ABSTRACT

Poly(vinyl alcohol) (PVA) ultrafine fibres were prepared by gas-jet/electrospinning of its aqueous solutions. The morphology of the gas-jet/electrospun PVA fibres was investigated by controlling parameters such as: polymer solution concentration, gas flow rate and the polymer solution feeding rate. The morphology of the PVA fibres changed when the solution concentration was increased from 7 wt% to 12 wt%. With concentration of 7 wt%, a combination of smooth and some beads ultrafine PVA fibres was observed. With higher concentration, smooth fibres were obtained and the beads disappeared. The average diameters of PVA fibres increased gradually from 165±4 nm to 263±8 nm with the concentration from 7 wt% to 12 wt%. In addition, the average diameters of these ultrafine fibres were decreased from 317±10 nm to 219±5 nm after an initial increase in the gas flow rate from 2.5 L/min to 7.5 L/min and then increased to 287±9 nm as the gas flow rate increased to 10.0 L/min. The morphological structure changed with the variety of the solution feeding rates. At the solution feeding rate of 3.3 mL/h, PVA fibres with beads were observed. The average diameters of PVA fibres increased with increasing solution feeding rate. Particularly, the production rate of the gas-jet/electrospinning of PVA solution could be up to 2.2 mL/h, which was 11 times higher than the conventional electrospinning (0.2 mL/h), while the difference between the average diameter of electrospun fibres and the gas-jet/electrospun fibres was slight.

INTRODUCTION

The study on ultrafine fibres has been a subject with extensive research because of their unique properties and widespread applications in many fields [1,2]. Among various methods of fabricating ultrafine fibres, electrospinning is a cheap and straightforward method to produce polymer fibres with diameter range from nanometers to a few microns using an electrically driven jet. The electrospinning process involves a polymer solution or melt being placed into a syringe with a millimeter size nozzle and subjected to high electric field. Under the applied electrostatic force, the polymer is
ejected from the nozzle, whose diameter is reduced significantly as it is transported and deposited on a collector, which also serves as the ground for the electrical charges [3]. Because of the very high aspect ratio, specific surface area, and porosity, electrospun fibres are used for various applications, including drug delivery and tissue engineering [4], wound dressings [5], and vascular grafts [6-8]. Poly(vinyl alcohol) (PVA) is an important water-soluble polymer. Due to the inherent non-toxicity, good biocompatibility and excellent mechanical properties, the electrospun PVA membranes have been applied in biosensor [9], carbon nanotubes [10,11], drug delivery and tissue engineering [4], wound dressings [5], and filtration applications [12].

However, the single-jet electrospinning throughput of PVA/water system ranged between 0.2 mL/h to 0.5 mL/h [13,14]. The low throughput may limit the industrial use of the PVA electrospun membranes [15]. To obtain high production rate, multiple nozzles were introduced in electrospinning apparatus [15,16]. Compared with the single nozzle electrospinning apparatus, the electrospinning device of the multiple nozzles is relatively complicated. In addition, in our laboratory, Yao et al. [17] designed a gas-jet/electrospinning apparatus combining electrospinning with a gas-jet device. Compared with the conventional single nozzle electrospinning, the gas-jet/electrospinning method could generate thinner and more uniform polysulphone nanofibres with a higher polymer solution feeding rate of 30 mL/h because of the drawing action of gas jet [17]. Up to now, PSU [17], poly(ether sulphone) (PES) [18,19], poly(ethylene terephthalate) [20] and poly(3-hydroxybutyrate) (PHB) [21] ultrafine fibres have been prepared by gas-jet/electrospinning. Furthermore, Wei et al. [19] and Guan et al. [21] have found that the gas-jet/electrospinning of PES and PHB membranes have the potential to be used as scaffolds for biomedical applications. However, so far it is not found yet that what value the production rate of the gas-jet/electrospinning can increase in relation to that of the single nozzle electrospinning.

Although Lin et al. [18] studied the effect of gas flow rate on the morphology and the diameter of PES fibres during the gas-jet/electrospinning, the solvent used in the experiments was N,N-dimethylformamide (DMF), a high boiling solvent (165°C). In the present research work water is used as solvent with boiling point (100°C) lower than DMF. The effect of gas flow rate on the morphology and the diameter of gas-jet/electrospun PVA may be changed with the change of polymer/solvent system.

