

Study on morphology of electrospun poly(vinyl alcohol) mats

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Abstract

Submicron poly(vinyl alcohol) (PVA) fiber mats were prepared by electrospinning of aqueous PVA solutions in 6–8% concentration. Fiber morphology was observed under a scanning electron microscope and effects of instrument parameters including electric voltage, tip–target distance, flow rate and solution parameters such as concentration on the morphology of electrospun PVA fibers were evaluated. Results showed that, when PVA with higher degree of hydrolysis (DH) of 98% was used, tip–target distance exhibited no significant effect on the fiber morphology, however the morphological structure can be slightly changed by changing the solution flow rate. At high voltages above 10 kV, electrospun PVA fibers exhibited a broad diameter distribution. With increasing solution concentration, the morphology was changed from beaded fiber to uniform fiber and the average fiber diameter could be increased from 87 ± 14 nm to 246 ± 50 nm. It was also found that additions of sodium chloride and ethanol had significant effects on the fiber diameter and the morphology of electrospun PVA fibers because of the different solution conductivity, surface tension and viscosity. When the DH value of PVA was increased from 80% to 99%, the morphology electrospun PVA fibers was changed from ribbon-like fibers to uniform fibers and then to beaded fibers. The addition of aspirin and bovine serum albumin also resulted in the appearance of beads.

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1. Introduction

Poly(vinyl alcohol) (PVA) is a water-soluble polymer produced industrially by hydrolysis of poly(vinyl acetate). A number of grades of PVA are commercially available, which can be divided into two types: the fully hydrolyzed and the partially hydrolyzed PVA depending on the amount of acetate groups left in the backbone [1]. The chemical stability of PVA at normal temperature

along with its excellent physical and mechanical properties have led to its broadly practical applications. PVA has been mainly used in fiber and film products for many years. It was also used as paper coating, adhesives and colloid stabilizer [2]. In recent years, much attention has been focused on the biomedical applications of PVA hydrogels including contact lenses, artificial organs and drug delivery systems [3,4].

Ultrafine PVA fibers, which may have potential applications in filtration and biomedical engineering, cannot be produced by conventional spinning techniques. Through the processes, such as melt spinning, dry spinning or wet spinning, fibers with diameters ranging from

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5 μm to 500 μm are generally obtained [5]. Electrospinning is a straightforward method to prepare fibers with diameters as small as several tens of nanometers [6]. In electrospinning, a high electrostatic voltage is imposed on a drop of polymer solution held by its surface tension at the end of a capillary. The surface of the liquid is distorted into a conical shape known as the Taylor cone. Once the voltage exceeds a critical value, the electrostatic force overcomes the solution surface tension and a stable liquid jet is ejected from the cone tip. Solvent evaporates as the jet travels through the air, leaving behind ultrafine polymeric fibers collected on an electrically grounded target. The jet often follows a bending or a spiral track resulting from the interaction between the external electric field and the surface charge of the jet. Bending instability of jets not only results in the electrospinning jet being elongated up to ultrafine fibers but also leads to the formation of randomly deposited nonwoven electrospun fiber mats [7–9]. Electrospun mats have a larger specific surface area and small pore size compared to commercial nonwoven fabrics. They are of interests in a wide variety of applications including semi-permeable membranes, nanocomposites, filters, protection clothing and biomedical applications such as wound dressings, tissue engineering scaffolds and drug delivery systems [10–13].

Polyethylene and polypropylene were electrospun from the melt while a wide variety of synthetic and natural polymers were electrospun from solutions. Among them are poly(vinyl chloride) [14], poly(ethylene-co-vinyl alcohol) [15], polycarbonates [16], nylon-6 [9], polyurethane [17], polyacrylonitrile [18] and so on. Bioabsorbable nanofibers prepared from polylactide, poly(lactide-co-glycolide) and poly(ϵ -caprolactide) were developed for tissue engineering [13,19]. Nature polymers such as collagen [20], silk fibroin [21], cellulose acetate [22] and even protein polymer synthesized using recombinant DNA biosynthesis technology [23] were electrospun into ultrafine fiber mats. Crosslinked PVA fiber mats was electrospun by Ding and the crystallinity, water solubility as well as mechanical properties of the mats were studied [24]. Electrospun fiber mats of organic–inorganic hybrids such as PVA/silica and PVA/ $\text{H}_4\text{SiMo}_{12}\text{O}_{40}$ fiber mats were prepared and characterized by Shao and Gong, respectively [25,26]. Effect of molecular weight on electrospun fibrous PVA was discussed by Koski et al. [27]. Stabilization of fully Hydrolyzed PVA fibers by treatment with methanol was investigated by Yao et al. [28].

In the present work, we have systematically evaluated the effects of instrument parameters, including electric voltage, tip–target distance, solution flow rate, and solution parameters, such as polymer concentration, on the morphology of electrospun PVA fibers. In addition, since solution properties of PVA with different contents of residual vinyl acetate group varied obviously [29], the influence of the hydrolysis degree (DH) of PVA on its fiber formation was also investigated. Moreover, the

feasibility and changes of the morphology of electrospun fibers of PVA solution blended with aspirin and bovine serum albumin (BSA) were also studied.

