

# Influence of the Molecular Weight of Chitosan on the Spinnability of Chitosan/Poly(vinyl alcohol) Blend Nanofibers

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**ABSTRACT:** The electrospinning of the biopolymer chitosan (CS) and poly(vinyl alcohol) (PVA) was investigated with 90% acetic acid as the solvent and with different CS/PVA ratios. The long chains of high-molecular-weight CS prevented it from forming nanofibers in a high-voltage field. The treatment of CS under high-temperature alkali conditions reduced its molecular weight exponentially with the treatment time and caused a reduction of the viscosity consequently. PVA, acting as a plasticizer and accompanied by the alkali-treated CS of lower viscosity, made the electrospinning of CS/PVA blends possible. The

effects of the duration of the alkali treatment on the molecular weight of CS and its viscosity were investigated and optimized. The diameter of the bicomponent nanofiber decreased proportionally with the increase in the CS portion, whereas the surface porosity increased inversely. Fourier transform infrared studies illustrated that the alkali treatment or blending of CS with PVA had no effect on its chemical nature. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2507–2513, 2009

**Key words:** blends; fibers; polysaccharides; viscosity

## INTRODUCTION

Biopolymers as natural-based polymers are of great interest in different fields of science. These materials are progressively used for various applications because of several advantages, such as their nontoxicity and availability, the plenitude of their agricultural or marine sources, their biocompatibility and biodegradability (which lead to ecological safety), and the possibility of producing a variety of chemically or enzymatically modified derivatives for specific uses.<sup>1,2</sup>

Polysaccharides are the major members of the biopolymer family. Cellulose, as the most widely known polysaccharide, is used in textile and paper industries, and chitin and its derivatives, as the next most important members, are used in food, pulp and paper industries, biotechnology, agriculture, cosmetics, wastewater treatment, and medicine.

Chitin is  $\alpha$ -(1 $\rightarrow$ 4)-linked 2-acetamido-2-deoxy- $\beta$ -D-glucose and is derived from crustacean shells, byproducts of lobsters, crabs, and the like. It can be found in other natural sources such as yeasts, fungi, and insects.

Chitosan (CS), the partially deacetylated and most operational derivative of chitin, is insoluble in water, alkali, and most mineral acidic systems. Its solubility in inorganic acids is quite limited, but it is soluble in organic acids such as dilute aqueous acetic, formic, and lactic acids. In the presence of a limited amount of acid, it is soluble in water–methanol, water–ethanol, and water–acetone mixtures. CS has incomparable specifications that enrich it with excessive physicochemical properties such as swelling, hydrogelation, wound healing, antibacterial attributes, and particular chemical and physical absorption properties; this makes it convenient for specific applications.<sup>3–6</sup>

Combining these properties with a nanoscale structure and preparing it in the form of nanofibers and nanowebs, which are actually random assemblies of nanofibers (similar to the structure of felt), optimize its other physical properties. In recent years, researchers have made attempts to produce it in the form of nanofibers, the finest morphology accessible by fibers, revealing a high porosity, a high aspect ratio, and structural compatibility with vital cells.<sup>7,8</sup>

However, CS is a polycationic polymer, and the fabrication of CS nanofibers through electrospinning, which is recognized as the most efficient method for producing ultrafine fibers with nanometric diameters, has attendant difficulties because of the high molecular weight, helical structure, and high

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positive charge density, which lead to a high viscosity, a gelation tendency, and a high surface tension.

With respect to all the difficulties with electrospinning pure CS, recent studies on CS have attracted interest by converting it into a more soluble derivative with a lower solution viscosity and a lower surface tension.<sup>7–11</sup>

As an alternative, CS is electrospun as a bicomponent nanofiber. Here, a second polymer, mostly with a flexible molecular structure and a low molecular weight, is used. These flexible molecules act as softening agents, reducing the average molecular weight, attenuating powerful hydrogen bonds between molecular chains of CS, and finally making the electrospinning of the polymer mixture possible. With respect to the specific characteristics of CS nanofibers that have attracted interest in medical fields, the second polymer has to be biocompatible, nontoxic, biodegradable, and without any allergic effect. However, this solution still needs more study. Literature reviews show that electrospinning CS with a second polymer also has many limitations.<sup>12–15</sup>

For example, Bhattarai et al.<sup>12</sup> used poly(ethylene oxide) (PEO) as the second polymer to improve the spinnability of CS. They placed 2 wt % CS (190 kDa) in 0.5M acetic acid (AcOH), mentioning that in such a situation the formation of nanofibers is highly dependent on the mass ratio of the two polymers. An increase in the portion of CS to more than 60 wt % led to difficulties in nanofiber formation; therefore, they applied dimethyl sulfoxide as a cosolvent.

