

RESEARCH ON MORPHOLOGIES OF POLYVINYL ALCOHOL/MILK NANOFIBERS

by

**Yan ZHANG^a, Chuan-Zheng ZHANG^a, Fu-Juan LIU^a,
Fei-Yan WANG^b, and Ping WANG^{a*}**

^a National Engineering Laboratory for Modern Silk, College of Textile and Clothing Engineering,
Soochow University, Suzhou, China

^b Nantong University Xinglin College, Nantong, China

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In this paper, the surface morphologies of polyvinyl alcohol/milk nanofibers produced via electrospinning technique were investigated. The electrospinning process was performed at various processing parameters (flow rate, applied voltage) and different polyvinyl acetate to milk ratios (100/0, 90/10, 80/20, 70/30, and 60/40). The scanning electron microscopy and Image J software were used to characterize the surface morphologies, especially the diameter distribution of electro spun nanofibers. The results of scanning electron microscopy show that the diameter of polyvinyl acetate/milk nanofibers increases with the increase of the spinning speed and spinning voltage but decreases with the increase of the weight percentage of milk in the spinning solution. The potential applications of this bicomponent nanofibers are numerous and diverse. The research results in present paper can contribute to better control of the electrospinning process and thus expanding the applicabilities, such as dressings for wound healing in sports.

Key words: *polyvinyl alcohol, milk, nanofiber, surface morphology, parametric research*

Introduction

Electrospinning technique is a traditional method which utilizes electrical forces to produce nanofibers with diameters ranging from 10 nm to 10 μm [1-4]. The nanofibers with small diameters have a broad range of potential applications such as biomedical, filtration/adsorption, functional materials [5]. An increasing attention has been attracted and paid on these nanomaterials due to their superior performances compared with classical polymer fibers. Further, bicomponent nanofibers which usually combine advantages of two or more than two different kinds of components have more potential applications. Ding *et al.* [6] electro spun polyvinyl alcohol/cellulose acetate nanofibers as biodegradable nanowoven mats. Bhattacharjee *et al.* [7] blended polyvinyl alcohol (PVA) and non-mulberry tasar silk fibroin to fabricate the nanofibrous matrices for bone regeneration. Song *et al.* [8] fabricated polyvinyl alcohol/collagen hydroxyapatite electro spun nanofibrous meshes which might be promising modifying materials on implant surfaces for orthopedic applications. Hsieh and Liao [9] cross-linked PVA