2. Experimental methods

2.1. Materials

PVA samples with degree of polymerization of 1700 ± 50 and DH values from 80% to 99% were obtained from Beijing Organic Chemical Plant, China and used without further purification. Distilled water was used as the solvent. Both sodium chloride and ethanol were chemical reagents. Aspirin was the product synthesized from salicylic acid and acetic anhydride, and recrystallized by ethanol before the use. BSA in the electrophoretic grade was purchased from Tianjin Blood Institute, China.

2.2. Preparation and properties of PVA solutions

PVA solutions were prepared at 40–98 °C depending on their DHs and gently stirred for 2 h. The concentration of polymer solution was 6–8% in mass. Occasionally, ethanol or sodium chloride was added to the PVA solution. Aspirin was dissolved in a small amount of ethanol and added to the PVA solution with agitation drop by drop. BSA was dissolved in water and blended with the PVA solution. The viscosity of polymer solution was determined by using a rotating viscometer (NDJ-79, Shanghai, China). Surface tension was measured with a digital tensiometer (DCAT21, Data Physics Co. Germany). The conductivity was measured in a conductivity instrument (DDS-11A, Shanghai, China).

2.3. Electrospinning

During electrospinning, a high voltage power (MGD-1A, Tianjin University, China) was applied to the PVA solution contained in a syringe via an alligator clip attached to the syringe needle. The applied voltage was adjusted at 5–15 kV. The solution was delivered to the blunt needle (Gauge 9, the nozzle diameter is about 0.9 mm) tip via a syringe pump (WZ-500C2, Zhejiang, China) to control the solution flow rate. Fibers were collected on an electrically grounded aluminum foil placed at 8–15 cm below the needle tip.

2.4. Characterization

The morphology of electrospun PVA fibers was observed with a Philips environmental scanning electron microscope (XL-30) after gold coating. The average fiber diameter of the electrospun fibers was measured by Adobe Photoshop 5.0 software from the SEM pictures in original magnification of 10 \times .

3. Results and discussion

3.1. Effect of voltage

A series of experiments were carried out when the applied voltage was varied from 5 to 13 kV and the tip to target distance was held at 15 cm. Results were shown in Fig. 1. There was a slightly increase in average fiber

diameter with increasing applied electric field. A considerable amount of thin fibers with diameters below 150 nm were found when the applied voltage is above 10 kV. A narrow distribution of fiber diameters was observed at a lower voltage of 5 kV, while broad distribution in the fiber diameter was obtained at higher applied voltages of 10–13 kV. Increasing the applied voltage, i.e., increasing the electric field strength will

