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Chitosan bicomponent nanofibers and nanoporous fibers

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Abstract—Nanofibers with average diameters between 20 and 100 nm have been prepared by electrospinning of 82.5% deacetylated chitosan ($M_v = 1600$ kDa) mixed with poly(vinyl alcohol) (PVA, $M_w = 124$–186 kDa) in 2% (v/v) aqueous acetic acid. The formation of bicomponent fibers was feasible with 3% concentration of solution containing up to an equal mass of chitosan. Finer fibers, fewer beaded structures and more efficient fiber formation were observed with increasing PVA contents. Nanoporous fibers could be generated by removing the PVA component in the 17/83 chitosan/PVA bicomponent fibers with 1 M NaOH (12 h). Fiber formation efficiency and composition uniformity improved significantly when the molecular weight of chitosan was halved by alkaline hydrolysis (50 wt % aqueous NaOH, 95 °C, 48 h). The improved uniform distribution of chitosan and PVA in the bicomponent fibers was attributed to better mixing mostly due to the reduced molecular weight and to the increased deacetylation of the chitosan.

Keywords: Chitosan; Nanofibers; Electrospinning

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1. Introduction

Chitosan is the N-deacetylated derivative of chitin, the second most abundant polysaccharide in nature after cellulose. Depending on the chitin source and the methods of hydrolysis, chitosan varies greatly in its molecular weight (MW) and degree of deacetylation (DDA). The MW of chitosan can vary from 30 kDa to well above 1000 kDa. The typical DDA of chitosan is over 70%, making it soluble in aqueous acidic solutions. Due to its biocompatible, biodegradable, antimicrobial, and nontoxic properties,[1] chitosan has been widely studied for applications as biomedical,[2–4] and antimicrobial materials,[5,6] and for drug delivery.[7–10]

The rigid D-glucosamine structures, high crystallinity and capacity to hydrogen bond intermolecularly lead to the poor solubility of chitosan in common organic solvents, limiting ways to process chitosan. Reduced molecular weight and lowered crystallinity by random deacetylation generally improve its solubility in dilute acids and enable processing chitosan into various forms, such as beads,[11,12] membranes,[13] and fibers.[14–17] Recent attention has been on making chitosan fibrous membranes by electrospinning. Electrospinning applies high voltages to a capillary droplet of polymer solution or a melt to overcome liquid surface tension and thus enables the formation of much finer fibers than conventional fiber spinning methods. Fiber formation from chitosan has, however, been met with challenges because of its limited solubility and polycationic nature in solution. Pure chitosan fibers have only been electrospun from 7% to 8% solutions of chitosan at relatively low molecular weights, such as 210 kDa (M_v) and 78% DDA in trifluoroacetic acid[18] and 106 kDa (M_v) and 54% DDA in 90% aqueous acetic acid.[19] Others reported fiber generation by electrospinning of chitosan mixtures with another polymer.[3,9,10,18,20,21] Very fine fibers (130 nm in diameter) were electrospun from mixing a low molecular weight chitosan ($M_v = 220$ kDa, 86% DDA) with silk fibroin (SF), however, with only 11 wt % of chitosan.[21] Beaded structures began to form along with fibers at a higher chitosan content of 23 wt %. By mixing with polyvinyl alcohol ($M_n = 88$ kDa), another low molecular weight chitosan ($M_v = 210$ kDa, 78% DDA) could

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generate 120 nm diameter fibers with up to 45% chitosan.[18] Again, beaded structures were observed, but at a higher chitosan content of 64.5%. All others reported fiber generation from mixtures that contained higher molecular weight chitosan with poly(ethylene oxide) (PEO) in aqueous acetic acid.[3,9,10,20] At equal mass composition of chitosan ($M_v = 654$ kDa, 90% DDA) and PEO (1500 kDa), ultra-fine fibers (~120 nm in diameter) containing both polymers were generated along with some micrometer-size fibers composed of nearly pure PEO.[20] Adding organic solvents, such as *N*,*N*-dimethylformamide and dimethyl sulfoxide at 0.3% and 10%, respectively, to 2.05 wt % 90/10 chitosan ($M_w = 1900$ kDa, 85% DDA)/PEO ($M_w = 900$ kDa) also improved fiber formation.[10]

This work aims to investigate fiber formation from high-molecular-weight chitosan via electrospinning. As electrospinning from solutions containing chitosan alone was expected to be unlikely, PVA was selected as the polymer additive because of its ease for fiber formation from electrospinning. Like chitosan, PVA is soluble in dilute aqueous acetic acid and is biodegradable.[22–24] The main focus is to understand the effects of polymer composition and chitosan molecular weight on fiber formation and on the morphology of chitosan/PVA bicomponent fibers. Furthermore, new fiber structure is probed by exploring the phase separation behavior between chitosan and PVA for the generation of nanoporosity within the fibers.

