Chapter 2
Effects of Working Parameters on Electrospinning

Abstract Working parameters are very important to understand not only the nature of electrospinning but also the conversion of polymer solutions into nanofibers through electrospinning. Those parameters can be broadly divided into three parts such as solution parameters, process parameters, and ambient parameters. Each of those parameters can affect the fibers morphologies and by proper control of those parameters we can fabricate electrospun fibers with desired morphologies and diameters. In this chapter, we will present a concise introduction of those parameters and their influence on fiber properties.

Keywords Electrospinning • Solution parameters • Process parameters • Ambient parameters

In Sect. 2.1, we describe the affections of solution parameters on the conversion of polymer solutions into nanofibers during the electrospinning. The affections of process parameters and ambient parameters will be discussed in Sects. 2.2 and 2.3. For each of these affections, examples are presented, respectively.

2.1 Solution Parameters

2.1.1 Concentration

The concentrations of polymer solution play an important role in the fiber formation during the electrospinning process. Four critical concentrations from low to high should be noted:

1. As the concentration is very low, polymeric micro (nano)-particles will be obtained. At this time, electrospray occurs instead of electrospinning owing to the low viscosity and high surface tensions of the solution [1].
2. As the concentration is little higher, a mixture of beads and fibers will be obtained [2–4].
3. When the concentration is suitable, smooth nanofibers can be obtained [2–4].
4. If the concentration is very high, not nanoscaled fibers, helix-shaped micro-ribbons will be observed [5].

To clearly see the evolution of the products with different critical concentrations from low to high, four typical SEM images have been used to illustrate the whole change (Fig. 2.1).

Usually, increasing the concentration of solution, the fiber diameter will increase if the solution concentration is suitable for electrospinning. Additionally, solution viscosity can be also tuned by adjusting the solution concentration.

### 2.1.2 Molecular Weight

Molecular weight of the polymer also has an important effect on morphologies of electrospun fiber. In principle, molecular weight reflects the entanglement of polymer chains in solutions, namely the solution viscosity. Keep the concentration fixed, lowering the molecular weight of the polymer trends to form beads rather than smooth fiber. Increasing the molecular weight, smooth fiber will be obtained. Further increasing the molecular weight, micro-ribbon will be obtained (Fig. 2.2) [6].

It is also important to note that too high molecular weight favors the formation of micro-ribbon even with the low concentration as shown in Fig. 2.3 [7]. Additionally, the authors also found that as the molecular weight is very high, some patterned fibers can also be obtained at low concentration (Fig. 2.4).

However, it is also important to point out that the molecular weight is not always essential for electrospinning if sufficient intermolecular interactions can be supplied by oligomers. For example, Long and McKee successfully obtained the
oligomer-sized phospholipid fibers from lecithin solutions via electrospinning. They found that as the concentration of phospholipid is higher than 35 wt. %, smooth fiber could be obtained [8].

Fig. 2.2 Photographs showing the typical structure in the electrospun polymer for various molecular weights. a 9000–10,000 g/mol; b 13,000–23,000 g/mol; and c 31,000–50,000 g/mol (solution concentration: 25 wt. %). Reprinted from Ref. [6], copyright 2004, with permission from Elsevier

Fig. 2.3 SEM images of the morphologies of the polyacrylamide with ultrahigh MW \(9 \times 10^6 \text{ g/mol}\). The concentration of a and b is 2 wt. % and 2.5 wt. %, respectively. Reproduced from Ref. [7] by permission of John Wiley & Sons Ltd

Fig. 2.4 SEM images of the helical fibers and zigzag ribbon. The molecular weight of the polyacrylamide is \(9 \times 10^6 \text{ g/mol}\). Reproduced from Ref. [7] by permission of John Wiley & Sons Ltd
2.1.3 Viscosity

Solution viscosity is the critical key in determining the fiber morphology. It has been proven that continuous and smooth fibers cannot be obtained in very low viscosity, whereas very high viscosity results in the hard ejection of jets from solution, namely there is a requirement of suitable viscosity for electrospinning [9, 10]. Generally, the solution viscosity can be tuned by adjusting the polymer concentration of the solution; thus, different products can be obtained as shown in Fig. 2.5. The viscosity range of a different polymer or oligomer solution at which electrospinning is done is different. It is important to note that viscosity, polymer concentration, and polymeric molecular weight are related to each other. For solution of low viscosity, surface tension is the dominant factor and just beads or beaded fiber formed. If the solution is of suitable viscosity, continuous fibers can be obtained. A number of papers on such interrelationships have been published [6, 11–15].

