# BUBBLE RUPTURE IN BUBBLE ELECTROSPINNING

by

# Rouxi CHEN<sup>a,b</sup>, Yuqin WAN<sup>d</sup>, Na SI<sup>c</sup>, Ji-Huan HE<sup>a,b\*</sup>, Frank KO<sup>d</sup>, and Shu-Qiang WANG<sup>e\*</sup>

<sup>a</sup> National Engineering Laboratory for Modern Silk, College of Textile and Clothing Engineering, Soochow University, Suzhou, China

 <sup>b</sup> Nantong Textile Institute of Soochow University, Nantong, China
<sup>c</sup> Nantong Bubbfil Nanotechnology Company Limited, Nantong, China
<sup>d</sup> Department of Material Engineering, University of British Colombia, Vancouver, Canada
<sup>e</sup> Research Center for High Performance Computing, Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, Shenzhen, China

> Review paper DOI: 10.2298/TSCI1504141C

As the distinctive properties and different applications of nanofibers, the demand of nanofibers increased sharply in recently years. Bubble electrospinning is one of the most effective and industrialized methods for nanofiber production. To optimize the set-up of bubble electrospinning and improve its mass production, the dynamic properties of un-charged and charged bubbles are studied experimentally, the growth and rupture process of a bubble are also discussed in this paper.

Key words: bubble electrospinning, bubbfil spinning, dynamic of bubble, growth and rupture of bubble, nanofiber, mass production

## Introduction

Nanofibers have been extensively explored in last decades [1]; their distinctive properties (high surface area in combination with different functionalities) make them one of the most promising candidates in diverse areas [2], such as filter, tissue engineering, drug delivery, protective clothing, advanced biomaterials, biosensors, *etc.* 

Conventional single-needle electrospinning is a simple, effective, versatile, costeffective method to produce polymer nanofibers. However, it has a small fiber production rate, typically less than 0.3 g per hour per needle [3], which greatly limits its practical applications in industrial and civil products. Recently the needle-less (free liquid surface) electrospinning technology have been reported as new viable possibilities to fabricate nanofibers in mass production [4]. Hundreds of labs and research institutions have attempted to find new methods to improve the production of nanofibers.

Bubble electrospinning is one of the most influential needle-less electrospinning methods, and it has been developed into a matured bubbfil spinning [5]. Inspired by the fantastic spider spinning, Liu and He [6] and Liu *et al.* [7] used a gas pump to generate bubbles on a polymer liquid surface which was charged with an electric voltage, a number of jets were generated from the surface of the bubbles. They also applied "theory of bubble dynamics" to explain the mechanism of mass nanofiber production [8, 9]. In a number of publications, efforts have been described in finding the controlling parameters for different polymers using bubble

<sup>\*</sup> Corresponding authors; e-mails: hejihuan@suda.edu.cn, sq.wang@siat.ac.cn

electrospinning. Yang et al. [10] investigated the effects of solution concentration and viscosity on the diameter and morphology of bubble electrospun polyvinyl alcohol (PVA) nanofibers. Kong et al. [11] suggested a new method for fabrication of nanofibers with a polymer bubble membrane, and studied the effects of applied voltage and collect distance on the fiber diameter. Gule et al. [12] used bubble electrospinning to prepare DMHF-containing PVA nanofibers, which demonstrated good antimicrobial and cell-adhesion inhibition efficiency. Dou et al. [13] investigated the morphology of nylon6/66 nanofibers yarns produced by bubble-spinning. Chen et al. fabricated crimped nanofibers by bubble electrospinning and explored its crimp mechanism [14]. The authors also described the surface tension of a bubble with a modified Young-Laplace equation [15], which can be widely applied for bubble spinning process analysis. Li et al. [16] studied the effect of airflow direction blowing on polymer bubble and the morphology difference of the superfine fibers. Li et al. [17] compared the fiber morphologies of polyether sulfone (PES) via bubble spinning vs. conventional single needle electrospinning under the same spinning conditions. Shen et al. [18] prepared multi-layer nanofiber nonwoven fabrics for PM2.5 mask, which admitted excellent filter capabilities and breathability. Sidaravicius et al. [19] fabricated PEO/PVA nanofibers using a bubble foamed polymer solution to promote high mass deposition and investigate its deposited intensity. Ren et al. [20] used the foaming-assisted electrospinning technique to get large-pore mesoporous ZnO nanofibers. Jiang et al. [21] demonstrated an improved approach of free surface electrospinning utilizing micro-bubble solution system and studied the effect of bubble size on the diameters of nanofibers. Figure 1 shows different nanofiber morphologies of different polymer via bubble electrospinning.



