

Studies of Chitosan. I. Preparation and Characterization of Chitosan/Poly(vinyl alcohol) Blend Films

Cheng-Ho Chen, Fang-Yu Wang, Ching-Feng Mao, Chien-Hsin Yang

Department of Chemical and Materials Engineering, Southern Taiwan University, Tainan, Taiwan

Received 1 July 2006; accepted 30 January 2007

DOI 10.1002/app.26257

Published online 9 April 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Various blending ratios of chitosan/poly(vinyl alcohol) (CS/PVA) blend films were prepared by solution blend method in this study. The thermal properties and chemical structure characterization of the CS/PVA blend films were examined by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), and Fourier transform infrared (FTIR). Based upon the observation on the DSC thermal analysis, the melting point of PVA is decreased when the amount of CS in the blend film is increased. The FTIR absorption characteristic is changed when the amount of CS in the blend film is varied. Results of X-ray diffraction (XRD) analysis indicate that

the intensity of diffraction peak at 19° of PVA becomes lower and broader with increasing the amount of CS in the CS/PVA blend film. This trend illustrates that the existence of CS decreases the crystallinity of PVA. Although both PVA and CS are hydrophilic biodegradable polymers, the results of water contact angle measurement are still shown as high as 68° and 83° for PVA and for CS films, respectively. A minimum water contact angle (56°) was observed when the blend film contains 50 wt % CS. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1086–1092, 2007

Key words: chitosan; poly (vinyl alcohol); solution blend

INTRODUCTION

Chitin, next to cellulose, is the second common polysaccharide on the earth. Meanwhile, chitin is the source material of chitosan (CS) and it can be prepared from the shells of crabs, shrimps, and other arthropods. Even fungi, yeasts, and squid pens may also be the source of this material.¹ CS, a deacetylated product of chitin, is a high molecular weight heteropolysaccharide composed mainly or fully of β -(1,4)-2-deoxy-2-amino-D-glucopyranose and partially or none of β -(1,4)-2-deoxy-2-acetamido-D-glucopyranose units.² CS is a fully or partially deacetylated form of chitin. Unlike chitin, CS is readily soluble in various acidic solutions, such as formic and acetic acids and others. Scheme 1 shows the chemical structure of CS with 95% degree of deacetylation.

Because of excellent biodegradability, biocompatibility, and bioactivity, chitin and CS become significantly attractive in biomedical applications, including antithrombotic, homeostatic, immunity enhancing, and wound healing.^{3–5} Therefore, many efforts have been tried to produce new biofunctional materials from chitin and CS in cotton, nonwoven fabric, sponge, film, and gel forms.⁶

The blending of two or more polymers has increasingly become an important technique for improving the cost-performance ratio of commercial products.⁷ Commonly, CS film has been investigated as a highly

potential biomedical material because of its good biocompatibility. However, CS films are brittle and not suitable for use in the dry state. To enhance the physical properties of CS films, PVA was chosen to blend with CS by adopting the solution blend method. Since CS contains hydroxyl and amine groups, CS may potentially be miscible with PVA because of the formation of hydrogen bonds.^{8,9}

Poly(vinyl alcohol) (PVA) is a water-soluble synthetic polymer. Because of easy preparation, biodegradability, excellent chemical resistance, and physical properties, PVA has been used for many biomaterial applications.¹⁰ For example, PVA membranes have been used in the artificial pancreas,^{11,12} hemodialysis,¹³ and other implantable biomaterials.^{9,14}

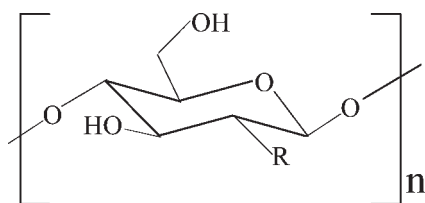
Although several researchers had studied chitosan/poly (vinyl alcohol) (CS/PVA) blend films, a systematic study on these blend films was still rare. In this study, the CS/PVA blend films with various blend ratios were prepared by solution blend method. Thermal properties, chemical structure, and surface morphology of CS/PVA blend films were examined by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), Fourier transform infrared (FTIR), contact angle instrument, and scanning electron microscopy (SEM), respectively.