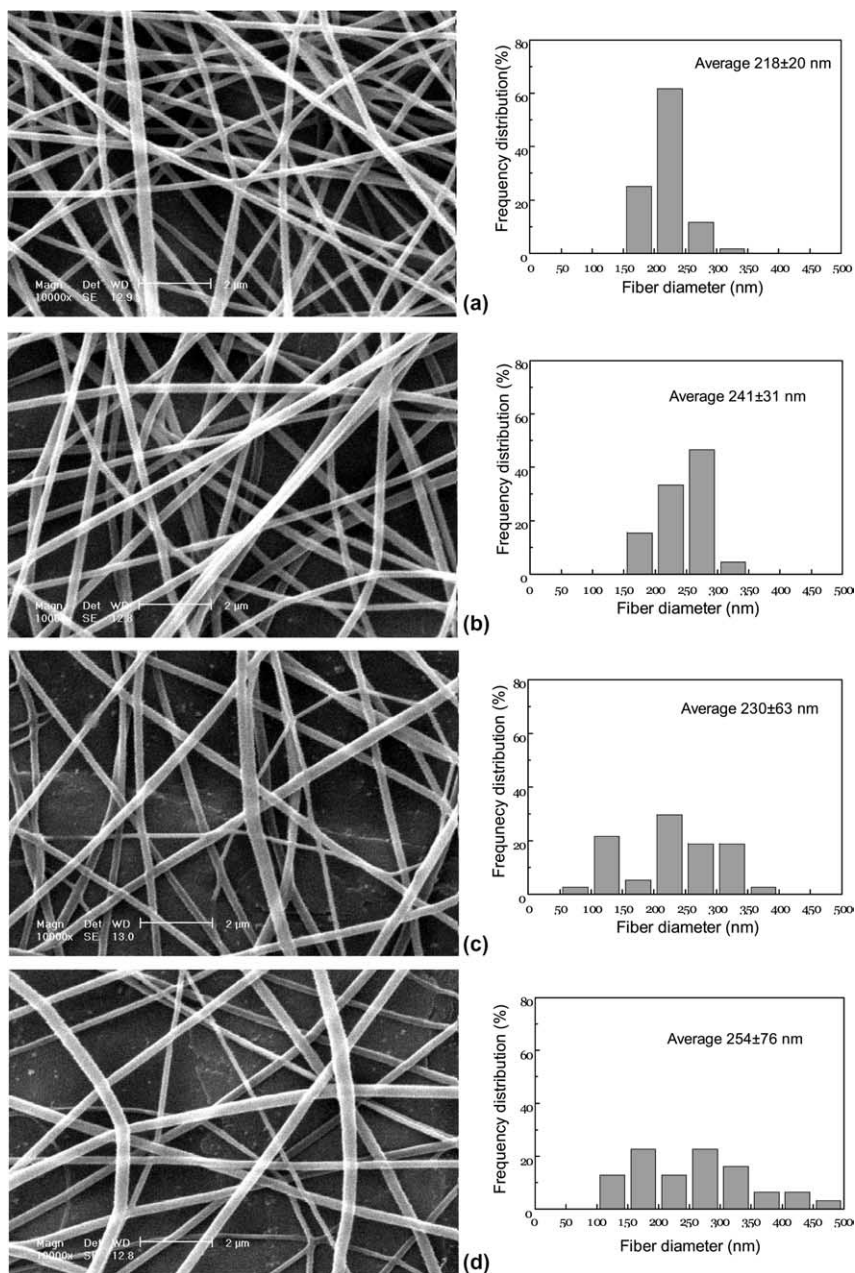


Fig. 1. Effect of voltage on morphology and fiber diameter distribution from a 7.4% PVA/water solution (DH = 98%, tip-target distance = 15 cm, flow rate = 0.2 ml/h). Voltage: (a) 5 kV; (b) 8 kV; (c) 10 kV; (d) 13 kV. Original magnification 10 k \times .

increase the electrostatic repulsive force on the fluid jet which favors the thinner fiber formation. On the other hand, the solution will be removed from the capillary tip more quickly as jet is ejected from Taylor cone. This results in the increase of the fiber diameter. Corona discharge was observed at voltages above 13kV, making electrospinning impossible.

3.2. Tip–target distance and flow rate

Tip–target distance had no significant effect on the electrospun fiber morphology of fully hydrolyzed PVA, as shown in Fig. 2. The micrographs were undistinguishable for electrospinning at 8–15cm of tip–target distance. It was assumed that solution jets were elongated and solidified quickly after they flowed out of the needle tip because of the high conductivity of fully hydrolyzed PVA used. The morphological structure can be slightly changed by changing the solution flow rate as shown in Fig. 3. At the flow rate of 0.3ml/h, a few of big beads were observed on the fibers. The flow rate could affect electrospinning process. When the flow rate exceeded a critical value, the delivery rate of the solution jet to the capillary tip exceeded the rate at which the solution was removed from the tip by the electric forces. This shift in the mass-balance resulted in sustained but unstable jet and fibers with big beads were formed.

3.3. Effect of concentration

Changing the polymer concentration could alter the solution viscosity, as shown in Table 1 (sample nos. 1–4). A series of samples with different PVA concentrations were electrospun, resulting in various fiber morphology, as shown in Fig. 4. At 6%, spindle-like beads were seen and the average fiber diameter between beads was 87 ± 14 nm. With increasing concentration, the morphology was changed from beaded fiber to uniform fiber structure and the fiber diameter was also increased to 246 ± 50 nm gradually. Above the concentration of 8.3%, the polymer solution did not form fibers but formed big droplets falling on the collection target regardless of the electrospinning voltage. A critical concentration of polymer solution needed to be exceeded in electrospinning as extensive chain entanglements are necessary to produce electrospun fibers. In electrospinning, the coiled macromolecules in solution were transformed by the elongational flow of the jet into oriented entangled networks that persist with fiber solidification. Below this concentration, chain entanglements were insufficient to stabilize the jet and the contraction of the diameters of the jet driven by the surface tension caused the solution to form beads or beaded fibers. At higher concentration, viscoelastic force which resisted rapid changes in fiber shape resulted in uniform fiber formation. However, it was impossible to electrospin if