2. Experimental

2.1. Materials

Chitosan (82.5% deacetylated, viscosity of 1% solution in 1% v/v acetic acid = 467 cps) and polyvinyl alcohol (PVA) (87–89% hydrolyzed, average $M_w = 124$–186 kDa) were obtained from Aldrich Chemical Company. Acetic acid (99.9%) was purchased from EM Science. Crude chitosan powder was hydrolyzed in 50 wt % aq NaOH solution at 95 °C for 2–48 h to lower its molecular weight.

2.2. Fiber formation by electrospinning

The PVA solution was prepared in water at 80 °C under magnetic stirring for 0.5 h, and then cooled to room temperature. Chitosan was dissolved in aq HOAc at 2%, 20%, and 90% v/v concentrations at room temperature with gentle magnetic stirring for 8 h. The chitosan solution prepared in 2% v/v aq HOAc was also mixed with the aq PVA solution to obtain chitosan/PVA compositions at 11/89, 17/83, 25/75, and 50/50 mass ratios. The concentrations of all polymer solutions were expressed in wt/wt %. Electrospinning of the solutions was performed by the procedure previously described.[25,26] The polymer solution was placed in a glass capillary with a 0.4-mm inner diameter tip. A stainless steel electrode was inserted to the polymer solution and connected to a power supply (Gamma High Voltage Supply, ES 30-0.1P). An electrospinning voltage ranging from 0 to 30 kV was tried for all solutions, and 18 kV was applied for those solutions that could generate fibers. Fibers were collected on an aluminum foil that was 25 cm from the capillary tip and connected to the ground.

2.3. Characterization and measurement

The morphology of electrospun chitosan/PVA bicomponent fibers was observed with a scanning electron microscope (SEM) (XL30-SFEG, FEI/Philips) without gold coating, and a transmission electron microscope (TEM) (Philips CM120). For TEM observation, fibers were electrospun directly onto a TEM copper mesh. Thermal analyses were conducted with a differential scanning calorimeter (DSC-60 Shimadzu, Japan) in N_2 using ca. 5.0 mg samples at a 10 °C/min heating rate. Fourier transform infrared spectroscopy (FTIR) measurements were performed (Nicolet Magna-IR 560) by the KBr method.

The chitosan and PVA compositions of the bicomponent fibers were estimated from the absorbance ratio at 898 and 850 cm^{-1} (A_{898}/A_{850}), which are characteristic of the saccharide structure of chitosan and the C–C stretching in PVA, respectively. A calibration curve was constructed from the FTIR spectra of cast films of chitosan/PVA mixtures with known chitosan compositions.

The viscosity-average molecular weight (M_v) of chitosan was determined by dilute solution viscosity measurement using a Cannon–Fenske viscometer. A mixture of 0.1 M HOAc–0.2 M NaCl was used as the solvent to prepare chitosan solutions with concentrations from 1×10^{-3} to 2.5×10^{-4} g/mL. The viscosity-average molecular weight (M_v, in Daltons or Da) was derived from the following Mark–Houwink equation:[27]

$$[\eta] = 1.81 \times 10^{-3} M_v^{0.93}$$

3. Results and discussion

3.1. Fiber formation from pure chitosan

The M_v of chitosan was calculated from solution viscosity measurement to be 1600 kDa. This high-molecular-weight chitosan was soluble in 2%, 20%, and 90% v/v aqueous acetic acid and could form homogeneous solutions at up to 3% concentration, above which the solutions gelled. Electrospinning of the above chitosan solutions at up to 2% concentrations produced droplets, whereas jet formation was not observed at 3%. Therefore, fibers could not be produced from electrospinning of this chitosan in aqueous acetic acid. The repulsive interaction among the polycations along the chitosan chains was thought to prevent sufficient chain entanglement that is necessary for fiber formation. In an attempt to shield the repulsion among chitosan molecules, sodium chloride (NaCl) was added to the 2% and 3% chitosan solutions at equal and 2:1 NaCl–amine molar ratio. Still no fibers were obtained.

