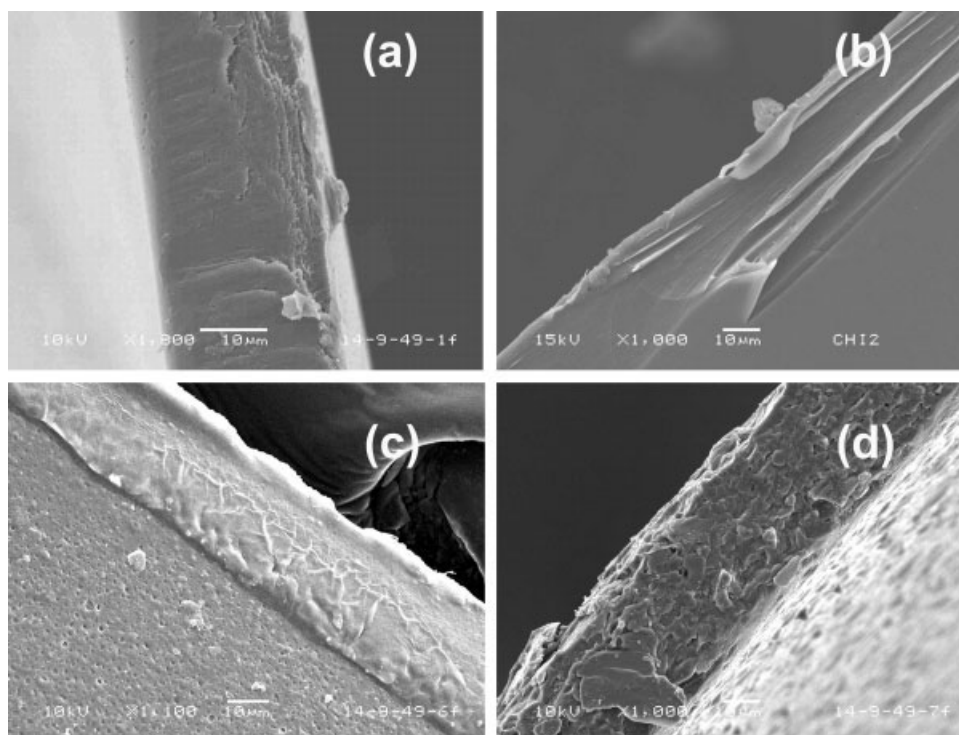
Figure 5 SEM micrographs of surfaces and fracture surfaces of (a) chitosan film, (b) 90/10 blend, (c) 80/20 blend and (d) 70/30 blend films.

(1587 cm^{-1}) was shifted to 1563 cm^{-1} for 90/10 (w/w) chitosan/MPEG-*b*-PCL blend film. When the MPEG-*b*-PCL ratios increased up to 20 and 30 for 80/20 and 70/30 blend films, the low shift of amino bands was slightly decreased (1558 and 1549 cm^{-1}, respectively). This suggested that the intermolecular
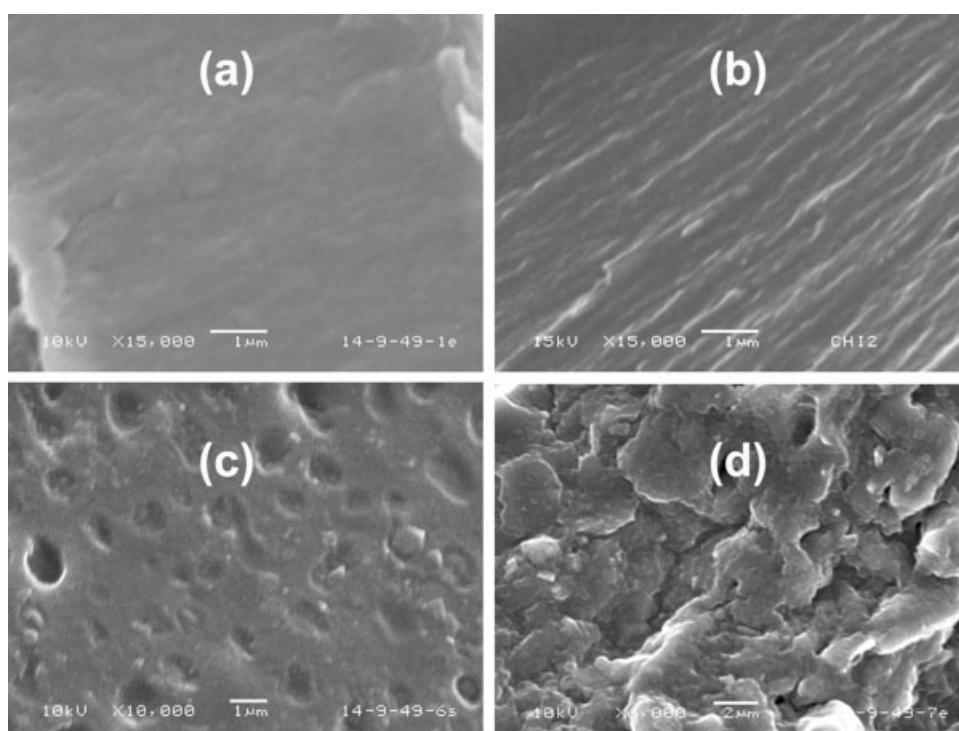