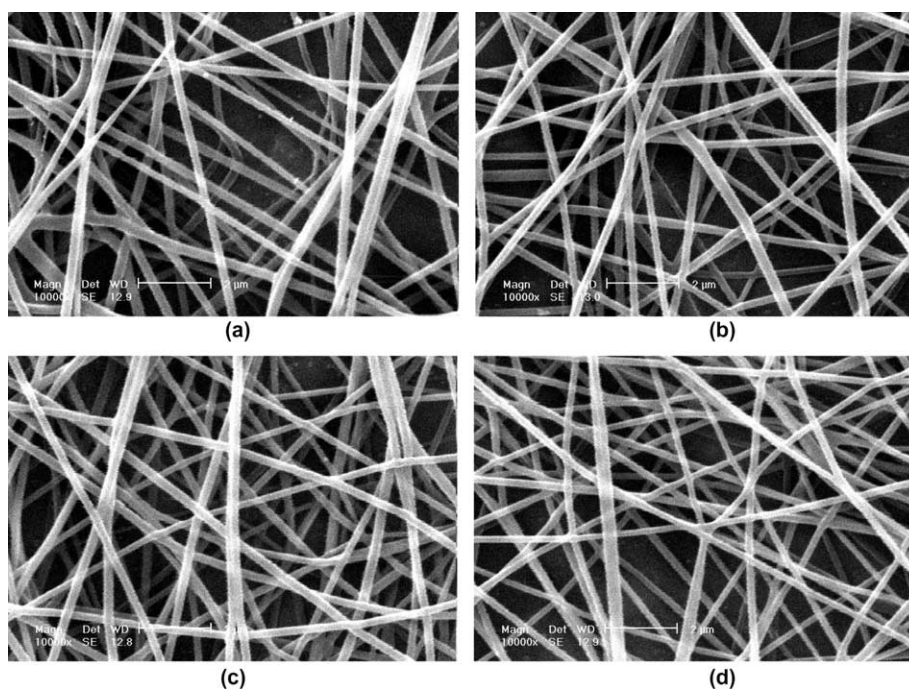


Fig. 2. Effect of tip–target distance on fiber morphology from a 7.4% PVA/water solution (DH = 98%, voltage = 5kV, flow rate = 0.2ml/h). Tip–target distance: (a) 8cm; (b) 10cm; (c) 12cm; (d) 15cm. Original magnification 10k \times .

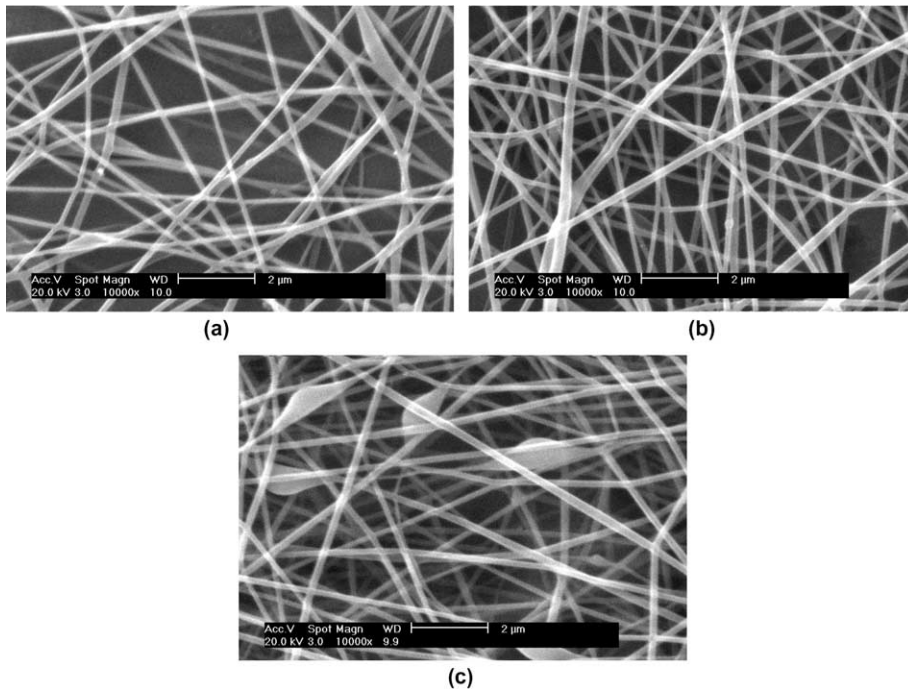


Fig. 3. Effect of flow rate of 7% PVA water solution on fiber morphology (DH = 98%, voltage = 8 kV, tip–target distance = 15 cm). Flow rate: (a) 0.1 ml/h; (b) 0.2 ml/h; (c) 0.3 ml/h. Original magnification 10k \times .

Table 1
Properties of PVA solution

Sample no.	PVA (g)	DH of PVA (%)	H ₂ O (ml)	NaCl (g)	Ethanol (ml)	Viscosity (Pa s)	Surface tension (mN/m)	Conductivity (mS/cm)
1	6	98	94			0.075	66.81	0.55
2	6.5	98	93.5			0.120	65.89	0.56
3	7	98	93			0.155	67.49	0.54
4	8	98	92			0.232	65.36	0.58
5	8	98	100	0.05		0.210	67.06	1.53
6	8	98	100	0.10		0.190	68.16	2.01
7	8	98	100	0.15		0.200	67.79	2.75
8	8	98	100	0.20		0.200	65.96	10.5
9	8	98	97		3	0.200	64.75	0.62
10	8	98	95		5	0.165	59.79	0.60
11	8	98	90		10	0.150	60.07	0.52
12	8	98	85		15	0.150	57.35	0.52
13	7	80	93			0.220	45.03	0.13
14	7	88	93			0.125	45.55	0.44
15	7	99	93			0.200	59.98	1.20

the solution concentration or the corresponding viscosity was too high due to the difficulty in liquid jet formation.

