

Effect of polyvinyl alcohol/chitosan blend ratios on morphological, optical, and thermal properties of electrospun nanofibers

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Abstract: In this study, the electrospinning method was used to prepare polyvinyl alcohol (PVA)/chitosan (CS) blend nanofibers from their solutions. The effect of blend ratios (PVA/CS: 1%, 3%, 5%, and 7% (w/w)), applied voltage, and flow rate on the morphological, optical, and thermal properties of electrospun nanofibers were investigated by scanning electron microscopy (SEM), fluorescence and UV-Vis spectroscopies, and thermogravimetric analysis (TGA), respectively. Fourier transform infrared spectroscopy analysis indicated the existence of related functional groups of both PVA and CS in the electrospun fibers. During the electrospinning process, the maximum possible ratio of CS was 7% (w/w). SEM images indicated that more flat nanofibers were synthesized at lower flow rates, but the shape of the fibers was more circular at higher flow rates. On the other hand, an increase in CS ratio, flow rate, and applied voltage caused a decrease in the transmittance values of the fibers while samples including higher concentrations of CS showed lower emission intensities. Furthermore, the thermal properties of the electrospun fibers were developed by incorporation of a high amount of CS.

Key words: Chitosan blends, electrospinning, nanofiber, polyvinyl alcohol

1. Introduction

Electrospinning is an important and promising method that is used to prepare micro- and nanofibers from polymer solutions. Working parameters strongly affect the morphology of fibers and it is possible to prepare fibers with desired morphologies and sizes by controlling the parameters appropriately. The working parameters of electrospinning can be classified as solution parameters (concentration, molecular weight of the polymer, viscosity, surface tension, and conductivity/surface charge density), process parameters (voltage, flow rate, collectors, distance between the collector and the tip), and ambient parameters (humidity and temperature of the medium).¹⁻³ Superhydrophobic and superoleophobic nanofibers can be prepared by applying electrospinning methods to several polymers such as fluorinated acrylates.⁴ Nanofibers can be used in many applications such as drug delivery, tissue engineering, and the medical sciences, depending on their characteristics.

Polyvinyl alcohol (PVA) is a semicrystalline, hydrophilic polymer with good chemical and thermal stability. PVA is a highly biocompatible, nontoxic, and water-soluble polymer and can be used as a nanofiber filler for some dental applications.⁵ Molecular weight and solution concentration strongly affect the structure of electrospun PVA polymers. More flat fibers with larger diameters can be prepared at higher molecular weights or concentrations. In the case of lower molecular weights or concentrations, PVA fibers become more circular

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and the diameter of fibers is reduced with the decrease of the molecular weight of the polymer.⁶ At a constant concentration, the structure of PVA fibers changes from beads to beaded fibers, to complete fibers, and to flat ribbons as the molecular weight is increased.⁷

Chitosan (CS) is insoluble in water, alkali, and most mineral acidic systems and it has limited solubility in inorganic acids. However, in the case of organic acids, such as dilute acetic acid, it becomes soluble.⁸ The presence of free amino groups in CS's structure makes it a positively charged electrolyte with low pH values; however, this becomes a disadvantage and complicates its electrospinning due to high viscosity.^{9,10} The electrospinnability of CS is not very good due to the rigid interaction of its molecules. The hydrogen bonds within the 3D network structure prevent the motion of polymer chains, which are exposed to the electric field.^{11–13} To overcome this problem, different solvents, such as dilute hydrochloric acid, acetic acid, formic acid, and trifluoroacetic acid (TFA), were tested, and it was found that TFA was the most successful due to its capability of destroying rigid molecular interactions between CS molecules.¹⁴

Highly volatile solvents cause more homogeneous CS nanofibers to form. Acetic acid is one solvent that can be generally used for the electrospinning of CS. Geng et al. and Homayoni et al. investigated the effect of acetic acid concentrations on CS fiber structures and found that with the increase of acetic acid concentration in water, the diameter of fibers was also increased.^{8,11} Various polymers, such as PVA, have also been used to prepare CS hybrids to improve the spinnability of pure CS.^{15–19} Gholipour et al. prepared CS/PVA blends with various blend ratios. They investigated the effect of voltage and extrusion rates on fiber diameter and found that an increase in voltage and decrease in extrusion rate caused a decrease in fiber diameters.²⁰ Giannakas et al. investigated the effect of PVA content and organoclay type on the morphological, mechanical, and antimicrobial properties of CS polymer blends and nanocomposite films. They reported that higher amounts of PVA resulted in plasticization of films and a decrease in stiffness and strength. Addition of organoclay also enhanced the stiffness and strength of the films.²¹ El Miri et al. prepared bionanocomposites of PVA/CS polymeric blends by using cellulose nanocrystals at different concentrations. They reported that the addition of cellulose nanocrystals improved the mechanical strength of the prepared blends.²² PVA/CS blend fibers can also be used for some potential applications in tissue engineering.^{23,24}

In the present work, we prepared PVA/CS blends from PVA (13% w/w) and CS (2% w/w) solutions at various blend ratios. The effect of experimental factors such as blend ratios, voltage, and flow rate on the morphological, optical, and thermal properties were evaluated. To our knowledge, there are only a few published papers in the literature that investigate the optical, fluorescence, and thermal properties of electrospun fibers as a function of processing parameters such as different polymer ratios, applied voltage, and flow rate. Electrospinnability of PVA/CS blends was not possible after the CS ratio of 7% (w/w) due to the rigid interactions of CS molecules. Flow rates strongly affected the shape of the fibers; at lower flow rates, fibers were much flatter, whereas more circular fibers were prepared at higher flow rates. An increase of the CS amount in blends caused a decrease in transmittance values due to the increase in fiber thickness. Thermal endurance of nanofibers was also investigated by using thermogravimetric analysis (TGA) under inert atmosphere. PVA/CS nanofibers exhibited a two-step degradation around 290 and 410 °C. Nearly 6% weight loss was observed before 100 °C due to vaporization of residual water and moisture inside the electrospun nanofibers.