Although they managed to increase the CS/PEO ratio from 60/40 to 90/10, the cosolvent is very toxic, and the concentration of 2 wt % CS is not productive enough.

Ignatova et al.<sup>13</sup> electrospun nanofibers from a blend of CS and poly(vinyl alcohol) (PVA). In this case, the molecular weight of CS was 400 kDa; they also produced bicomponent nanofibers with a 20/80 CS/PVA ratio. Their report stated that the electrospinning of pure CS was impossible.

Park et al.<sup>14</sup> underlined the role of ionic amino groups of CS and their repulsive forces in preventing the formation of nanofibers. Therefore, they used silk fibroin as the second polymer. The most accessible portion of CS in this bicomponent nanofiber was 20%. The molecular weight of the applied CS was 220 kDa, and the concentration of CS was 3.6 wt % in a solution of formic acid.

Li and Hsieh<sup>15</sup> tried a mixture of CS and PVA again. The molecular weight of their examined CS was 1600 kDa; therefore, they reached just the ratio of 17/83 CS/PVA, but using an alkali treatment, they increased this ratio to 50/50.

According to this literature review, the molecular weight of CS plays a critical role; that is, electrospinning CS blends is easier when the molecular weight of CS is not very high. Hence, in this study, we inves-

tigated the influence of the molecular weight of CS on the spinnability of CS/PVA blends. As the starting point, high-molecular-weight CS (1094 kDa) was chosen; a wide range of molecular weights were available via the alkali treatment in sodium hydroxide (NaOH).

## EXPERIMENTAL

### Materials

CS powder with a viscosity-average molecular weight ( $M_v$ ) of 1095 kDa and a degree of deacetylation of 75–85% was purchased from Sigma–Aldrich Co. (Milwaukee, WI).

PVA ( $M_v = 70$  kDa, degree of hydrolyzation = 98%), glacial AcOH, and NaOH were supplied by Merck (Oarmstadt, Germany).

### Reducing the molecular weight of CS

To reduce the molecular weight of CS, the polymer powder was treated in a 50% NaOH solution with a CS/NaOH ratio of 1/25 (w/v). The temperature was 95°C, and the procedure continued for 5, 16, 32, and 48 h; this resulted in different molecular weights. To keep the temperature constant and to prevent the vaporization of the solvent, a polymath bath (made by Datacolor, United Kingdom) was used.

### Measurement of the molecular weight

The molecular weights of the neat CS and the hydrolyzed CS powders were measured with viscometry. CS solutions in a 0.2M NaCl/0.1M AcOH solvent system<sup>16,17</sup> were prepared in four different concentrations for each sample: 0.01, 0.03, 0.07, and 0.1 g/L.<sup>18</sup> The dropping times of the solvent and CS solutions through an Ubbelohde capillary tube were denoted  $t_0$  and  $t_1$ , respectively. Equation (1) provides an estimation of the reduced viscosity ( $\eta_{red}$ ). The intrinsic viscosity ( $[\eta]$ ) was calculated by the extrapolation of eq. (1) to a concentration of 0. Plotting the measured  $\eta_{red}$  values against the concentration provided a linear graph, the intersection of which could be considered to be  $[\eta]$  ( $[\eta] = \frac{1}{C} \left( \frac{t_1}{t_0} - 1 \right)_{C=0}$ ), where C is the concentration.

$$\eta_{red} = \frac{1}{C} \left( \frac{t_1}{t_0} - 1 \right) \quad (1)$$

The Mark–Houwink equation,  $[\eta] = k_m M_v^a$  (where  $k_m$  and  $a$  are the constants for the selected solvent system and are equal to  $1.8 \times 10^{-3} \text{ cm}^3/\text{g}$  and 0.93, respectively), gives an approximation of  $M_v$ .<sup>16,17</sup>

### Preparation of the CS/PVA solutions

Untreated and treated CS solutions were prepared in 0.2M AcOH and 90% AcOH, respectively, by the

gradual addition of portions of CS and by increases in the temperature up to 70°C while the solution was being stirred on a magnetic heater. The beaker containing the solution was tightly sealed. The duration of stirring, depending on the concentration of CS, was varied from 1 to 4 days.