EXPERIMENTAL

Materials

Chitosan (CS) with 95% deacetylation (prepared from β -chitin) was supplied by Ohka Enterprises, Taiwan.

Correspondence to: C.-H. Chen (chchen@mail.stut.edu.tw).



R: containing 5% NHCOCH_3 and 95% NH_2

Scheme 1 Chemical structure of CS with 95% degree of deacetylation.

The molecular weight of CS is about 200,000. Acetic acid was purchased from Union Chemical Works, Taiwan. Poly (vinyl alcohol) (PVA) was purchased from Merck. The molecular weight of PVA is about 72,000.

Preparation of CS/PVA blend films

CS powder (chemical structure as shown in Scheme 1) was added into a 0.1M acetic acid solution and stirred to form a 2.5 wt % clear CS solution. Meanwhile, PVA powder was charged into 80°C hot purified water with stirring to form a 2.5 wt % clear PVA solution. Different weight percentage (as indicated in Table I) of CS and PVA solution were homogeneously blended and then poured into the PP petridishes. After 48-h settle, the CS/PVA blend solution was debubbled and then moved into 60°C oven for about 24-h drying to remove the water content. Then, the blend sample was further vacuum dried for additional 24 h at 80°C to remove the residue of water and the acetic acid.

DSC analysis

A differential scanning calorimeter (DSC; Perkin-Elmer, model: DSC 7) was used to examine the thermal property of the CS/PVA blend film. The test was performed under nitrogen purge. The sample was two-stage heated. Firstly, the sample was heated from 50 to 220°C with a heating rate of 5°C/min and then cooled to room temperature to release the internal stress of the sample. Secondly, the sample was reheated from 50 to 250°C with a heating rate of 5°C/min. The results were recorded and analyzed.

TGA analysis

A thermogravimetric analyzer (TGA; Perkin-Elmer, model: TGA 7) was conducted to measure the thermal weight loss of the CS/PVA blend film in the temperature, ranging from 50 to 700°C. The sample was tested with a heating rate of 10°C/min and under a nitrogen stream. The weight losses at different stages were analyzed.

DMA analysis

The CS/PVA blend film was cut into pieces with dimensions of 20 mm long, 4 mm wide, and 0.009 mm thick. A dynamic mechanical analyzer (DMA; Perkin-Elmer, model: DMA 7e) was conducted to measure the thermal dynamic mechanical properties of the CS/PVA blend films. The sample was also two-stage heated. Firstly, the sample was heated from 0 to 120°C with a heating rate 5°C/min and then cooled to 0°C to release the internal stress of the sample. Secondly, the sample was heated from 0 to 200°C with operation conditions of heating rate 2°C/min, amplitude 10 μm , and tension 105%. The result was recorded and analyzed.

FTIR analysis

The chemical structure of the CS/PVA blend film was identified by a Fourier-transformed infrared (FTIR; Perkin-Elmer, model: Spectron One). This analysis was done at wavenumber ranged from 400 to 4000 cm^{-1} and with a scan frequency of 32 times per second.

X-ray diffraction analysis

X-ray diffraction patterns of these CS/PVA blend films were obtained by using an X-ray diffractometer (XRD; Rigaku Company, model: DMAX-2200, Japan). A $\text{Cu K}\alpha$ radiation with a wavenumber of 0.154 nm was used. The scanning rate was 2°/min ranging from 5 to 35° (2 θ).

