Front. Chem. China (2006) 3: 334–339
DOI 10.1007/s11458-006-0041-4

RESEARCH ARTICLE

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Polysulfone nanofibers prepared by electrospinning and gas/jet-electrospinning

Abstract Polysulfone nanofibers were prepared by electrospinning. The electrospinning equipment was designed in a new way, wherein the spinneret was combined with a gas jet device. The intrinsic viscosity of the used polysulfone was 0.197 dL/g in dimethyl acetamide, which was also the solvent in electrospinning. The gas used in this gas jet/electrostatic spinning was nitrogen. The relationship between the process parameters and the average diameter of polysulfone nanofibers was investigated. The main process parameters studied in this work were the voltage, the flow rate of the spinning fluid, the distance between the spinneret and the nanofiber collector and the temperature in the spinning chamber. The other important factors determining the nanometer diameter were the spinning fluid properties including its viscosity, surface tension and electrical conductivity. The average diameter and the diameter distribution of electrospinning nanofibers were measured experimentally by using scanning electron microscopy. The diameter of polysulfone nanofibers prepared by the gas jet/electrostatic spinning was in the range 50–500 nm. It was found that the diameter of nanofibers mainly depended on high voltage, the gap between the spinneret and the collector and the concentration of polymer solutions. It is concluded that the gas-jet/electrospinning is a better method than the conventional electrospinning, in that it makes the nanofibers finer and more uniform and exhibits higher efficiency in the process of electrospinning.

Keywords electrostatic spinning, polysulfone, nanofibers, gas jet, electrospinning equipment

Translated from *Acta Polymerica Sinica*, 2005, (5) (in Chinese)

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1 Introduction

The topics on nanometer fibers (nanofibers) have attracted wide interests both in the scientific community and industries because of their unique performances. There is a lot of research papers published in this field [1–5]. Among various methods for nanofiber preparation, the electrospinning is the most direct way of obtaining polymer nanofibers. When the electrical force at the surface of a polymer solution or polymer melt overcomes the surface tension, a charged jet is ejected. The jet extends in a straight line for a certain distance, and then bends and follows a looping and spiraling path. The electrical force elongates the jet by thousand or even million times, and then the jet becomes very thin. At the same time, because the solvent evaporates or the melt cools down, the jet solidifies and becomes superfine nanofibers with diameter of 50–500 nm under proper conditions. Finally, the nanometer fibers are collected in the form of nonwoven fabrics on an electrically grounded metal sheet, a winder or some other collectors.

Electrospinning of polymer solutions can be traced back to 1934, when Formhals [6] invented a process for making polymer fibers by electrostatic force. His fiber was made from acetate cellulose solutions by electrospinning. The needed voltage depended on the character of the polymer and its solution, such as the molecular weight of the polymer and the viscosity of the spinning fluid. In order to make more stable fibers, Gladding [7] and Simins [8] improved the electrospinning apparatus, which collected electrospun fibers with a continuum conveyor belt. Later, Bornat [9, 10] published a patent related to a electrospinning apparatus, in which there was a collector on the swivel. Recently, Chu et al [11] further improved the electrospinning device, using their double electric field to make charged polymer jets and to spin nanofibers. In order to resolve the instability of the jet, Deitzel [12] set several charged rings to change the micro-configuration of electric lines between the spinneret and the collector, by which the

deposit path of the fiber was controlled. Reneker and Doshi [13] fulfilled the electrospinning of water-soluble PEO (Polyethylen Oxide) nanofibers with diameters of 0.05–5 μm. They described the electrospinning process, technical conditions, fiber morphology and some possible applications of electrospinning fibers. Kosuke [14] prepared nanofiber nonwoven fabrics of fibroin by using electrospinning and described the optimal conditions and discussed the diameter distribution of the fibers. Electrospinning of many other kinds of materials is described in details in monographs[1, 2].

In this paper, a novel type of electrospinning apparatus is presented. It is the gas-jet/electrospinning apparatus (for short, gas-electrospinning apparatus). Based on the standard electrospinning machine, a gas-supply system was added. In this novel process, the uniform nanometer fibers were obtained from a jet elongated by combined forces, including the electrostatic force and the frictional forces between polymer jet and air. Electrospinning and gas-electrospinning were compared and the effects of the processing parameters on the diameter and its distribution of the obtained nanofibers during spinning were investigated for the case of polysulfone.