* Corresponding author; e-mail: pingwang@suda.edu.cn

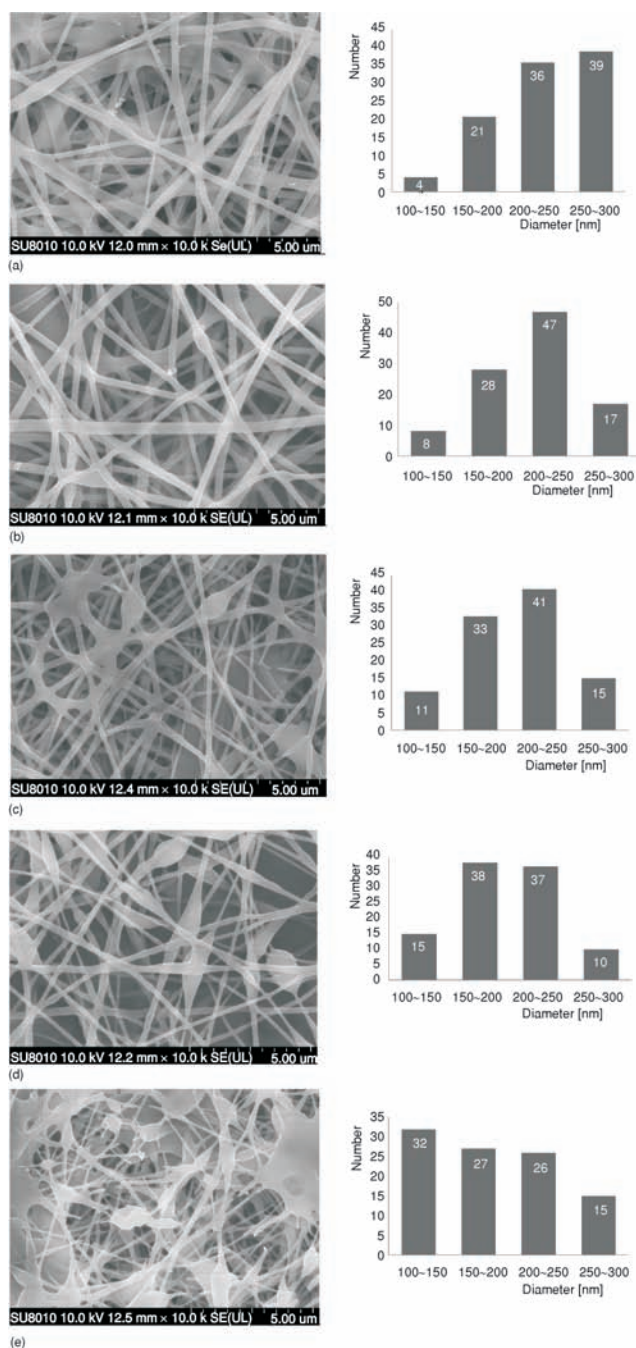


Figure 1. The SEM images for different ratios between PVA and milk; (a) 100/0, (b) 90/10, (c) 80/20, (d) 70/30, (e) 60/40

seven-gauge stainless steel needle. A grounded Al-foil served as the collector. The distance between syringe-tip to the collector was fixed at 15 cm. First, five different kind solutions

and starch to form a 3-D scaffold that is effective water absorbent, has a stable structure, and supports cell growth. Maleki *et al.* [10] electro spun aqueous mixture of PVA and honey with different PVA to honey ratios. The authors [11, 12] of this article also attempted to electro spun PVA-milk and PVA-honey nano- fibers with potential application in biodegradable field.

Based on the previous researches [13-19], this article deeply discussed the effects of electro spun parameters for electro spun PVA/milk nanofibers. A simple theoretical analysis on the base of the conservation equation of mass is also provided. The surface morphologies of the PVA/milk nanofiber verify the theoretical analysis results.

Experimental work

Materials

The PVA, Sigma, mixed with whole milk powder were used as the model polymer. The solutions were prepared by dissolving the PVA powder and whole milk powder in deionized water and then transferred to a water bath at 90 °C for three hours with continuous stirring. In this study, five different proportions of PVA and milk (100/0, 90/10, 80/20, 70/30, 60/40) were prepared, while all the solutions have the same weight ratio of 7%.

Electrospinning

The homogeneous PVA/milk mixed solutions were pumped through a syringe with a

(PVA/milk 100/0, 90/10, 80/20, 70/30, and 60/40) were electro spun with the applied voltage of 25 kV and flow rate of 0.7 mL/h, which aims to find out the best proportion of PVA and milk. Following, the PVA/milk 80/20 solution was selected to study the changes of fiber diameter with different flow rates and voltages. In this study, five different flow rates (0.1 mL/h, 0.3 mL/h, 0.5 mL/h, 0.7 mL/h, and 0.9 mL/h) and five different voltages (10 kV, 15 kV, 20 kV, 25 kV, and 30 kV) are applied.

Results and discussion

Electro spun PVA/milk nanofibers

Figure 1 shows the scanning electron microscopy (SEM) images of electro spun PVA/milk nanofibers and fig. 2 illustrates the nanofiber diameters for different ratios between PVA and milk. It is easily to find out that the diameter of pure PVA nanofiber is more uniform without beaded fibers. With the increases of the proportion of milk, the diameter of nanofiber decreases linearly, meanwhile the beaded fiber increases significantly. When the proportion of milk reaches to more than 40%, the solution cannot be electro spun steadily. The changes mainly caused by the decrease of the viscosity of the mixed solutions. For the solutions of low viscosities, the molecular chain is easily to fracture under the tensile effect of electric field force. Based on the effect of surface tension, beaded fibers are formed easily.

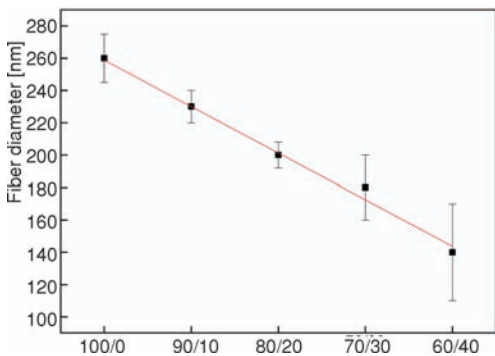


Figure 2. The fiber diameters for different ratios between PVA and milk

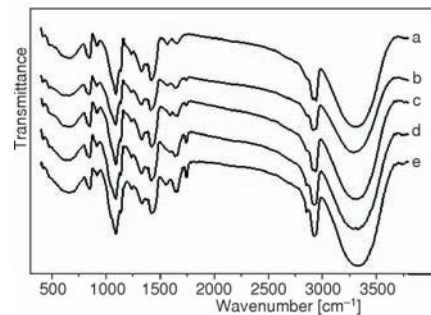


Figure 3. The FTIR spectra of PVA/milk nanofibers. (a) 100/0, (b) 90/10, (c) 80/20, (d) 70/30, (e) 60/40

