EFFECT OF CONCENTRATION OF METAL INORGANIC SALT ON FIBER DIAMETER IN ELECTROSPINNING PROCESS: MATHEMATICAL MODEL AND EXPERIMENTAL VERIFICATION

by

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Electrospinning is used to produce polyvinylidene fluoride (PVDF) nanofibers under various the ferric chloride ($FeCl_3$) contents. The effect of $FeCl_3$ concentration on fiber diameter is investigated theoretically and experimentally. A critical value of the concentration is found, below which fiber diameter decreases with its concentration, and an opposite prediction is observed when the concentration is larger than the critical value.

Key word: *electrospinning, fiber diameter, metal inorganic salt*

Introduction

Electrospinning is a micro/nano scale flow, which is widely used to fabricate fibrous materials with diameters ranging several micrometers from a few nanometers from a polymer solution [1-4]. In this process, a jet is ejected and accelerated from a spinneret by a high electrostatic force, and then deposited on a grounded-metal collector as a nanofiber, which can be widely used in many high-tech areas where the fiber diameter is crucial to its applications. The fiber diameter mainly depends on solution properties, e.g. the viscosity, conductivity, surface tension, and so forth [5, 6], see also some review articles[7,8]. In the electrospinning process, additive (e.g. metal inorganic salt) is a versatile method to change the solution property and to control fiber morphology. Alpha-Fe_2O_3[9], Na_2CO_3[10], Cu nanoparticles[11], milk[12] and chitosan[13] were used in practical applications. In this paper $FeCl_3$ will be used as an additive, due to its inexpensive price its ferromagnetic property.

The electrospinning has been developing very fast, and various new technologies were appeared recently, for examples, the bubble electrospinning[14,15] and bubbfil spinning[3], which are the promising technologies for mass-production of nanofibers, and new applications of nanofibers have been appeared, for examples, oxygen-enrichment nanofiber membrane[16] and nanofiber membrane for enhancing silver ion release[17].

This paper will prepare for PVDF fibrous membrane with different $FeCl_3$ contents via electrospinning. At the same time, the influence of $FeCl_3$ concentration on fiber diameter of

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electrospun PVDF fibrous material will be studied. Finally, a mathematical model of the relationship between the $FeCl_3$ concentration and fiber diameter is proposed and experimentally verified.

Experiment

In this work, PVDF particles were dissolved in N,N-dimethylacetamide (DMF) and acetone (ACE) mixtures (weight ratio 1:1) under constant and vigorous magnetic stirring. Subsequently, $FeCl_3$ with different contents were added respectively into above solution and kept vigorous magnetic stirring at room temperature. The concentration of $FeCl_3$ (i.e., 2 wt%, 4wt%, 6 wt%, 8 wt%, and 10 wt%) in the mixture was based on the weight of PVDF, DMF and ACE. In this experiment, all solutions were the concentration of PVDF 6 wt% and chemicals were used without further purification. In the spinning process, the applied electric voltage is 25kV and the collector distance is 15 cm. All the experiments were performed at similar ambient temperature and relatively humidity.