Contact angle measurements

Contact angle measurement of CS/PVA blend films were performed by following the sessile drop method.¹⁵ A contact angle instrument equipped with an Image Analysis Attachment (First Ten Angstroms, Model FTA 100) was used for this test. The probe liquid used in the experiment was deionized distillation water. Measurements were consistently conducted at the condition of relative humidity 70% and tempera-

TABLE I
Compositions of CS/PVA Blend Films

Sample	Blend ratio, CS solution (g)/ PVA solution (g)
CS	10/0
CS8	8/2
CS6	6/4
CS5	5/5
CS4	4/6
CS2	2/8
PVA	0/10

ture 24°C. The water drop (2 μL) was carefully deposited on the surface of the blend film by using an assemble micrometer syringe. Since both PVA and CS are hydrophilic polymers, the contact angle measurement was immediately recorded right after the water drop was deposited on the surface of the blend film. If the contact angle measurement was not immediately recorded right after the water drop was deposited on the surface of the blend film, the water drop became flat gradually. Each reported data represents an average measured contact angle of at least three individual drops that were tested in different locations on a given blend film. The drop size was kept constant to minimize the experimental variances for the contact angle measurements.¹⁵

SEM examination

The surface morphologies of the CS, PVA, and CS/PVA films were examined. Each sample was coated with the gold palladium film and examined by a field-emission scanning electron microscopy (FE-SEM, Jeol Ltd., Japan, model JSM 6700F).

RESULTS AND CONCLUSIONS

A two-stage heating process was conducted for the DSC analysis. The first-stage heating is used to decrease the water content in the blend films and also release the stress of the blend films. Since CS contains $-\text{NH}_2$ and $-\text{OH}$ functional groups, the hydrogen bonding force is strongly formed among moleculars. It is difficult to identify the T_g of CS, since this compound is a semicrystalline structure. DSC curves of

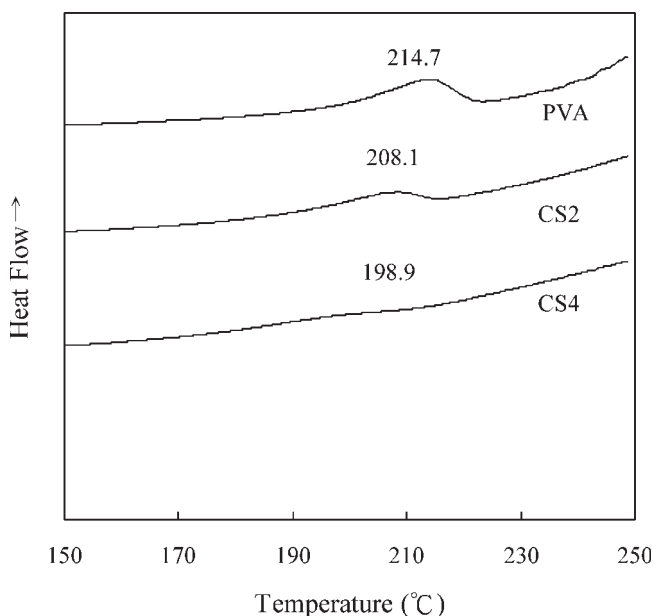


Figure 1 DSC analysis curves of PVA, CS2, and CS4 films.

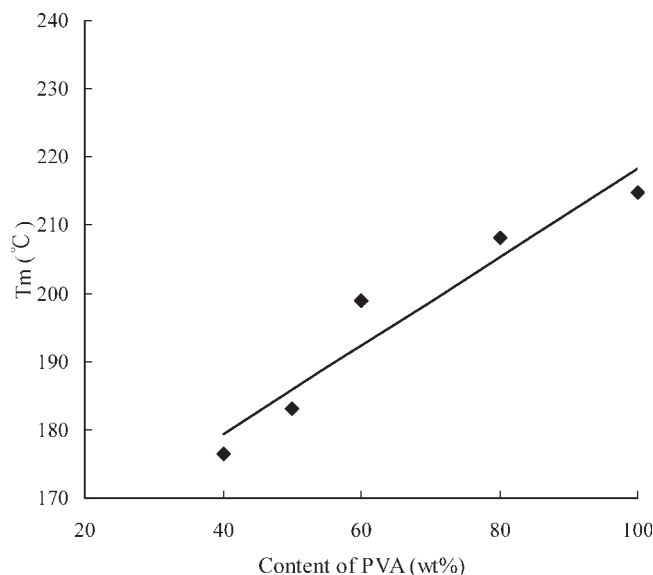


Figure 2 Influence of PVA contents on the melting temperatures (T_m) of CS/PVA blend films.