The Fourier transform infrared (FTIR) spectroscopy spectra of electro spun nanofibers are shown in fig. 3. Obviously, the PVA/milk nanofibers have a strong absorption peak at the wavenumber of 1730, which due to the carbonyl vibration of the fat in milk. With the increases of milk, the absorption peak becomes much stronger. Therefore, the difference in FTIR shows the success of electro spun PVA/milk nanofibers.

Parametric discussions

Considering a 1-D jet, a part of the stream tube as shown in fig. 4 can be chosen as the research object. Based on the classical conservation equation of mass, the rate of increase of mass within the fluid element equals to the net rate of mass which enters into the element volume. Then a partial differential equation of the conservation of mass can be derived:

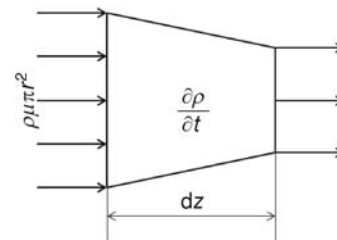


Figure 4. An element volume

$$\pi r^2 dz \frac{\partial \rho}{\partial t} - \frac{\partial}{\partial z} (\rho \mu \pi r^2) = 0 \quad (1)$$

where r is the radius of jet flow, ρ – the density of jet flow, μ – the velocity of jet flow which is positive correlation with the applied voltage. When ignoring the compressibility of the jet flow, the $\rho / t = 0$. Therefore, eq. (1) can be derived:

$$\rho \mu \pi r^2 = \text{constant number} = Q \quad (2)$$

where Q is the flow rate. When the applied voltage keeps as a constant number, the relationship between the radius of the nanofiber and flow rate can be derived:

$$r \propto \sqrt{Q} \quad (3)$$

Figure 5 shows the effects of the flow rate on the diameter of the electro spun PVA/milk nanofibers. It can be seen that the diameter of the PVA/milk nanofiber increases with the increase of the flow rate. The experimental results show non-linear relationship between nanofiber diameter and flow rate. Meanwhile, the experimental results greatly agree with the results obtained from applying theoretical analysis.

Figure 6 shows the relationship between applied voltage and fiber diameter. The diameter of electro spun PVA/milk nanofiber increases with the increase of applied voltage. The higher applied voltage is attributed to the more solutions pumped out the needle. At the same time, the higher applied voltage may increase the velocity of solutions pumped out the needle. Therefore, the time for the solutions to the collector is short. The electric field force which has the effect to draft the solutions becomes weak. All previous reasons are lead to the increase of the nanofiber diameter.

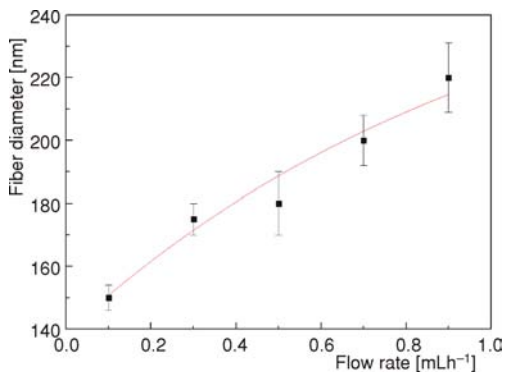


Figure 5. The relationship between flow rate and fiber diameter

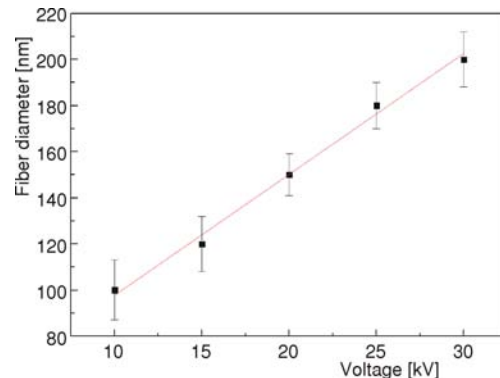


Figure 6. The relationship between voltage and fiber diameter

Conclusions

The article focused on the electro spun properties of PVA/milk nanofibers. Five different kind of proportions for PVA to milk solutions were studied. The higher proportion for milk leads to finer nanofibers but much more beaded nanofibers. The FTIR results clearly show the absorbed peak for carbonyl which only existed in milk rather than PVA. For the PVA/milk 80/20 solutions, the electro spun nanofiber diameter increases with the increase of flow rate and ap-

plied voltage which agreed with the theoretical analysis. The research results show great understand of the surface morphologies of PVA/milk nanofiber.

