

Effect of Experimental Parameters on Nanofiber Diameter from Electrospinning with Wire Electrodes

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Abstract. Polyvinylidene Fluoride (PVDF) nanofibers were electrospun by Nanospider equipment with wire electrodes. The parameters which would influence the fiber diameter were investigated in terms of solution concentration, cartridge speed (feed rate of solution), voltage, electrode distance, rotating wire speed, winding speed and slit diameter. The morphology and diameter of fibers were observed by scanning electron microscope. The results revealed that the solution concentration had significant influence on both fiber morphology and fiber diameter; the cartridge speed, voltage, electrode distance and slit diameter had slight effect on fiber diameter since the standard deviations were large; the rotating wire speed and the winding speed had insignificant influence on fiber diameter.

1. Introduction

A nanofiber is a fiber with a diameter of 100 nanometers or less[1]. The most attractive feature of nanofiber is its very high specific surface area, which provides it some remarkable properties, i.e., high capacity for the attachment or release of functional groups, absorbed molecules, ions, catalytic moieties and nano-scale particles[2], great effect on the chemical, biological reactivity, electro-activity[3], better rectification properties as well as better transport[4], higher tensile strength and strain energy[5, 6].

The birth of nanofiber can be traced back to 1934 when Formhals produced nanoscale fibers by electrospinning for viscoelastic solutions[7]. But the nanofiber had not stirred up much interest for its limitation in production and applications until 1990s when D.H. Reneker's group demonstrated that many organic polymers could be electrospun into nanofibers [8-10].

Even though several techniques appeared for generating nanofibers in the past several decades, i.e., conjugate spinning, chemical vapor deposition, drawing, template synthesis, self-assembly, meltblown, and electrospinning [2]. Among these techniques, only meltblown and electrospinning can reach the industrial scale production, which make the practical applications possible. But the diameters of fibers from meltblown technology often have a broad range from nano-scale to above 20 μm [11], which limits the usage of meltblown nanofibers when the small diameters of fibers and uniformity of fiber diameters are required. Electrospinning has been proven to be an ideal method of producing continuous nanofibers. The biggest advantages of this technology is the great simplicity of the electrospinning process[2, 11], its versatility in processing a wide range of polymers, and the consistency in producing nanofibers with controllable fiber diameter and morphology[12].

The principle of electrospinning is to produce nanofiber by electrostatic forces[13]. The process of electrospinning is to draw electrically charged jets from polymer solution or melts in an electric field



caused by high voltage towards to an oppositely charged collector[14]. In a conventional electrospinning setup system, a needle nozzle/syringe is often used as a jet outlet. But the production rate of nanofiber is very low which limits its commercial applications. In order to improve the productivity of nanofibers, several significant innovations in electrode have been done i.e., multi-needle system[15], cylindrical porous hollow tube system[16], roller electrode system [17], bubble free-surface system[18], and wire electrodes system [19]. The fiber production from needle, cylinder and coil technology was introduced by [20-23], but the fiber from wire technology hasn't been reported. Poly (vinylidene fluoride) (PVDF) has been widely used as a membrane material thanks to its good chemical resistance, great mechanical properties and high thermal stability [24-27]. It is broadly applied in ultrafiltration (UF), microfiltration (MF), membrane distillation (MD) and other membrane processes[27, 28]. Therefore, the diameter of nanofibers from wire electrospinning technology was investigated under different conditions for better controlling the quality of fibers and final products.

2. Materials and methods

Polyvinylidene Fluoride Powder (average molecular weight 600,000~700,000) was provided by Arkema Group, Dimethylacetamide (DMAc) was provided by PENTA Chemicals. Tetraethylammonium bromide (TEAB) was obtained from Sigma Aldrich.

PVDF was dissolved in DMAc with concentration of 8%, 10%, 12% and 14% in w/w, and before electrospinning process, 2% TEAB was added into the PVDF solution. Nanofibers were electrospun from PVDF solution under different operating conditions in terms of cartridge speed, rotation wire speed, winding speed, electrodes distance, slit diameter, and voltage. The temperature and humidity were controlled at 23 ± 0.5 °C and 18 ± 1 %. The specific process parameters are given in table 1.