An 8 wt % PVA solution was prepared in deionized water. Here the temperature rose up again to 70°C until a homogeneous milky syrup was obtained. This part was critical because of the possibility of agglomeration. Then, the temperature was increased up to 100°C to yield a clear, transparent solution.

CS/PVA solutions were prepared in proportions of 50/50, 60/40, and 70/30 (v/v).

### Electrospinning of untreated and treated CS/PVA blends

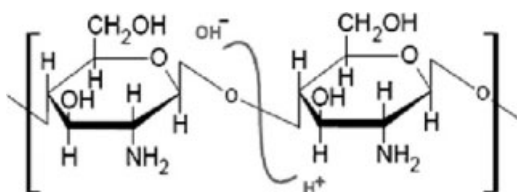
The electrospinning solution was fed into a 1-mL syringe fitted with a pipette tip 0.7 mm in diameter. The electrospinning system used in this study was horizontal. The syringe tip was connected to the cathode, and an aluminum sheet, used as a collector, was connected to the anode.

With a high direct-current power supply, a direct-current voltage of 7–17 kV was applied between the syringe tip and the aluminum sheet collector with a glass slide in the middle. The typical distance between the syringe tip and the collector was 4–14 cm. During the spinning process, the solution droplet at the syringe tip was split by a repulsion force set by the charge in the droplet, and it formed a cone-shaped jet, drawing toward the collector. During the drawing time, the solvent evaporated, and polymer fibers were deposited on the collector in the form of a nanofibrous web. All the spinning experiments were performed at 23–24°C.

## RESULTS AND DISCUSSION

### Molecular weight

The alkali treatment reduces the molecular weight of the CS polymer through the decomposition of molecular chains and hydrolyzation, as shown in Figure 1. Table I shows the effects of the alkali treatment time on the molecular weight of CS macromolecules.



**Figure 1** Decomposition mechanism of CS with the alkali treatment.

**TABLE I**  
Effect of the Alkali Treatment Time on the Molecular Weight of CS

| Treatment time (h) | $M_v$ (g/mol) |
|--------------------|---------------|
| 0                  | 1,094,804     |
| 5                  | 1,043,791     |
| 16                 | 645,023       |
| 32                 | 341,782       |
| 48                 | 293,763       |

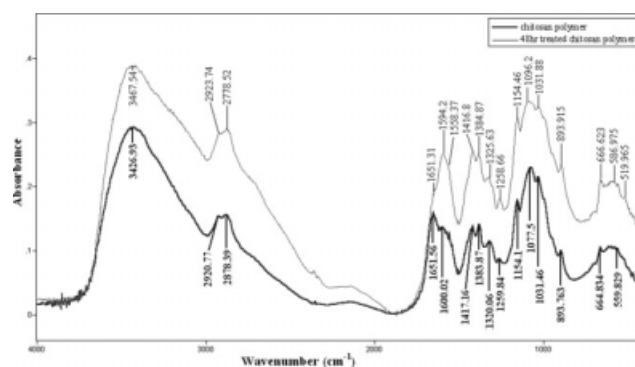
The decomposition of CS macromolecules occurs in the position of oxygen bonding the glucose amine groups together. Therefore, it is just a depolymerization reaction that does not change the chemical nature of CS.<sup>5,6,15</sup>

This feature was proved with Fourier transform infrared (FTIR) spectra of untreated and 48-h-treated CS polymers (Fig. 2). Both spectra show the saccharide absorption peaks around 1154 and 893  $\text{cm}^{-1}$ , the peak at 1600  $\text{cm}^{-1}$  for primary amino group bending, and the peaks at 1651 and 3425  $\text{cm}^{-1}$  for carbonyl and N–H group stretching, respectively. Small deviations in the positions of these peaks in the spectrum of the treated CS corroborate the physical changes naturally appearing because of the molecular weight reduction and its distribution variations.