2. Results and discussion

2.1. Structural characterization

Fourier transform infrared (FT-IR) spectroscopy was used to verify the functional groups of PVA, CS, and PVA/CS blends. As can be seen in Figure 1, PVA showed a characteristic broad band between 3000 and 3600 cm^{-1} , which refers to strong interaction of -OH intramolecular and intermolecular -H bonding, and bands at 2920 cm^{-1} for $-\text{CH}_2$ and at 1425 cm^{-1} for CH-O-H, respectively. Moreover, the characteristic saccharine structures both at 1125 and 900 cm^{-1} , as well as the band between 3000 and 3600 cm^{-1} for $-\text{NH}_2$ and -OH groups, were good evidence for the CS structure. Overall, the structures of fibers were strongly confirmed by FT-IR spectroscopy by comparing the PVA, CS, and PVA/CS blend spectra, which have been attributed to similar functional groups.^{16,25,26}

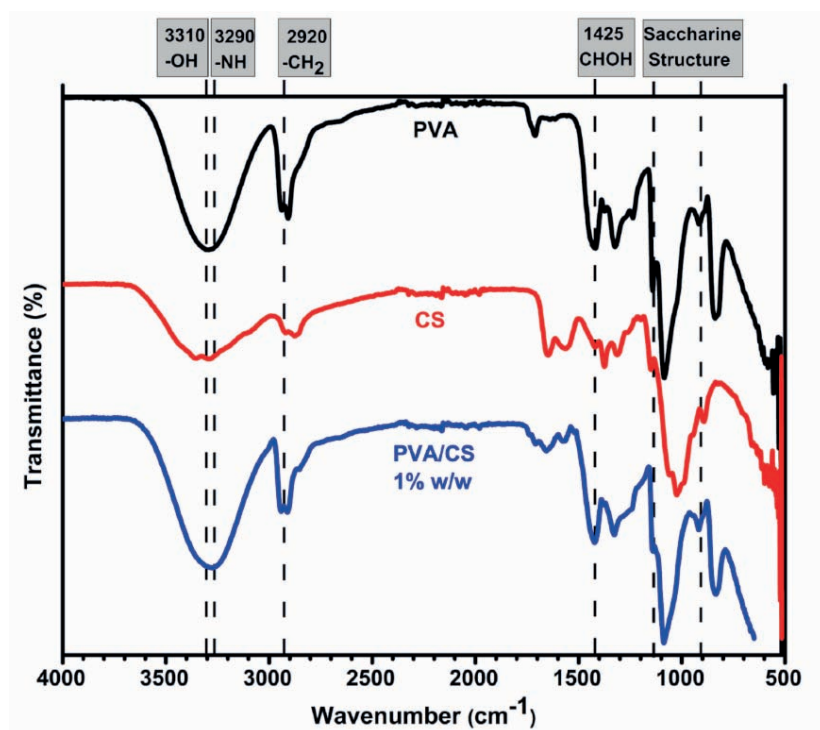


Figure 1. FT-IR spectra of PVA, CS, and PVA/CS blends.

2.2. Morphological properties

A field emission scanning electron microscope (FE-SEM; Leo Supra 35 VP) was used for investigation of the surface morphologies of the PVA and PVA/CS blend fibers. All images were taken with 30,000 \times magnification and some selected scanning electron microscopy (SEM) images are given in Figure 2. As can be seen from Figure 2, PVA/CS blend ratios strongly affect the shape and size of the nanofibers.

The electrospinnability of pure CS polymer is not very good due to the rigid interactions between the polymer molecules.^{11,13} Consequently, instead of electrospinning pure CS polymer, PVA/CS blends were used to prepare electrospun fibers. However, an increase of CS concentration caused weak electrospinning conditions; therefore, the maximum possible ratio of CS in blends was 7% w/w. The molecular weight of PVA also strongly affects the shape of the fibers.⁶ We used slightly lower molecular weight PVA ($M_w = 60,000$ g/mol); thus, it

