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Fabrication and characterization of poly (vinyl alcohol)/chitosan blend nanofibers produced by electrospinning method

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Abstract

A series of poly (vinyl alcohol) (PVA)/chitosan (CS) blend nanofibrous membranes with different weight ratio of PVA to CS were fabricated by electrospinning method. The morphology, diameter, and structure of electrospun nanofibers were investigated by scanning electron microscopy (SEM), fourier transform infrared (FT-IR), X-ray diffraction (XRD) and differential scanning calorimetry (DSC). SEM images showed that the morphology and diameter of the nanofibers were mainly affected by concentration of the blend solution, weight ratio of the blend, respectively. FT-IR, XRD, and DSC demonstrated that there were strong intermolecular hydrogen bonds between the molecules of CS and PVA. The crystalline microstructure of the electrospun fibers was not well developed.

Keywords: Poly (vinyl alcohol)/chitosan blend; Nanofiber; Electrospinning

1. Introduction

The development of electrospinning has been rapidly increasing in the past years because it can consistently generate polymer fibers ranging from 50 to 500 nm in diameter, depending on the polymer and processing conditions (Deitzel, Kleinmeyer, Harris, & Beck Tan, 2001; Phillip, Heidi, & Donald, 2001). The nanofibers produced by electrospinning method have showed amazing characteristics such as very large surface area-to-volume ratio and high porosity with very small pore size (Shin, Hohman, Brenner, & Rutledge, 2001; Park, Jeong, Yoo, & Hudson, 2004). Therefore, electrospun nanofibers have become promising materials for many biomedical applications such as wound dressing, drug delivery, and scaffold for tissue engineering (Li, Laurencin, Caterson, Tuan, & Ko, 2002; Kenawy et al., 2003; Yoshimoto, Shin, Terai, & Vacanti, 2003; Bhattarai et al., 2004; Zong et al., 2002). Recently, researchers have investigated electrospinning of blend polymers as candidate materials for biomedical applications because polymer blends have provided an efficient way to fulfil new requirements for material properties (Sajitha & Mohan, 2003; Kenawy et al., 2002; Min, You, Kim, Lee, & Park, 2004; You et al., 2005).

Poly (vinyl alcohol) (PVA) is a non-toxic, water-soluble, biocompatible, and biodegradable synthetic polymer, which is widely used in biomedical field. PVA has better fiber-forming and highly hydrophilic properties, and its fibers have been commercialized since the 1950s (Zheng, Du, Yu, Huang, & Zhang, 2001). Chitosan (CS), a (1-4)-linked 2-amino-2-deoxy-β-D-glucopyranose, is derived from chitin, (1-4)-linked 2-acetamido-2-deoxy-β-D-glucopyranose. As

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one of the most abundant natural polysaccharides, CS is well known for its biocompatible and biodegradable properties (Mi, Tan, Liang, & Sung, 2002). As candidate materials, CS and PVA have been investigated for biomedical applications, such as sutures and wound dressings (Senel & McClure, 2004; Yuan, Zhang, Yang, Wang, & Gu, 2004; Stammen, Williams, Ku, & Guldberg, 2001; Schwenter, Bouche, Pralong, & Aebischer, 2004).

As biomedical materials, PVA/CS blended membrane is more favorable for the cell culture than the pure PVA membrane (Chuang, Young, Yao, & Chiu, 1999). So, it is reasonable to expect that the membrane composed of nanofibers of PAV/CS blend produced by electrospinning will play a more important role in the biomedical field. To our knowledge, there has been no report on electrospinning of PVA/CS blend, except for Ref. (Ohkawa, Cha, Kim, Nishida, & Yamamoto, 2004). Meanwhile, only the effect of volume ratio of PVA to CS on the diameter and morphology of the nanofibers has been briefly discussed. The effects of processing parameters on the electrospinning of the PVA/CS blend have not been well understood. Especially, the relationship between processing parameters and microstructures in the electrospun nanofibers has not been reported.