3.4. Effect of NaCl amount

Previous results of Fong showed that the addition of NaCl to the PEO solution increased the net charge den-

sity carried by the moving jet and beaded fibers were less likely to be formed [7]. The beads on electrospun poly(D,L-lactic acid) fibers also become smaller and more spindle-like with the addition of salts [30]. In this study, the effect of NaCl addition on the morphology of electrospun PVA fibers was shown in Fig. 5. Even a little sodium chloride added in the solution made its conductivity increase sharply as shown in Table 1 (sample

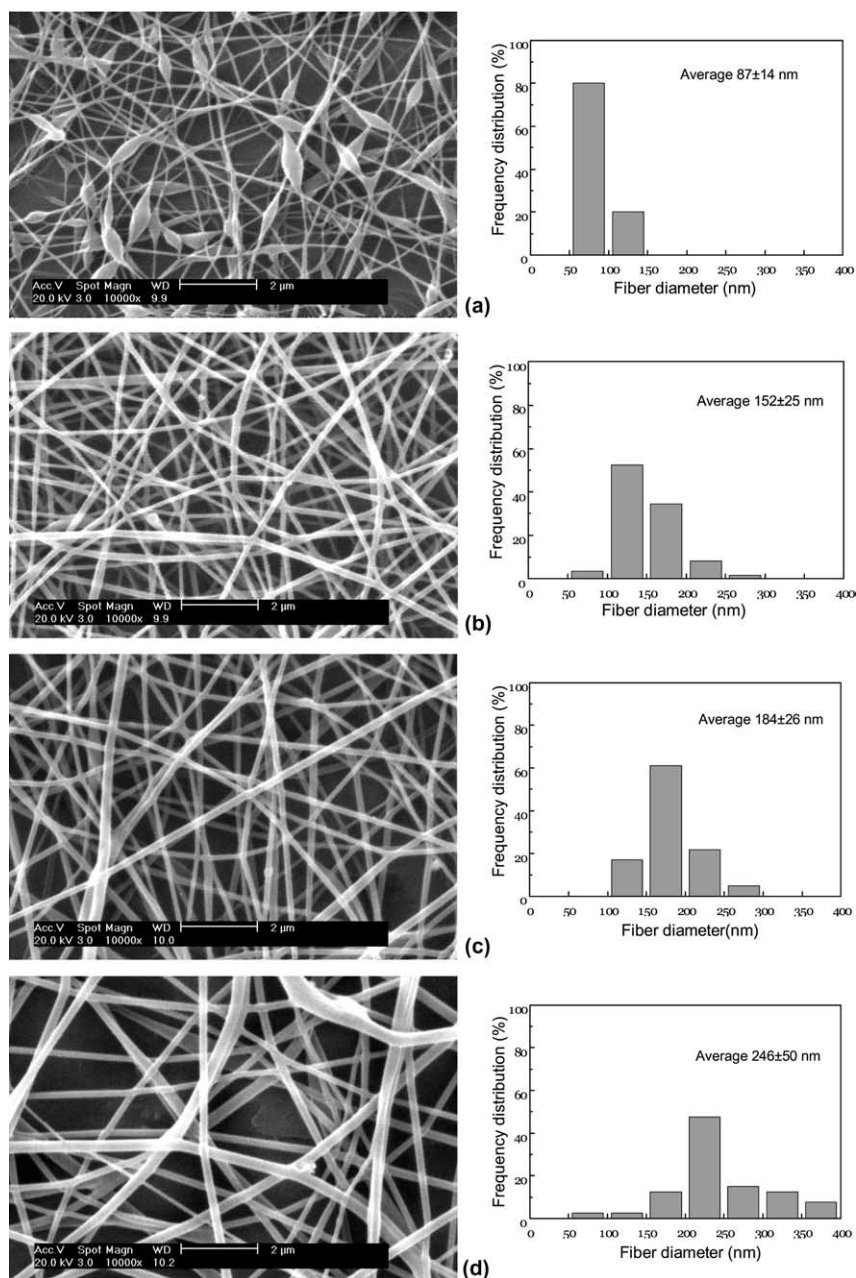


Fig. 4. SEM micrographs of electrospun fibers from PVA solutions with different solution concentration (DH = 98%, voltage = 8kV, tip–target distance = 15cm, flow rate = 0.2ml/h). PVA concentration: (a) 6%; (b) 6.5%; (c) 7%; (d) 8%. Original magnification 10k \times .

nos. 5–8). Net charge density carried by the jet in the electrospinning process can be affected by the conductivity of the solution. PVA fiber diameters were gradually decreased from 214 ± 19 nm to 159 ± 21 nm with increasing content of NaCl from 0.05% to 0.2%, for the higher net charge density increased the electrical force exerted on the jet and led to decreased fiber diameter. When 0.2% NaCl was added in PVA solution,

many small particles, perhaps sodium chloride crystals were observed on the SEM micrograph [Fig. 5(d)].