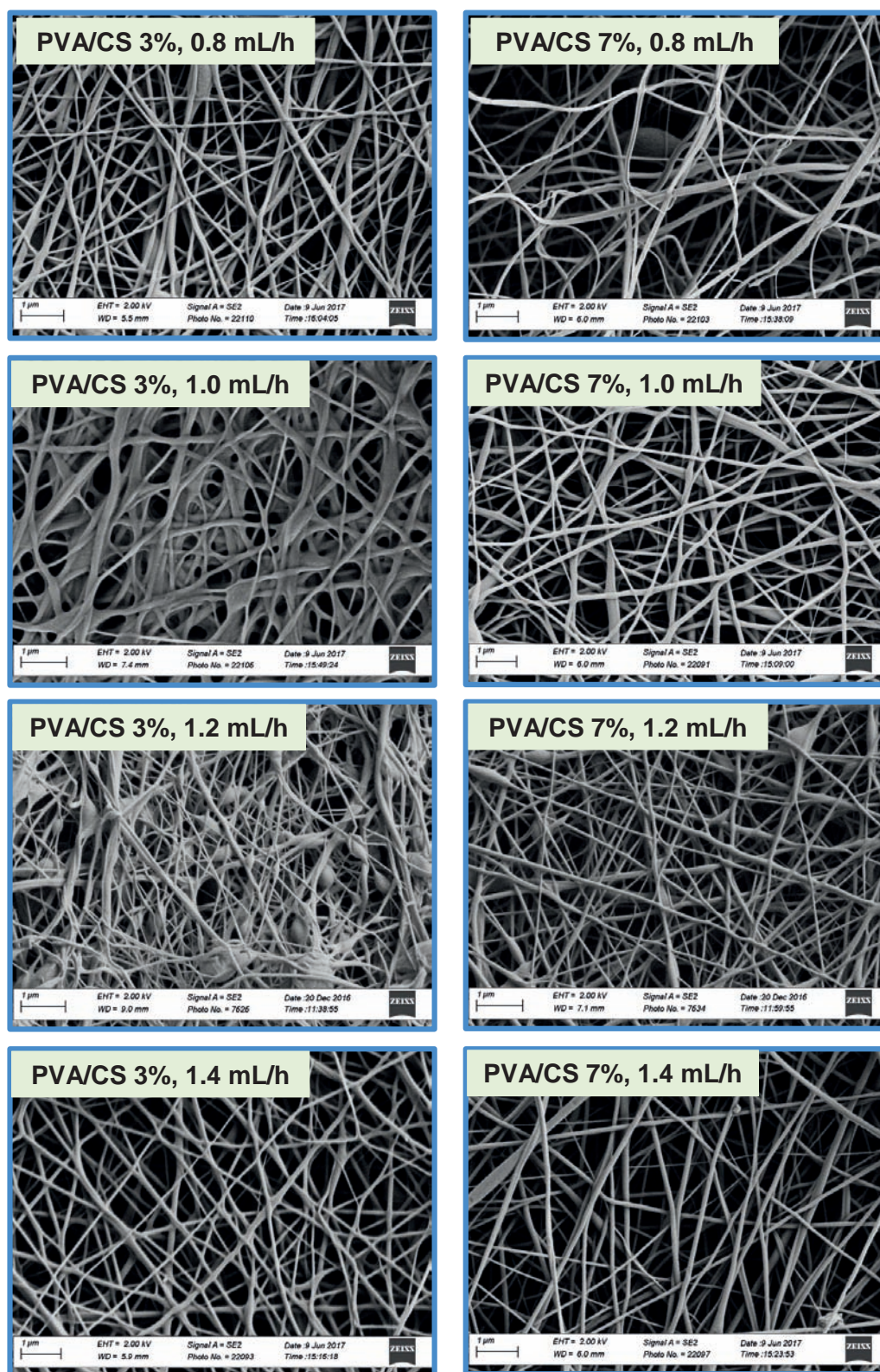


Figure 2. SEM images of PVA/CS 3% and PVA/CS 7% (w/w) blends with 30,000× magnification at various flow rates.

was possible to synthesize more circular fibers. One other important effect on fiber shapes is the applied flow rate of the polymer solutions. We applied flow rates ranging from 0.8 mL/h to 1.4 mL/h and found that at lower flow rates more flat nanofibers were synthesized, whereas at higher flow rates the shape of the fibers became more circular. At high flow rates (1.2 mL/h), when CS concentrations were lower, the resultant morphology comprises beaded-fiber structures; however, with the increase of CS concentration up to 7% w/w, fibers became more circular and beaded structures were almost destroyed. At higher flow rates, bead fibers with thicker diameters will form due to the short drying time prior to reaching the collector and the polymer solution will not get enough time for polarization. All the prepared fibers are durable and robust under room conditions for a 1-year time period.

2.3. Optical properties of electrospun fibers

The effects of experimental factors such as CS ratio, applied voltage, and flow rate on optical properties of the electrospun fibers were evaluated. In all measurements, PVA solution concentration and tip-collector distance were kept constant at 13% (w/w) and 10 cm, respectively. The effect of variation of CS ratio on the optical properties of the fiber surfaces is shown in Figures 3a and 3b. These measurements were carried out at either constant voltage (21 kV) or constant flow rate (1.0 mL/h). The transmittance curves of PVA fibers containing various amounts of CS ranging from 1% to 7% (w/w) are given in Figure 3a. Highest light transmittance, which is approximately 90%, was found for PVA/CS 1% (w/w) fibers. However, when the CS ratio ranged between 3% and 7%, a decrease was found in the transmittance values of fiber surfaces. This may be due to the increase in the CS ratio of the fibers. When a higher amount of CS was added, a larger number of optical interfaces were produced and a decrease in light transmittance values was found.²⁴ Moreover, the ratio of CS in PVA solution strongly affected the fiber diameters. At lower CS ratios, the viscosity of PVA solution was relatively lower than the surface tension and this property leads to nonuniform fiber formation.²⁶ Our results were in accordance with other papers in the literature.²⁷

The transmittance values of fibers in the visible region, at 700 nm, are given in Figure 3b. When the CS ratio was increased from 1% to 7% w/w, a decrease was found in the transmittance values of the fibers. This result could probably be due to the formation of uniform fibers depending on the solution viscosity at high CS ratios.