In the present work, a series of PVA/CS blend nanofibrous membranes were fabricated by electrospinning method. The effects of the weight ratio and the concentration on morphology and diameter of the fibers were investigated by SEM technique. Fourier transform infrared (FT-IR), X-ray diffraction (XRD), and differential scanning calorimetry (DSC) were used to characterize the electrospun fiber membranes.

2. Experimental

2.1. Materials

CS (degree of deacetylation 0.78) was purchased from Sichuan Biochem-ZX Research Co., Ltd., China. PVA (degree of hydrolysis, 96%; degree of polymerization, approximately 2500; $M_n = 9.4 \times 10^4$) and acetic acid (AA) were purchased from Sichuan Biochem-ZX Research Co., Ltd., China. All materials were used without further purification.

2.2. Electrospinning procedures

The apparatus for electrospinning experiments was assembled based on the previous study (Jia, Kim, Gong, & Lee, 2006). Briefly, the polymer solution was placed into a 3 ml syringe with a capillary tip whose inner diameter is 0.3 mm. A copper wire connected to the positive electrode was inserted into the polymer solution. A copper plate wrapped with aluminum foil was used as the collector, which was connected to the ground. A high voltage power supply (0–30 kv) was employed to generate the electric filed. PVA was dissolved in distilled water (DW) at a concentration of 20 wt%, and CS was dissolved in AA-water solution (2 wt%) at a concentration of 3 wt%. A PVA-DW solution (20 wt%) was mixed with a CS-AA solution (3 wt %) in weight ratios of (PVA/CS) 90/10, 80/20, 75/25, and 70/30, respectively. Then, the mixed solutions were subjected to the electrospinning experiment. The applied voltage was 15 kv, the elecrospinning distance (tip-to-collector distance: TCD) was 15 cm, and the concentration of PVA/CS blend solutions were from 3 wt% to 9 wt%.

2.3. Film preparation

Thin films of PVA/CS blend with different weight ratio were prepared by casting the solution on the surface of polytetrafluoroethylene film. The thin films were dried under atmospheric temperature for three days, then, dried under vacuum at 50 °C for another day.

2.4. Measurement and characterization

Conductivity of each PVA/CS blend solution was measured by electric conductivity mete. The intrinsic viscosity ($[\eta]$) of the solution was measured by using Ubbelohde viscometer.

The morphologies and diameters of the electrospinning fibers were determined with SEM. A small section of the fiber mat was placed on the SEM sample holder and sputter- coated with gold (Denton Desk-1 sputter coater). An Amray 3000 SEM with an accelerating voltage of 20 kv was employed for SEM photographs.

FT-IR spectra of the electrospinning fibers and the films were recorded with a Nicolet 17DSX FT-IR Spectrometer.

XRD patterns of the electrospinning fibers and the films were recorded with a Rigaku Dmax-II X-ray diffractometer, using Nickel-filtered C_u K_α radiation at 40 kv and 50 mA in the 2θ range of 5–36°.

The thermal behavior of the electrospinning fibers and the films were studied with a DSC technique. DSC was performed with a DuPont 2100 thermoanalyzer under a nitrogen atmosphere. DSC traces were recorded between 50 and 250 °C at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Effect of blend weight ratio

Zong et al. (Zong et al., 2002) reported that the addition of a small amount of salt increased the charge density in ejected jets. Thus the addition of salt was found to greatly change the morphology of the electrospun fibers from beads-on-fiber structure to uniform fiber-structure. Moreover, the diameter of the nanofibers also decreased with the addition of salt. Son et al. (Son, Youk, Lee, & Park, 2004) reported that the addition of cationic and anionic polyelectrolytes would increase the conductivity of polymer solution and result in thinner fiber diameter. In this study, we prepared the nanofibrous membrane of PVA/CS blend