CS/PVA blend films are shown on the Figure 1. The absorption peak on Figure 1 is the melting point of PVA. From Figure 2, it is observed that the melting point of PVA is decreased when the amount of CS in the blend film is increased because of the partial miscibility between PVA and CS. If the content of PVA in a CS/PVA blend film is lower than 40 wt %, the melting point of PVA is not easy to be determined. Thus, the addition of CS reduces the PVA crystallinity and then decreases PVA melting point.

TGA and DTG curves of CS are shown on Figure 3. Notations on Figure 3 are: ΔY , which is the weight loss due to the thermal degradation of chitosan and T_{onset} is the thermal degradation onset temperature for CS. Figure 4 shows TGA curves of PVA,

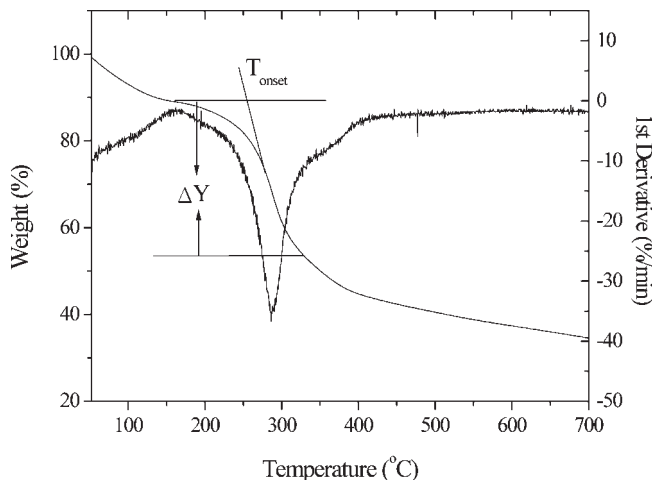


Figure 3 TGA curve of CS with 95% degree of deacetylation.

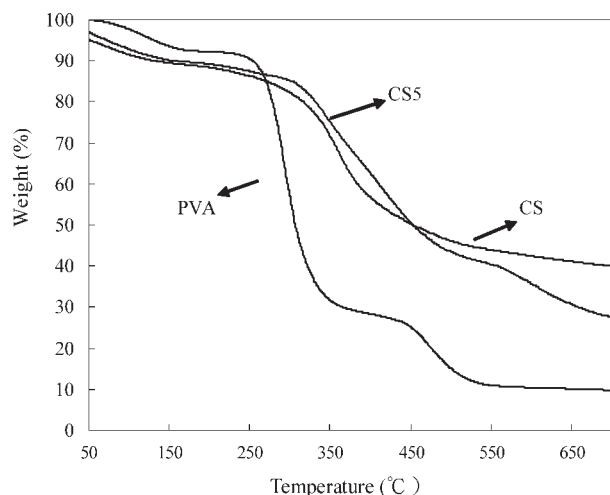


Figure 4 TGA curves of PVA, CS, and CS5 films.

CS5, and CS. Two weight losses are observed in the CS TGA curves. Weight loss at 50–100°C is due to the moisture vaporization. Another weight loss at 200–300°C is due to the degradation of CS. This process ascribes to a complex process which includes not only the dehydration of the saccharide rings but also the decomposition of the acetylated and deacetylated units of CS.