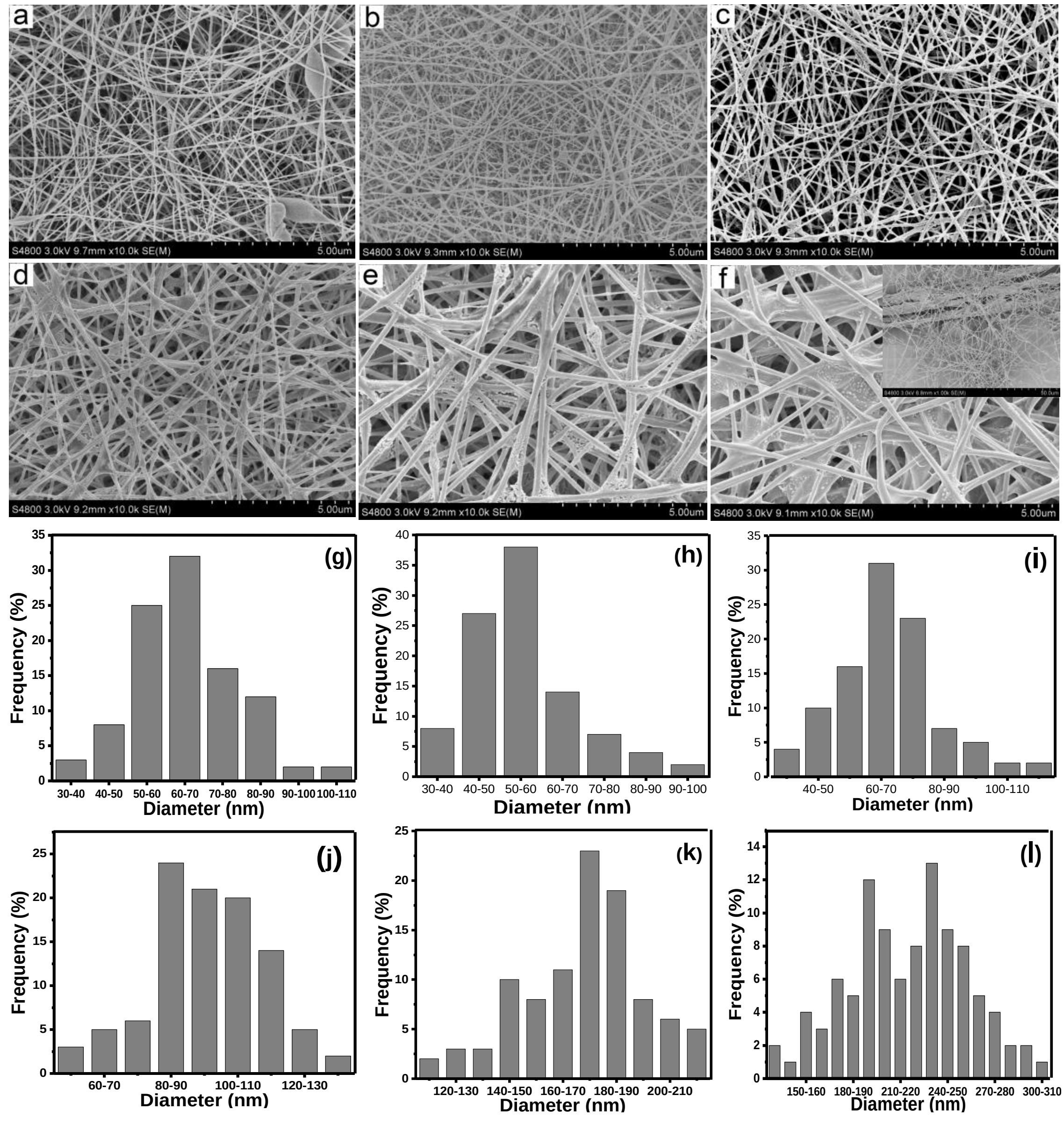

Figure 1. FESEM images and diameter distribution of the PVDF fibrous with different $FeCl_3$ contents: (a, g) 0, (b, h) 2, (c, i) 4, (d, j) 6, (e, k) 8, and (f, l)10 wt%

Theoretical analysis and experimental verification

The SEM images of electrospun fibrous membrane with different $FeCl_3$ contents are presented in fig. 1a-f. It is obvious that electrospun pure PVDF nanofiber membrane shows beads on string morphology from fig. 1a. Differently, there are no significant beads in the fibrous membrane from the solutions with a small amount of $FeCl_3$ (fig. 1b, c, and d). Interestingly, when the $FeCl_3$ concentration was relatively high, lots of beads were appeared again. In addition, the surface becomes rough with the increase of $FeCl_3$. Figure 1e and 1f clearly display this phenomenon. It was concluded that increased $FeCl_3$ concentration leads to poor spin-ability.

The diameter distribution curves of as-spun fibrous membrane with different $FeCl_3$ concentration have been demonstrated in fig. 1g-l. It shows a narrow fiber diameter distribution at low $FeCl_3$ concentration, while wide fiber diameter distribution at relatively high-level. Meanwhile, it is obvious that the fibers diameter noticeably decreased in the relatively low-level $FeCl_3$ concentration and dramatically increased in the relatively high-level $FeCl_3$ concentration.

The fiber diameter is mainly influenced by conductivity, viscosity, and surface tension of the electrospinning solution. The properties of electrospinning solutions are displayed in table 1. It is clear that solution conductivity acutely increased while viscosity increased fiercely then decreased slightly at the beginning with the increasing of $FeCl_3$ concentration. However, the surface tension of solution has no significant variation with the increase of $FeCl_3$ concentration.