3.2. Fiber formation from chitosan/PVA mixtures

As PVA was demonstrated to be effective in enhancing fiber formation,[18] an 87–89% hydrolyzed and high-molecular-weight PVA ($M_w = 124$–186 kDa) was added to the chitosan solution prepared in 2% v/v aqueous acetic acid to moderate the repelling interaction between polycationic chitosan molecules and to enhance the molecular entanglement. Fiber formation could be sustained from electrospinning of mixtures with chitosan/PVA mass ratio ranging from 11/89 to 50/50 at decreasing total polymer concentrations from 6% to 3% (Table 1). The fibers electrospun from the 6% mixtures of chitosan/PVA at 11/89 (Fig. 1a) or 17/83 (Fig. 1b) mass ratio were varying sizes. The fibers were as thin as 100 ± 20 nm in diameters and interspersed with enlarged spindle-like sections of about 500 ± 100 nm in widths. The average fiber length between the spindle-like structures was 10 ± 3 μm. As the chitosan/PVA mass ratio increased to 25/75 (4% solution), the enlarged sections became more bead-like structures in larger numbers (Fig. 1c). The fibers between the beads were much finer, about 20 ± 5 nm in diameter and 7 ± 3 μm in length, which was likely due to the lowered polymer concentration. The mixture with 50/50 chitosan/PVA generated significantly fewer fibers, but some very larger micrometer size beads (Fig. 1d). These results showed that the addition of PVA facilitated the electrospinning of chitosan into nanofibers, but only with up to 25% chitosan.

Table 1. Fiber formation from chitosan/PVA mixed solutions in 2% acetic acid

Chitosan/PVA (mass ratio)	Total polymer concentration (wt %)		
	3	4	6
11/89	—	—	Fibers (∼100 nm)
17/83	—	—	Fibers (∼100 nm)
25/75	—	Fibers (∼20 nm)	None[a]
50/50	Very few fibers	None	None[a]

[a] Solution was too viscous.

The DSC thermogram of PVA fibers electrospun from 10% aqueous solution showed a melting endotherm at

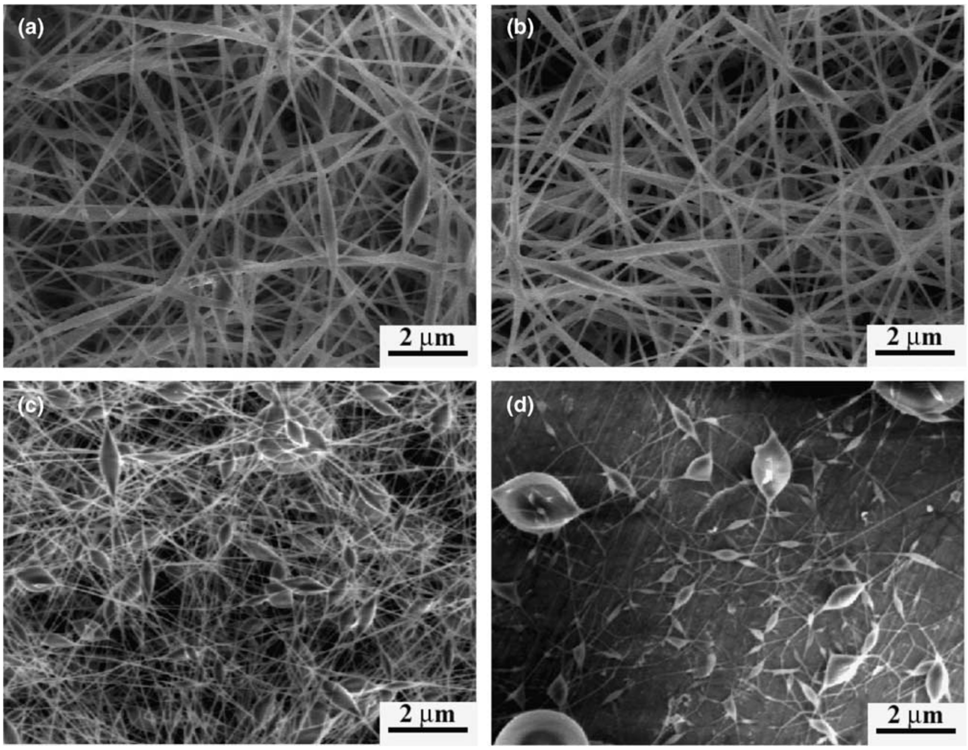
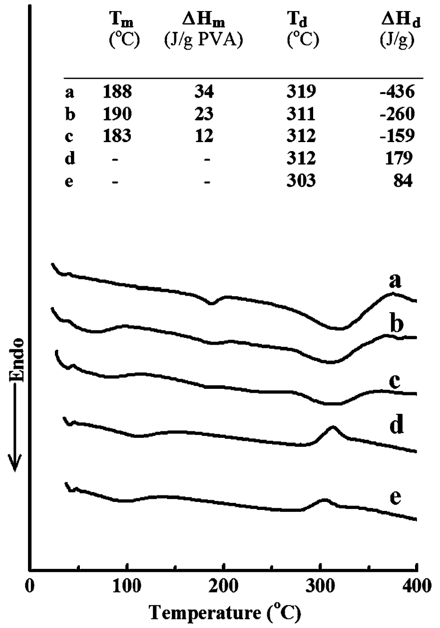