The conductivity of solution was measure by SCHOTT instruments (Model: k00090-L), and the solution viscosity was measured by HAAKE Viscotester E from Thermos Scientific Company. The fiber morphology was observed under scanning electron microscope (SEM). The average fiber diameter was calculated from the SEM images using image analysis software. More than 100 fibers were counted from at least 3 SEM images which were taken from different places of a sample.

The main part of electrospinning is shown in figure 1. The polymer solution was contained in a cartridge which has a slit on it; a steel wire acted as an electrode passed the cartridge through the slit and contacted with polymer solution; the cartridge was able to have reciprocating motions onto the steel wire, and left solution droplets on it. Therefore, the solution droplets were exposed to a strong electrical field which provided by high voltage power supply through two electrodes. Once the applied voltage exceeded a critical value, jetting of polymer solution was initiated, and collected by the supporting material. As the charged jets travel toward the supporting material, the solvent evaporates, resulting in solid fibers.

Table 1. Process parameters of electrospinning

Parameters	Values					
Concentration (%)	8	10	12	14		
Cartridge speed (mm/s)	200	300	400	500		
Voltage (kV)	-10/+40	-10/+45	-10/+50	-10/+55	-10/+60	
Electrodes distance (mm)	160	170	180	190	200	
Rotating wire speed (mm/min)	40	80	125	165	215	
Winding speed (mm/min)	100	200	300	400	500	600
Slit diameter (mm)	0.5	0.6	0.7	0.8	1.0	

Note: all the combinations of these process parameters were carried out.

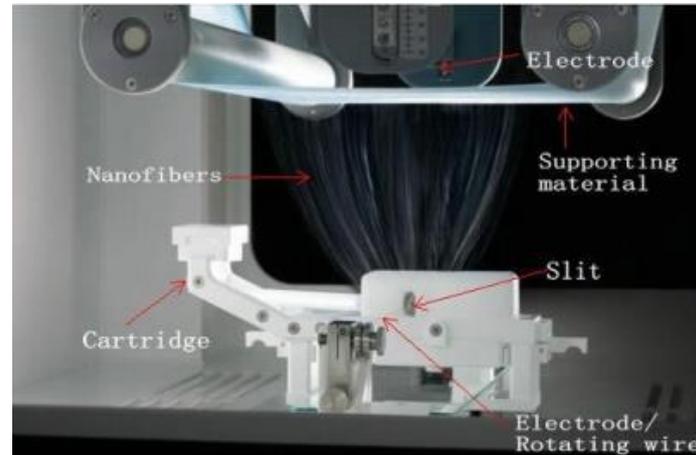


Figure 1. Picture of electrospinning[29]

3. Results and discussions

Both viscosity and conductivity are important factors for electrospinning, which are given in table 2 responding to different solution concentrations. The conductivity of solutions decreased with the increase of solution concentration; however, all these values are higher enough for electrospinning[30]. The increase of viscosity of solutions occurred responding to the solution concentration.

Table 2. Viscosity and conductivity of PVDF solutions

Solution Concentration (%)	Viscosity (mPa s at 23 °C)	Conductivity ($\mu\text{S}/\text{cm}$ at 23 °C)
8	304.2	103.4
10	553.6	96.1
12	1317.1	90.4
14	1845.3	83.8

3.1. Effect of solution concentration on fiber diameter

Solution concentration was taken as variable while other process parameters were kept constant as given in table 3.

Table 3. Process parameters during electrospinning

Temperature (°C)	Humidity (%)	Electrode distance (mm)	Voltage (kv)	Cartridge speed (mm/s)	Rotation wire speed (mm/s)	Slit diameter (mm)	Winding speed (mm/min)
23	18	180	-10/50	300	40	0.5	200

T: temperature, H: humidity, ED: electrode distance, V: voltage, CS: cartridge speed, RWS: rotating wire speed, SD: slit diameter, WS: winding speed

The images of nanofibers from different solution concentrations are given in figure 2. Almost all the fibers had the beads in their structure when the concentration was 8 wt% (as shown in Fig. 2A). The beads disappeared when concentration increased to 10 wt%; however, many fibers were attaching to each other and extended like webbed hands (as shown in Fig. 2B). When the concentration was over 10 wt%, the more obvious solid fiber-structure fibers appeared (as shown in Fig. 2 C&D). These images revealed that the solution concentration had a very important influence on morphology of fibers.