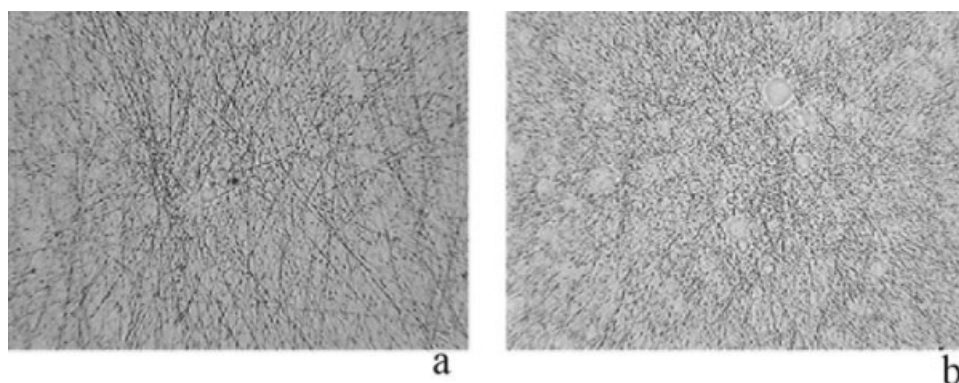
### Electrospinning of the CS/PVA blends

Blending CS with a low-molecular-weight polymer provides an easier spinning process; however, this does not mean that electrospinning will be possible under any condition. Figure 3 shows optical microscopy images of untreated CS/PVA electrospinning according to the conditions presented in Table II.

According to the results of optical microscopy, when the portion of untreated CS is too great, the electrospinning of untreated CS/PVA is impossible. Patchy, fibrous-shaped structures accompanied by solution droplets, obviously unqualified to be considered nanoweb, are the only product of the



**Figure 2** FTIR spectra of the untreated CS polymer and 48-h-treated CS polymer.



**Figure 3** Optical microscopy images of untreated CS/PVA nanofibers (magnification: 1000): (a) 50/50 and (b) 70/30.

application of untreated CS. As an alternative, a reduction of the molecular weight of CS is supposed to produce remarkable results.

Figures 4–6 show scanning electron microscopy (SEM) images for 5-, 16-, and 48-h-alkali-treated CS/PVA blends with different CS/PVA ratios. The most considerable achievement is the possibility of increasing the CS concentration from 2 to 5 wt %.

Treating CS under high-temperature alkali conditions depolymerizes polymer chains and decreases the molecular weight and viscosity of its solution in AcOH. According to Table I, the molecular weight reduction of 5-h-treated CS is less than 5%, but it evidently improves the spinnability of the blend, particularly when the portion of CS is not more than 50%. However, despite nanofiber formation, the electrospinning process is not continuous and efficient yet. An excessive reduction of the molecular weight by alkali treatment leads to more electrospinnable CS, providing a steadier and more uniform CS/PVA nanoweb.

Concerning the quality of CS/PVA nanowebs and the continuity and stability of the electrospinning process, treating the CS polymer for 48 h, which reduces its molecular weight to 294 kDa (a 73% reduction in the primary molecular weight), leads to significantly high-quality nanofibers and electrospinning. The reduction of the molecular weight of CS to less than 294 kDa increases the quality of electrospun CS nano-

webs. According to the results of this study,  $M_v = 294$  kDa can be considered an optimum molecular weight for the electrospinning of CS/PVA blends when the ratio of the CS polymer is higher than 50%.

At a lower molecular weight, the molecular chains of CS can be straightened more easily in the electrical field, and because of the simplicity of their movement, they can better resist the repulsive forces of their neighbor chains. As is evident in Table II, when the portion of CS increases, the voltage has to be increased accordingly.

