

PARTICLE-LIKE BEADS AND DAUGHTER JET CASCADES IN ELECTROSPINNING

by

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Nanofibers with high surface-to-volume ratio are of significant applications. This paper proposes a novel method for fabrication of particle-like beaded nanofibers and their daughter nanofibers, which are ejected from the surface of charged jets. Polyvinyl alcohol/ash solution is used in the electrospinning process.

Key words: *electrospinning, daughter jet cascades, whelk-like protuberances*

Introduction

Electrospinning is the cheapest and the most straightforward way to produce nanomaterials. Electrospun nanofibers are of indispensable importance for the scientific and economic revival of developing countries [1-4].

Structured polymer fibers with diameters in the range from several micrometers down to tens of nanometers are of considerable interest for various kinds of applications. Electrospun fibers can be used in different kinds of applications such as non-woven fabrics, reinforced fibers, support for enzymes, drug delivery systems, fuel cells, conducting polymers and composites, photonics, sensors, medicine, pharmacy, wound dressings, filtration, tissue engineering, catalyst supports, fiber mats serving as reinforcing preparation of functional nanotubes and so on [5-12].

There is difficulty in precisely controlling the diameter, morphology and porosity of electrospun fibers, which means that a new theory linked to classical mechanics and quantum mechanics should be developed to control the process of electrospinning to obtain nanofibers with homogenous diameters or to reveal different morphologies of the fabricated nanofibers [13-15]. This paper proposes a novel method to produce particle-like beaded fibers and daughter fibers.

Experimental

Polyvinyl alcohol (PVA) with a degree of 1750 ± 50 was supplied by Sinopharm Chemical Reagent Co. Ltd., and ash, black powdery substance that is left after something is burned, was used as an additive.

The electrospinning set-up used here was customized and demonstrated schematically in fig. 1. The solution was placed in a 10 mL syringe. The needle tip with a diameter 0.7 mm was connected to a DC high-voltage generator (Dongwen High Voltage Co., Ltd.) via an

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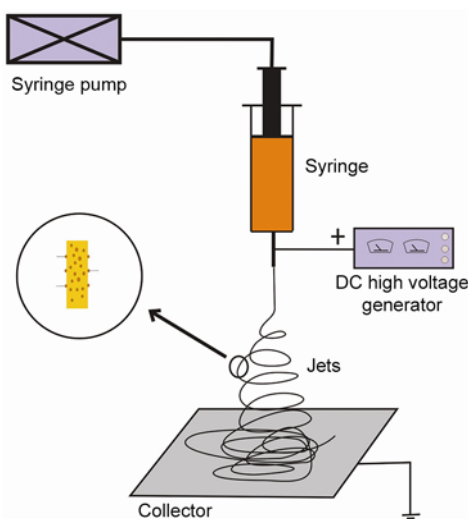


Figure 1. The set-up of electrospinning

The mixed solution was then put into an ultrasonic cell disruption system for 60 minutes to make them homogeneously mixed.

During the spinning process, the flow rate was 1 mL/h and the voltage applied was maintained at 20 kV.

Results and discussion

Electrospinning is a novel process for producing superfine fibers by forcing a viscous polymer, composite, sol-gel solution or melt through a spinneret with an electric field to a droplet of the solution, most often at a metallic needle tip. In the electrospinning process, there are surface charges on the jets which were shown in fig. 2.

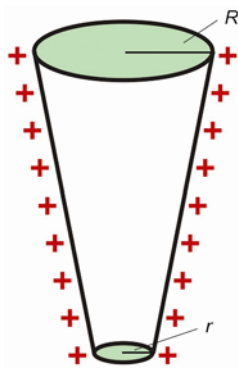


Figure 2. The charged jet

According to the mass conservation of the jet, the radius of the fiber can be predicted using the equation:

$$ur^2 = C \quad (1)$$

where r is the radius, u – the velocity, and C – a constant. A higher electrostatic field leads to a higher jet velocity and smaller jet radius.

According to the conservation of surface charges, the density of surface charges can be obtained using the equation:

$$2\pi R\bar{\sigma} = 2\pi r\sigma \quad (2)$$

where R is the initial radius of the jet, r – the radius of the jet, $\bar{\sigma}$ – the initial density of surface charges of the inlet, and σ is the density of surface charges of the jet.