The PVA is biodegradable and harmless to humans. The PVA/honey nanofibrous scaffold with anti-inflammatory drug has been reported to improve the wound dressing efficiency [9]. The PVA/milk nanofibers can also be considered as drug-load materials for wound dressing and increasing the heal rate. The new materials may apply in vast domain especially for the bruises in sports. Further research will prove the suppose.

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References

- [1] Cramariuc, B., et al., Fiber Diameter in Electrospinning Process, *Journal of Electrostatics*, 71 (2013), 3, pp. 189-198
- [2] Ahn, Y. C., et al., Development of High Efficiency Nanofilters Made of Nanofibers, *Current Applied Physics*, 6 (2006), 6, pp. 1030-1035
- [3] Lannutti, J., et al., Electrospinning for Tissue Engineering Scaffolds, *Materials Science and Engineering: C*, 27 (2007), 3, pp. 504-509
- [4] Hunley, M. T., Long, T. E., Electrospinning Functional Nanoscale Fibers: A Perspective for the Future, *Polymer International*, 57 (2008), 3, pp. 385-389
- [5] Bhardwaj, N., Kundu, S. C., Electrospinning: A Fascinating Fiber Fabrication Technique, *Biotechnology Advances*, 28 (2010), 3, pp. 325-347
- [6] Ding, B., et al., Fabrication of Blend Biodegradable Nanofibrous Nonwoven Mats via Multi-Jet Electrospinning, *Polymer*, 45 (2004), 6, pp. 1895-1902
- [7] Bhattacharjee, P., et al., Nanofibrous Nonmulberry Silk/PVA Scaffold for Osteoinduction and Osseointegration, *Biopolymers*, 103 (2015), 5, pp. 271-284
- [8] Song, W., et al., Electrospun Polyvinyl Alcohol-Collagen-Hydroxyapatite Nanofibers: A Biomimetic Extracellular Matrix for Osteoblastic Cells, *Nanotechnology*, 23 (2012), 11, p. 115101
- [9] Hsieh, W. C., Liau, J. J., Cell Culture and Characterization of Cross-Linked Poly(Vinyl Alcohol)-G-Starch 3D Scaffold for Tissue Engineering, *Carbohydrate Polymers*, 98 (2013), 1, pp. 574-580
- [10] Maleki, H., et al., A Novel Honey-Based Nanofibrous Scaffold for Wound Dressing Application, *Journal of Applied Polymer Science*, 127 (2013), 5, pp. 4086-4092
- [11] Wang, P., He, J.-H., Electrospun Polyvinyl Alcohol-Milk Nanofibers, *Thermal Science*, 17 (2013), 5, pp. 1515-1516
- [12] Wang, P., He, J.-H., Electrospun Polyvinyl Alcohol-Honey Nanofibers, *Thermal Science*, 17 (2013), 5, pp. 1549-1550
- [13] Li, W. J., et al., A Nonlinear Pyrolysis Layer Model for Analyzing Thermal Behavior of Charring Ablator, *International Journal of Thermal Science*, 98 (2015), Dec., pp. 104-112
- [14] Li, W. J., et al., Nonlinear Analysis on Thermal Behavior of Charring Materials with Surface Ablation, *International Journal of Heat and Mass Transfer*, 84 (2015), May, pp. 245-252
- [15] Li, W. J., et al., Nonlinear Pyrolysis Layer Model for Thermal Behavior of Non-Homogeneous Charring Materials, *Journal of Applied Polymer Science*, 132 (2015), 31-32, p. 42331
- [16] He, C. H., et al., Bubbfil Spinning for Fabrication of PVA Nanofibers, *Thermal Science*, 19 (2015), 2, pp. 743-746

- [17] Liu, Z., *et al.*, Tunable Surface Morphology of Electrospun PMMA Fiber Using Binary Solvent, *Applied Surface Science*, 364 (2016), Feb., pp. 516-521
- [18] Liu, Z., *et al.*, Active Generation of Multiple Jets for Producing Nanofibres with High Quality and High Throughput, *Materials & Design*, 94 (2016), Mar., pp. 496-501
- [19] Chen, R., *et al.*, Bubble Rupture in Bubble Electrospinning, *Thermal Science*, 19 (2015), 4, pp. 1141-1149