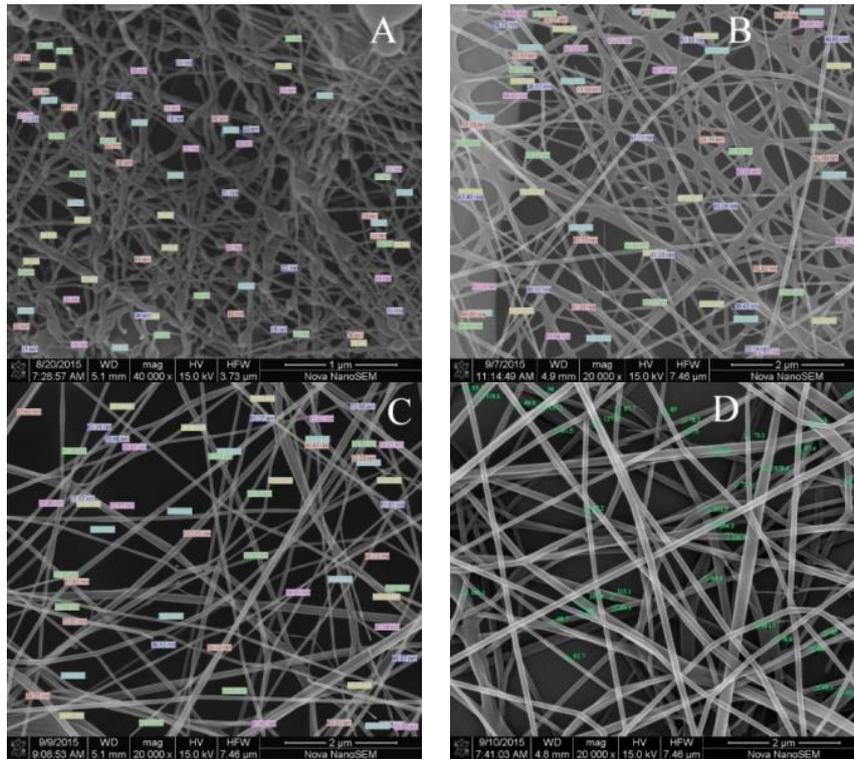


Figure 2. The SEM images of fibers from solutions with different concentrations (A) 8%; (B) 10%; (C) 12%; (D) 14%.

The fiber diameter increased significantly with the increase of concentration; however, the standard deviation indicated that the diameters of fibers were distributed in a large range (as shown in figure 3). The phenomenon of fiber diameter increase with concentration was observed by many researchers [20-22]. This phenomenon could be easily explained by the polymer concentration in solution. However, it's worth noting that the mass of droplet separated from solution induced for electrospinning by strong electric field must be different due to the different surface tensions of solutions with different concentrations. This could also be helpful for explaining the relationship (linear or non-linear) between fiber diameter and solution concentration.

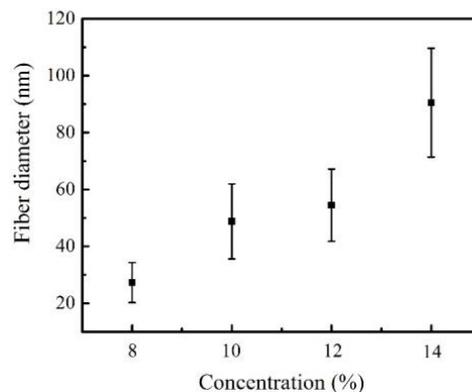


Figure 3. Relationship between solution concentration and fiber diameter

3.2. Effect of cartridge speed on fiber diameter

The solution was evenly deposited onto the wire electrode as the back-and-forth motion of cartridge. The cartridge speed (or frequency) is adjustable; more solution will be deposited onto the wire electrode

when the cartridge speed is higher, vice versa. This process is equivalent to the feed rate of needle electrospinning. The SEM images of fibers and the relationship between cartridge speed and fiber diameter are given in figure 4 and figure 5.