The effect of the applied voltage on the transmittance values of fibers was also investigated and transmittance curves of fibers at different voltages are given in Figure 3c. PVA/CS 5% (w/w) fiber surface was used in the measurements and the flow rate was adjusted to 1.0 mL/h. Aliabadi et al. reported that nonuniform fibers were obtained at lower voltages due to the weak electrical field strength and uniform fiber was obtained around 20 kV voltage values.²⁸ In addition, average fiber diameter was increased with increase in applied voltage.²⁵ According to transmittance curves of fibers at different applied voltages, the fibers obtained by applying 15 kV showed 60% transparency, whereas the fibers lost their transparencies due to the average value of fiber diameters and formation of uniform fibers at higher voltages around 25 kV.

The relationship between the transmittance and the applied voltage values of PVA/CS fibers in the visible region, at 700 nm, are given in Figure 3d. The fibers obtained by applying 15 kV voltage exhibited the highest transmittance. When the applied voltage was increased, transmittance values showed a decrease from 44% to 1% due to the formation of more uniform fibers at high voltages.²⁷

Another electrospinning parameter affecting fiber morphology is the flow rate. The transmittance curves

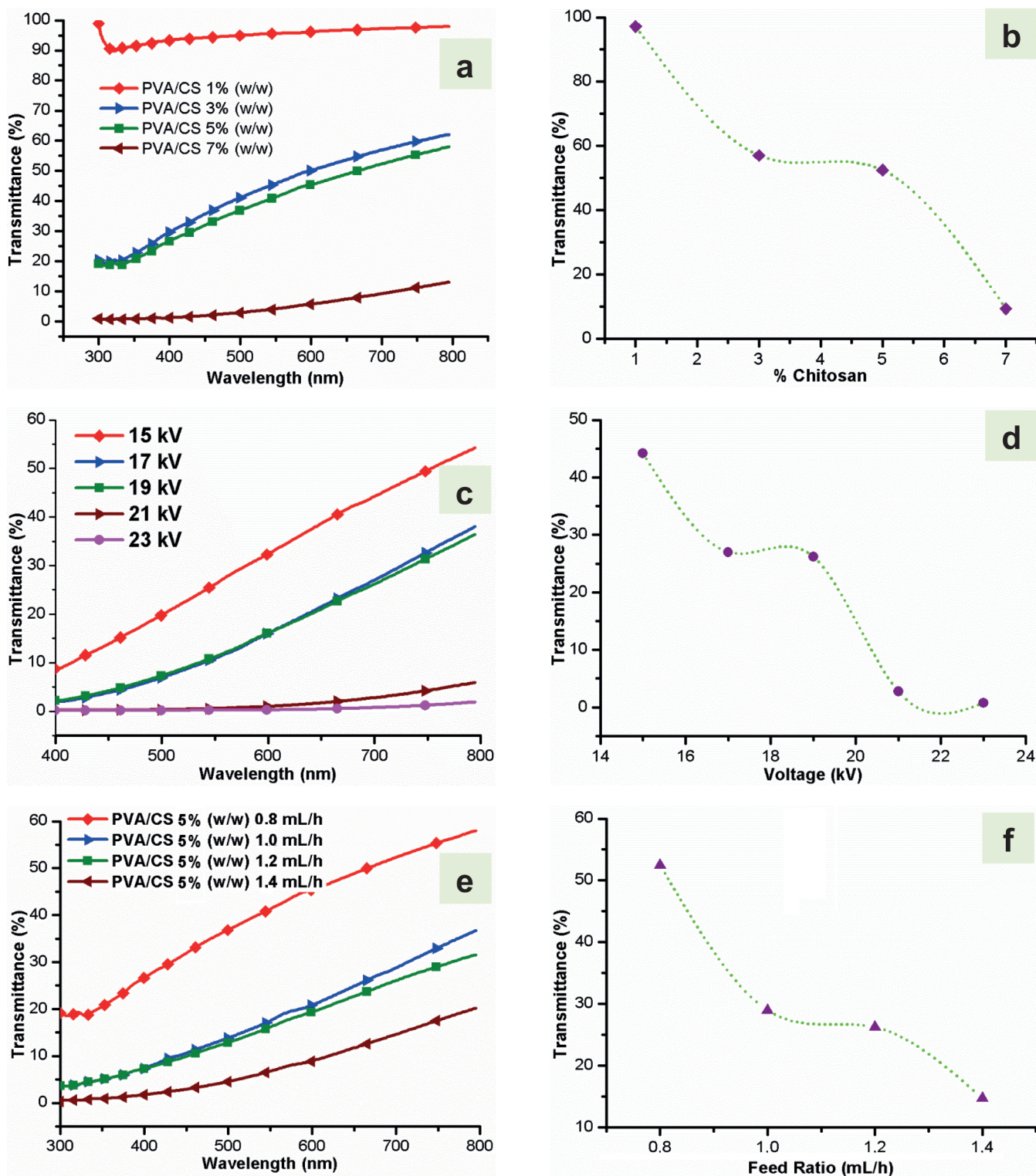


Figure 3. Transmittance curves of the fibers at different CS ratios (a, b), applied voltages (c, d), and flow rates (e, f).

of the fibers at various flow rates are given in Figure 3e. In these measurements, the applied voltage was adjusted to 21 kV and PVA/CS 5% (w/w) fiber surface was used. At lower flow rates, surfaces exhibited higher transparencies due to the fineness of fibers. With the increase of flow rates between 0.8 and 1.4 mL/h, thicknesses of the fibers increased and, as a result of this, lower transmittance values were exhibited due to average diameter of fibers. Park et al. reported that average diameter of fibers increased with the increase of flow rate due to the decrease in electrostatic density.²⁵ Transmittance values as a function of the flow rate in the visible region, at 700 nm, are comparatively given in Figure 3f. A similar tendency with the flow rate change was observed in the mentioned region.