Figure 1. SEM of bicomponent fibers electrospun from solutions of decreasing concentration and increasing chitosan/PVA mass ratios: (a) 6% at 11/89, and (b) 6% at 17/83; (c) 4% at 25/75; and (d) 3% at 50/50.



	T_m (°C)	ΔH_m (J/g PVA)	T_d (°C)	ΔH_d (J/g)
a	188	34	319	-436
b	190	23	311	-260
c	183	12	312	-159
d	-	-	312	179
e	-	-	303	84

Figure 2. DSC of (a) PVA fibers; (b) 17/83 chitosan/PVA bicomponent fibers; (c) 25/75 chitosan/PVA bicomponent fibers; (d) crude chitosan; and (e) NaOH treated (1 M, 12 h) bicomponent fibers (as in b).

188 °C and a decomposition peak at 319 °C (a, Fig. 2). Crude chitosan exhibited an exothermic decomposition peak at 312 °C (d, Fig. 2). The bicomponent fibers containing 17% (c, Fig. 2) and 25% (c, Fig. 2) of chitosan showed reduced melting behavior of the PVA component, that is, lower melting temperatures and much lower melting enthalpies, that is, 67% and 34%, respectively. The presence of PVA melting in the bicomponent fibers, though much reduced, indicated that PVA could still crystallize, indicative of phase separation from the chitosan domains in the fibers. Both bicomponent fibers also exhibited decomposition endotherms as the PVA fibers, but the endotherms were smaller and at slightly lower temperatures. The decomposition enthalpies of PVA in these bicomponent fibers were about 78% and 56% of the values calculated based on their compositions. The less heat required to decompose PVA in the bicomponent fibers is another indication that the structure of PVA was compromised by the presence of a minor chitosan component, again possibly due to the hydrogen bonding interaction between chitosan and PVA.[28] Similar results have also been reported on the chitosan/PEO (33/67 mass ratio) bicomponent electrospun fibers.[9] The melting temperature and heat of fusion of the PEO component in the bicomponent electrospun fibers were found to decrease by 17% and 38%, respectively, when compared with PEO powder.

Although fibers could not be electrospun from the chitosan alone in aqueous acetic acid, adding PVA to the solutions enabled fiber formation. The bicomponent fibers could be efficiently generated from the chitosan/PVA mixtures with up to 25% chitosan. These fibers had diameters in the 20–100-nm range. The spindle-like or bead-like structures appeared with increasing chitosan in the mixtures. Thermal behaviors gave evidence to both partially phase-separated, crystallized PVA domains as well as certain interaction between the two polymers in the bicomponent fibers.

3.3. Porous chitosan fibers

At a higher magnification, the TEM of the thin fibers from the 17/83 chitosan/PVA mixture (Fig. 1b) showed nanometer-size surface features (Fig. 3). In an attempt to remove the phase-separated PVA, the bicomponent fibers were treated in 1 M aqueous NaOH solution for 12 h and vacuum dried overnight at room temperature. This treatment resulted in an 83% weight loss, which was identical to the PVA content in the bicomponent fibers. The TEM of the resulted nanofibers showed a highly irregular surface structure and fiber widths (Fig. 4a). The entire fiber was covered by elongated surface grooves and pores (Fig. 4b), and some pores appeared laterally across the entire fiber width (Fig. 4c). These porous features had dimensions ranging from a few nanometers to several tens of nanometers. The porous fibers indicated that the insoluble portion, presumably chitosan, existed in a continuous phase in the original bicomponent fibers.

The porous fibers only showed an exothermic peak at 303 °C, a slightly lower temperature than that of crude chitosan (e, Fig. 2). The lack of PVA melting indicates that most, if not all, of the PVA in the bicomponent fibers had been removed. The lowered chitosan decomposition temperature and enthalpy in the fibers (Fig. 2) were thought to be related to the porous fiber structure.