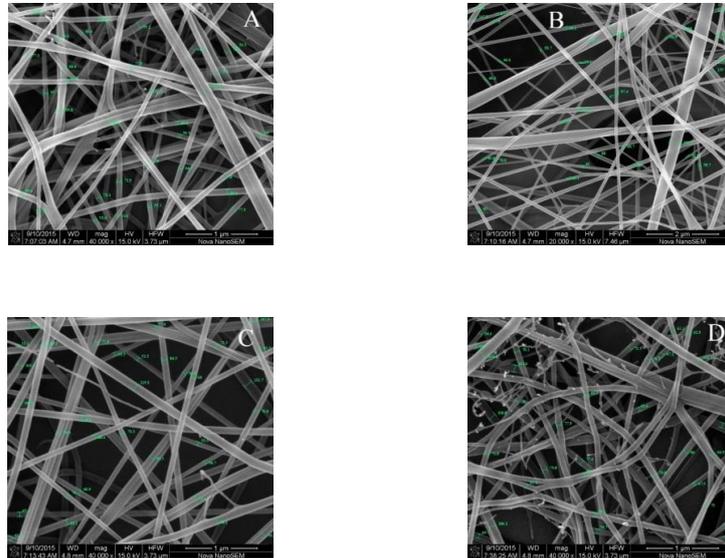


Figure 4. Images of fibers from 14 % solution at different cartridge speed, (A) 200 mm/min, (B) 300 mm/min, (C)400 mm/min , (D) 500 mm/min

There is no significant difference in fiber diameter by changing the cartridge speed (as shown in Fig. 5). Once the feed rate is sufficient for forming fibers, and the electric force is able to overcome the capillary force, then the mass of droplet separated from solution by electric force should be the same. Therefore, the higher cartridge speed only provided more polymer solution and then more fibers. In another case, if the cartridge speed is too high, and the feed solution is over the capacity of fiber formation by electric field, then the over-feed solution will drop down from the wire electrode (this phenomenon was observed during electrospinning process).

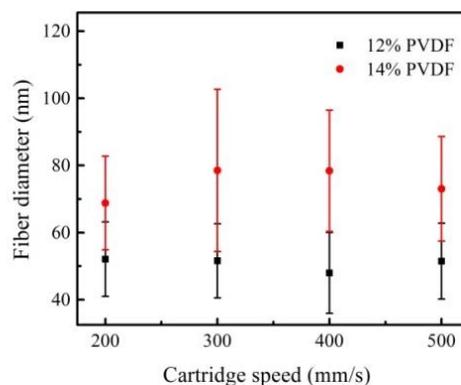


Figure 5. Relationship between cartridge speed and fiber diameter

3.3. Effect of voltage on fiber diameter

The SEM images of fibers under different voltages are given in figure 6, all the fibers had very good morphology, and a few fibers had much larger diameter when the applied voltage was over 60 kV.

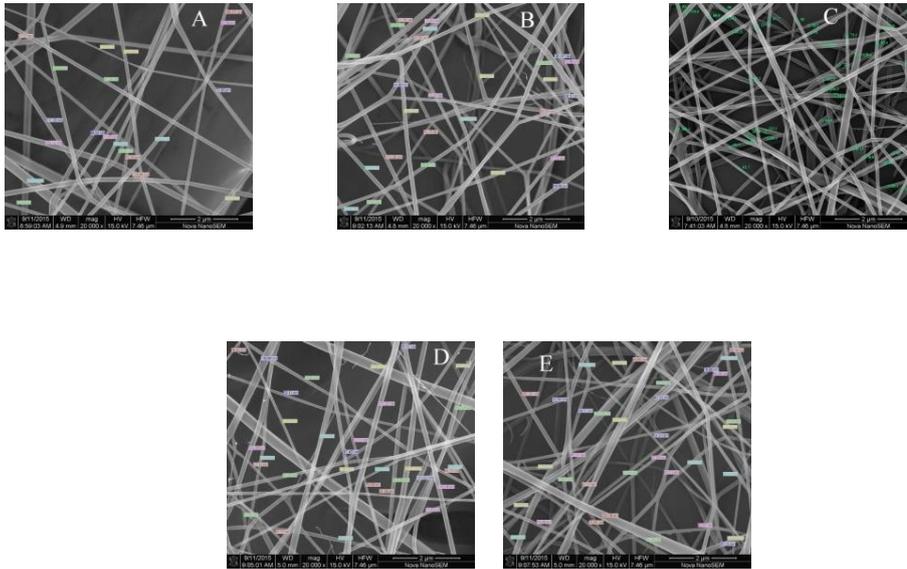


Figure 6. Images of fibers under different voltage (A) 50 kV, (B) 55 kV, (C) 60 kV, (D) 65 kV, (E) 70 kV

