NANOSCALE MULTI-PHASE FLOW AND ITS APPLICATION TO CONTROL NANOFIBER DIAMETER

by

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Nanoscale flows appear widely in nanofiber fabrication especially in electrospinning, where a nanoscale jet is a multi-phase fluid including solvents and additives. This paper shows that the fiber morphology can be effectively controlled by adjusting the density of the multi-phase jet. TiO_2 is used as an additive to produce polyacrylonitrile nanofibers by electrospinning; the results elucidate that uniform nanofiber can be obtained, and this phenomenon is explained theoretically.

Key words: *nanofibers, TiO_2 nanoparticle, polyacrylonitrile, electrospinning*

Introduction

Nanoscale hydrodynamics [1-4] becomes a hot topic in nanotechnology and thermal science as well. A nanoscale flow [5, 6] always behaves extremely. For example, an extreme efficiency in heat transfer [5] and water transportation is predicted through a carbon nanotube and blood capillaries. Majumder *et al.* [2] found that liquid flow through a membrane composed of an array of aligned carbon nanotubes is 4 to 5 orders of magnitude faster than would be predicted from conventional fluid-flow theory.

Electrospinning [7, 8], bubble electrospinning [9] and bubbfil spinning [10-12] are examples of nanoscale flows. In this paper we will use the basic concepts of multi-phase fluid mechanics to control fiber diameter in electrospinning process.

Nanoscale flow in electrospinning process

It is extremely easy to adjust the density of a jet in electrospinning process by adjusting concentration of the spun solution and by adding nanoparticles as additives. The density can be written in the form:

$$\rho = \rho_{\mathrm{p}} c_{\mathrm{p}} + \rho_{\mathrm{s}} c_{\mathrm{s}} + \rho_{\mathrm{a}} c_{\mathrm{a}} \tag{1}$$

$$c_{\mathrm{p}} + c_{\mathrm{s}} + c_{\mathrm{a}} = 1 \tag{2}$$

where subscripts p, s, and a imply polymer, solvent, and additive, respectively, and c is the concentration.

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Additives are also widely used in nanofiber fabrication to enhance some surface properties.

During the spinning process, the continuity equation can be expressed as [5]:

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}(\rho u) = 0 \tag{3}$$

where u is the velocity of the jet, and ρ – the density of the jet. For steady flow, eq. (3) becomes:

$$\pi r^2 \rho u = Q \tag{4}$$

where Q is the flow rate, and r – the fiber radius. In view of eq. (1), we write eq. (4) in the form:

$$\pi r^2 u \rho_a \left(\frac{\rho_p}{\rho_a} c_p + \frac{\rho_s}{\rho_a} c_s + c_a \right) = Q \tag{5}$$

In case for no additives ($c_a = 0$), the density varies in time due to solvent evaporation, and the fiber diameter mainly depends upon solvent evaporation. This is the reason for wide distribution of nanofibers with different fiber diameters, and non-uniform nanofibers are always obtained.

In case $\rho_a \gg \rho_p$ and $\rho_a \gg \rho_s$, eq. (5) can be approximately written in the form:

$$\pi r^2 \rho_a c_a u = Q \tag{6}$$

That means solvent evaporation will not affect much fiber's radius for a fixed spinning velocity, therefore, we can use additives with large density, *e. g.*, copper nanoparticles, to control fiber diameters in electrospinning and bubble electrospinning.

Experiment design

Uniform and parallel nanofibers [13] are needed in some advanced applications in, *e. g.*, tissue engineering, invisibility surface, and highly selective absorption [14]. The TiO_2 nanoparticles are widely used for surface treatment of nanofibers for enhancement of air purification and other fields [15-18]. In this paper TiO_2 nanoparticles are used to control the morphology of nanofibers.

It is well-known that the diameter of fibers during the electrospinning process is almost impossible to be controlled, and the distribution of fiber sizes is random and casual. It is almost impossible to repeat a same experiment to obtain the same morphology of the nanofibers by electrospinning. This paper aims to making the experiment repeatable with almost same fiber size using the above theoretical prediction.

The TiO_2 sol was prepared by using Sol-gel method. Subsequently, as-prepared sol was calcined to obtain pure TiO_2 nanoparticles at 450, 500, and 600 °C, respectively. The 1.2 g polyacrylonitrile (PAN) powders were dissolved absolutely in DMF (wt:wt = 12%) under vigorous magnetic stirring to form a homogeneous solution. Then 0.6 g TiO_2 nanoparticles were dispersed into PAN solution to form electrospun solution. Further, the PAN/TiO_2 blend solution was filled in to a 5 mL syringe. In this experiment, an adjustable high voltage power supply was applied to provide a voltage of about 18 kV. The rate of flow for electrospinning was 0.5 mL/h. The distance between needle and collector was maintained in 17 cm. The PAN/TiO_2 composite nanofibers were prepared *via* electrospinning at room temperature for 4 hours. The morphology

characteristics of nanofibers were measured by scanning electron microscope (SEM). The diameters of nanofibers were determined by using Image J 1.40 G.