The FTIR of crude chitosan exhibited the resonance bands at 1154 and 898 cm^{-1} characteristic of its saccharide structure, and those at 3423, 1654, and 1598 cm^{-1},

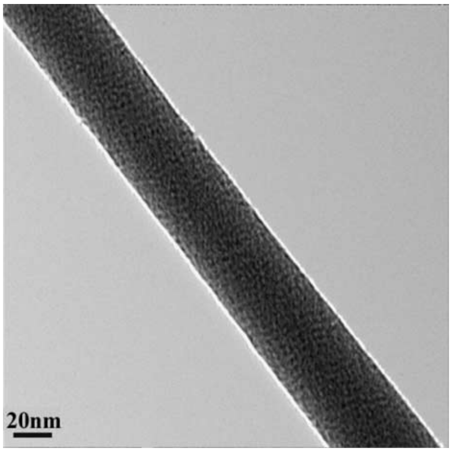


Figure 3. TEM of 17/83 chitosan/PVA bicomponent fibers.

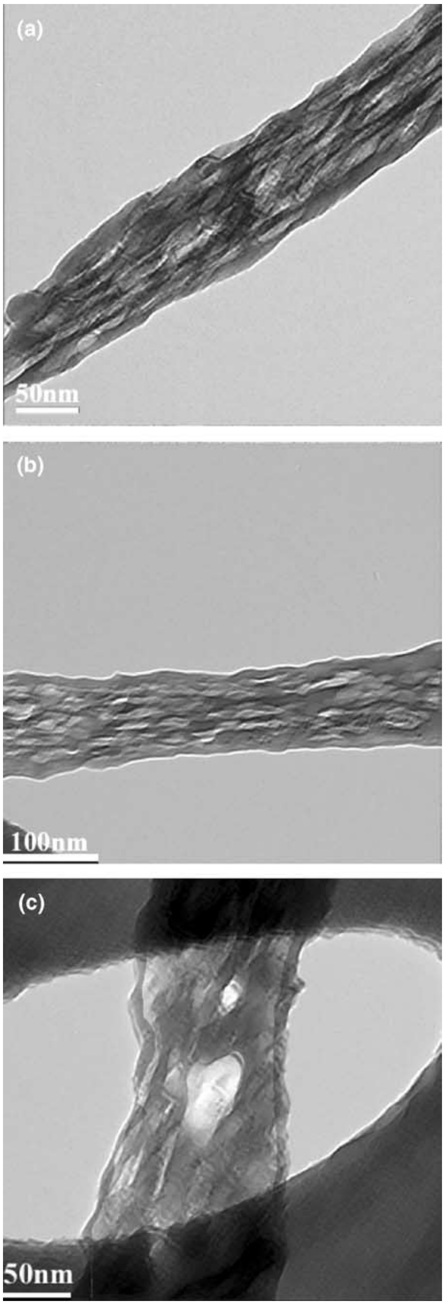


Figure 4. TEM of NaOH treated (1 M, 12 h) 17/83 chitosan/PVA bicomponent fibers: (a) continuous ditch along the fiber direction; (b) pores; and (c) holes.

commonly known for the N–H stretching of the primary amino groups, the carbonyl stretching of the secondary amide band (amide I) and the N–H bending of the primary amino groups, respectively (a, Fig. 5). A very weak N–H bending of the secondary amides (amide II) appeared at 1555 cm^{-1}. The electrospun PVA fibers showed absorption bands at 3383, 2941, 1734, 1098, and 850 cm^{-1}, characteristic of the $\nu(\text{OH})$, $\nu(\text{CH}_2)$, $\nu(\text{C=O})$, $\nu(\text{C–O})$, and $\nu(\text{C–C})$ resonances, respectively (b, Fig. 5). The nanoporous chitosan fibers resulted from treating the 17/83 chitosan/PVA bicomponent fibers with 1 M aqueous NaOH solution showed the characteristic absorbance bands of both chitosan and PVA (c, Fig. 5), which indicated residual PVA in the porous fibers. Based on the absorbance ratio, A_{898}/A_{850}, the chitosan content in the porous fibers was estimated to be 84%.

Therefore, nanoporous chitosan fibers could be prepared by treating the 17/83 chitosan/PVA bicomponent fibers with aqueous NaOH. Although PVA was not observed from the DSC, FTIR appeared to be more sensitive and showed 16% residual PVA in the porous fibers.