3.5. Effect of ethanol amount

The surface tension of the PVA solution depends on both the polymer and the solvent. Changing ethanol amount could alter the surface tension of PVA solution

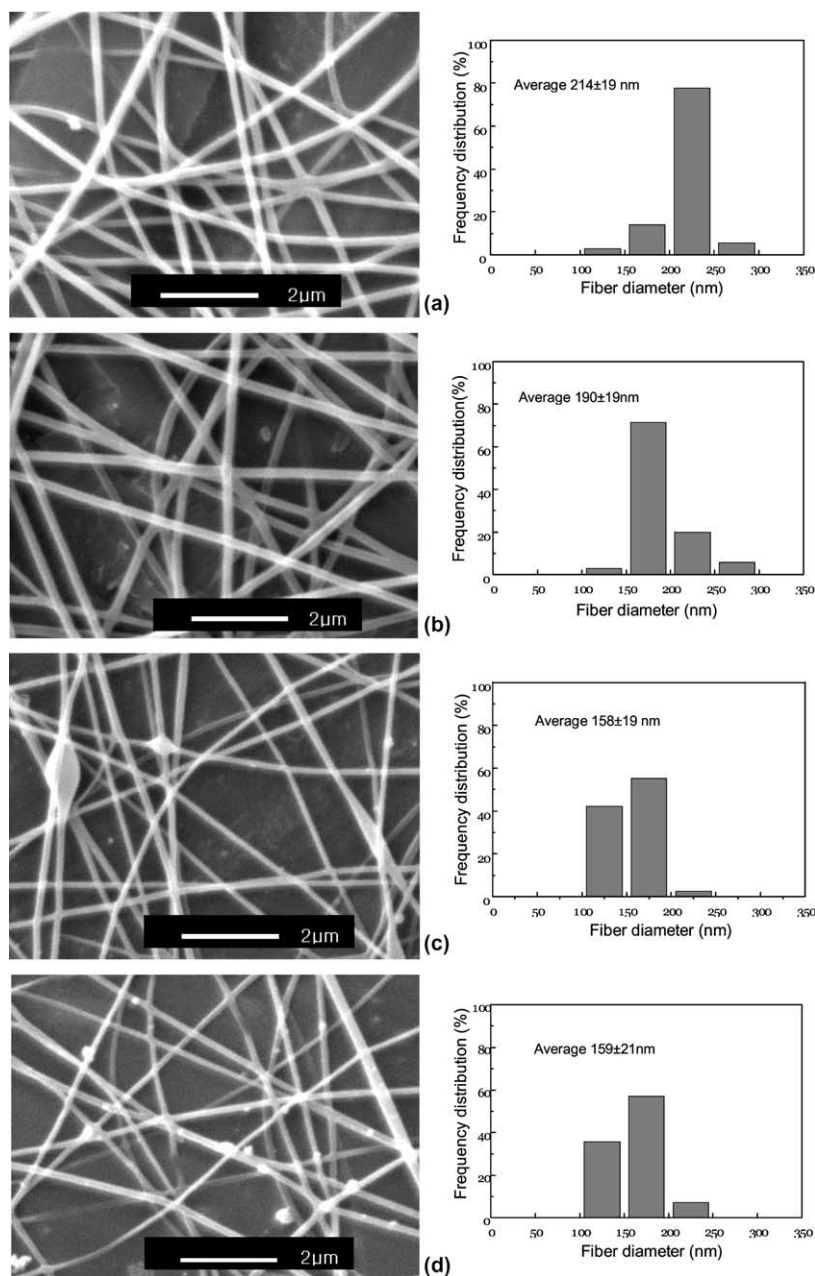


Fig. 5. Effect of NaCl amount in the PVA solution on fiber morphology (DH = 98%, voltage = 5kV, tip–target distance = 10 cm; flow rate = 0.2 ml/h). NaCl amount based on H₂O: (a) 0.05%; (b) 0.10%; (c) 0.15%; (d) 0.2%. Original magnification 10 k \times .

(Table 1 sample nos. 9–12). Fong et al. reported that beaded fibers of PEO were changed gradually from bead-fibers to ultrafine-fibers by addition of ethanol [7]. It showed that lower surface tension and higher evaporation rate of the solvent due to the addition of ethanol weakened the opportunities of bead formation. In our work, smooth fibers were changed to beaded fibers when ethanol/water ratio was more than 5:95

[Fig. 6(b–d)]. Ethanol is a solvent of PEO and its addition increased the solution viscosity [7]. However, in our work, ethanol is a nonsolvent of PVA and ethanol addition could decrease surface tension of aqueous PVA solutions, accompanied with a reduction in viscosity (Table 1). The viscosity was not high enough for stable liquid jet formation and then beaded fibers were formed.