Meanwhile, three weight losses are observed in the PVA TGA curves: ΔY_1 at 50–100°C is due to the moisture vaporization, ΔY_2 at 200–300°C is due to the thermal degradation of PVA, and ΔY_3 at 400–450°C is due to the by-product generation of PVA during the TGA thermal degradation process. According to Hay's report,¹⁶ thermal degradation could lead to the production of aldehyde and alkene end-groups in the molten state. And, this could lead to the formation of a vinyl ester by the rearrangement. CS5 (containing 50 wt % CS and 50 wt % PVA) shows a mixture char-

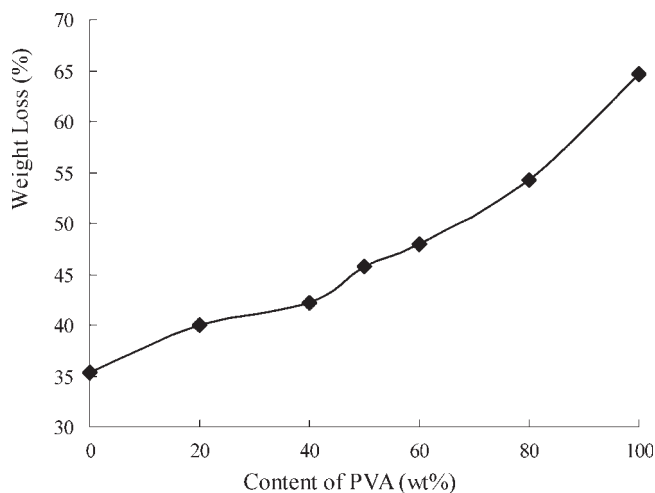


Figure 5 Relationship between the weight loss (ΔY_2) and the content of PVA in the CS/PVA blend films.

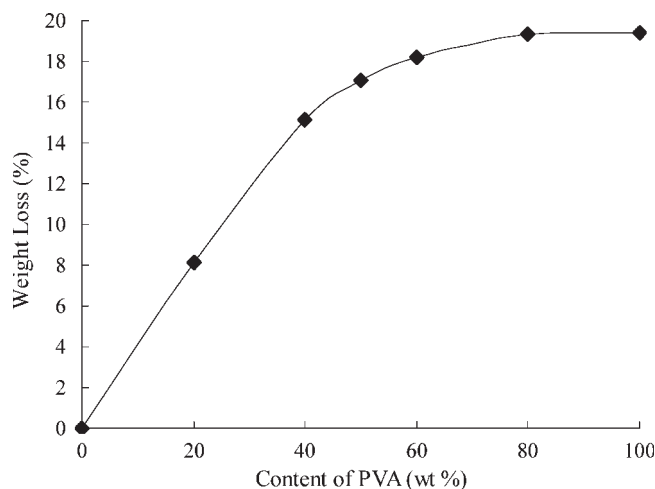


Figure 6 Relationship between the weight loss (ΔY_3) and the content of PVA in the CS/PVA blend films.

acteristic of CS and PVA from the observation on Figure 4. From Figures 5 and 6, it indicates that ΔY_2 and ΔY_3 are increased when the PVA in the blend film is increased. Figure 7 reveals the DMA analysis of the CS5 blend film. Since the partial miscibility of PVA and CS, two T_g s are found in the DMA analysis of the CS5 blend film.

Figure 8 shows the FTIR spectra of PVA, CS5, and CS films. The frequencies and their assignments of CS are indicated as followed: 655 and 1076 cm^{-1} for the characteristic peaks of crystallization of CS,⁶ 1642 cm^{-1} for the bending vibration of $-\text{NH}_2$ group, 1560 cm^{-1} for the bending vibration of amide group, and 3367 cm^{-1} for the combination of $-\text{OH}$ and $-\text{NH}$ functional groups. Also, the frequencies and their assignments of PVA are indicated as follows: 2943 cm^{-1} for $-\text{CH}_2$ group stretching vibration and 1096 cm^{-1} for C—O group. The major differences between CS and PVA from FTIR spectra are amine and amide functional groups. The FTIR spectrum of CS5 contains the characteristics of both CS and PVA. The intensity