3.4. Fiber formation from hydrolyzed chitosan

Attempt was made to improve the solubility of chitosan, thus fiber formation from chitosan/PVA mixtures, by lowering its molecular weight. Alkaline hydrolysis in 50 wt % NaOH at 95 °C caused molecular weight reduction of chitosan from 1600 to 1500, 1200, 1000, and 800 kDa after for 2, 6, 12, and 48 h, respectively (Fig. 6). Fiber formation was improved with the chitosan hydrolyzed for just 2 h (Fig. 7a) in comparison to the original chitosan (Fig. 1d) at the same equal mass composition. The amount and morphology of the bicomponent fibers appear similar with chitosan hydrolyzed for 2, 6, and 12 h. The total polymer concentration suitable for fiber formation increased from 3% to 5% with longer hydrolysis time from 2 to 48 h. With the 800 kDa chitosan, fiber formation could be sustained continuously for several hours at a rate of 60 mg in dry fiber mass per hour (Fig. 7b). The average fiber diameter was around 50 ± 10 nm and with very few beads.

The homogeneity of the membrane composition was also improved with reducing the molecular weight of chitosan. The FTIR of the fibrous membrane electrospun from solution containing chitosan hydrolyzed for 12 h showed a much larger A_{898}/A_{850} value of 0.38 near the center (b, Fig. 8) than the 0.17 from the edge (c, Fig. 8). Based on the composition calibration, these A_{898}/A_{850} values correspond to 68/32 and 30/70 chitosan/PVA mass ratios for fibers from the center and edge of the membrane, respectively. Following a 24-h water immersion, the membrane from the edge dissolved completely, whereas fibers from the center partially kept their fibrous structure (Fig. 7c). This dissolution behavior seems to be consistent with the higher chitosan content near the center of the membrane. The varied fiber compositions by locations on the same membrane indicate that these two polymers behave differently during electrospinning. In acidic solution, chitosan is polycationic, and its charged nature causes it to be drawn more strongly toward the collecting target by the applied electric potential, thus concentrating more in the center. Even after the 12-h hydrolysis, the degree of

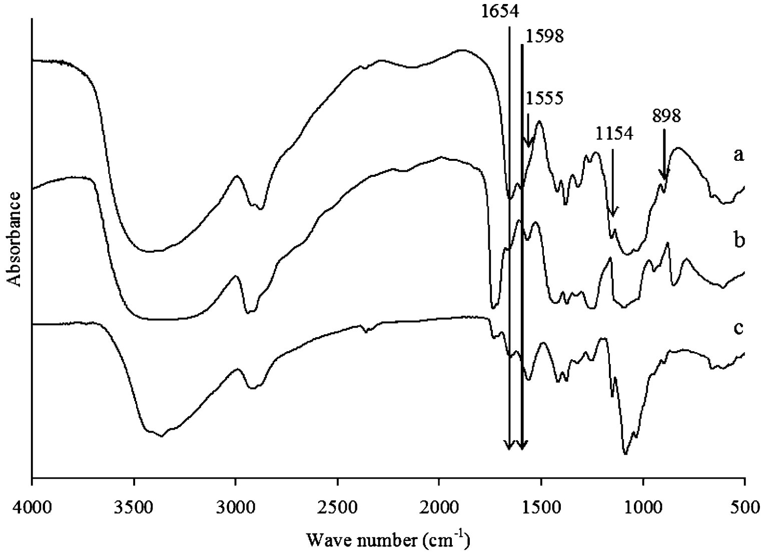


Figure 5. FTIR of (a) crude chitosan; (b) PVA fibers; and (c) NaOH treated (1 M, 12 h) 17/83 chitosan/PVA bicomponent fibers.

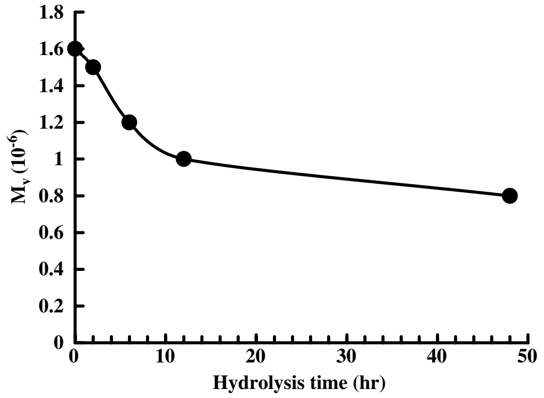


Figure 6. The effect of hydrolysis (50% NaOH, 90 °C) time on the molecular weight of chitosan.

polymerization of chitosan was 6000, nearly twice that of the PVA used. The longer, bulkier and more rigid saccharidic backbone of the chitosan chains may reduce the bending instability of the jet, causing it to travel in a relatively straight path to be deposited at the center of the collector. Phase separation between chitosan and PVA is expected due to the significant differences in their molecular structures. Enhanced phase separation due to differential charge behavior is also expected, which is similar to the report on the chitosan/PEO bicomponent fibers.[20]