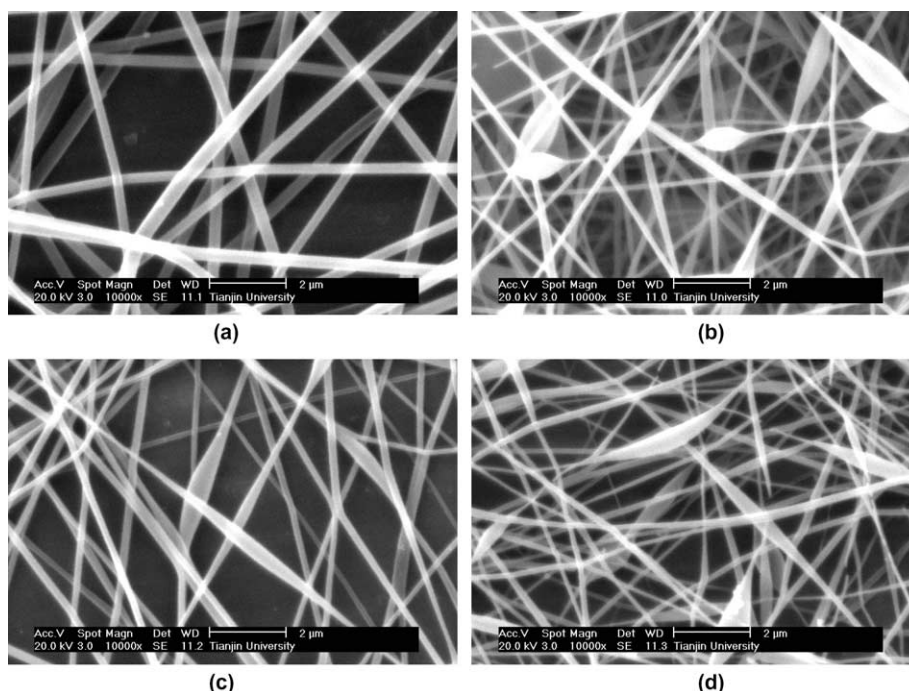


Fig. 6. Effect of addition of ethanol in PVA solution on fiber morphology (voltage = 8 kV, tip–target distance = 15 cm, flow rate = 0.2 ml/h). Ethanol/water ratio (v/v): (a) 3:97; (b) 5:95; (c) 10:90; (d) 15:85. Original magnification 10k \times .

3.6. Effect of DH

The solubility behavior of PVA with different DH values exhibits marketable changes. PVA with DH above 98% is insoluble in cold water but soluble in hot water, whereas PVA with residual acetate more than 20% is soluble in cold water but insoluble in hot water [29]. To clarify whether the solution behavior of PVA with different DHs influences the fiber morphology, electrospinning of three PVA samples with the same degree of polymerization but different DHs (Table 1, sample nos. 13–15) were carried out. Fig. 7(a) shows that flat ribbon-shaped fibers were obtained and agglomeration was apparent at some junction points of the fibers. This feature demonstrates that the electrospun PVA with 80% DH was still wet at the time it was deposited on the collector. Flat PVA fibers were also reported by Koski et al. [27]. This phenomenon began to appear at higher solution viscosity caused by higher concentration or higher molecular weight of PVA [27]. In addition to higher viscosity, it was found in our work that the conductivity of PVA with 80% DH is only 0.13 mS/cm (Table 1 sample no. 13), about an order of magnitude lower than that of PVA with 99% DH (Table 1 sample no. 15). Solution jet with lower conductivity showed relatively lower net charge density in electrospinning. It could not be stretched as much as the jet of solution with higher

conductivity. This also prevented the solution jet of PVA with 80% DH from drying thoroughly and quickly during electrospinning. Electrospun PVA with 88% DH displayed the most uniform fiber structure [Fig. 7(b)] as well as the smallest fiber diameters, 151 ± 24 nm, because of its relatively lower viscosity and higher conductivity (Table 1 sample no. 14). Beaded-fibers were observed on PVA with 99% DH. Smaller amount of fibers [Fig. 7(c)] were collected on the target than others although the electrospinning time was the same. The conductivity was gradually increased with DH increasing, as shown in Table 1 (sample no. 15). Higher solution conductivity not only resulted in thinner fiber formation but also resulted in increased instability of liquid jet in electrospinning. The homogeneous solutions of PVA with higher DH were subject to aggregation and crystallization which take place particularly at the air/solution interface [1]. These effects made the electrospinning of PVA with very high DH much more difficult. In Yao's work, aqueous solutions of 99% hydrolyzed PVA without additives could not electrospin and sporadic electrospraying of droplets was observed [28]. However, in our work, beaded fibers of PVA with 99% DH were found. This difference could be attributed to the different molecular weights of PVA. In our work, the molecular weight of PVA was 74.8 kDa, much lower than that in Yao's work (115 kDa) [28].