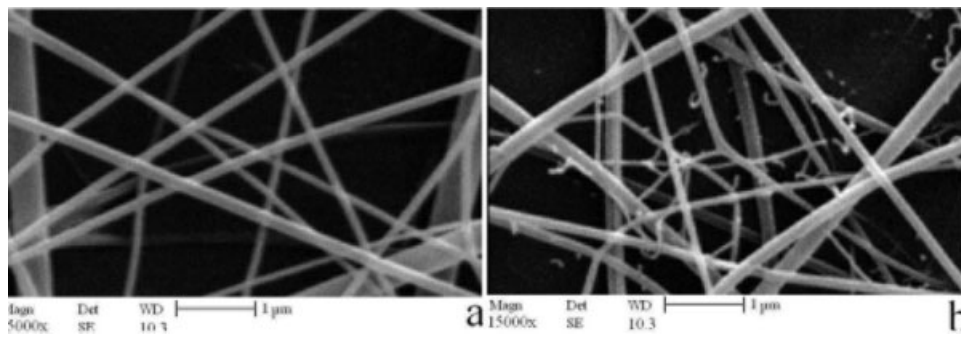
### Characterization of the CS/PVA nanofibers

#### Diameter

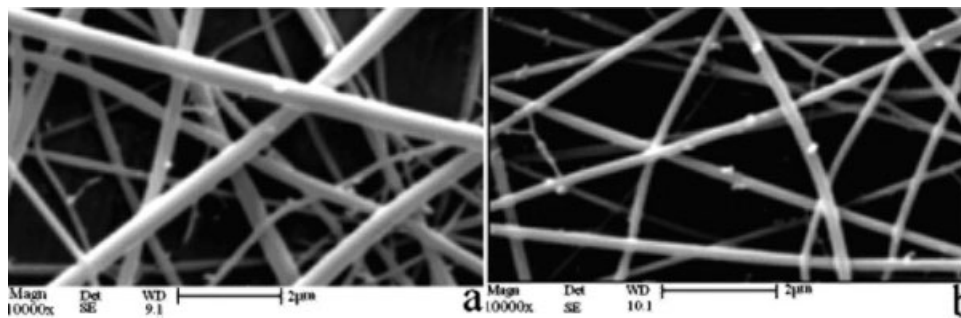
Electrospun nanofibers were sputter-coated with Au/Pd, and the morphology of the nanofibers was examined with SEM (XL 30, Philips, Eindhoven, The Netherlands) at an accelerating voltage of 10 kV. The average diameter of the electrospun nanofibers was determined by the measurement of the diameters of the nanofibers at 100 different points in SEM images. The averages and percentages of the coefficient of variation [Coefficient of variation (%) = (Standard deviation/Average)  $\times$  100] of the diameters of the nanofiber produced from 5- and 48-h-treated CS are presented in Table III.

**TABLE II**  
Electrospinning Parameters of the CS/PVA Blends

| Solution concentrations               | CS/PVA (v/v) | Electrospinning parameter |                                |              |
|---------------------------------------|--------------|---------------------------|--------------------------------|--------------|
|                                       |              | Diameter (cm)             | Flow rate (mm <sup>3</sup> /h) | Voltage (kV) |
| 2 wt % untreated CS and 9 wt % PVA    | 70/30        | 3.5–4.5                   | 0.48                           | 10           |
|                                       | 60/40        | 3.5–4.5                   | 0.48                           | 9            |
|                                       | 50/50        | 3.5–4.5                   | 0.48                           | 7            |
| 5 wt % 5-h-treated CS and 8 wt % PVA  | 70/30        | 6–6.5                     | 0.74                           | 17           |
|                                       | 60/40        | 6–6.5                     | 0.74                           | 15           |
|                                       | 50/50        | 6–6.5                     | 0.48                           | 10           |
| 5 wt % 48-h-treated CS and 8 wt % PVA | 70/30        | 13.5                      | 0.24                           | 17           |
|                                       | 60/40        | 13.5                      | 0.24                           | 17           |
|                                       | 50/50        | 13.5                      | 0.24                           | 16           |