2.1.4 Surface Tension

Surface tension, as the function of solvent compositions of the solution, is quite important factor in electrospinning. In 2004, Yang and Wang systematically investigated the influence of surface tensions on the morphologies of electrospun products with PVP as model with ethanol, DMF, and MC as solvents (Fig. 2.6) [5]. They found that different solvents may contribute different surface tensions. With the concentration fixed, reducing the surface tension of the solution, beaded fibers can be converted into smooth fibers.
Additionally, they also demonstrated that the surface tension and solution viscosity can be adjusted by changing the mass ratio of solvents mix (Fig. 2.7) and fiber morphologies (Fig. 2.8). Basically, surface tension determines the upper and lower boundaries of the electrospinning window if all other conditions are fixed [16–18].

2.1.5 Conductivity/Surface Charge Density

Solution conductivity is mainly determined by the polymer type, solvent sort, and the salt. Usually, natural polymers are generally polyelectrolytic in nature, in which the ions increase the charge carrying ability of the polymer jet, subjecting to higher tension under the electric field, resulting in the poor fiber formation in contrast to the synthetic counterpart [19]. Additionally, the electrical conductivity of the solution can be tuned by adding the ionic salts like KH$_2$PO$_4$, NaCl, and so on [20]. With the aid of ionic salts, nanofibers with small diameter can be obtained. Sometimes high solution conductivity can be also achieved by using organic acid as the solvent. For example, Hou et al. [20] used formic acid as the solvent to

**Fig. 2.6** TEM images of the PVP nanofibers electrospun from ethanol (a), MC (b), and DMF (c), respectively. The concentration of PVP is fixed at 4 wt. %. Reproduced from Ref. [5] by permission of John Wiley & Sons Ltd

**Fig. 2.7** Surface tension and viscosity as functions of mass ratio of ethanol/DMF. Reproduced from Ref. [5] by permission of John Wiley & Sons Ltd
dissolve the nylon and obtained ultrathin (3 nm) electrospun nylon-beaded fibers (Fig. 2.9). In their study, small amount of pyridine has been also added into the solution to eliminate the beads by increasing the conductivity of the solution. All those data mentioned above indicate that increase in the solution conductivity favors the formation of thinner fibers.

2.2 Processing Parameters

2.2.1 Voltage

Within the electrospinning process, applied voltage is the crucial factor. Only the applied voltage higher than the threshold voltage, charged jets ejected from Taylor Cone, can occur. However, the affection of the applied voltages on the diameter of
electrospun fibers is a little controversial. For example, Reneker and Chun [21] have demonstrated that there is not much effect of electric field on the diameter of electrospun polyethylene oxide (PEO) nanofibers. Several groups suggested that higher voltages facilitated the formation of large diameter fiber. For example, Zhang et al. [18] investigated the effect of voltage on morphologies and fiber diameters distribution with poly (vinyl alcohol) (PVA)/water solution as model (Fig. 2.10).

Several groups suggested that higher voltages can increase the electrostatic repulsive force on the charged jet, favoring the narrowing of fiber diameter. For example, Yuan et al. [22] investigated the effect voltage on morphologies and fiber alignment with polysulfone (PSF)/DMAC/acetone as model (Fig. 2.11).

In addition to those phenomena, some groups also demonstrated that higher voltage offers the greater probability of beads formation [1, 23, 24].

Thus, we can found that voltage does influence fiber diameter, but the level of significances varies with the polymer solution concentration and on the distance between the tip and the collector [25].

### 2.2.2 Flow Rate

The flow rate of the polymer solution within the syringe is another important process parameter. Generally, lower flow rate is more recommended as the polymer solution will get enough time for polarization. If the flow rate is very high, bead fibers with thick diameter will form rather than the smooth fiber with thin diameter owing to the short drying time prior to reaching the collector and low stretching forces. For example, Yuan et al. [23] investigated the effect of the flow rate on the morphologies of the PSF fibers from 20 % PSF/DMAC solution at 10 kV (Fig. 2.12). In their study, bead fibers with thicker diameters can be obtained as the flow rate is 0.66 ml/h.