The fiber diameter had a very slight increase with the increase of applied voltage, but the difference is insignificant owing to the large range of standard deviation (as seen in figure 7). Vince Beachley and Dhananjay reported the decrease of fiber diameter with the increase of applied voltage for needle electrospinning [21, 31]. In contrary, Huan stated that the fiber diameter increased with the increase of applied voltage for needle electrospinning, and also pointed out the existence of optimal applied voltage for narrowing the fiber diameter distribution [23]. Wang investigated the fiber diameter by free surface electrospinning, revealed the slight finer fibers from higher applied voltage; however, the productivity of fibers dramatically increased under higher voltage [22]. However, the author tends to believe that the higher voltage (stronger electric field intensity) is able to draw bigger droplets from solution; therefore, the fiber diameter could be larger (figure 6 D&E).

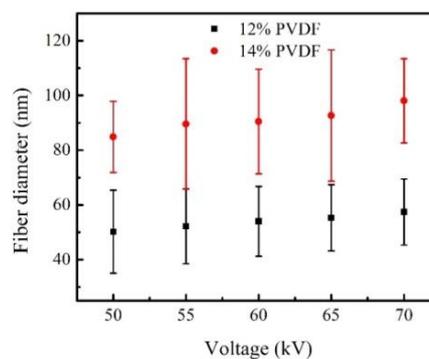


Figure 7. Relationship between voltage and fiber diameter

3.4. Effect of electrode distance on fiber diameter

The images of fibers at different electrode distances are given in figure 8.

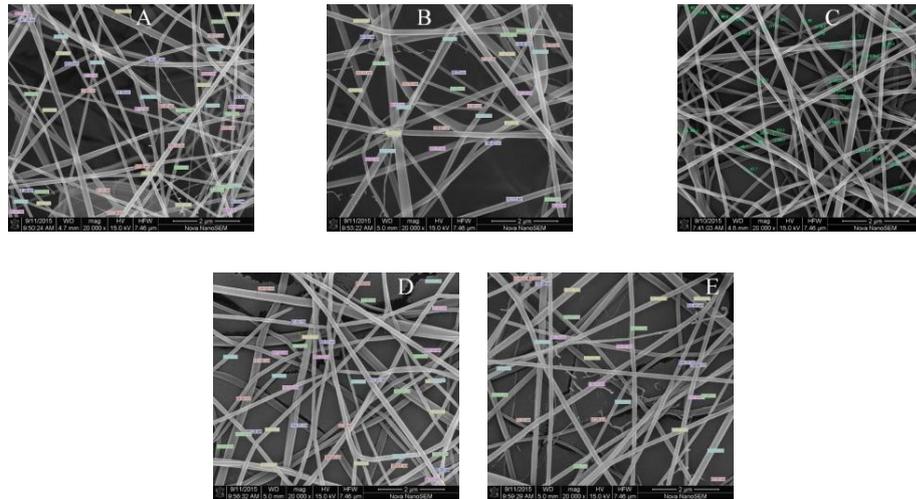


Figure 8. Images of fibers at different electrode distances (A) 160 mm, (B)170 mm, (C)180 mm, (D) 190mm, (E) 200mm

As shown in figure 9, the fiber diameter from 12% solution had a slight decrease when the electrode distance increased; but there is no regular trend to describe the change of fiber diameter from 14% solution. The increase of distance between two electrodes will lead to weaker electric field intensity, and longer travelling path of fibers, which could be the reasons for decrease of fiber diameter at larger distance between electrodes. However, there was an uncertain factor would influence the fiber diameter, i.e. the airflow exchange between electrospinning chamber and external environment. The motion of airflow would change the travelling path of fibers.

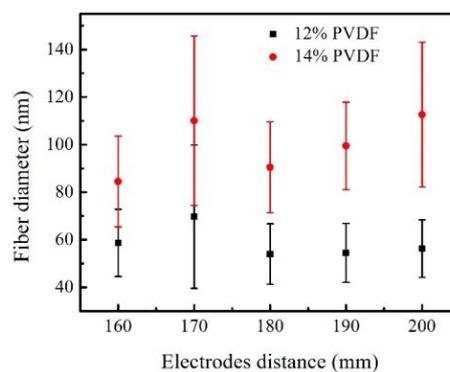


Figure 9. Relationship between electrode distance and fiber diameter

3.5. Effect of rotating wire speed on fiber diameter

The bottom wire electrode is dynamic, and transferred from one glide wheel to another in order to make sure that the electrode is always clean keeping the electrospinning process in a good condition. The images of fibers at different rotating wire speed are given in figure 10, and the relationship between rotating wire speed and fiber diameter is given in figure 11. The influence in fiber diameter was small when rotating wire at low speed, only one obvious drop in fiber diameter occurred when rotating wire speed was 215 mm/min.