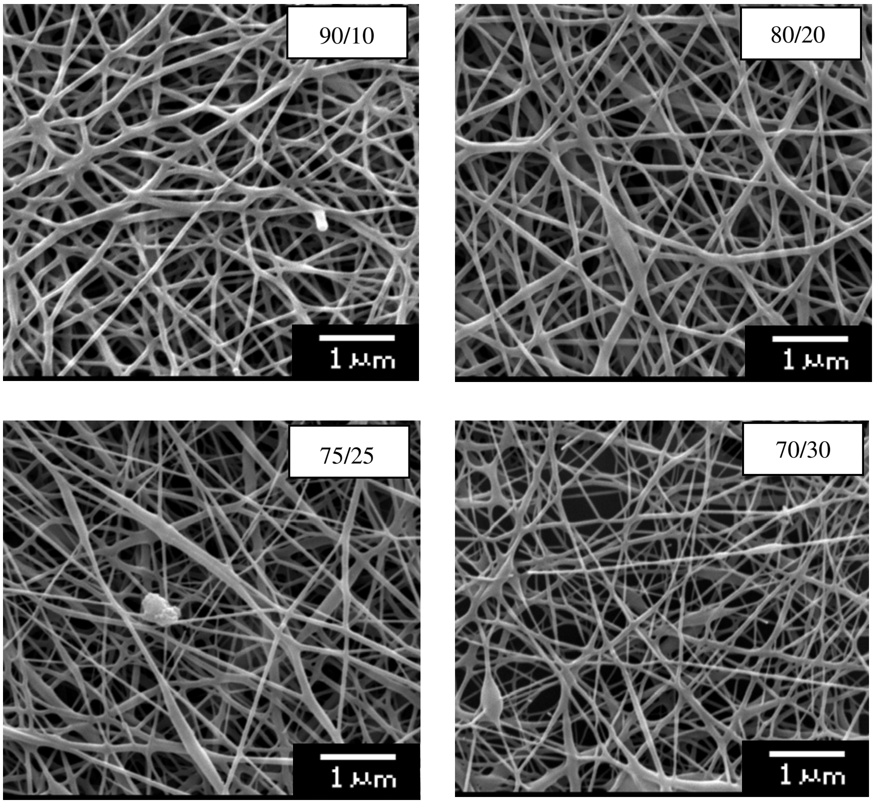

Fig. 1. SEM photographs of nanofiber mat with different weight ratio of PVA to CS (Concentration, 7.4 wt%; voltage, 15 kv; TCD, 15 cm).

using acetic acid-water solution as a spinning solvent. As we know, CS is a cationic polysaccharide with amino groups at the C2 position, which are ionizable under acidic or neutral pH conditions. Therefore, the morphology and diameter of electrospun fibers will be seriously influenced by the weight ratio of PVA/CS. Fig. 1 shows SEM images of CS/PVA blend fibers with different weight ratio of CS to PVA under the same processing condition (Concentration, 7.4 wt%; voltage, 15 kv and TCD 15 cm). Fig. 2 shows the average diameter and the electrospinning weight of per-hour (EW) as a function of the weight ratio. The fiber diameter gradually decreased with increasing CS content in the blend. When the CS content was more than 30%, fibers could hardly form. These behaviors can be explained as the following. CS is ionic polyelectrolytes, a higher charge density on the surface of ejected jet form during electrospinning. As the charges carried by the jet increase, higher elongation forces are imposed to the jet under the electrical field. It has been known that the overall tension in the fibers depend on the self-repulsion of the excess charges on the jet. Thus, as the charge density increase, the diameter of the final fibers becomes smaller (Zong et al., 2002). We noted that when the diameter of the fibers decreased with increasing CS content in the blend, as shows in Fig. 2, EW also decreased. When the CS content in the blend was more than 30%, the fibers could not form. This indicated that the repulsive force between ionic groups within the polymer backbone was expected to inhibit the formation of continuous fiber during electrospinning (Park et al., 2004).