2 Experimental

2.1 Structure of gas-jet/electrospinning apparatus

Gas-electrospinning apparatus is shown in Fig. 1. It is composed of a sample supplier, a spinneret, a high voltage supplier, a gas supplier and a collecting screen.

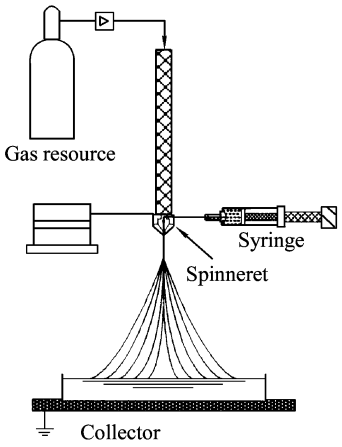

Fig. 1 Schematic diagram of gas-jet/electrostatic spinning setup

This gas-jet/electrostatic spinning set-up was different from the standard electrospinning apparatus, in that the spinneret only was the capillary tube of the spinning fluid. The gas-jet/electrospinning equipment was designed in a new way that in the spinneret, the capillary tube of spinning fluid is circled with the tube of the gas jet (Fig. 2).

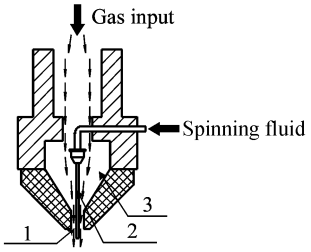

Fig. 2 Schematic diagram of spinneret used in gas-jet/electrostatic spinning setup 1) Orifice, 2) Capillary, 3) Gas Buffer

The inert gas was introduced from the inlet and passed through the buffer reservoir, which stabilized the gas flow in the form of the laminar flow. The gas flow additionally stretched the jet of the polymer solution. The polymer solution was slowly injected into a capillary by injector and flowed through a capillary with a definite length. The liquid could form the jet at the capillary nozzle due to the surface tension of the solution. In order to realize the gas electrospinning process, the polymer solution with a certain concentration was put into the sample injector. The polymer solution was educed by spinneret, which was connected to the anode of a high-voltage supplier. The cathode was the metal collector or coagulating bath and is connected with the ground. Under the proper conditions including the solution properties (viscosity, surface tension and conductivity) and operating conditions (voltage, flow rate, temperature, the distance between capillary and collector and the rate of gas jet), the jet of the spinning dope was accelerated and split into superfine jets by electrostatistic force and the force of air stream. The solvent in the jets was vaporized and the jets were solidifying. The forming nanofiber was collected on an electrically grounded metal sheet often in the form of nonwoven fabrics. In the coagulating bath as the collector, the solvent was transferred from fibers to the coagulating bath; the adhesion phenomena for the jets could not appear owing to the phase transformation in the forming nanofibers.

2.2 Materials and methods

Polysulfone (PSU) was supplied by the Anhua Company, its intrinsic viscosity [η] = 0.97dl/g. As the solvent, dimethylacetamide (DMAc) was the analytical reagent purchased from the Shanghai Chemical Regent Company. Nitrogen was an industrial product. The gas-electrospinning equipment was designed and made by the present authors. A scanning electron microscope (SEM) JSM-5900LV(Jeol Company) was used.

The spinning fluid was solutions of PSU in DMAc, the concentration was between 10%–20%. Before dissolving in DMAc, PSU was dried at 105℃ for 30 hours. The range of high voltage used was 27–50 kV, the anode was connected with the spinneret, the cathode was connected with the collector, which was connected with the ground. Nitrogen of 15 kPa was supplied from the gas resource by a PP pipe. The

flow rate of nitrogen was 5–15 L/min, measured by a gas flow meter. Ten milliliters of the polymer solution was put in the injector with the volume of 20 mL, which was driven by a screw driver, and in this way the polymer solution was injected into the spinneret. For this spinneret, the inner diameter of capillary was 0.4 mm. When other parameters were fixed, the distance between the spinning orifice and the collector was changed in order to determine the effect of this distance on the diameter of the nanofibers. The morphology and diameter of gas-electric spun nanofibers were observed by SEM. Data of SEM photography were treated by SigmaScan Pro2.0 software.

3 Results and discussion

3.1 Comparison of gas-jet/electrospinning with electrospinning

In an electrospinning process, a hemispherical drop of the spinning fluid is formed first at the top of the capillary. Then, if some voltage is applied on the surface of the liquid drop, the curvature of the drop surface will be changed. When a critical value of voltage is reached, the hemispherical drop becomes a conic one with a conical angle of 49.3°. This charged cone is called the Taylor cone [15]. The spinning fluid can be extruded from the Taylor cone and form a jet from the capillary under the action of the high-voltage electric field. This charged jet is accelerated further in the electric field, and its diameter decreases as shown in Fig. 3(a).