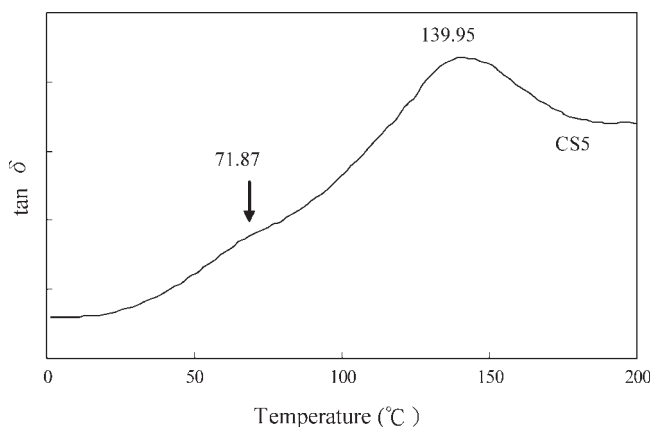


Figure 7 DMA curve of CS5 blend film.

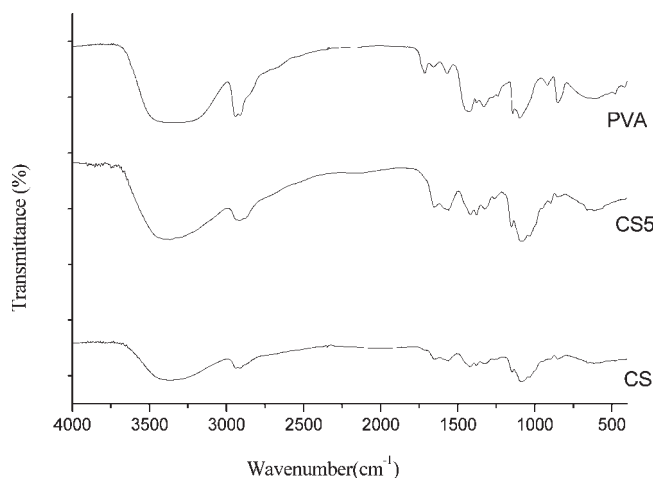


Figure 8 FTIR spectra of PVA, CS, and CS5 films.

of the characteristic peaks of CS functional groups is significantly changed when the amount of CS in the blend film is changed. Especially, 1642 cm^{-1} for $-\text{NH}_2$, 655 cm^{-1} and 1076 cm^{-1} for the characteristic peaks of crystallization of CS have the most obvious change.

XRD results of CS, CS5, and PVA films are shown in Figure 9. The CS film dried from acetic acid solution shows two diffraction peaks at about 15° and 21° , which are characteristics of the hydrated crystalline structure of CS.¹⁷ The PVA film dried from aqueous solution shows a significant crystalline peak at about 19.5° , which is because of the occurrence of strong inter- and intramolecular hydrogen bonding. As the amount of CS in the CS/PVA blend film is increased, the intensity of diffraction peak at 19° of PVA becomes lower and broader. It illustrates that the existence of CS decreases the crystallinity of PVA. Meanwhile, two diffraction peaks (at about 15° and 21°) resulting from the hydrated crystalline structure in

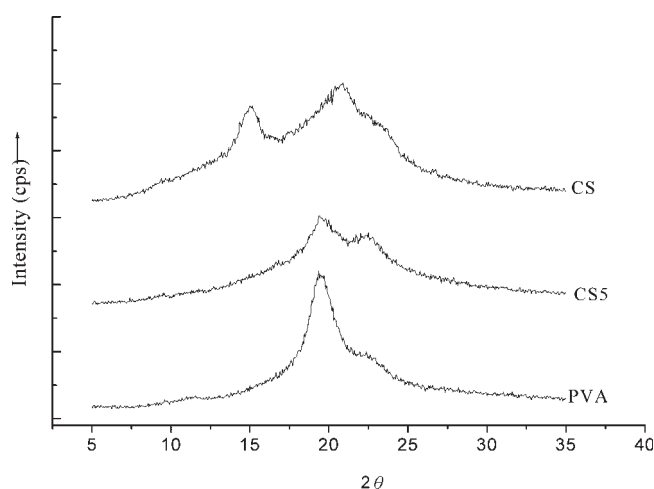


Figure 9 XRD patterns of PVA, CS, and CS5 films.