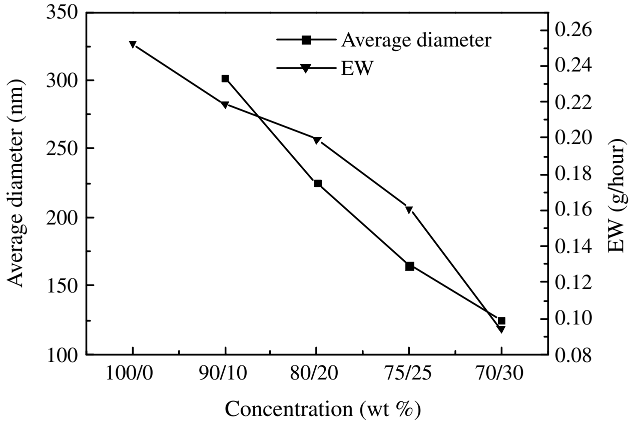

Fig. 2. Average diameter and EW of the electrospun fibers as a function of the weight ratio (PVA/CS; voltage, 15 kv; TCD, 15 cm).

3.2. Effect of solution concentrations

The morphology and diameter of electrospun nanofibers depended on the various parameters such as solution concentration, applied electric field strength, TCD, etc. (Fong, Chun, & Reneker, 1999; Bognitzki et al., 2001; Lee, Kim, La, Lee, & Sung, 2002). Among these parameters, the concentration or the corresponding viscosity of the electrospinning solution was one of the most effective variables to control the fiber morphology and diameter (Zong et al., 2002). Results obtained from our study showed that the morphology and average diameter of electrospun nanofibers did not change significantly within the applied voltage and TCD. Thus, the effects of the concentration on fiber morphology and diameter were emphatically investigated. The similar results of effect of concentration on the fibers morphology and diameter were obtained from the various weight ratios of PVA to CS. Fig. 3 shows SEM photographs of the electrospinning fibers as a function of concentration (PVA/CS = 80/20). It was found that the morphology of the fibers changed gradually from the more beads structure to the uniform fiber-structure with increasing concentration of the solution. Fig. 4 expresses the average diameter of the electrospinning fibers of CS/PVA blend as a function of solution concentration. The average diameter of the fibers increased with increasing the concentration. Beads were only generated by electrospinning the CS/PVA blend solution at the concentration below 3 wt% (no images). In contrast, when the concentration of PVA/CS blend solution was more than 10 wt%, the electrospinning process was hard to maintain due to the high viscosity of the solution.

Fig. 5 gives the conductivity and the [η] as functions of concentration. It was found that the conductivity slightly increased, and the [η] obviously increased with increasing the solution concentration. However, the fiber diameter increased with increasing concentration of the solution (Fig. 4). This indicated that the fiber diameter is mainly affected by the concentration of solution under the same weight ratio.

3.3. FT-IR spectra

Fig. 6 gives FT-IR spectra of PVA/CS blend nanofibers with different weight ratios. The PVA nanofibers exhibited