Figure 1. The scanning electron microscopy of the nanofiber membrane *via* bubble spinning set-ups; (a) PVA (DI water) nanofiber, (b) PES (DMF) nanofiber, (c) PLA(DMF) nanofiber, (d) PES (DMF) nanopore fibers; (e) nylon (formic acid) nanofibers; (f) PS(THF) nanofibers

These researches mainly focused on the preparation and application of various polymer nanofibers *via* bubble electrospinning, but fewer literature reported the dynamical mechanism of bubble forming and its application in electro-spinning for mass production of nanofibers. In view of this, in this paper, the growth situation and rupture process of un-charged and charged polymer bubble were discussed, which further explained the reasons why bubble electrospinning will be one of the most effective methods for mass production of nanofiber.

1142

#### **Experimental**

Materials: PVA, with an average molecular weight of 95,000 g/mol purchased from Aladdin, sodium dodecyl benzene sulfonate (SDBS) purchased from Sinopharm Chemical Reagent Co., Ltd, and deionized water were used in these experiments. All materials used without further purification.

Solution preparation: PVA particles and SDBS powder were dissolved into DI water at the room temperature. The mixture was then placed on a 120 °C heating plate and stirred until a homogeneous and transparent solution was obtained. The solution was then cooled down to room temperature for experiment. The concentration of PVA solution was 6 wt.%.

Electrospinning set-up: fig. 2 shows the schematic of a classical bubble spinning set-up, which includes a bubble generator, a spinneret, an air pump, a solution reservoir, a high-voltage power supply, and a grounded collector. The grounded collector was placed 20 cm upper to the spinneret.

The forming and vanishing process of uncharged and charged polymer bubbles were respectively recorded with a high speed camera (HSC). The photos were further dissected to investigate the growth and rupture process of bubble.

During the experimental process, to begin with, the air pump was switched on until the generated bubbles were continuously pumped into the spinneret; the growth and rupture process of the un-charged bubble was videoed. And then, the ap-



Figure 2. The schematic of a classical bubble spinning set-up

plied voltage was applied and increased until a number of jets were observed from the top of the spinneret, the movement of the charged bubbles was also videoed. The experiments were carried out at room temperature in the air.

## Discusses

Shown as fig. 1, nanofibres with various morphologies, such as smooth, nanoporous, micro-spherical with nanoporous, can be fabricated. The key to a successful bubble electrosping is the steady continuous generation and rupture of polymer bubbles.

The nanofiber formation and the obtained nanofiber properties in bubble electrospinning depend on polymer solution properties including viscosity, solution concentration, surface tension and electrical conductivity.

### Young-Laplace equation

When an air bubble generates from the surface of a polymer solution, the force pushing it upward can be expressed in the form:

$$F_{\rm upward} = (P_{\rm in} - P_{\rm out})\pi R^2 \tag{1}$$

where  $P_{in}$  is the inner pressure of the bubble,  $P_{out}$  – the out pressure of the bubble, and R – the radius of the bubble. The gravitation could be ignored as the mass of bubble is extremely low.

The downward force of bubble, related with the surface tension of polymer solution, can be expressed in the form:

$$F_{\rm downward} = \gamma 2\pi R \tag{2}$$

where  $\gamma$  is the surface tension of polymer solution.

Since

$$F_{\rm upward} = F_{\rm downward} \tag{3}$$

it's surface tension T can be expressed in the form [2]:

$$T = \frac{1}{2}R(P_{\rm in} - P_{\rm out}) \tag{4}$$

When the bubble has an aspheric surface, the inner radius of the bubble can be expressed as  $R_1$  and  $R_2$ , according to the Laplace equation, it's surface tension T can be also expressed in the form:

$$T = \frac{P_{\rm in} - P_{\rm out}}{\frac{1}{R_1} + \frac{1}{R_2}}$$
(5)

According to eqs. (4) and (5), we can see that the surface tension is related with the diameter of the bubble and the inner and outside pressure difference on the bubble, but not with whatever the polymer is. Therefore, as long as a solution can form bubbles, these equations can be used to guide the fabrication nanofibers in bubble electrospinning. What's more, the pressure difference of bubble between inside and outside is the most important parameter which has effects on the rupture of polymer bubble (fig. 3).

### Unstable growth of bubble

HSC was used to record the growth process of polymer bubbles. Figure 4 shows the

photos of growth process. To quantify this process, the height, width and angel of the bubble were measured per 10 ms and the methods of measurement were shown as figs. 5(a) and (b). The height, width and angel of the bubble were always changing during the growth process, figs. 5(a) and (b) show the increasing tendency of the height, width and angel.