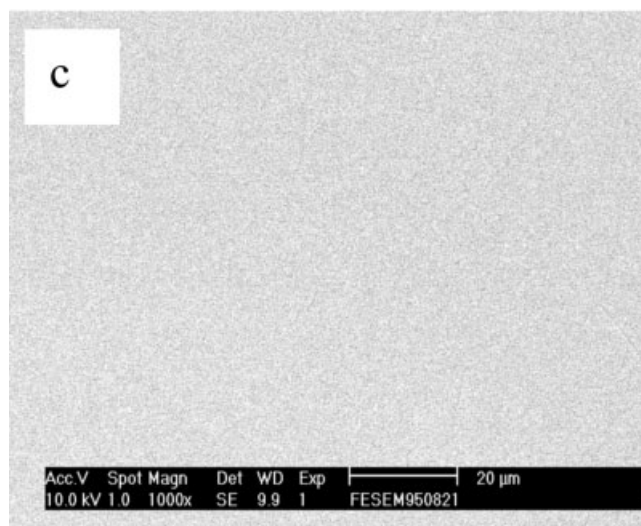
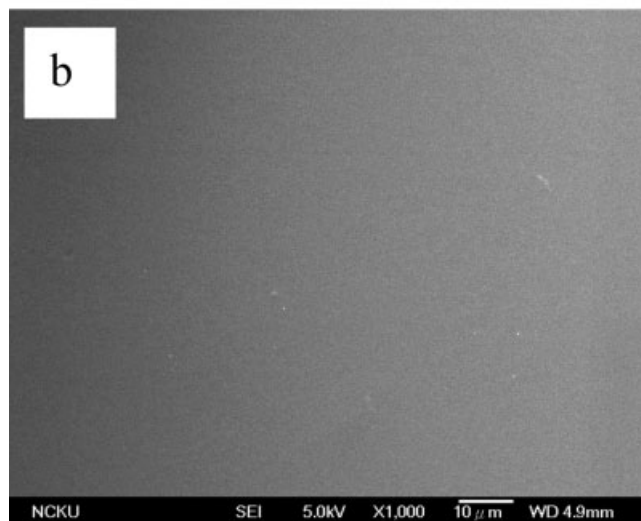
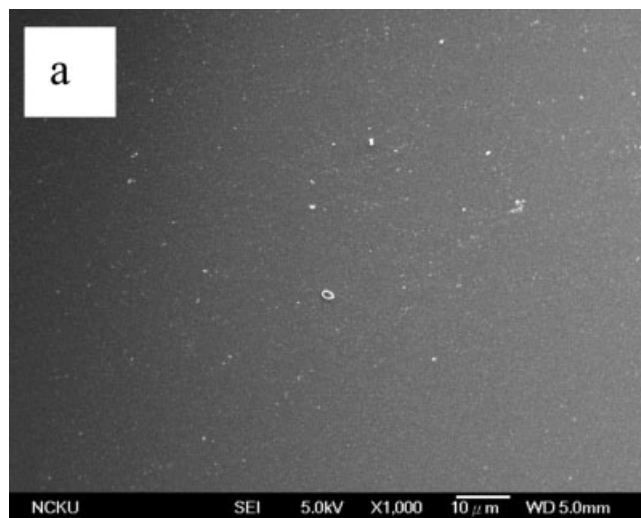


Figure 10 SEM photographs of the top surfaces of (a) PVA, (b) CS, and (c) CS5 films.