The optical band gap (E_g) of electrospun fibers was calculated by using the Tauc method.^{29,30} This method is used to determine the optical band gap of both semiconductors and amorphous materials such as polymers. The Tauc plots of PVA/CS 1% (w/w), PVA/CS 3% (w/w), and PVA/CS 5% (w/w) are given in Figure 4 and E_g results are summarized in Table 1.

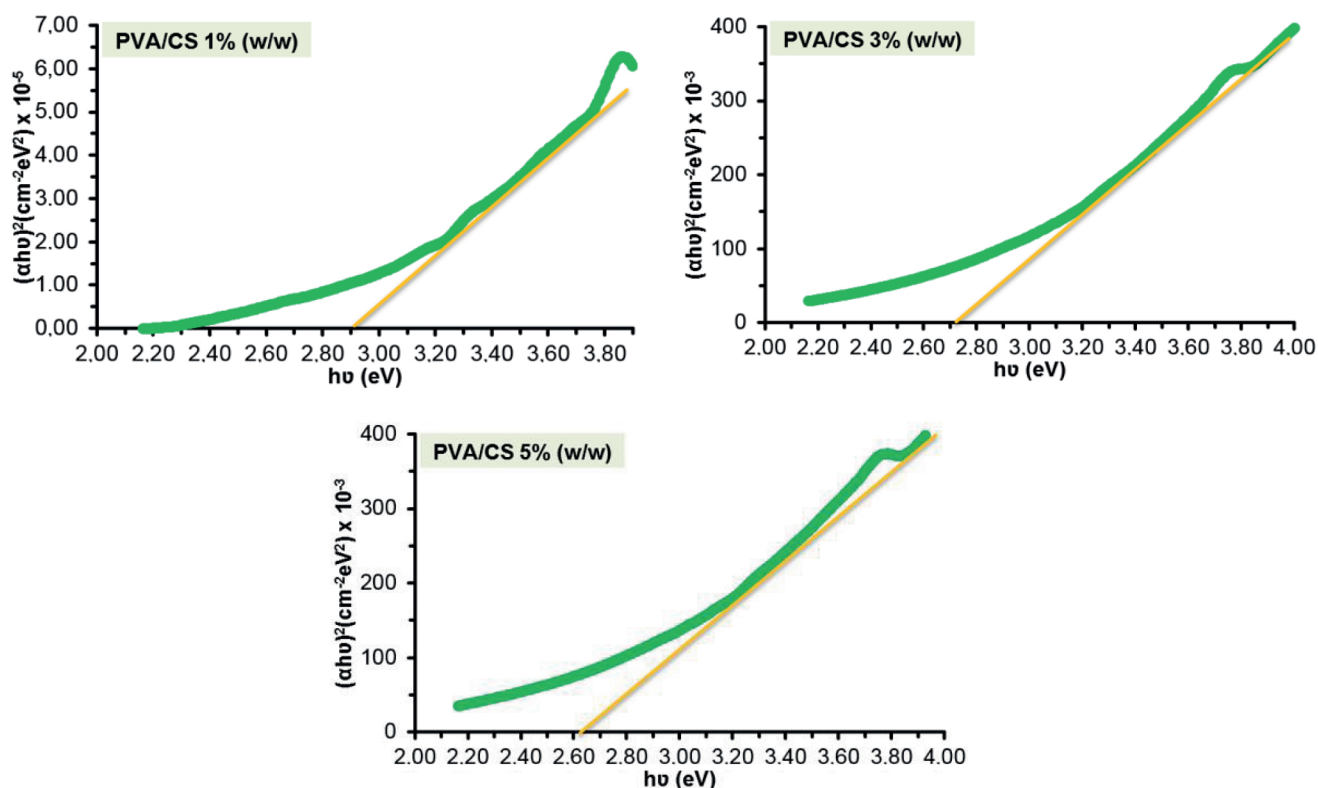


Figure 4. Plots of $(\alpha h\nu)^2$ versus $h\nu$ for PVA fibers containing 1%, 3%, and 5% CS (w/w).

The optical band gap was found to be 2.57 eV for PVA/CS 1% (w/w) and E_g values decreased from 2.72 to 2.57 eV with the increase of CS ratio from 3% to 7% (w/w). Similarly, the optical band gap of PVA/CS fibers decreased from 2.55 to 2.41 eV as the applied voltage was increased from 15 to 23 kV. In addition, the optical band gap of the electrospun fibers at various flow rates was determined in the range from 2.68 to 2.93 eV and the optical band gap of fibers increased with the increase of flow rate. Jahan et al. prepared CS/PVA film (50/50, w/w) and calculated the optical band gap of this film using the Tauc method.³¹ The optical band gap of the blend film was found as 2.30 eV and this result was in accordance with our results.

These results indicated that the optical band gap of the electrospun fiber decreased with the increase of

Table 1. Optical data of the electrospun fibers.