It is obvious that $\bar{\sigma}$ must be large enough to ensure enough electronic force to overcome the surface tension of the Taylor cone, R is generally several millimeters, and r can be from several micrometers to tens of nanometers. According to eq. (2), the density of surface charge of the charged jet increase almost 1,000 times.

alligator clip. A flat piece of aluminum foil on the grounded receiver, placed 20 cm below the needle tip was served as the collector. The ultrasonic cell disruption system, SL-650D, was used for solution preparation. Fiber morphology images of PVA/ash were analyzed using a scanning electron microscope (SEM).

All concentration measurements were done in weight by weight (w/w). PVA was dissolved into distilled water with the temperature 16.2 °C and the humidity 43%. Then the mixture was stirred with the aid of electromagnetic stirrer at 90 °C for 3 hours to get homogeneous and transparent solution, and cooled to the room temperature before the experiment. The PVA concentration was 10%. Some plant charcoal ash was added gradually into the PVA solution until its concentration is 0.5%.

The surface of the charged jet in the electrospinning process does not appear to be calm there always exist thermally excited capillary waves, this results in beaded as discussed in [16]. The capillary waves typically have small amplitudes (~ 1 nm) and small wavelength (~ 100 μm). The behavior of capillary waves is restored by the surface tension, and is damped by the viscosity.

When the beads are to be formed on the opposite sides of the jet, the Coulomb force acting on the couple (fig. 3) is:

$$f_e = k \frac{\sigma^2}{r} \quad (3)$$

where f_e is the Coulomb force, which is directed outward, and k – a constant. It is obvious that the Coulomb force increases almost 1,000,000,000 times compared with that acting on the initial jet, this force is large enough to overcome the surface tension of the unformed beads to eject daughter jets. A similar phenomenon occurs in a daughter jet, and a sub-daughter jet can be ejected, thus a hierarchical jet cascade is formed which is shown in fig. 6, an event that typically occurs within milliseconds.

In the traditional electrospinning process, the Coulomb force can be ignored on a macro-scale, but it might increase large enough to relax the jet surface when the radius of the jet becomes small in micro/nano scale. The coupling of surface tension and the Coulomb force creates a tangential stress and extrudes the surface to form particle-like beaded fibers as shown in figs. 4 and 5. These particle-

-like fibers results in an unsmooth surface remarkably increase the surface-to-volume ratio.

A hierarchical fiber cascade obtained by the electrospinning is illustrated experimentally in fig. 1, where we also observe many bubbles-in-half on the fibers' surface. The diameter of the obtained fibers in last cascade can reach as small as 5-8 nm.

Conclusions

In the paper, we demonstrate that when a charged jet is accelerated by an electrostatic field, its diameter tends to micro/nano scale, and its surface can eject many wheel-like protuberances due to the growing Coulomb force acting on its surface. Once the electric force exceeds the critical value which is needed to overcome the surface tension, one daughter charged jet can be ejected.