The theoretical basis for the mechanical analysis of the spinning processes was provided systematically by Ziabick [16]. Based on this theory, Shambaugh [17] analyzed the mechanics of the deformation of the filament flow during drawing by gas jet as shown in Fig. 3(b).

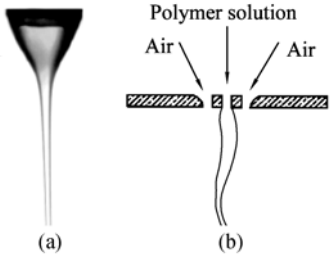

Fig. 3 Principles of drawing in traditional electrospinning and gas-jet/electrostatic spinning
a) Drawing by eletrostatic force, b) Drawing by gas jet

According to these principles, the deformation of spinning jet in an electrospinning process is the result of various instabilities of the charged jet [18–20]. For analyzing the mechanics of jet flow in gas-electrospinning, obviously, we should combine the theory of gas-spinning and electrospinning. In this work, the comparison of the two spinning processes was studied experimentally.

It was shown in Fig. 4 that the diameter of gas-electrospinning nanofiber was 200 nm, which was obviously finer than the average diameter (350 nm) of electrospinning nanofiber. This phenomenon indicated the additional drawing action of the gas jet on the polymer fluid jet during the spinning process.

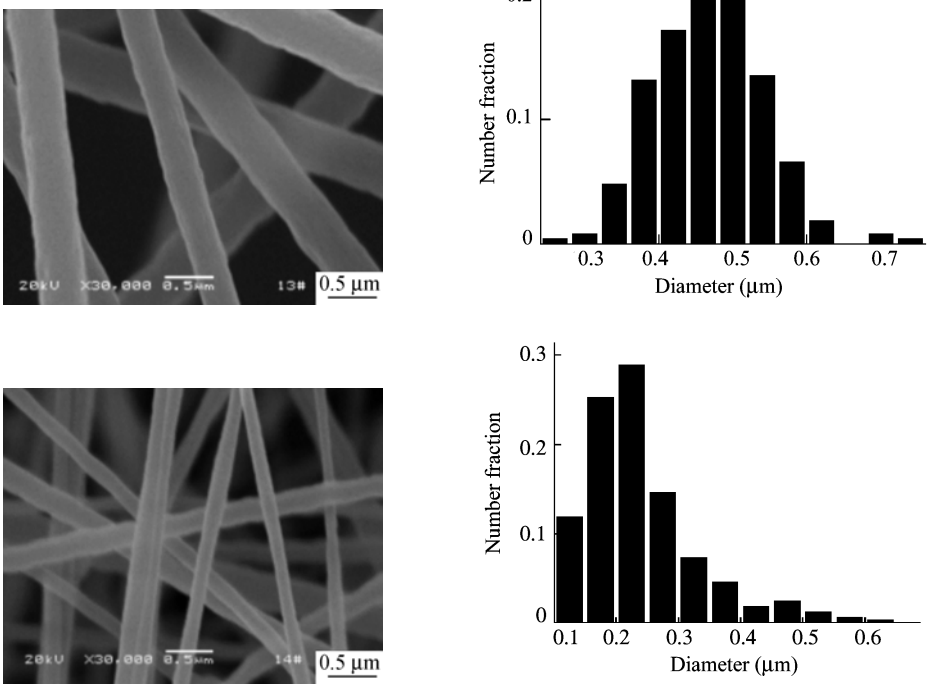

Fig. 4 SEM photographs and image manipulation graphs of PSU nanofibers spun by (a) electrospinning and (b) gas-jet/electrostatic spinning

The PSU/DMAc solution concentration was 20%, the distance between the spinneret and collector was 19 cm, the gas flow rate was 10.0 L/minute, and the applied voltage was 32.5 kV.

It was found in comparison of Fig. 4 (a) with Fig. 4(b) that the diameter of the electrospun nanofiber was in the range of 200–700 nm, but that of the gas-electrostatic spun nanofiber was in the range of 100–600 nm. The distribution of the diameter of the gas-electrospun nanofiber was narrower than that of the standard electrospun one, and was concentrated in the range of 100–300 nm.