Fibers	UV-Vis		Fluorescence	
	^a Eg (eV)	^b T ₇₀₀ (%)	^c Wmax (nm)	^d Iem
PVA/CS 1% (w/w)	2.85 ± 0.04	97	330	763
PVA/CS 3% (w/w)	2.72 ± 0.03	57	330	113
PVA/CS 5% (w/w)	2.64 ± 0.03	53	330	97
PVA/CS 7% (w/w)	2.57 ± 0.02	9	330	86
PVA/CS 5% (w/w), 15 kV	2.55 ± 0.02	44	330	170
PVA/CS 5% (w/w), 17 kV	2.52 ± 0.02	27	330	152
PVA/CS 5% (w/w), 19 kV	2.48 ± 0.01	26	330	129
PVA/CS 5% (w/w), 21 kV	2.45 ± 0.01	3	330	123
PVA/CS 5% (w/w), 23 kV	2.41 ± 0.01	1	330	103
PVA/CS 5% (w/w) 0.8 mL/h	2.93 ± 0.04	52	365	299
PVA/CS 5% (w/w) 1.0 mL/h	2.76 ± 0.03	29	365	113
PVA/CS 5% (w/w) 1.2 mL/h	2.71 ± 0.03	26	365	110
PVA/CS 5% (w/w) 1.4 mL/h	2.68 ± 0.03	15	365	74

^aOptical band gap.^bTransmittance at 700 nm.^cMaximum emission wavelength.^dMaximum emission intensity.

CS amount, applied voltage, and flow rate. This can be due to the average diameter of fibers and formation of uniform fibers at high CS ratios, voltages, and flow rates.^{25,28}

The emission spectra of PVA/CS fibers with various CS ratios, applied voltage, and flow rate are given in Figures 5a–5c, respectively, and the results are summarized in Table 1. The obtained fluorescence spectra clearly indicated that the emission intensity of electrospun fibers decreased with the increase of CS ratio (1%–7%), voltage (15–23 kV), and flow rate (0.8–1.4 mL/h), as shown with the results obtained from transmittance spectra. As can be seen in the fluorescence spectra, fibers produced by using a different CS ratio and applied voltage showed in the 330 nm (3.76 eV) emission band, while the emission band of fibers at a different flow rate was observed at 365 nm (3.40 eV). Moreover, the flow rate and CS ratio caused a significant change in emission intensity of the electrospun fibers, while the emission intensity of fibers at different applied voltages was not affected.

2.4. Thermal characterization

Thermal endurance of PVA and PVA/CS blend fibers was investigated by using TGA under inert atmosphere (Figure 6) and the results are summarized in Table 2. Based on the obtained thermal data, PVA/CS fibers exhibited a two-step degradation around 290 and 410 °C. In addition, nearly 6% weight loss was observed before 100 °C due to vaporization of residual water and moisture inside the electrospun fibers. The first and major degradation step in the range from 100 to 320 °C is attributed to the decomposition of CS. In this degradation step, around 60% weight loss was observed. The second degradation step was due to the decomposition of fiber structure at high temperatures ranging between 320 and 600 °C.^{32–34}

As depicted in Figure 6a, the thermal decomposition behavior of bulk PVA fiber is different when