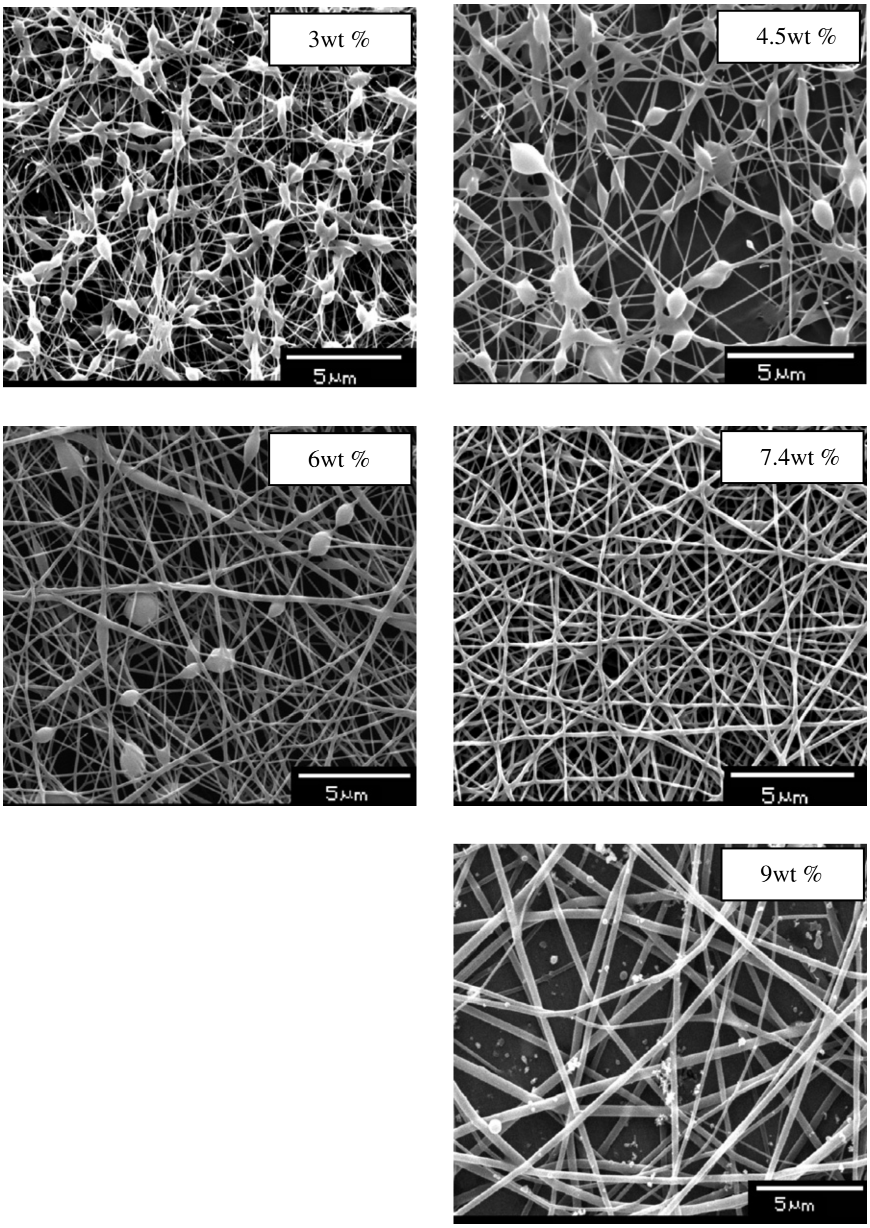

Fig. 3. SEM photographs of the electrospinning fibers as a function of the concentration (PVA/CS = 80/20; voltage, 15 kv; TCD, 15 cm).

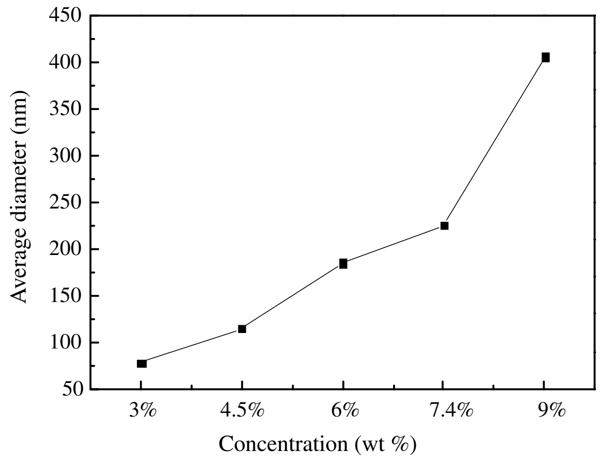

Fig. 4. Average diameter of the electrospinning fibers as a function of the solution concentration. (PVA/CS = 80/20; voltage, 15 kv; TCD, 15 cm).