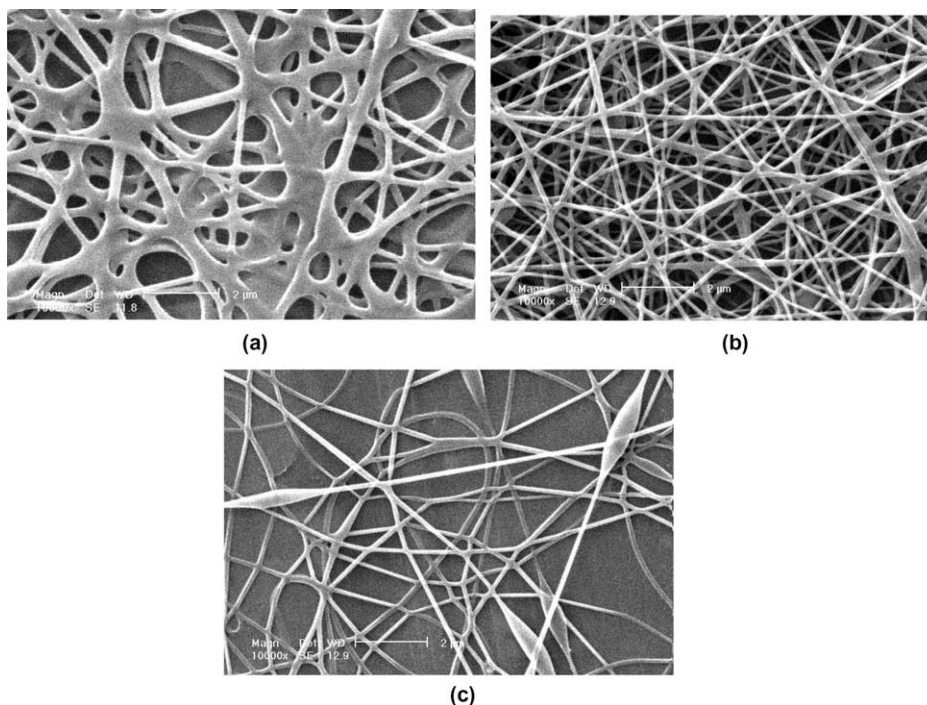


Fig. 7. Morphology of PVA fibers with different DH values from 7% PVA (voltage = 11 kV, tip–target distance = 8 cm, flow rate = 0.1 ml/h). PVA DH: (a) 80%, (b) 88%, (c) 99%. Original magnification 10k \times .

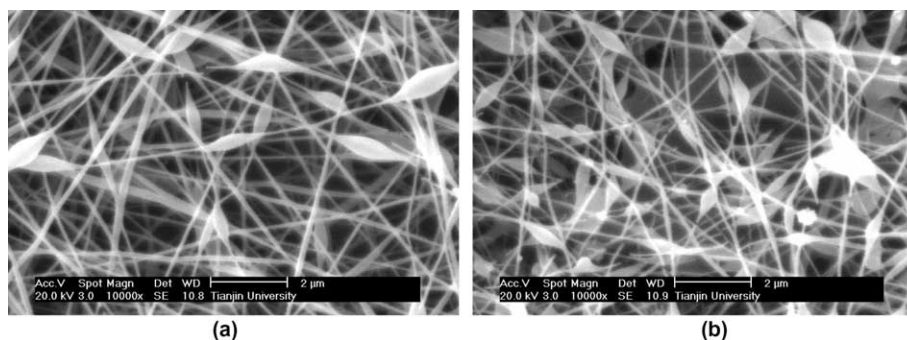


Fig. 8. SEM micrographs of electrospun fiber mats from 7% PVA solutions with aspirin and BSA respectively. (a) PVA/aspirin ratio = 100/2.5 (voltage = 8 kV, tip–target distance = 15 cm, flow rate = 0.2 ml/h); (b) PVA/BSA = 100/10 (voltage = 5 kV, tip–target distance = 10 cm, flow rate = 0.1 ml/h). Original magnification 10k \times .

3.7. Effect of aspirin and BSA

Aspirin was chosen to investigate the effect of the addition of small molecular drugs on the morphology of the electrospun PVA fibers. As shown in Fig. 8(a), with the addition of a little amount of aspirin, there appeared a great deal of beads, whose typical diameter was less than 500 nm. It was assumed that ethanol was added as the solvent of aspirin to PVA solution and induced the reduction of viscosity of blended solution, just like

the discussion in the above section of effect of ethanol amount.

The morphology of electrospun PVA blended with BSA as a type of protein drugs was also studied. Similar like aspirin, the addition of small amount of BSA brought out a lot of beads as shown in Fig. 8(b). The conductivity of PVA/BSA (90:10) solution were 1.3 mS/cm, much higher than that of pure PVA solution (0.54 mS/cm). The high conductivity of blended solution is the main reason of the instability of the process of

electrospinning and the appearance of beads and strips. On the other hand, as a protein, the molecule of BSA can't array regularly due to their complicatedly three-dimensional structures as well as strong inter- and intra-molecular forces. The blend of BSA with PVA can interrupt its complex structure and destroy molecular interactions because PVA has capacity to form secondary bonding with protein. Accordingly, the interaction of PVA and BSA resulted in the reduction of ability of forming jets of PVA solution and induced the appearance of beads.

Although the addition of aspirin and BSA to PVA solution decreased the ability of forming uniform fibers, it could demonstrate the potential of preparation of ultrafine fibers carrying drugs by electrospinning.

4. Conclusions

Submicron PVA fiber mats were prepared by electrospinning of aqueous PVA solutions. There was a slightly increase in average fiber diameter with increasing applied electric voltage. Tip–target distance had no significant effects on fiber morphology, however the morphology was slightly changed by the flow rate. With increasing the concentration of PVA solution, the morphology was changed from beaded fiber to uniform fiber structure and the fiber diameter was also increased from 87 ± 14 nm to 246 ± 50 nm. PVA Fiber diameters were gradually decreased from 214 ± 19 nm to 159 ± 21 nm with increasing amount of NaCl. It was also found that smooth fibers were changed to beaded fibers when ethanol amount was higher than 5%. The morphology of electrospun PVA changed from the ribbon-like fibers to uniform fibers and then to beaded fibers when the DH value of PVA was increased from 80% to 99%. The addition of aspirin and BSA made the formation of beads in the electrospun PVA mats.

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