The longitudinal and transverse growth rates in per 10ms can be calculated by

$$V_l = d_j - d_i \tag{6}$$

$$V_t = d_n - d_m \tag{7}$$

where  $V_l$  and  $V_t$  are the longitudinal and transverse growth rates per 10 ms,  $d_j - d_i$  and  $d_n - d_m$  are the difference of height and width per 10 ms.

Shown as figs. 5(c) and (d),  $V_l$  and  $V_t$  vary greatly during the whole growth process. Sometimes they get bigger, sometimes they get smaller. After about 300 ms, they even drop

Figure 3. The force analysis model of bubble



#### Chen, R., *et al.*: Bubble Rupture in Bubble Electrospinning THERMAL SCIENCE, Year 2015, Vol. 19, No. 4, pp. 1141-1149





Figure 4. High speed photography of polymer bubble growth process

below zero which means the size of bubble is smaller than the size last 10 ms. What's more, the difference between adjacent peak and valley point greaten, which means the growth situation become more and more unstable. All descripted phenomena indicated that the growth process of bubble was extremely unstable, especially in the very short time-frame before the rupture process. As we all know, more Tylor corns can be generated under a higher voltage which makes the polymer surface unstable more easily in needle-less electrospinning. For bubble electrospinning, the unstable surface is ingenerate during the whole growth process, which is very advantageous for generating more Tylor cones at the same voltage.

# The movement and morphology of polymer bubble film

Figure 6 shows that the polymer solution flowed fast along the bubble surface. There were many polymer solution ripples and tiny bubbles, caused by the incoming airflow, which made a rough bubble surface. In this case, Taylor-like cones could be easily generated and many jets were produced on the rough polymer surface if a voltage was applied.

That is to say, during the growth process, the nanofibers can be easily fabricated from the unstable and rough polymer bubble surface; the spinning process was shown as fig. 7.

# Rupture of polymer bubble

When a bubble on a liquid-gas interface ruptures, the general expectation is that the bubble vanishes. But this is not what happened. Figure 8 is a collection of photos of a rupturing polymer bubble, which were videoed by HSC at 2000 frames per second. It shows that the

polymer bubble ruptures into many smaller thin films and tiny droplets. Therefore, the ruptured thin film is more precisely expected to retract rapidly until it becomes part of the interface, which typically occurs within milliseconds.



Figure 5. The changes during the growth of polymer bubble; (a) the changing of the bubble high and width, (b) the changing of the bubble angel, (c) longitudinal growth rate, and (d) transverse growth rate

As we all know, during the industrialization process of nanofiber production, one of the most profound difficulties is how to increase the number of Tylor cones, and many researchers explored lots of methods to improve it, the typically one was increasing the number of needles. However, for the bubble spinning, this problem can be solved considerably easier, because a bubble ruptures into hundreds of tiny thin films and droplets which are the Tylor cones for fabricating mass nanofibers.



Figure 9 shows the rupture process of charged polymer bubble, which was videoed by HSC at 500 frames per second. Lots of jets go up to the ground collector after the charged polymer bubble rupture, which typically occurs within milliseconds. All these jets are formed from these tiny droplets and shredded bubble films. Figure 10 shows the bubble electrospinning process, which was taken by digital single lens reflex camera. Thousands of polymer jets, looks like a waterfall, are spraying toward the ground collector after applying high-voltage direct-current power. The production of PVA nanofibers are about 3 g/hour *via* single bubble electrospinning.

Chen, R., et al.: Bubble Rupture in Bubble Electrospinning THERMAL SCIENCE, Year 2015, Vol. 19, No. 4, pp. 1141-1149



Figure 9. The rupture of charged polymer bubble, videoed by HSC



Figure 10. The bubble spinning for mass production

### Conclusions

The paper reported the dynamics mechanism of polymer bubble and its application in electro-spinning for mass production of nanofibers. According to the Yang--Laplace equation, the surface tensile of bubble is only related with the diameter and pressure difference of bubble between inside and outside. Therefore, the growth and rupture of bubble can be controlled by changing the inside pressure of bubble, which affect the stability, continuity, efficiency of bubble electrospinning. Based on high speed photos, the dynamic mechanism, including growth, and rupture process, of polymer bubble was investigated. The unstable growth situation of bubble made the

electrospinning more easily under a lower voltage; Tylor cones could be easily generated and many jets were produced on the rough polymer bubble surface after applying a voltage. What is more, thousands of tiny droplets and shredded bubble films, which were generated from the ruptured bubbles, were Taylor-like cones for producing polymer jets and fabricating mass nanofibers.