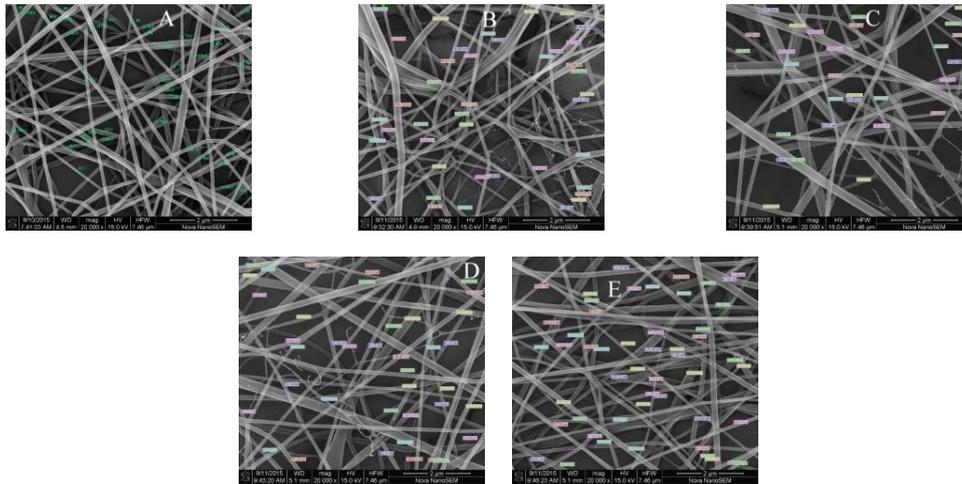


Figure 10. Images of fibers at different rotating wire speed (A) 40 mm/min, (B) 80mm/min, (C) 125mm/min, (D) 165mm/min, (E) 200mm/min

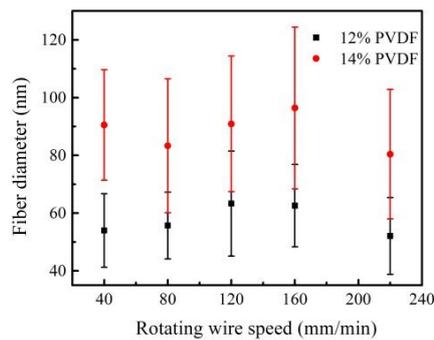
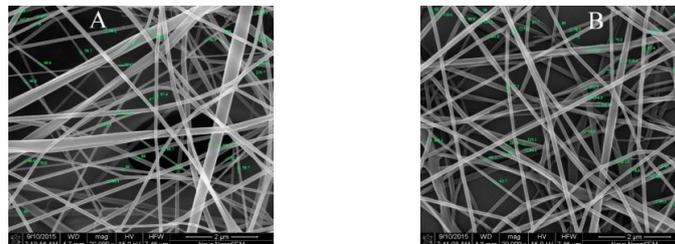


Figure 11. Relationship between rotating wire speed and fiber diameter

3.6. Effect of winding speed on fiber diameter

The winding speed had significant effect on the areal density of nanofibrous mat (figure 12). However, it did not show obvious effect on fiber diameter as shown in figure 13. The higher winding speed provided larger area of supporting material; and in the same period of time, the amount of fibers was the same. Thereby, less fibers and thinner layer of nanofibrous mat were appeared on the supporting material.