### 2.2.3 Collectors

During the electrospinning process, collectors usually acted as the conductive substrate to collect the charged fibers. Generally, Al foil is used as a collector but it is difficult to transfer the collected nanofibers to other substrates for various applications. With the need of fibers transferring, diverse collectors have been developed including wire mesh [26], pin [27], grids [28], parallel or gridded bar [29], rotating rods or wheel [29], liquid bath [30], and so on (Fig. 2.13).
Fig. 2.10 Effect of voltage on morphology and fiber diameter distribution from a 7.4 wt. % PVA/water solution (DH = 98 %, tip–target distance = 15 cm, flow rate = 0.2 ml/h). Voltages: a 5; b 8; c 10; and d 13 kV. Reprinted from Ref. [18], copyright 2005, with permission from Elsevier.
2.2.4 Distance (H) Between the Collector and the Tip of the Syringe

It has been proven that the distance (H) between the collector and the tip of the syringe can also affect the fiber diameter and morphologies [12]. In brief, if the distance is too short, the fiber will not have enough time to solidify before reaching the collector, whereas if the distance is too long, bead fiber can be obtained. It is well known that one important physical aspect of the electrospun fiber is the dryness from the solvent, so optimum distance is recommended. For example, Yuan et al. [22] demonstrated that a little long distance favors the thinner fiber diameter as shown in Fig. 2.14.

Fig. 2.11  SEM images of the ultrafine fibers electrospun from a 20 % PSF solution in DMAC/acetone (9:1) under different voltages. The applied voltages of A, B, and C are 10, 15, and 20 kV, respectively. The average diameters of A, B, and C are 344 ± 51, 331 ± 26, and 323 ± 22 nm, respectively. Reproduced from Ref. [22] by permission of John Wiley & Sons Ltd

Fig. 2.12  SEM images of the effect of the flow rate on the morphologies of the PSF fibers from 20 % PSF/DMAC solution at 10 kV. Flow rates of A and B are 0.40 and 0.66 ml/h, respectively. Reproduced from Ref. [22] by permission of John Wiley & Sons Ltd

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Fig. 2.13 SEM images of the different electrospun products with different types of collectors. 

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d and e Reproduced from Ref. [29] by permission of John Wiley & Sons Ltd; 
f Reproduced from Ref. [30] by permission of John Wiley & Sons Ltd.
2.3 Ambient Parameters

Ambient parameters can also affect the fiber diameters and morphologies such as humidity, temperature. For example, Mituppatham et al. [31] had proven that increasing temperature favors the thinner fiber diameter with polyamide-6 fibers for the inverse relationship between the solution viscosity and temperature (as shown in Fig. 2.15).

As for the humidity, low humidity may dry the solvent totally and increase the velocity of the solvent evaporation. On the contrary, high humidity will lead to the thick fiber diameter owing to the charges on the jet can be neutralized and the stretching forces become small. Recently, Casper et al. [32] demonstrated that the variety of humidity can also affect the surface morphologies of electrospun PS fibers (Fig. 2.16).

![Fig. 2.14](image1.png) SEM images of the electrospun PSF fibers from 20 wt. % PSF/DMAC solution at 10 kV with different distances. The distances of A and B are 10 and 15 cm, respectively. The diameters of A and B are 438 ± 72 and 368 ± 59 nm, respectively. Reproduced from Ref. [22] by permission of John Wiley & Sons Ltd

![Fig. 2.15](image2.png) SEM images of the electrospun PA-6-32 fibers under different temperatures. The temperatures of A and B are 30 and 60 °C, respectively. The diameters of A and B are 98 and 90 nm, respectively. Reproduced from Ref. [30] by permission of John Wiley & Sons Ltd
Fig. 2.16 FESEM images of surface morphologies of electrospun PS fibers under varying humidity: a 25%, b 31–38%, c 40–45%, d 50–59%, e 60–72%. Reprinted with the permission from Ref. [32]. Copyright 2004 American Chemical Society
References


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