**Figure 4** SEM images of 5-h-alkali-treated CS/PVA nanofibers (magnification: 15,000): (a) 50/50 and (b) 70/30.

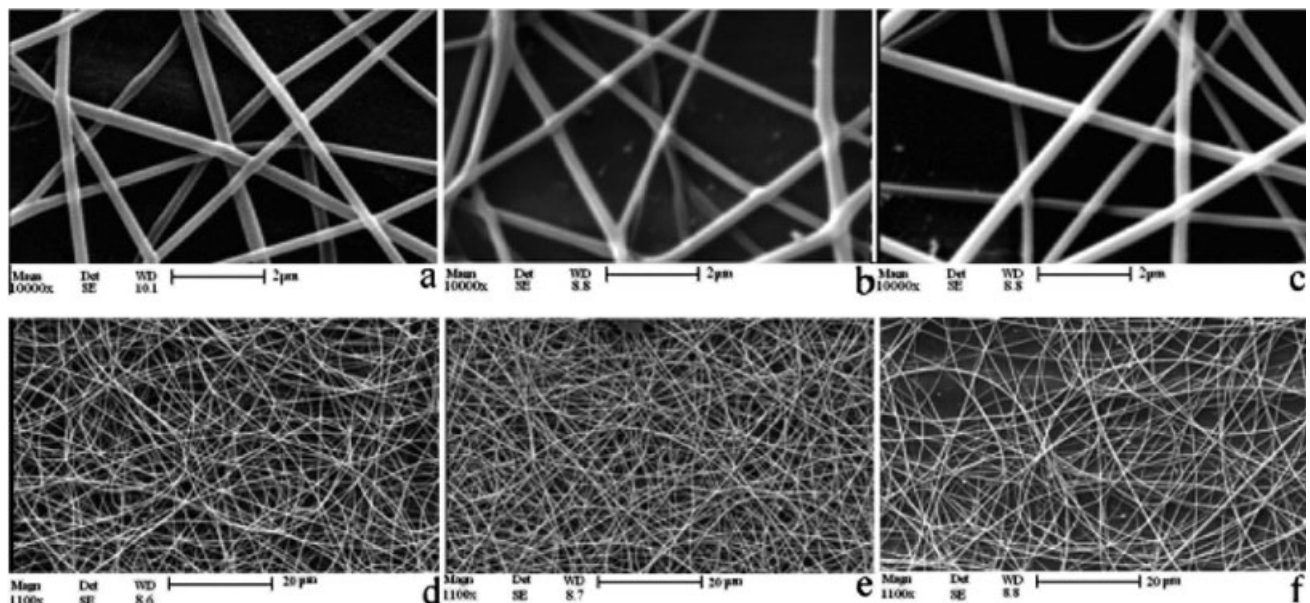


**Figure 5** SEM images of 16-h-alkali-treated CS/PVA nanofibers (magnification: 10,000): (a) 50/50 and (b) 70/30.

The reduction of the molecular weight of CS not only makes its electrospinning easier and more efficient but also leads to finer nanofibers, particularly when the portion of CS is increased. Figure 7 reveals the histograms of nanofiber diameters of 48-h-treated CS/PVA for different fractions of CS in the blend. Here, nanofibers are more even and uniform;

therefore, they are more proper for final applications.

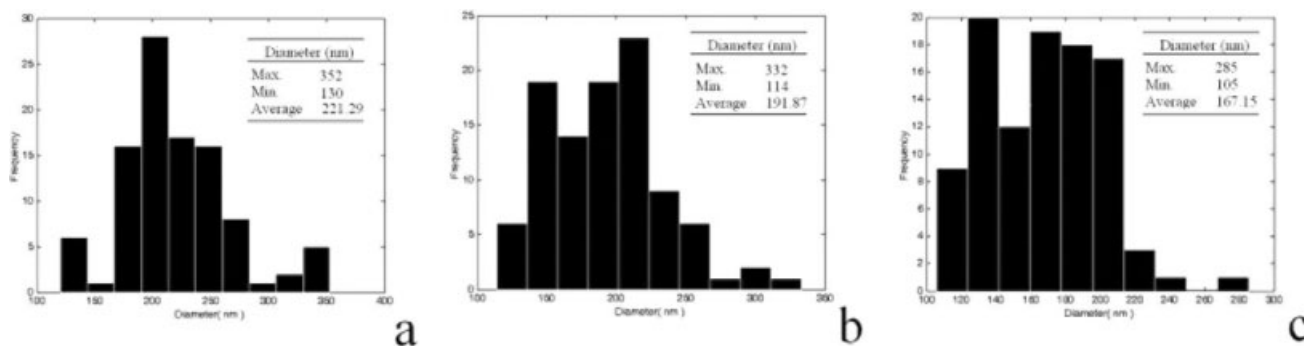
FTIR spectra of these fibers illustrate that CS and PVA are blended just physically and that this mixing will not affect the chemical properties of CS or PVA. Figure 8 shows the FTIR spectra of PVA powder and 48-h-treated CS/PVA nanofibers. In these spectra,



