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Nanofibrous membrane through multi-needle electrospinning with multi-physical field coupling

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Abstract

The mass electrospinning is the key way to promote the industrial application of nanofibrous membrane, in which the multi-parameter controlling is the challenge for the multi-needle electrospinning. A constant temperature and humidity environment was introduced to studied the effect of process parameters on the ejection process of multi-needle electrospinning process. This article focused on the nanofiber deposition behaviors of multi-needle electrospinning from two different polymer solution of aqueous solution of poly (ethylene oxide) and the non-aqueous solution of polyvinylidene fluoride. We found that the same humidity has opposite effects on the deposition morphology of the water-soluble material PEO and the non-water-soluble material PVDF electrospun fiber. At the same time, we explored the effects of solution conductivity, solvent volatility, temperature and viscosity on electrospinning on water-insoluble and water-soluble materials. What this paper aim is to provide a process debugging reference for the batch preparation of nanofibers of different materials by multi-needle electrospinning.

1. Introduction

Electrospinning is a typical multi-physical coupled fields process, in which the morphology of electrospun nanofiber is influenced by lots of parameters, such as applied voltage, space electric field distribution, surface charge density, liquid supply rate, solution surface tension, viscosity, conductivity, environment temperature and humidity [1–9]. At the same time, the preparation of more and more versatile fibers has become a research trend [10–17]. The environment humidity is the key factor to the electrospinning process, the diameter and morphology of electrospun nanofiber. In 2004, Cheryl found that when the humidity was lower than 25%RH for spinning, the polystyrene (PS) nanofiber with smooth surface can be gained; when the humidity was greater than 30% porous structures were appeared on the nanofiber surface, and the pores became larger with the increasing of humidity [18]. In 2007, Sureeporn used aqueous solution of polyethylene oxide (PEO) to study the effect of environment humidity on the nanofibrous nanofiber, with the increasing of humidity increased, the average diameter of the fibers became smaller, but the string of beads in the fibers became larger [19]. In 2009, Vrieze found that with the decreasing of the lower the solubility of polyvinyl pyrrolidone (PVP) solution concentration, higher humidity is required for the production of nanofibrous membrane, but nanofiber diameter decreased with the increasing of humidity, the fiber [20]. Kazuto studied electrospinning process of PA6 solution, the fiber diameter decreased with the increasing of humidity [21]. In 2011, Huang found that humidity not only affected the surface morphology of nanofibers, but also affected the diameter distribution of nanofibers [22]. In 2011, Oliver found that the cellulose acetate (CA) nanofiber diameter decreased with the
increasing of temperature, but increased with the increasing of humidity [23]. Fashandi’s studied the surface and internal morphology of polystyrene (PS) nanofiber, which were related to the solvent of the raw material as well as to the temperature and humidity [24]. The higher the humidity, the rougher the surface; and the higher the temperature, the smoother the surface. With the increase of humidity or the temperature, the beading phenomenon will weaken. With the increase of temperature, the fiber diameter will become thicker [24]. Roya studied the effect of humidity on fiber morphology in 2013, proposed that low concentration solution and low humidity environment are easy to produce beads in PCU materials [25]. In 2013, Cai found that with the increase of humidity, the current and jet diameter of water-soluble PEO materials become smaller. For PVP materials, the fiber diameter is positively correlated with the jet diameter. It is found that the fiber diameter decreases with the increase of ambient humidity [26]. In 2013, Jan found that the average fiber diameter of water-soluble PVA and PEO solutions decreased with the increase of humidity [27].

The systematic study on the influence of multi-parameter coupling on electrospinning deposition process is required urgently for the industry application. Therefore, the process guidance for electrospinning industry production is not enough. This paper will make an in-depth study of water-soluble materials and non-water-soluble materials respectively. The comparison of the effect of temperature and humidity on the morphology of multi-needle electrospun fiber in the two solvent systems has important guiding significance for the industrial production of electrospinning.

2. Experiment

2.1. Experiment equipment

As shown in the schematic diagram of figure 1, a mass electrospinning spinneret with 32-needle is assembled into the equipment. The distance between the needles is 20 mm, the length of the needle is 15 mm, and the distance between the collector needle and collector is 200 mm. The constant temperature and humidity machine is designed to study the process controlling of multi-needle electrospinning, the controllable range of humidity and temperature is 15% ~ 90% and 15 °C ~ 50 °C, respectively. The detection accuracy of humidity sensor and temperature sensor is ±2% RH and ±1 °C, respectively. The collector high voltage power supply (Tianjin Dongwen high voltage power supply), of which the max output is 50 kV and 2 mA.