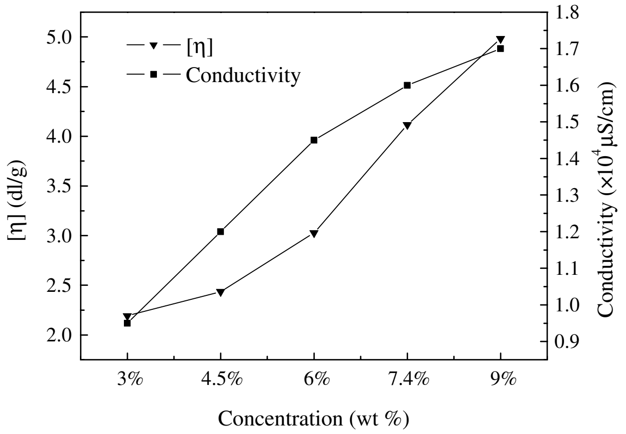

Fig. 5. The conductivity and [η] as a function of the solution concentration. (PVA/CS = 80/20; voltage, 15 kv; TCD, 15 cm).

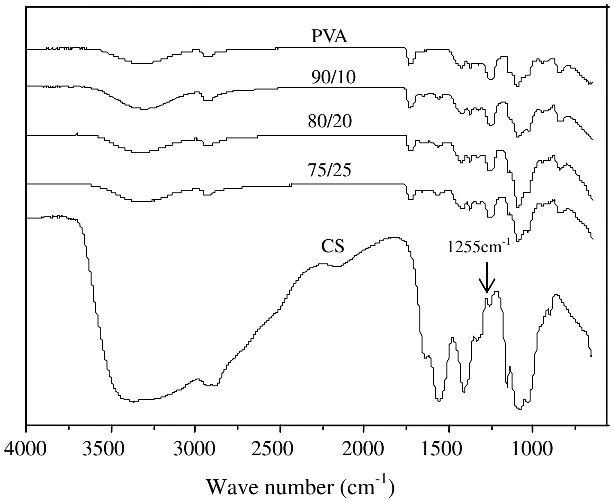

Fig. 6. FT-IR spectra of the nanofibrous membranes with different weight ratio of PVA/CS (Concentration, 7.4 wt%; voltage, 15 kv; TCD, 15 cm).

a number of absorption peaks at 2940, 1448, 1333, 1248, 1095, and 847 cm^{-1}, which were attributed to the ν_α (CH_2), δ (CH–OH), δ (CH–OH), ω (CH), ν (C–O), and ν (C–C) resonance, respectively (Zheng et al., 2001). CS membrane showed FT-IR absorption features around 898 and 1151 cm^{-1} peaks assigned saccharine structure and a weaker amino characteristic peak at 1255 cm^{-1} was the absorption of δ (O–H), and the peak at 1383 cm^{-1} was assigned to the CH_3 symmetrical deformation mode (Zheng et al., 2001). It was observed that the absorption peak at about 3441 cm^{-1} concerned with –OH and –NH stretching vibrations shifted to a lower wave number with the increase of PVA content in the blends. Moreover, compared with FT-IR spectra of pure CS membrane, the absorption peak of CS/PVA nanofibers at 1255 cm^{-1} disappeared. These results suggested the formation of hydrogen bond between CS and PVA molecule.