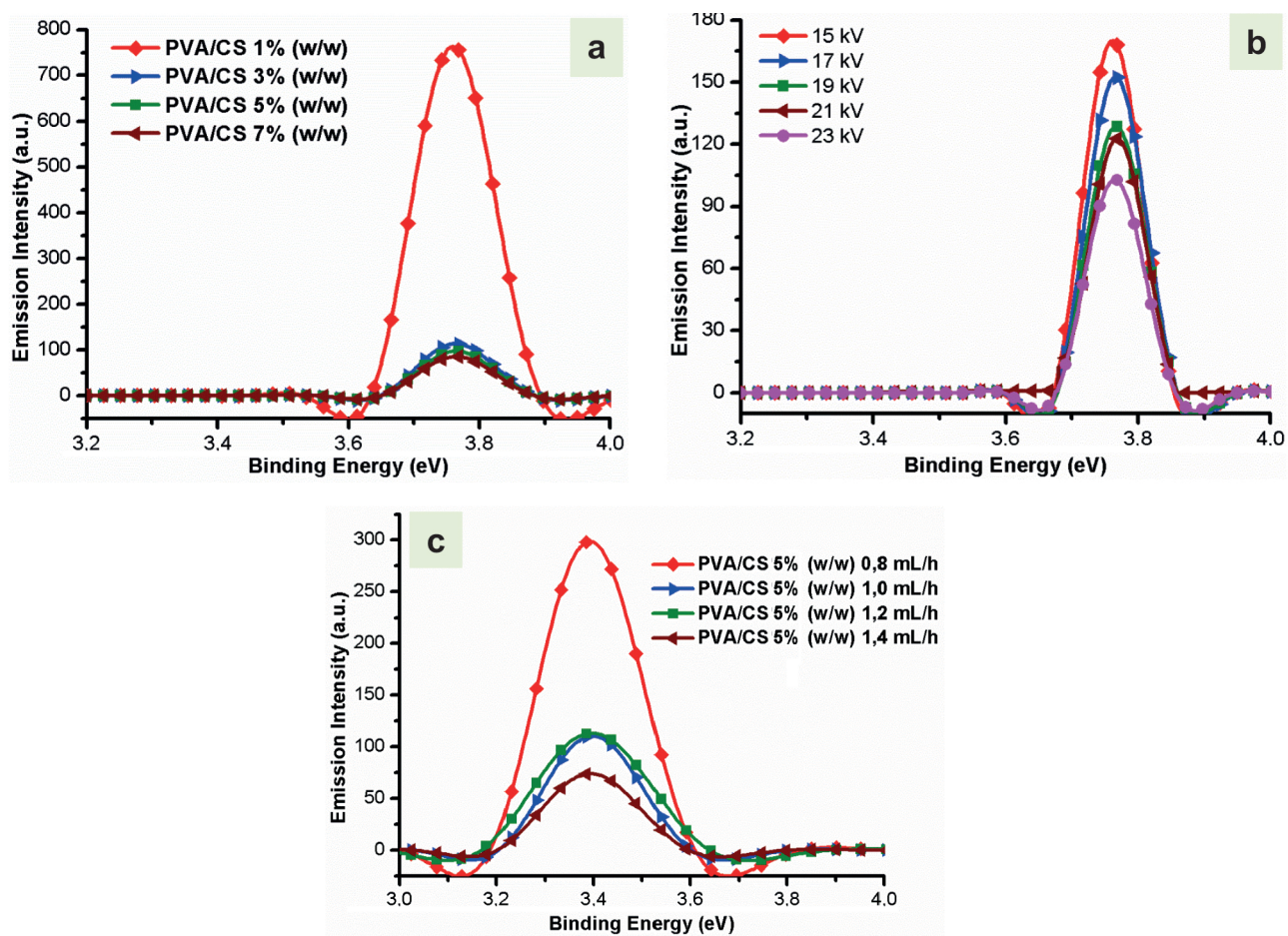


Figure 5. Fluorescence spectra of fibers at different CS ratios (a), applied voltages (b), and flow rates (c).

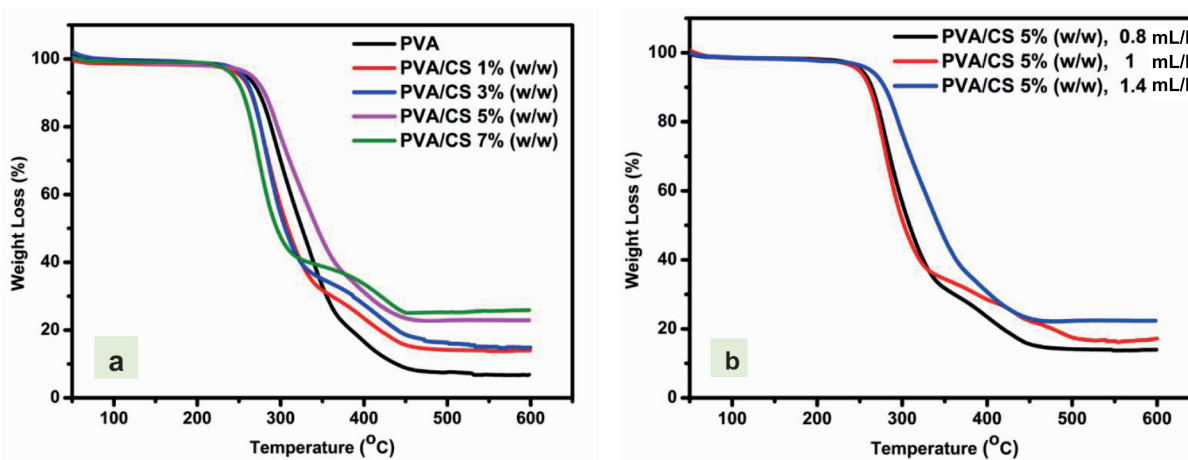


Figure 6. TGA curve of PVA and PVA/CS blend fibers with various weight ratios (a) and flow rates (b).

compared to PVA/CS blend fibers. It is clearly seen from Figure 6a that higher endurance is obtained with an increase of CS weight ratio.³⁵ This can be due to the thermal stability of CS and PVA. When compared to the thermal stability of CS and PVA, the % mass loss of CS was significantly lower than that of PVA around 500 °C.³⁵

Table 2. TGA data of the electrospun fibers at different electrospinning parameters.

Fibers	^a T _{on} (°C)	^b T _{max} (°C)	^c T20 (°C)	^d T50 (°C)
PVA	276	296, 415	280	317
PVA/CS 1% (w/w)	282	301, 396	276	305
PVA/CS 3% (w/w)	283	299, 398	277	309
PVA/CS 5% (w/w)	297	318, 425	287	334
PVA/CS 7% (w/w)	300	320, 428	290	338
PVA/CS 5% (w/w), 0.8 mL/h	281	295, 418	268	296
PVA/CS 5% (w/w), 1.0 mL/h	283	290, 416	266	295
PVA/CS 5% (w/w), 1.4 mL/h	274	306, 420	261	288

^aOnset temperature.

^bMaximum weight temperature.

^c20% weight loss temperature.

^d50% weight loss temperature.

Additionally, TGA was also performed to investigate the effect of flow rate on thermal endurance of fibers,³⁵ and the results are given in Figure 6b. From the respective curves, the thermal characteristics of related blends interestingly improved with the increase of flow rate as 0.8, 1.0, and 1.4 mL/h.

2.5. Conclusions

In this study, PVA/CS blend fibers were prepared from their solutions by using an electrospinning method. PVA/CS blend ratios, flow rate, and the molecular weight of PVA strongly affected the shape and size of the nanofibers; with the increase of CS concentration, due to the rigid interactions of CS molecules, weak electrospinning conditions occurred and the maximum possible ratio of CS was 7% (w/w). At lower flow rates, more flat nanofibers were prepared; however, with the increase in flow rates, deviations from the flat structures occurred and the shape of the fibers became more circular.

Increase in CS amount in the blend ratio, flow rate, and applied voltage caused a decrease in the transmittance values of the fibers. The optical band gap of the electrospun fibers also decreased with the increase of CS ratio. These results were due to production of more optical interfaces and more uniform electrospun fibers.