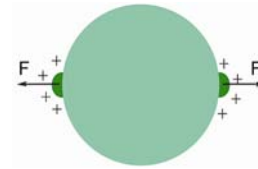


Figure 3. The Coulomb force of surface charges

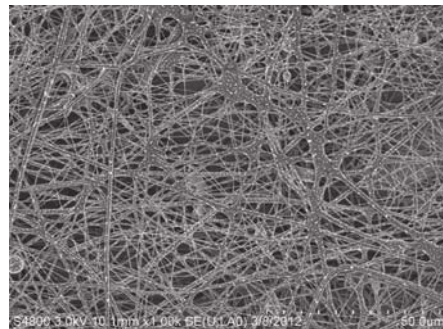


Figure 4. A SEM picture of PVA/ash fibers with 1.00 K

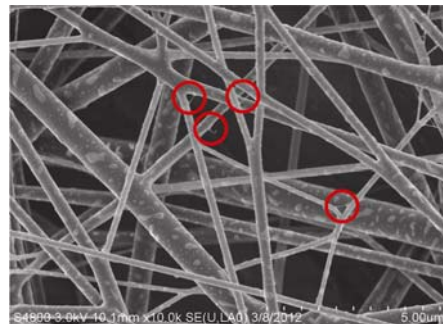


Figure 5. PVA/ash fibers with bubbles-in-half and daughter charged jets

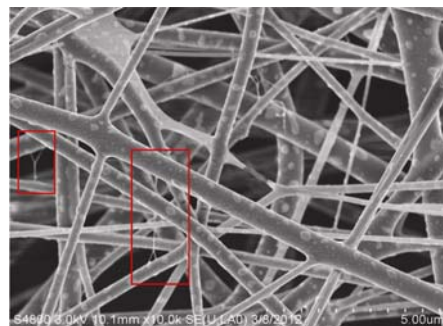


Figure 6. Hierarchical jet cascade

Sub-daughter jets are formed when the Coulomb force can overcome the surface tension of the daughter charged jet, as a result, we can observe a multi-stage cascade, which is received as superfine fibers, the diameter of the minimal fiber reaches as small as few nanometers.

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References

- [1] He, J.-H., et al., *Electrospun Nanofibres and Their Applications*, Smithers Rapra Update, Shawbury, UK, 2008
- [2] He, J. H., et al., Apparatus for Preparing Electrospun Nanofibres: a Comparative Review, *Materials Science and Technology*, 26 (2010), 11, pp. 1275-1287
- [3] 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
- [4] He, J. H., An Elementary Introduction to Recently Developed Asymptotic Methods and Nanomechanics in Textile Engineering, *International Journal of Modern Physics B*, 22 (2008), 21, pp. 3487-3578
- [5] McKee, M. G., et al., Phospholipid Nonwoven Electrospun Membranes, *Science*, 311 (2006), 5759, pp. 353-355
- [6] Viswanathamurthi, P., et al., Preparation and Morphology of Palladium Oxide Fibers via Electrospinning, *Materials Letters*, 58 (2004), 26, pp. 3368-3372
- [7] Wang, X. F., et al., Electro-Netting: Fabrication of Two-Dimensional Nano-Nets for Highly Sensitive Trimethylamine Sensing, *Nanoscale*, 3 (2011), 3, pp. 911-915
- [8] Gibson, P., et al., Transport Properties of Porous Membranes Based on Electrospun Nanofibers, *Colloids and Surfaces A, Physicochemical and Engineering Aspects*, 187-188 (2001), August, pp. 469-481
- [9] Tsai, P. P., et al., Strength, Surface Energy, and Ageing of Meltblown and Electrospun Nylon and Polyurethane (PU) Fabrics Treated by a One Atmosphere Uniform Glow Discharge Plasma (OAUGDP™), *Textile Research Journal*, 75 (2005), 12, pp. 819-825
- [10] Chen, D., et al., Electrospinning Fabrication of High Strength and Toughness Polyimide Nanofiber Membranes Containing Multiwalled Carbon Nanotubes, *The Journal of Physics Chemistry B*, 113 (2009), 29, pp. 9741-9748
- [11] Egevskaia, T., Borisov, G., Superthin Polymeric Film and Its Application in Optics, *Vibrational Spectroscopy*, 30 (2002), 1, pp. 3-6
- [12] Tessonier, J. P., et al., Carbon Nanotubes: a Highly Selective Support for the C=C Hydrogenation Reaction, *Studies in Surface Science and Catalysis*, 143 (2002), pp. 697-704
- [13] He, J.-H., et al., BioMimic Fabrication of Electrospun Nanofibers with High-Throughput, *Chaos, Solitons and Fractals*, 37 (2008), pp. 643-651
- [14] He, J.-H., Effect of Temperature on Surface Tension of a Bubble and Hierarchical Ruptured Bubbles for Nanofiber Fabrication, *Thermal Science*, 16 (2012), 1, pp. 327-330
- [15] Liu, Y., et al., The Principle of Bubble Electrospinning and its Experimental Verification, *Journal of Polymer Engineering*, 28 (2008), 1-2, pp. 55-65
- [16] He, J.-H., et al., Review on Fiber Morphology Obtained by Bubble Electrospinning and Blown Bubble Spinning, *Thermal Science*, 16 (2012), 5, pp. 1363-1379

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