**Figure 6** SEM images of 48-h-alkali-treated CS/PVA nanofibers: (a,d) 50/50, (b,e) 60/40, and (c,f) 70/30 (magnifications: 10,000 and 110, respectively).

**TABLE III**  
**Number-Average Diameter, Coefficient of Variation, and Surface Porosity of the CS/PVA Nanofibers**

| CS/PVA blend        | CS/PVA (v/v) | Number-average diameter (nm) | Coefficient of variation (%) | Surface porosity (%) |
|---------------------|--------------|------------------------------|------------------------------|----------------------|
| 5-h-treated CS/PVA  | 50/50        | 249.8                        | 72                           | —                    |
| 48-h-treated CS/PVA | 70/30        | 167.15                       | 21.63                        | 46.16                |
|                     | 60/40        | 191.87                       | 20.14                        | 41.62                |
|                     | 50/50        | 221.29                       | 21.32                        | 37.25                |



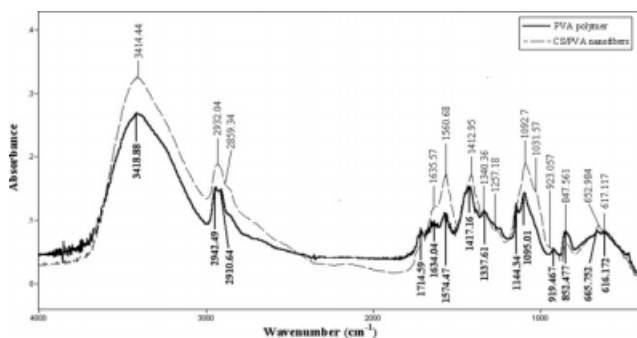
**Figure 7** Histograms of nanofiber diameters of 48-h-treated CS/PVA: (a) 50/50, (b) 60/40, and (c) 70/30.

functional bonds of both pure CS and PVA remain in the same place, showing small shifts because of new secondary bonds of PVA–CS molecule interactions.

#### Surface porosity of the electrospun web

As a physical property, the surface porosity of the whole electrospun membrane of 48-h-treated CS/PVA nanofibers was measured. To this end, nanofibers were electrospun for 5 min for each blend. The surface porosity of the electrospun web was calculated by image processing of SEM images and by computation of the ratio of free spaces to fibers. The surface porosity was considered the ratio of free spaces, which is the dark area in the image of the whole area.

The results are shown in Table III. As expected, the surface porosity increases proportionally with the reduction of the nanofiber diameter.



**Figure 8** FTIR spectra of the PVA polymer and 48-h-treated CS/PVA nanofibers.

## CONCLUSIONS

In this study, the effect of the molecular weight of CS on the spinnability of CS/PVA blends was investigated with an electrospinning method. Electrospinning high-molecular-weight CS is impossible because of the strong polycationic effects of CS amine groups.

The alkali treatment of CS decreases the molecular weight by depolymerization of CS chains, and the consequent reduction of the viscosity of the electrospinning solution makes the electrospinning of CS/PVA blends possible. FTIR spectra show that alkali treatment or mixing CS with PVA does not change the chemical nature of these polymers.

Among the different molecular weights used in the electrospinning of CS/PVA blends, CS with a molecular weight of 294 kDa provided the best results in terms of the quality and evenness of the nanofibers as well as the continuity of the electrospinning process.

The investigation of the characteristics of these nanofibers from CS/PVA blends of different ratios reveals that an increase in the portion of CS decreases the diameter of the nanofibers and increases the surface porosity of the whole electrospun membrane simultaneously.

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