3.2 Relation between diameter of nanofiber and process parameters

3.2.1 Effect of applied voltage on diameter of nanofiber and its distribution

When other parameters were fixed, the SEM photographs of nanofibers obtained by gas-jet/electro-static spinning with different voltages were shown in Fig. 5 and Fig. 4(b).

The solution concentration of PSU in DMAc was 20 %, the distance between the spinneret and collector was 19 cm, the gas flow rate was 10.0 L/min and the applied voltages were (a) 27.5 kV and (b) 45.0 kV, respectively.

When the applied voltage increased from 27.5 kV to 45.0 kV, the average diameter of nanofibers was reduced from 250 nm to 150 nm. It was suggested that the surface charge density of the polymer solution jet was increased with the rise in the applied voltage, and the electrostatic force of repulsion was also increased. At the same time, the jet obtained by a greater intensity of electric field would have a greater acceleration in the spinning line. These two factors resulted in a greater tensile stress exerted on the jet and the forming nanofibers, and led to a higher rate of tensile strain. So the increase of electric voltage is favorable to obtaining finer nanofibers. However, this variation of diameter with the change of electric field intensity is not very large.

3.2.2 Dependence of diameter of nanofiber and distribution on the distance between spinning orifice and collector

When other parameters were fixed, the SEM photographs of PSU nanofibers obtained by gas-jet/electrostatic spinning with different distances between the spinneret and the collector is shown in Figs 4(b) and 6.

The solution concentration of PSU/DMAc was 20%, the applied voltage was 32.5 kV, the gas flow rate was 10 L/min.

When the distance between spinneret and collector was increased from 15 to 19 cm, the average diameter of PSU nanofibers was decreased from 300 to 150 nm (see Figs 4(b) and 6). The flying distance of fibers was decreased with the decrease of the distance between spinneret and collector. In this case, the splitting degree of the jet flow and the drawing ratio were decreased, as a result the increase in the diameter of electrospun fibers.

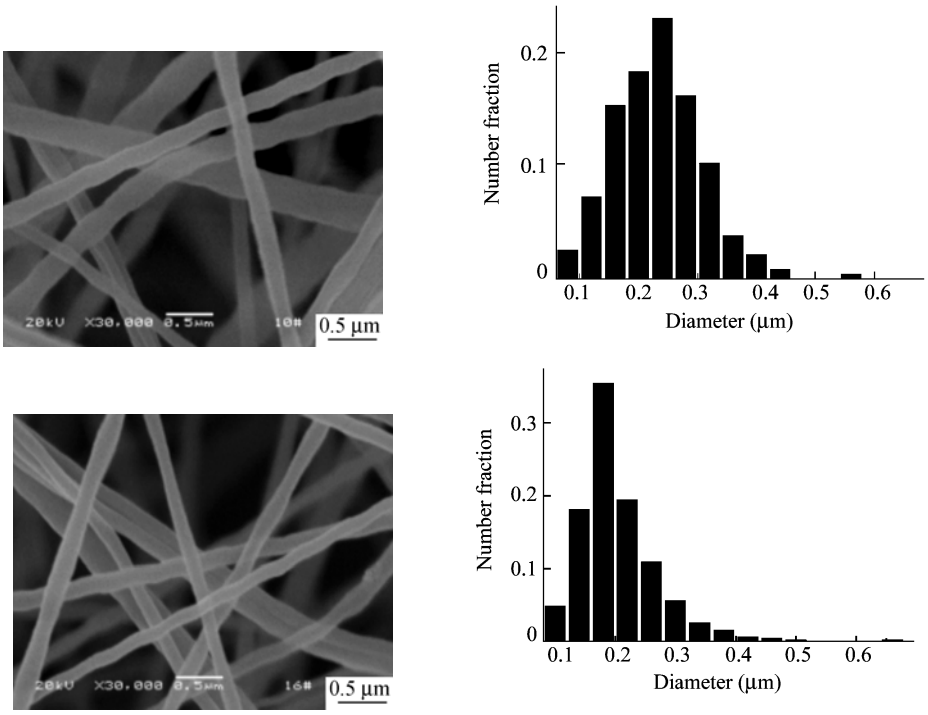

Fig. 5 Voltage dependence of average diameter and distribution of PSU nanofibers obtained by gas-jet/electrostatic spinning