Figure 6 SEM micrographs of expand fracture surfaces of (a) chitosan film, (b) 90/10 blend, (c) 80/20 blend and (d) 70/30 blend films.

TABLE II
Transparency and Moisture Uptake of Chitosan and Blend Films

Chitosan/MPEG-*b*-PCL blend films	Transparency (%T_{660})	% Miosture uptake
100/0	78.7	29.5
90/10	49.3	24.6
80/20	39.6	22.5
70/30	32.7	20.3

bonds between the chitosan and the MPEG-*b*-PCL were slightly decreased. Then, the microphase separation or the surface roughness of the blend films occurred as increasing the MPEG-*b*-PCL ratios. However, the film roughness was continuous on the film surfaces indicated that the chitosan/MPEG-*b*-PCL blend films were homogeneous films.

Film transparency

The films were transparent with slight yellowish and whiteness tint in the chitosan and blend films, respectively. Film transparency was measured from %transmittance at λ_{max} 660 nm (%T_{660}) and presented in Table II. The %T_{660} of the film was directly related to the film transparency. From Table II, the transparency of the blend films are less than the chitosan film. The transparency of the blend films decreased as increasing the MPEG-*b*-PCL ratios. This due to the MPEG-*b*-PCL is an opaque semicrystalline polymer.

Moisture uptake

Moisture uptake of the films was measured instead of water uptake (immersion in water) since chitosan partially dissolved in water. The %moisture uptakes of film were calculated after 2 weeks of moisture absorption testing and the calculated results were summarized in Table II. The %moisture uptake of the chitosan film was 29.5% due to its hydrophilic property. The %moisture uptakes of the blend films were lower than the chitosan film suggested that the blending of water-soluble MPEG-*b*-PCL reduced moisture absorption of the chitosan film. The %moisture uptake of the blend films decreased when the MPEG-*b*-PCL ratio was increased. The results indicated that the hydrophobic PCL block of MPEG-*b*-PCL can be improved moisture resistance which directly related to water-resistance properties of the chitosan films.

CONCLUSIONS

The chitosan/MPEG-*b*-PCL blend homogeneous films with different blend ratios were successfully prepared by film casting of their blend aqueous solu-tions. The intermolecular bonds between chitosan and MPEG-*b*-PCL were detected from the band shifting of amide I and free amino groups of FTIR spectra to lower wave number. The blend films showed endothermic melting peak of the semicrystalline MPEG-*b*-PCL which depended upon the blend ratios. The MPEG-*b*-PCL could improve thermal stability of chitosan films in the range of 50–400°C. The SEM micrographs indicated the homogeneous blend films. Finally, film roughness increased whereas transparency and moisture uptake of the blend films decreased as the MPEG-*b*-PCL ratios increased. The blend films have potential for wound dressing and food packaging applications with lower moisture sensitivity than the chitosan film.

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