3.4. XRD spectra

Fig. 7 presents XRD patterns of PVA/CS blend nanofibers. For the pure PVA fibers, there were two peaks around $2\theta = 10.7°$ and $2\theta = 20.4°$ (Nakane, Yamashita, Iwakura, & Suzuki, 1999).The diffraction model of CS fiber showed three typical peaks at $2\theta = 10.5°$, $2\theta = 15.4°$, and $2\theta = 20.1°$ (Samuels, 1981). If there were no or weak interaction between CS and PVA molecules in the blend fibers, each component would has its own crystal region in the blend fibers, and XRD patterns would be expressed as simple mixed patterns of CS and PVA with the same ratio as those for mechanical blending. In fact, the peak of PVA at $2\theta = 10.7°$ became weak until disappearing with increasing CS content in the blend. The diffraction peak of CS at 15.4° disappeared in the blends. Moreover, the peak of electrospun fibers of CS/PVA blends around $2\theta = 20.4°$ slightly shifted towards high 2θ from 20.7° to 21.4° with increasing CS content in the blend. These evidences further concluded

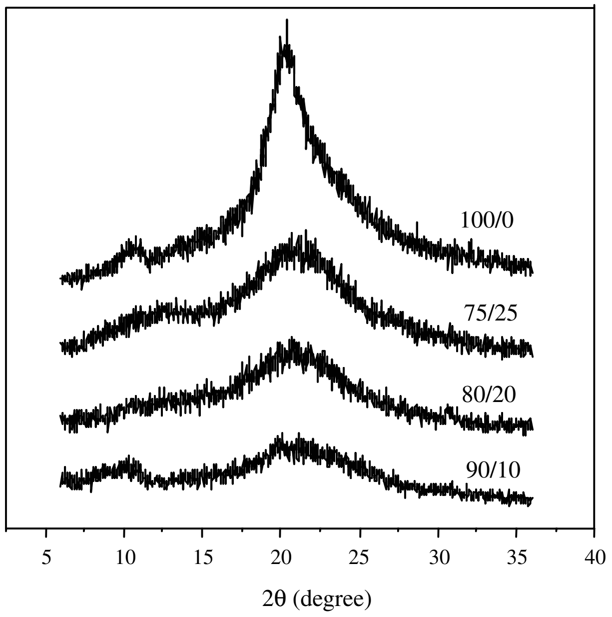

Fig. 7. XRD patterns of the nanofibrous membranes with different weight ratio of CS/PVA (Concentration, 7.4 wt%; voltage, 15 kv; TCD, 15 cm).

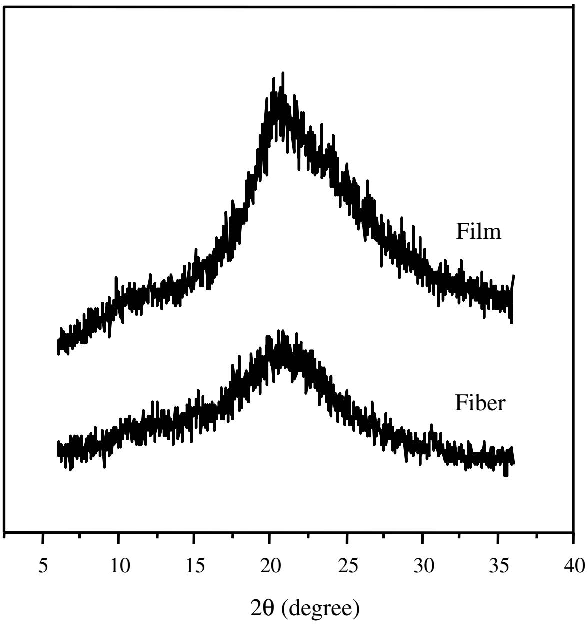

Fig. 8. XRD patterns of the nanofibrous membrane and the corresponding film (PVA/CS = 80/20; Concentration, 7.4 wt%; voltage, 15 kv; TCD, 15 cm).

that strong interaction occurred between CS and PVA molecule in the blends.