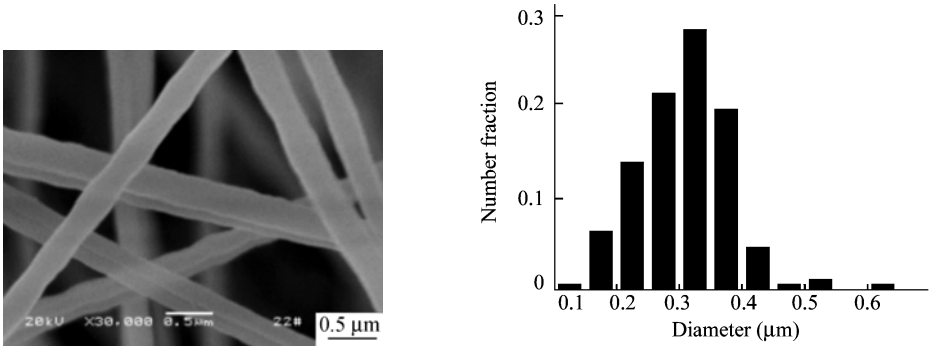

Fig. 6 SEM photograph and image manipulation graph of PSU nanofibers obtained by gas-jet/electrostatic spinning with a shorter distance of 15 cm between spinneret and collector

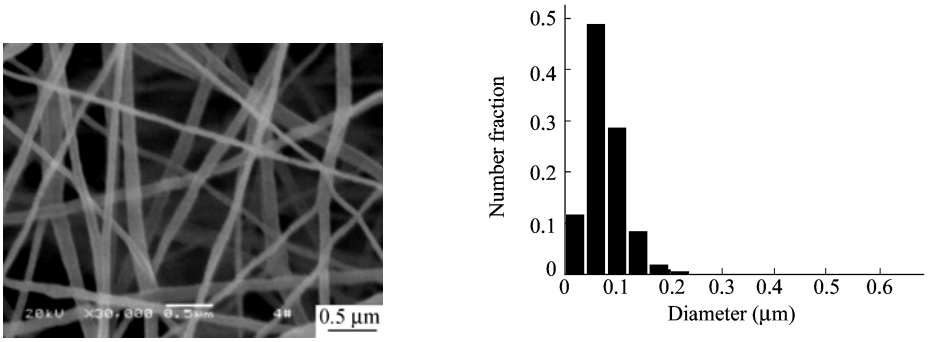

Fig. 7 SEM photograph and image manipulation graph of PSU nanofibers ontained by gas-jet/electrostatic spinning with a lower concentration 10% of the polymer solution

3.2.3 Dependence of the diameter of nanofiber and the distribution of the concentration of spinning solutions

Figs. 5(b) and 7 and show the dependence of nanofiber diameter and its distribution on the concentration of the spinning solution, i.e., the solution of PSU in DMAc. The distance between the spinneret and collector was 19 cm, the gas flow rate was 10.0 L/min and the applied voltage was 32.5 kV.

When the concentration of PSU/DMAc solution was 10%, the average diameter of fibers obtained was 130 nm (see Fig. 7). When the concentration was increased to 20%, the diameter was increased to 250 nm (see Fig. 4(b)). Many parameters (such as surface tension and viscosity) of the spinning fluid are determined by the concentration of polymer solutions. For example, when the concentration of the polymer solution was increased, both the surface tension and the viscosity were increased. Therefore, in the electrospinning process, the increase in concentration may lead to an increase in the total resistance to the hydrodynamic and electric force. As a result the increase of concentration will decrease both the splitting degree and draw ratio of the jet, and thicker nanofibers will be obtained.

4 Conclusions

A novel gas-jet/electrospinning method is presented on the basis of the standard electrospinning method for producing polymer nanofibers. The PSU nanofibers with diameter ranging from 50 to 500 nm were obtained. The diameters of the nanofibers are obviously depended on the process parameters of the gas-jet/electrospinning. When the voltage is increased from 27.5 to 45.0 kV, the average diameter of nanofibers is decreased from 250 to 150 nm. when the distance between spinneret and collector is decreased from 19 cm to 15 cm, the average diameter increases from 150 to 300 nm. The average diameter of electrospun nanofibers is equal to 130 nm for spinning with a polymer solution of 10%. While the concentration of the polymer solution goes up to 20%, the diameter of electrospun nanofibers increases to 250 nm. It is concluded that the gas-jet/electrospinning is better than the conventional electrospinning, making the nanofibers finer and more uniform, and exhibiting higher efficiency in the electrospinning process.

Acknowledgment This work was supported by the National Natural Science Foundation of China (No.50473050) and the Specialized Research Fund for the Doctoral Program of Higher Education of China under Grant No. 20010610024.

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