$FeCl_3$ (wt.%)	conductivity (μs /cm)	Viscosity [a] (Pa.s)	Surface Tension [b] (Dyn/cm)	Diameter [c] (nm)
0	0.388	0.11	29.197±0.029	64.8±13.7
2	200.6	0.07	30.528±0.029	55.2±12.5
4	352.3	0.06	30.564±0.014	66.9±16.4
6	564.5	0.09	30.528±0.013	95.8±16.3
8	624.1	2.44	30.622±0.0.13	172.5±24.1
10	759.7	4.59	30.571±0.029	219.7±37.6

[a] shear rate is 0.34 s^{-1}. [b,c] values are expressed as means±SD.

Table 1. Characteristics of the electrospinning solutions and the fiber diameters of the resultant fibrous membrane with different $FeCl_3$ concentration

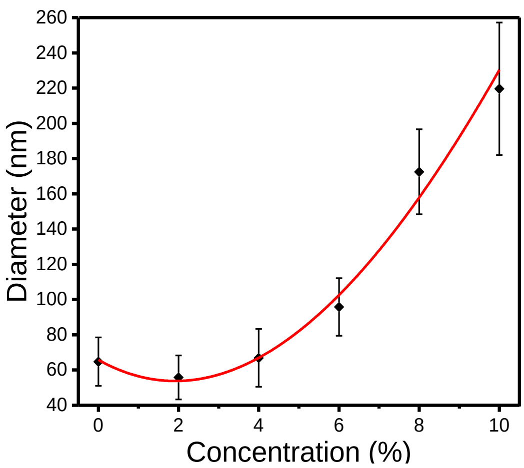

Figure 2. A plot of the fiber diameter as a function of $FeCl_3$ concentration

Previous report [18,19] indicated the diameter of electrospun fiber mainly depends upon solution viscosity, and higher viscosity leads to thicker fibers:

$$d \propto \eta^{\alpha} \tag{1}$$

where d is fiber diameter, η is viscosity, and α is a constant varying for different solutions.

On the other hand, higher concentration results in higher viscosity, which means [8]

$$d \propto c^{\beta}, \quad c \le c_0 \tag{2}$$

Where c_0 is threshold value for c, β is a constant varying for different solutions.
We write

$$d = k_1 + k_2 c + k_3 c^2 + k_4 c^3 + \alpha(c), \quad c \le c_0 \tag{3}$$

Where k_i constant is further determined experimentally, $\alpha(c)$ is a matching term for $c > c_0$.

However, when the concentration increases to a threshold value, the electrospinning's spin-ability reduces, and when the concentration is larger than the threshold value, the fiber diameter increases greatly, which means

$$d \propto \frac{1}{c^{\delta}}, \quad c \ge c_0 \tag{4}$$

where δ is a constant varying for different solutions.
We write

$$d = \frac{1}{b_1 + b_2 c + b_3 c^2 + b_4 c^3} + \beta(c), \quad c \ge c_0 \tag{5}$$

Where b_i constant is further determined experimentally, $\beta(c)$ is a matching term for $c < c_0$.

Combining Eq.(3) with Eq.(5), we have the following relation between the fiber diameter and the concentration:

$$d = k_1 + k_2 c + k_3 c^2 + k_4 c^3 + \frac{1}{b_1 + b_2 c + b_3 c^2 + b_4 c^3} \tag{6}$$

Using above experimental data, we can approximately identify constants in Eq.(6) as follows:

$$k_1 = 65.73 \qquad k_2 = -12.68 \qquad k_3 = 3.47 \qquad k_4 = -0.06$$

$$b_1 = 65.73 \qquad b_2 = -12.68 \qquad b_3 = 3.47 \qquad b_4 = -0.06$$

Eq.(6) becomes

$$d = 65.73 - 12.68c + 3.47c^2 - 0.06c^3 + \frac{1}{65.73 - 12.68c + 3.47c^2 - 0.06c^3} \tag{7}$$

It is easy to find that the threshold value of concentration is $c_0 = 2$ and minimal fiber diameter is 53.8 nm, which agree well with experimental data, see fig. 2.