2.2. Materials and testing apparatus

The materials used in this work include poly (ethylene oxide) (PEO) and polyvinylidene fluoride (PVDF). The solvent is pure water or N-dimethylformamide (DMF) and acetone. The test results of the spinning solution material parameters at 20 °C are shown in table 1. From this table, it can be seen that the viscosity of the material
increases with the increase of concentration. On the other hand, the electrical conductivity and surface tension are relatively little affected by the change of concentration. The instruments used in this research are shown in table 2.

3. Results and discussion

As shown in figure 2, the surface of the jet is positively charged and water molecules are negatively charged by the electric field, which are derived by the Coulomb force. Finally, a large number of water molecules attach to the surface of the jet, weaken the volatilization process of the solvent in jet. For water-soluble materials, after the jet absorbs more water molecules, the volatilization is weakened at higher humidity environment. As for non-water-soluble materials, the solute precipitation of the jet is accelerated, and the jet solidification process becomes faster.

3.1. Electrospinning experiment of poly (ethylene oxide)

PEO is the representative of water-soluble materials in electrospinning. In the process of electrospinning of PEO, when the humidity is low, after the jet is ejected from the tip, the volatilization rate of the water solvent is high, and the jet solidifies not far from the tip. With the increase of humidity, it is easy to absorb water molecules in the air, which makes the water in the jet volatilize more slowly. The longer the distance between the solidification point of the jet and the tip of the needle, the better the fluidity of the jet, and the greater the drawing force of the jet by the electric field, and the jet will be more easily refined.

Firstly, the law of fiber deposition of PEO material under different voltage and humidity is studied. By electrospinning the PEO solution with 6.5 wt% concentration, the SEM diagram of fiber deposition is sampled at 30 °C and the liquid supply rate is 30 ml h⁻¹. The results are shown in figure 3. It can be seen from the figure that with the increase of humidity and applied voltage, the fiber diameter decreases. However, when the ambient humidity is 70%RH, the fiber deposition occurs with beads. This is mainly because, with the increase of humidity, the surface tension of the water-soluble material jet is lower, but the fluidity of the jet is good. The charge is easy to drive the fluidity jet to gather in the electric field, and the beads are formed after the jet is solidified. Compared with the SEM morphology of the fibers with different voltages in 30%RH, the morphology of the fibers is better with the increase of the voltage, since the higher the

| Sequence number | Materials | Model | Solvent | Mass fraction | Conductivity (μs cm⁻¹) | Viscosity (mPa·s) | Surface tension (mM m⁻¹) |
|-----------------|-----------|-------|---------|---------------|------------------------|-------------------|------------------------|
| 1               | PEO       | N3000 | Pure water | 4.50%       | 92.4               | 1786             | 70.3                   |
|                 |           |       |          | 5.50%       | 110.9              | 4655             | 70.6                   |
|                 |           |       |          | 6.50%       | 124.1              | 11546            | 73.9                   |
| 2               | PVDF      | 1010  | DMF     | 18%          | 1.22                | 598              | 43.3                   |
|                 | PVDF + LiCl |       |         | 20%          | 1.08                | 1891             | 43.5                   |
|                 | PVDF + LiCl |       |         | 22%          | 1.004               | 2840             | 43.9                   |
|                 | PVDF + LiCl |       |         | 24%          | 1.32                | 9850             | 46.5                   |
|                 | DMF: acetone = 3:1 |       |         | 22%          | 1.0                | 2790             | 41.5                   |
|                 | DMF + 0.001% LiCl |       |         | 22%          | 6.29                | 2740             | 44.1                   |
|                 | DMF + 0.002% LiCl |       |         | 22%          | 10.64               | 2746             | 44.3                   |
|                 | DMF + 0.003% LiCl |       |         | 22%          | 15.78               | 2753             | 44.2                   |
|                 | DMF + 0.004% LiCl |       |         | 22%          | 20.35               | 2760             | 44.6                   |

Table 2. Apparatus used in this research.

| Apparatus                  | Manufacturer                                      | Version            |
|----------------------------|---------------------------------------------------|--------------------|
| Conductivity instrument    | Tianjin Shengbang Scientific instrument Technology Development Co. Ltd. | DDJ-A automatic conductivity instrument |
| Viscometer                 | Shanghai Tianmei balance instrument Co. Ltd.     | NDJ-1 Rotary Viscometer |
| Surface tension instrument | Chengde Youte testing instrument Co. Ltd.        | JYW-200 series automatic surface and interface tension instrument |
| Electrospinning Machine    | Foshan lepton Precision Measurement and Control Technology Co. Ltd. | QZNT-MF01-002 |
| Scanning electron microscope | Hitachi                                         | TM3030             |
**Figure 2.** Schematic diagram of surface charge distribution of electrospinning jet.