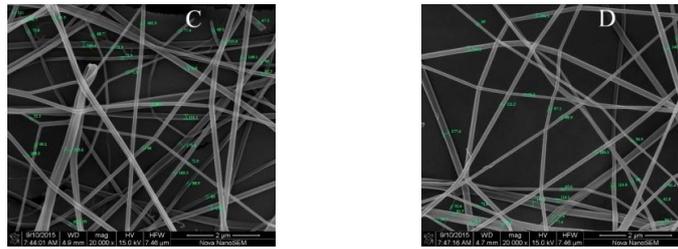


Figure 12. Images of fibers at different winding speed (A) 00 mm/min, (B) 200mm/min, (C) 300 mm/min, (D) 400mm/min

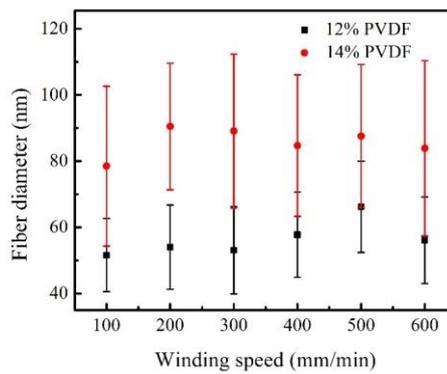


Figure 13. Relationship between winding speed and fiber diameter

3.7. Effect of slit diameter on fiber diameter

The larger the slit diameter is, the more solution would leak out from the cartridge, and attaches onto the wire electrode. The images of fibers are given in figure 14.

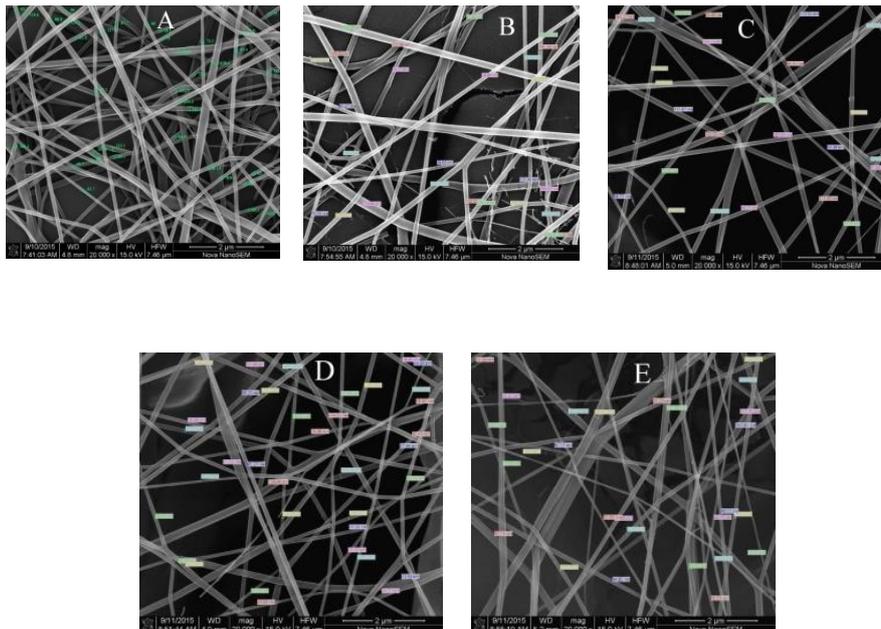


Figure 14. Images of fibers from different slit size (A) 0.5 mm, (B) 0.6 mm, (C) 0.7 mm, (D) 0.9 mm, (E) 1 mm

The fiber diameter increased when the slit diameter increased for solution of 12% concentration. But there was a slight decrease in fiber diameter for solution of 14% concentration when slit diameter changed from 0.5 mm to 0.9 mm. An obvious fiber diameter increase for both solutions when 1 mm slit diameter was applied (as shown in figure 15).

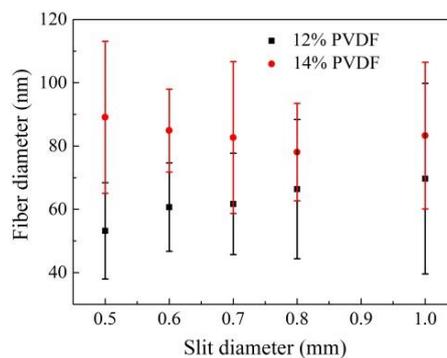


Figure 15. Relationship between slit diameter and fiber diameter

4. Conclusion

Nanofibers were produced by electrospinning equipment with wire electrodes, and the process parameters were adjusted according to the experimental design in order to investigate the influence of process parameters on fiber diameter. After evaluating the fiber diameter, some conclusions can be drawn. The morphology and fiber diameter were significantly influenced by solution concentration; the cartridge speed, voltage, electrode distance and slit diameter had slight effect on fiber diameter, meanwhile, the standard deviation were large; the rotating wire speed and the winding speed hardly had influence on fiber diameter.

5. References

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