The FTIR spectrum of the bicomponent fibrous membrane electrospun from the mixture containing the chitosan hydrolyzed for 48 h exhibited the same A_{898}/A_{850} ratio of 0.28 (Fig. 8d), corresponding to equal chitosan/PVA ratio as derived from the composition calibration curve. Therefore, the bicomponent fibrous membrane not only contains the same polymer composition as the solution, but also a uniform distribution of both polymers. The shorter chain length and higher DDA of chitosan following hydrolysis is thought to improve mixing with PVA. Since 48-h hydrolysis decreased the molecular weight by 50% but increased the DDA of chitosan by at best 20%, the more uniform distribution of polymers is attributed more to the reduced molecular weight than the increased deacetylation. At the same 50/50 hydrolyzed (48 h) chitosan/PVA composition, both the bicomponent fibers (b, Fig. 9) and cast films (c, Fig. 9) showed the same water evaporation peaks near 100 °C, and exothermic decomposition peaks of chitosan at 280 °C. The decomposition temperatures of chitosan in both bicomponent fibers and film were 25 °C lower than those of the cast film of chitosan alone (a, Fig. 9), indicating that chitosan in both bicomponent materials was affected by the presence of the PVA, irrespective of the forms. Both the melting temperature (176 °C) and enthalpy of PVA in the bicomponent film (c, Fig. 9) were also much lower than those of pure PVA fibers (d, Fig. 9), also showing the effect of chitosan on PVA. This is similar to the previous observation with the original chitosan (Fig. 2). Both the effects of each component on the other indicate the existence of molecular interaction between hydrolyzed chitosan and PVA. The bicomponent fibers exhibited an obviously broader chitosan decomposition peak than the corresponding cast film, but no PVA melting peak. Therefore, the effects of each component on each other are higher in the fibers than in the film.

4. Conclusions

At a high average molecular weight (M_v) of 1600 kDa, chitosan (82.5% DDA) alone could not be electrospun

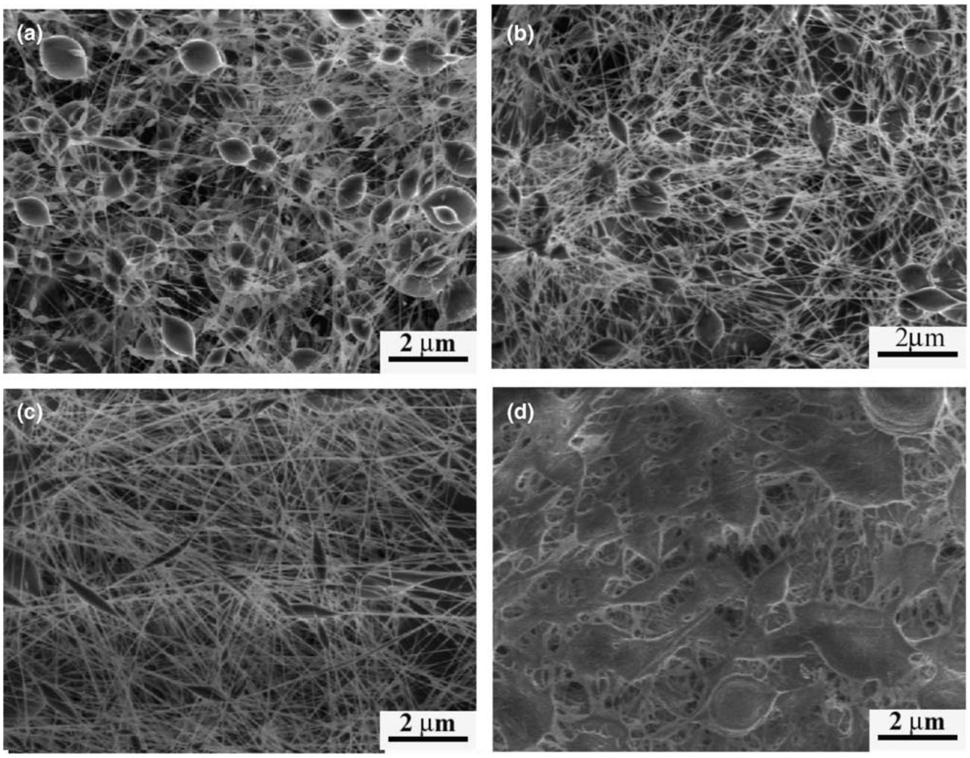


Figure 7. SEM of bicomponent fibers electrospun from 5% solution containing 50% mass of chitosan hydrolyzed (50% NaOH, 90 °C) for (a) 2 h; (b) 12 h; (c) 48 h; and (d) fibers in (b) after an 8-h immersion in water.