The morphology characteristics were measured by SEM, fig. 1. The average diameters of TiO_2/PAN nanofibers were showed in fig. 2.

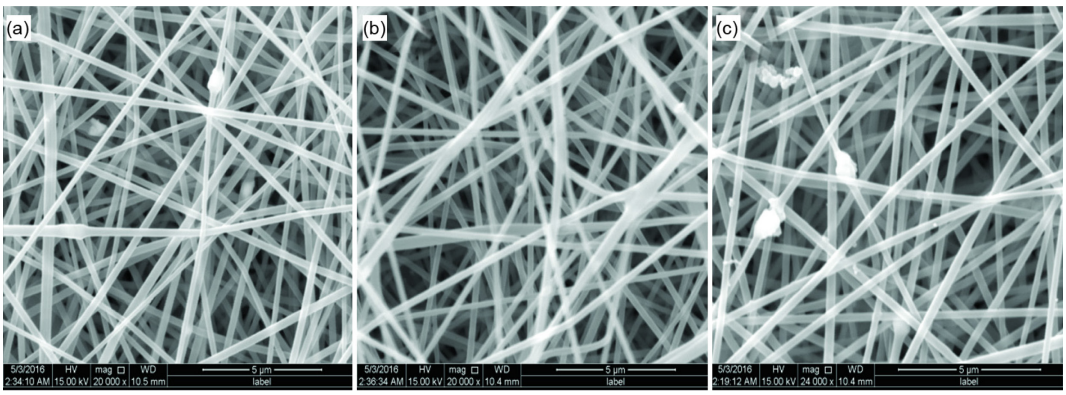

Figure 1. The SEM images of composite nanofibers of TiO_2/PAN; (a) 450 °C, (b) 500 °C, and (c) 600 °C

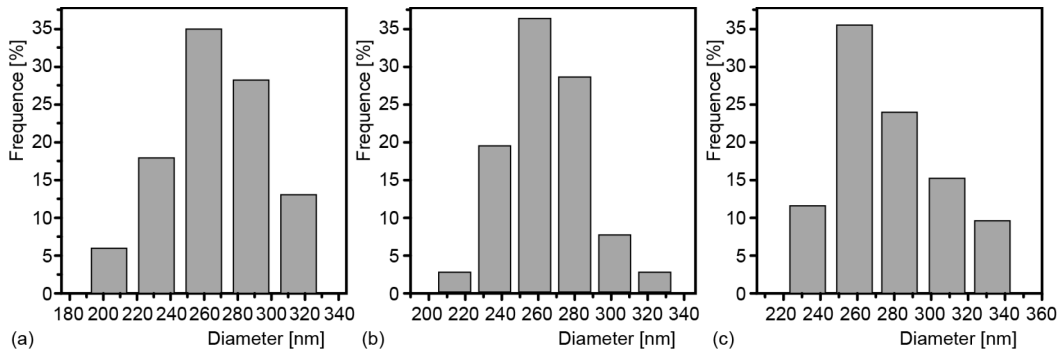

Figure 2. Diameter distribution of composite nanofibers of TiO_2/PAN; (a) 450 °C, (b) 500 °C, (c) 600 °C

Discussion and conclusion

In our study, TiO_2 nanoparticles are used as a massive additive, $\rho_a c_a \gg \rho_s c_s$; eq. (5) can be approximately expressed as:

$$\pi r^2 (\rho_p c_p + \rho_a c_a) u = Q \tag{7}$$

The velocity in eq. (7) is mainly determined by the voltage, a higher voltage results in a higher velocity. In our study the voltage is kept unchanged. So according to eq. (3) the radius of the fiber will be almost same as illustrated in fig. 1. The main distribution of fiber diameters for TiO_2/PAN (450 °C), TiO_2/PAN (500 °C), and TiO_2 /PAN (600 °C) nanofibers are kept unchanged; that is 266 nm.

This paper gives an easy way to control fiber diameters by TiO_2 nanoparticles as a massive additive, and uniform nanofibers are obtained for advanced applications. For mass-

production of TiO_2/PAN nanofibers, bubble electrospinning [9], and bubbfil spinning [10-12] has to be adopted.

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