**Figure 3.** SEM image of fiber deposition with different voltages and different humidity.
voltage, the greater the tensile force of the electric field on the jet, the easier the jet is refined in the air, and the more volatile the solvent will be, so the fiber stickiness will not occur.

The fiber morphology of 6.5 wt% PEO aqueous solution at different temperatures was sampled. As shown in figure 4, the fiber morphology was extracted under the conditions of spinning voltage of 40 kV, feeding rate of 30 ml min$^{-1}$, temperature of 25 °C, 30 °C, 35 °C and humidity of 30%RH, 40%RH, 50%RH, 60%RH and 70%RH respectively. As can be seen from figure 4, there are a large number of beads at 25 °C when the humidity is 60%RH, and there is no fiber film formed at 70%RH. This is mainly because in this environment, the solvent volatilization of the jet is not timely, and the jet dissolves completely after it is deposited on the collector, so there is no fiber structure. By comparing the situations according to three temperatures, it can be found that the increase of temperature can improve the fiber-forming performance of jet deposition, and can reduce the bead morphology of water-soluble materials in high humidity environment. This is mainly due to the increase of temperature, which leads to the increase of saturated vapor pressure of water vapor, and accelerates the

![Figure 4. SEM of 6.5 wt% PEO aqueous solution with different temperature and humidity.](image-url)
evaporation of the jet solvent and the fiber solidification of the jet. In addition, by comparison, it is found that the increase of temperature can reduce the wire diameter of the fiber, mainly because the increase of temperature reduces the viscous force of the jet and makes the electric field stretch whipping more fully.

The fiber deposition morphologies of 6.5 wt%, 5.5 wt% and 4.5 wt% PEO aqueous solution were extracted at 30 °C, 40 kV and 30 ml h\(^{-1}\), respectively. As shown in figure 5, the film-forming property of the jet becomes worse with the decrease of the solution concentration. Hereinto, the film-forming property of 4.5 wt% PEO aqueous solution is the worst at 30 °C. Under the ambient humidity of most of the experiments, the jet volatilization was not completed, and the serious fiber adhesive morphology appeared. Therefore, although the low concentration material has a good traction force by electric field in the air because of its low viscosity, the volatility of jet solvent is not strong. To sum up, in the production process, the temperature should be increased in order to obtain better fiber deposition morphology.

3.2. Electrospinning Experiment of Polyvinylidene fluoride
Polyvinylidene fluoride (PVDF) is a kind of water-insoluble material commonly used in electrospinning. The fiber morphologies of four kinds of DMF solutions of 18 wt%, 20 wt%, 22 wt% and 24 wt% were tested under different humidity. The test voltage was 45 kV and set temperature is 30 °C. The results are shown in figure 6. All the materials with all concentrations of PVDF have beaded microspheres to a certain extent in the ambient
humidity of 30%RH-50%RH. At the same humidity, the beading situation is alleviated with the increase of the concentration, which shows that one of the parameters affecting the bead morphology is the viscosity of the material, that is, the viscous force of the jet in the electric field. Compared with the materials of the same concentration, the bead situation in the fiber was alleviated with the increase of humidity. For non-water-soluble materials, with the increase of humidity in the spinning environment, the jet absorbs more water molecules in the air, so the solvent in the jet is extracted faster, and the viscosity of the jet will be greatly increased, thus affecting the formation of bead morphology.

Comparing the effect of different temperature and voltage on the morphology of PVDF fiber, 22 wt% PVDF was used to test the fiber morphology at 25 °C, 30 °C and 35 °C, respectively. The ambient humidity was 50% RH. The test results are shown in figure 7(a)–(c). Figure 7(a)–(c) are the fiber SEM diagrams at 25 °C, 30 °C and 35 °C, respectively. However, there is no beading in figure 7(c), which can be seen that increasing the temperature can alleviate the beading problem of PVDF fiber. Figure 7(d) is the fiber morphology diagram at 50 kV and 35 °C and there are no beads in the picture. Figure 7(e) shows the average value and deviation of fiber diameter under the four different parameters of figure 7(a)–(d), from which we know that the fiber diameter is the smallest and the fiber uniformity is the best at 40 kV at 30 °C.