In conclusion, bubble electrospinning has some innate advantages in electrospinning. It definitely is one of the most effective methods for mass production of nanofibers and its set-up also deserves further exploration on the improvement and optimizing.

# Acknowledgment

The work is supported financially by PAPD (A Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions), Natural Science Foundation of the Jiangsu Higher Education Institutions of China (Grant No. 12KJB130002), National Natural Science Foundation of China under Grant Nos. 10802021 and 10972053, and Nantong Textile Institute of Soochow University, Academic new artist doctoral post graduate of Soochow University.

### References

- Reneker, D. H., Chun, I., Nanometre Diameter Fibres of Polymer, Produced by Electrospinning, Nanotechnology, 7 (1996), 3, pp. 216-223
- [2] Fujihara, K., et al., An Introduction to Electrospinning and Nanofibers, World Scientific, Singapore, 2005

1148

- Wang, X., et al., Needleless Electrospinning of Uniform Nanofibers Using Spiral Coil Spinnerets, Journal of Nanomaterials, 2012 (2012), ID 785920
- [4] Petrik, S., Maly, M., Production Nozzle-Less Electrospinning Nanofiber Technology, *Proceedings*, MRS 1240 (2009), DOI: http://dx.doi.org/10.1557/PROC-1240-WW03-07
- [5] Chen, R. X., et al., Bubbfil Spinning for Mass-Production of Nanofibers, Thermal Science, 18 (2014), 5, pp. 1718-1719
- [6] 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
- [7] Liu, Y, et al., Bubble-Electrospinning: A Novel Method for Making Nanofibers, Proceedings, 2007 International Symposium on Nonlinear Dynamics, Pts 1-4. Vol. 96. Ed. J.-H. He; 2008: Journal of Physics Conference Series
- [8] He, J.-H., The Smaller, the Better: From the Spider-Spinning to Bubble-Electrospinning, *Acta Physica Polonica A*, *121* (2012), 1, pp. 254-256
- [9] Liu, Y., et al., The Principle of Bubble Electrospinning and Its Experimental Verification, Journal of Polymer Engineering, 28 (2008), 1-2, pp. 55-65
- [10] Yang, R. R., et al., Effect of Solution Concentration on Diameter and Morphology of PVA Nanofibres in Bubble Electrospinning Process, *Materials Science and Technology*, 26 (2010), 11, pp. 1313-1316
- [11] Kong, H.-Y., et al., Polymer Liquid Membrane for Nanofiber Fabrication, Thermal Science, 17 (2013), 5, pp. 1479-1482
- [12] Gule, N. P., et al., Furanone-Containing Poly (Vinyl Alcohol) Nanofibers for Cell-Adhesion Inhibition, Water Research, 47 (2013), 3, pp. 1049-1059
- [13] Dou, H., et al., Effect of Solution Concentrations on the Morphology of Nylon6/66 Nanofibrous Yarns by Blown Bubble-Spinning, Materia, 19 (2014), 4, pp. 358-362
- [14] Chen, R.-X., et al., Mechanism of Nanofiber Crimp, Thermal Science, 17 (2013), 5, pp. 1473-1477
- [15] Chen. R.-X., On Surface Tension of a Bubble under Presence of Electrostatic Force, *Thermal Science*, 19 (2015), 1, pp. 353-355
- [16] Li, Z.-B., et al., On Air Blowing Direction in the Blown Bubble-Spinning, Materia, 19 (2014), 4, pp. 345-349
- [17] Li, Y., et al., Comparison between Electrospun and Bubbfil-Spun Polyether Sulfone Fibers, Materia, 19 (2014), 4, pp. 363-369
- [18] Shen, J., et al., Bio-Mimic Design of PM2.5 Anti-Smog Masks, Thermal Science, 18 (2014), 5, pp. 1689-1690
- [19] Sidaravicius, J., et al., The Influence of Solution Parameters on the Electrospinning Intensity from Foamed Surface, Journal of Applied Polymer Science, 132 (2015), 23, pp. 42034-42041
- [20] Ren, X., et al., Foaming-Assisted Electrospinning of Large-Pore Mesoporous ZnO Nanofibers with Tailored Structures and Enhanced Photocatalytic Activity, RSC Advances, 5 (2015), 21, pp. 16361-16367
- [21] Jiang, G., et al. An Improved Free Surface Electrospinning with Micro-Bubble Solution System for Massive Production of Nanofibers, *Materials Letters*, 144 (2015), 4, pp. 22-25

Paper submitted: January 28, 2015 Paper revised: May 18, 2015 Paper accepted: May 26, 2015