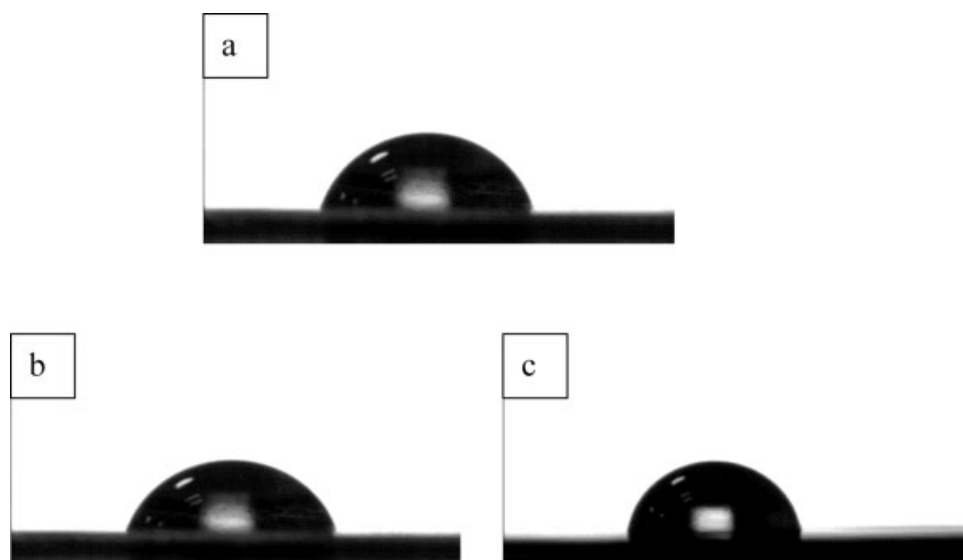


Figure 11 Photo images of water drops on the (a) PVA film, water contact angle = 68° , (b) CS5 film, water contact angle = 56° , and (c) CS film, water contact angle = 83° .

CS disappeared in all CS/PVA blend films. This phenomenon is because of the existence of PVA in CS/PVA blend films and the hydrogen bonding interaction between CS and PVA, which eliminates the hydrated crystalline structure of CS.

Figure 10(a–c) shows SEM photographs of the top surfaces of PVA, CS, and CS5 films, respectively. It indicates that PVA, CS, and CS5 films all have a thick and dense top layer with almost no pores. Figure 11 (a–c) shows the photo images of water drops on the surfaces of CS, CS5, and PVA films, respectively. According to the sessile drop method, the water contact angle of the PVA film (68°) is lower than that of the CS film (83°). It implies that PVA is more hydrophilic than CS. As mentioned in the experimental section, the contact angle measurements were recorded immediately right after the water drop was deposited on the surface of the blend film. Although both PVA and CS are hydrophilic biodegradable polymers, their water contact angles are still as high as 68° and 83° , respectively. This high water contact angle is mainly resulted from two factors. The first factor is associated with the hydrophobic backbone of the polymer chains.¹⁸ The second factor in both PVA and CS films have a thick and dense top layer with almost no pores, according to the result of Figure 10. Similar research results had also reported by Chiu and coworkers.⁹

When the amount of CS is increased in the CS/PVA blend film, the water contact angle of the CS/PVA blend film is initially decreased and then increased. It indicates that there is a minimum water contact angle (56°) that occurred when the blend film contains 50 wt % CS. This phenomenon may be resulted from the reorientation of polar functional

groups toward the top surface of CS/PVA blend films during the formation of the blend film, especially, when the blend film contains 50 wt % CS. Polar group reorientation could be especially important for polymers with asymmetric repeating units.¹⁹ The lower water contact angle indicates the more polar group on the surface of CS5 than that of other blend films.

CONCLUSIONS

The thermal properties of CS/PVA blend films are studied. The melting point of PVA is decreased when the amount of CS in the blend film is increased from the DSC thermal analysis. Two weight losses are observed in the CS TGA curves and three are formed in the PVA TGA curves. It is found that ΔY_2 and ΔY_3 are increased when the content of PVA in the blend film is increased. Since PVA and CS are not completely miscible, two T_g s are shown in the DMA curve of the CS5 blend film. The FTIR absorption characteristic is changed when the amount of CS in the blend film is changed. Besides, the intensity of XRD peak at 19° of PVA becomes lower and broader when the amount of CS in the CS/PVA blend film is increased. It illustrates that the existence of CS decreases the crystalline of PVA. From the water contact angle measurement, it indicates that there is a minimum water contact angle, which occurred when the blend film contains about 50 wt % CS. According to the discussions mentioned above, CS and PVA are identified as partially miscible.

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