Discussion and Conclusion

In this paper, the effect of $FeCl_3$ concentration on fiber diameter of electrospun PVDF membrane has been investigated. All additives will greatly affect morphology of nanofibers, this is because the additive will greatly affect the solution’s density:

$$\rho = \rho_p c_p + \rho_s c_s + \rho_a c_a \tag{8}$$

where subscribes p, *s* and *a* imply PVDF, solvent, and additive, *c* is concentration.

Fiber diameter depends mainly upon solvent evaporation. In case $\rho_a c_a >> \rho_s c_s$, the solvent evaporation will not affect morphology of nanofibers, so additives are widely used to control morphology of nanofibers.

With 2 wt% addition of $FeCl_3$, the average fibers diameter decreases compared with pure PDVF nanofibers. However, the average diameter of the fibers dramatically increased as the concentration of $FeCl_3$ increased to 10 wt%. Meanwhile, we have also proposed a mathematical formulation of the relationship between metal inorganic salt concentration and fiber diameter based on the experimental result. This result will benefit further research with regard to diameter control in electrospinning.

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References

[1] Liu, Z., *et al.*, Active Generation of Multiple Jets for Production Nanofibers with High Quality and High Throughput, *Material & Design, 94* (2016), pp. 496-501

[2] Liu, Z., *et al.*, Tunable Surface Morphology of Electrospun PMMA Fiber Using Binary Solvent, *Applied Surface Science, 364*(2016), pp. 516-521

[3] He, C. H., *et al.*, Bubbfil Spinning for Fabrication of PVA Nanofibers, *Thermal Science, 19*(2015), 2, pp. 743-746

[4] Liu, P., *et al.*, Micro-Nanofibers with Hierarchical Structure by Bubbfil-Spinning, *Thermal Science, 19*(2015), 4, pp. 1455-1456

[5] Cengiz, F., *et al.*, Influence of Solution Properties on the Roller Electrospinning of Poly(vinyl alcohol), *Polmer Engineering and Science, 50*(2010), pp. 936-943

[6] Teeradech J., *et al.*, Effect of Solvents on Electro-Spinnability of Polystyrene Solutions and Morphological Appearance of Resulting Electrospun Polystyrene Fibers, *European Polymer Journal, 41* (2005), pp. 409-421

[7]Huang, Z.M., et al., A review on polymer nanofibers by electrospinning and their applications in nanocomposites, Composites Science and Technology, 63(2003),15,pp.2223-2253

[8] Greiner, A., et al., A Electrospinning: A fascinating method for the preparation of ultrathin fibres, Angewandte Chemie-International Edition,46(2007),30,pp.5670-5703

[9]Liu, P., et al., Facile preparation of alpha-Fe2O3 nanobulk via bubble electrospinning and thermal treatment, Thermal Science,20(2016),3,pp.967-972

[10]Liu, Z., et al., Effect of Na2CO3 degumming concentration on LiBr-FORMIC ACID-silk fibroin solution properties, Thermal Science,20(2016),3,pp.985-991

[11]Li, Y., et al. Bubbfil electrospinning of PA66/Cu nanofibers, Thermal Science,20(2016),3,pp.993-998

[12] Zhang, Y., et al., Research on morphologies of polyvinyl alcohol/milk nanofibers, Thermal Science,20(2016),3,pp.961-966

[13]Zhao, L., et al., Microstructure and property of regenepercentaged silk fibroin/Chitosan nanofibers, Thermal Science,20(2016),3,pp.979-983

[14] Liu, Y., He, J.H. Bubble electrospinning for mass production of nanofibers , International Journal of Nonlinear Sciences and Numerical Simulation, 8(2007),3,pp.393-396

[15]Ren, Z.F, et al. Effect of bubble size on nanofiber diameter in bubble electrospinning, Thermal Science,20(2016),3,pp.845-848

[16]Shen, J., et al., Primary study of ethyl cellulose nanofiber for oxygen-enrichment membrane, Thermal Science,20(2016),3,pp.:1008-1009

[17]Li, H., et al., Influence of nano-fiber membranes on the silver ions released from hollow fibers containing silver particles, Thermal Science,20(2016),3,pp. 859-862

[18] Cui, Q. N., *et al.*, Effect of Temperature on the Morphology of Bobble-electrospun Nanofibers, *Thermal Science, 18*(2014), 5, pp. 1707-1709

[19] He, J. H., *et al.*, Effect of Concentration on Electrospun Polyacrylonitrile (PAN) Nanofibers, *Fibers and Polymers, 9*(2008), 2, pp. 140-142

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