Fig. 8 shows XRD patterns of the electrospun fibers and the corresponding films of CS/PVA blend. Compared with the film, PVA/CS blend nanofibers showed a relative obtuse and broad peak around $2\theta = 21.1°$. This phenomenon confirmed that electrospinning retarded the crystallization process of PVA/CS blend, which did not lead to the development of the crystalline microstructure of electrospun fibers. The retardation of crystalline microstructure of electrospun fibers during electrospinning has been also reported by Deitzel et al. and Zong et al. (Deitzel et al., 2001; Zong et al., 2002), respectively. The reason for the retardation could be explained as following. During electrospinning, the stretched molecular chains of the fiber solidified rapidly at high elongate rates, which significantly hindered the formation of crystals.

3.5. DSC analysis

DSC thermograms of the electrospinning fibers of CS/PVA blends are shown in Fig. 9. The pure PVA fibers showed a relatively large and sharp endothermic curve with a peak at 200 °C. However, for CS/PVA blend fibers, endothermic curve became broad and obtuse, and the peak shifted toward the low temperature. This indicated that the crystalline microstructure of electrospun fibers did not develop well. This was because the majority of the chains are in the non-crystalline state due to the rapid solidification process of stretched chains during electrospinning. The results from DSC were supported by XRD analysis. Table 1 lists thermal properties of the fibers. It was observed that the peaks of the endothermic curves shifted toward the low temperature from 194.1 to 190.1 °C and the ΔH_m values also decreased from 44.0 to 27.0 J/g with increasing CS content in the blend. This demonstrated that the CS content in the blend leaded to worse condition for crystallization of the fiber.

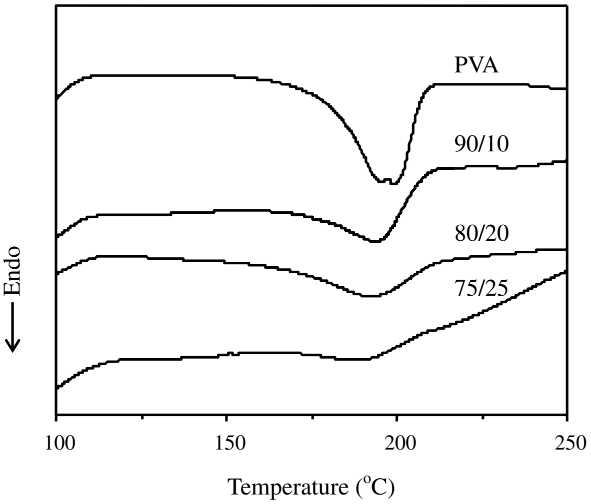

Fig. 9. DSC curves of the nanofibrous membranes with different weight ratio of PVA/CS (Concentration, 7.4 wt%; voltage, 15 kv; TCD, 15 cm).

Table 1
DSC data obtained from the electrospun fibers of PVA/CS blend

Weight ratio (PVA/CS)	T_m (°C)	ΔH_m (J/g^{-1})
100/0	199.1	54.3
90/10	194.1	44.0
80/20	192.4	42.8
75/25	190.1	27.0

4. Conclusions

The electrospun nanofibrous membrane of CS/PVA blends was fabricated. The effects of the blend weight ratio and the solution concentration on structure and morphology of the fibers were investigated for the fist time. The result indicated that the average diameter of the fiber gradually decreased with increasing CS content from 10% to 30%. Above 30% CS, the blend nanofibers could not form. On the other hand, the morphology and diameter of the fiber were principally affected by the solution concentration with the same blend weight ratio. The average diameter of the fibers increased and the morphology changed gradually from the more beads structure to the uniform fiber-structure with increasing concentration of the solution from 3% to 9 wt%. Below 3 wt %, only beads generated. In contrast, when the concentration of PVA/CS blend solution was more than 10 wt%, the electrospinning process was hard to maintain due to the high viscosity of the solution. FT-IR, XRD, and DSC analysis demonstrated that there were strong intermolecular hydrogen bonds between CS and PVA molecular. The crystalline microstructure of electrospun fibers did not well develop due to the rapid solidified of the fibers during electrospinning and the existence of CS content in the blend.

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