In the above content, we can know that although there are no beads in PVDF electrospinning morphology at high humidity, the fiber diameter will increase accordingly, so it is necessary to explore how to obtain uniform nanofibers in low humidity environment. We have attempted to change the solution composition system to obtain a better morphology of nanofibers. The pure DMF solution of 22 wt% of PVDF is compared with the solution with 0.001 wt%, 0.002 wt%, 0.003 wt% and 0.004 wt% lithium chloride, respectively. The spinning effect of 22 wt%PVDF solution with solvent at a volume ratio of DMF: acetone = 3:1 is also compared. The spinning voltage is 50 kV, the temperature is 30 °C, and the liquid feeding rate is 50 ml h⁻¹. The fiber morphologies of different solutions under different humidity are compared, and the results are shown in

![Figure 6. Fibers SEM morphology of different PVDF solution concentrations at different humidity.](image)
Figure 8. The addition of LiCl to improve the electrical conductivity of PVDF solution can alleviate the beading situation, especially when 0.004 wt% LiCl solution is added, where the beading situation will not occur at a humidity of 40%RH. This is mainly because after the electrical conductivity of the jet becomes better, the electric field tensile force of the jet is greatly improved, and a more uniform fiber diameter can be obtained. After changing the solution of the solvent system and adding acetone, the volatility of the solvent was changed, and there was no beading phenomenon.
The fiber diameter statistics of the fibers in figure 8 are carried out, and the results are shown in table 3 and figure 9. It can be seen from figure 9 that the average filament diameter of the solution added with acetone is much larger than that of other materials, which is mainly due to the strong volatility of acetone. The solution with acetone volatilizes rapidly after the jet is ejected, and the viscous force of the jet increases rapidly. The jet is not stretched enough by the electric field, so it is difficult to form whipping. As a result, the diameter of the jet is thicker after solidification, and it is easy to cause wire hanging phenomenon. The solution with or without lithium chloride was compared, and the result showed that the diameter of the fiber with lithium chloride is smaller than that without lithium chloride under the humidity of 30%RH; and the higher the concentration of lithium chloride is, the smaller the fiber diameter is. However, when the humidity is above 40%RH, the filament diameter of PVDF solution with 0.001 wt% lithium chloride is larger than that of other lithium chloride concentration and the solution without lithium chloride. Except for 0.001 wt% lithium chloride solution, the spinning diameter of the solution with other concentration of lithium chloride is smaller than that without lithium chloride. This is mainly because after the improvement of the electrical conductivity of the jet, the electric field force of the jet is greater, and the jet can be better stretched and refined. Generally speaking, with the increase of humidity, the fiber diameter becomes larger. When the ambient humidity of 0.001 wt% lithium chloride is greater than 40%RH, the fiber diameter of the solution with 0.001 wt% lithium chloride is larger than that of the unadded solution, which is mainly because the electrical conductivity of the jet becomes better. But it is not enough to cause a more severe whipping effect, for the positive charge on the surface of the jet is denser and the amount of adsorbing water molecules is larger. So, this process accelerates the solidification of the jet and causes thicker fibers. The electrical conductivity of other concentrations of lithium chloride solution is stronger, and the whipping is more intense than that without lithium chloride, so the spinning diameter is smaller.

4. Conclusion

For the water-soluble material (PEO), the charged jet is easier to absorb water vapor in the air, which makes the solvent volatility of the jet worse, the fluidity of the jet better, and decrease the nanofiber diameter and beads structure appeared. When the humidity is relatively high, the water in the jet is more difficult to volatilize. The jet
with more solvent cannot be form uniform nanofiber membrane on the collector. The lower the concentration of the spinning solution, the better the fluidity of the jet, the finer the fiber diameter, and the more easily the bead morphology is affected by humidity. Besides, the higher the humidity, the worse the film-forming property. Increasing the temperature can accelerate the volatilization of the solvent on the surface of the jet, thereby change the fluidity of the jet and the film-forming performance of the fiber.

For water-insoluble materials, the effect of humidity on fiber deposition morphology is contrary to that of water-soluble materials. Beads are easy to occur when the humidity is low, mainly because the morphology is affected by humidity. Besides, the higher the humidity, the worse the fluidity of the jet, the DMF solvent in the jet can be extracted quickly. As a result, the viscosity of the jet increases rapidly and the fluidity becomes worse, but the diameter of the deposited fiber becomes larger at the same time. The electrical conductivity of the solution will also affect the formation of bead morphology. The higher the conductivity of the solution, the less easy to form bead structure, for the effect of electric field force on the jet is greater than the resilience force of the solution. The addition of volatile acetone material to the solution also helps to solve the bead problem of nanofibers. It is mainly due to the rapid volatilization of the solvent, which makes the viscosity of the jet increase rapidly, the resilience becomes smaller, and beads are not easy to formed. But correspondingly, it will cause the fiber diameter to become thicker. The effect of temperature and viscosity on water-insoluble materials is the same as that of water-soluble materials.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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