PVA/CS blends containing 1% CS had the highest emission intensity and an increase in CS ratios caused a slight decrease in emission intensities due to their uniform fiber structure. PVA/CS blend fibers exhibited a two-step degradation around 290 and 410 °C. In addition, nearly 6% weight loss was observed before 100 °C due to vaporization of residual water and moisture inside the electrospun fibers.

3. Experimental

3.1. Materials

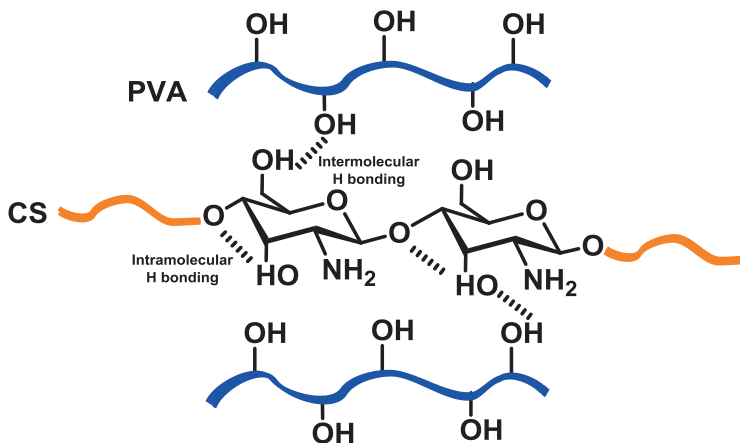
PVA (fully hydrolyzed, Mw = 60,000 g/mol) and Tween 80 (viscous liquid) were purchased from Merck (Darmstadt, Germany). CS (medium molecular weight) and acetic acid (AA, ≥99%) were obtained from Sigma-Aldrich (Steinheim, Germany). All chemicals were used without purification.

3.2. Preparation of electrospinning solutions

First, PVA was dissolved in distilled water at 60 °C for 3 h to obtain 13% w/w solution. CS was dissolved in diluted acetic acid solution (2% v/v) at room temperature for about 18 h to obtain 2% w/w solution. After the preparation of solutions, PVA (13 w/w%), CS (2 w/w%), and five drops of Tween 80 were introduced into a 20-mL beaker and the mixture was left under continuous vigorous stirring for 15 min at room temperature in order to yield electrospinning solutions having concentrations of 1%, 3%, 5%, and 7% w/w CS to PVA, respectively. Tween 80 was chosen as a surfactant due to its nontoxic and biocompatible properties and the reason for the addition of a surfactant was to decrease the surface tension of the final electrospinning solution. Decreasing the surface tension of the electrospinning solution causes the electrospinnability characteristics of the blend solutions to improve.

3.3. Electrospinning procedure

Laboratory-scale NE-100 model electrospinning equipment (Inovenso, Turkey) with a syringe pump (New Era Pump Systems Inc., USA), high DC voltage power supply (0–40 kV) (PW1010, Elektrosis, Turkey), and mobile aluminum ground collector was used to conduct the electrospinning process. The typical electrospinning procedure for a series of PVA and PVA/CS blend solutions (Scheme) is as follows: an electrospinning system, consisting of applied adjustable +21 kV DC voltage to generate potential difference, 5-mL plastic feeding syringe, needle with an inner diameter of 11.99 mm, and a needle tip to aluminum plate collector at a working distance fixed at 10 cm, is utilized at room temperature. Nanofibers were accumulated on glass slides, which were stuck on the collector, and the flow ratios were chosen as 0.8, 1.0, and 1.4 mL/h (Table 3). Glass slides were cleaned in chromic acid solution before the electrospinning process. All nanofibers were stored in a desiccator at room temperature to remove the residual solvent before characterization. All the prepared fibers are durable and robust under room conditions.



Scheme. Schematic illustration of PVA/CS blends.

3.4. Structural characterization

FT-IR analysis was performed to verify functional groups of PVA, CS, and PVA/CS blends by using a PerkinElmer (Lambda 25, Waltham, MA, USA) FT-IR Spectrum Two Spectrometer equipped with a diamond ATR device at room temperature and a scanning range that covered 4000 cm^{-1} to 400 cm^{-1} . TGA was

Table 3. Parameters for electrospinning of PVA/CS fibers.

Solutions	Voltage (kV)	Flow rate (mL/h)	Tip-to-collector distance (cm)	Ambient conditions
PVA (13 wt.%)	15, 17, 19, 21, 23	0.8, 1.0, 1.2, 1.4	10	~25 °C
CS (2 wt.%)				

conducted on a PerkinElmer Diamond TA/TGA with a heating rate of 10 °C/min under nitrogen flow (200 mL/min) to investigate the thermal endurance of the PVA/CS blends. Merck grade water was used for the PVA and PVA/CS blends' contact angle (CA) measurements and CAs were measured using a KSV Attension Theta Optical Tensiometer at room temperature under air. A FE-SEM (Leo Supra 35 VP) was used for investigation of the surface morphologies of the PVA and PVA/CS blends.

3.5. Optical properties

Optical properties of electrospun fibers were investigated using UV-Vis and fluorescence spectrophotometers. Transmittance spectra were recorded using a PerkinElmer Lambda 25 UV-Vis spectrophotometer in the range from 300 to 800 nm. Fluorescence measurements were carried out using a PerkinElmer LS-55 fluorescence spectrometer in the range from 300 to 800 nm. In these measurements, excitation wavelength and slit width were adjusted as 330 and 2.5 nm, respectively. The samples for UV-Vis and fluorescence measurements were obtained directly by collecting the as-electrospun fibers on a quartz plate.

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