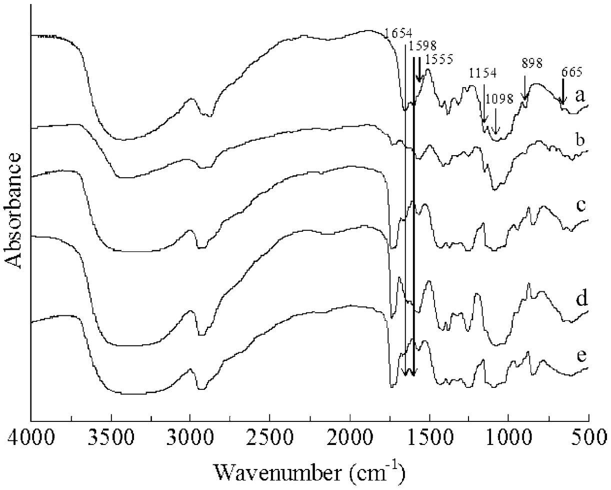
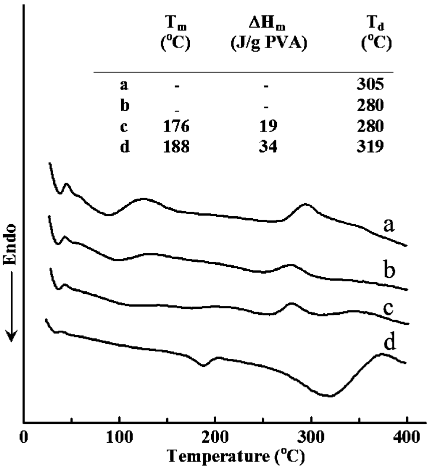


Figure 8. FTIR of (a) crude chitosan; (b) 50/50 bicomponent fibers with hydrolyzed chitosan (12 h) from the center of the membrane; (c) 50/50 bicomponent fibers with hydrolyzed chitosan (12 h) from the edges of the membrane; (d) 50/50 bicomponent fibers with hydrolyzed chitosan (48 h); and (e) electrospun PVA fibers.



	T_m (°C)	ΔH_m (J/g PVA)	T_d (°C)
a	-	-	305
b	-	-	280
c	176	19	280
d	188	34	319

Figure 9. DSC of (a) chitosan cast film; (b) 50/50 bicomponent fibers with hydrolyzed chitosan (48 h); (c) 50/50 bicomponent cast film with hydrolyzed chitosan (48 h); and (d) electrospun PVA fibers.

into fibers from solutions in 2%, 20%, and 90% v/v aqueous acetic acid. The addition of PVA ($M_w = 124$–186 kDa) to this long-chain chitosan allowed the formation of bicomponent fibers from 2% v/v aqueous acetic acid. The bicomponent fibers with chitosan/PVA mass ratio up to 25/75 were 20–100 nm in diameter and contained some spindle-like or bead-like structures. A large amount of beads with very few fibers were observed when the chitosan content was increased to 50%. Nanoporous fibers could be obtained by treating the 17/83 chitosan/PVA bicomponent fibers in aqueous NaOH (1.0 M, 12 h) to remove most of PVA component, leaving 16% PVA.

Alkaline hydrolysis (50 wt % NaOH at 95 °C) lowered the molecular weight of chitosan from 1600 to 1500, 1200, 1000, and 800 kDa after for 2, 6, 12, and 48 h, respectively. With equal mass of chitosan and PVA, reducing chitosan chain lengths significantly improved the formation efficiency and uniformity of the bicomponent fibers. The total polymer concentration appropriate for fiber formation also increased from 3 to 5 wt % with increasing hydrolysis from 2 to 48 h. With the higher molecular weight chitosan, the two polymers appeared to be distributed nonuniformly in the fibrous membranes. Chitosan (1000 kDa) appeared to be more concentrated near the center of the fibrous membrane than at the edges. With further reduced molecular weight of 800 kDa, the fibrous membrane contained not only the same polymer composition as the solution, but also uniform distribution of both polymers throughout the membrane. The improved uniform distribution of chitosan and PVA in the bicomponent fibers is attributed to better mixing mostly due to the reduced molecular weight and somewhat to the increased deacetylation of the chitosan.

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