In this paper, PVA fibres were prepared by gas-jet/electrospinning of its solutions in water. The effects of controlling parameters including the concentration of polymer solution, gas flow rate, and polymer solution feeding rate on the morphology of PVA ultrafine fibres were investigated. Especially, the production rate of gas-jet/electrospinning of PVA solution could be up to 2.2 mL/h and this production rate was 11 times greater than the conventional electrospinning (0.2 mL/h). In addition, the average diameter of the electrospun PVA fibres was 210±7 nm, whilst that of PVA fibres gas-jet/electrospun at the solution feeding rate of 2.2 mL/h was 231±7 nm. The difference between the electrospun fibres and the gas-jet/electrospun fibres was insignificant. The gas-jet/electrospun PVA fibres were characterized by scanning electron microscopy.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVA) with degree of polymerization of approximately 1700 and degree of hydrolysis (DH) of 92%, was purchased from Sichuan Weinilun Industry Corp. (Chongqing, China). Nitrogen gas (99.9%) was supplied by Chengdu Haoru Gas Sale Co. Ltd. PVA was dissolved in deionized water to make solutions with concentrations range between 7 wt% to 12 wt%. The solutions were gently stirred for 1 h at 90°C in order to obtain homogeneous solutions.

Gas-jet/Electrospinning

The PVA solution was gas-jet/electrospun using the gas-jet/electrospinning apparatus shown in refs 17, 18. The gas-jet/electrospinning equipment was designed in a new way in which the spinneret was combined with a gas jet device. The spinneret consisted of two coaxial tubes. The inner capillary delivered PVA solution, while the outer tube delivered nitrogen gas. The gas-jet/electrospinning was carried out at
room temperature and the temperature of nitrogen gas was about 20. The PVA solution was transferred into a syringe and delivered to the tip of the inner capillary of the spinneret. The metal spinneret was connected to the negative electrode of a high voltage power supply (ZGF-60, Chengdu Chuandian Huayun High Voltage Electrical Apparatus Co. Ltd., China). A flat metal plate was placed below the nozzle as a grounded counter electrode to collect the fibres. During the gas-jet/electrospinning, the polymer solution was gas-jet/electrospun with the actions of high voltage and gas jet. The feeding rates of the polymer solution were 1.1, 2.2, and 3.3 mL/h and were controlled by a syringe pump. The gas flow rates were 2.5, 5.0, 7.5, and 10.0 L/min, and they were controlled by a gas flow meter. Unless otherwise specified, the applied voltage was 25 kV, the tip-collector distance was 25 cm, and the inner diameter of the inner capillary was 0.24 mm.

Characterization
The morphology of gas-jet/electrospun PVA mats was characterized by a scanning electron microscopy (SEM) (FEI Inspect F). The average diameters (P = 95%) of the PVA ultrafine fibres were measured by SigmaScan Pro 2.0 software based on 10 different SEM images with a magnification rate of ×10000. The fibre number of every sample was 500. The images of the capillary tip were taken with a digital camera (Nikon Coolpix 5600).

RESULTS AND DISCUSSION
Effect of Solution Concentration
The concentration of the polymeric solution is an important parameter in the process of electrospinning. The effect of the polymer solution concentration on the morphology of the gas-jet/electrospun PVA fibres is shown in Figure 1. Varying the PVA concentration from 7 wt% to 12 wt%, the solution feeding rate was 1.1 mL/h and the gas flow rate was 7.5 L/min. When the concentration was 7 wt%, a combination of smooth and some beaded ultrafine fibres was obtained. During electrospinning, beaded fibres were generally obtained at lower concentrations [22]. As the concentration was increased to 8, 10, and 12 wt%, respectively, smooth ultrafine fibres were obtained and the beads disappeared. It has been recorded that at lower concentration, the viscoelastic force was not large enough to counter the higher coulombic force, resulting in the break-up of the charged jet into smaller jets, which later rounded up to form minute and discrete droplets. At higher concentrations, with increased chain entanglements, the viscoelasticity was sufficient enough to prevent the total break-up of the charged jet and to allow the coulombic stress to further elongate the charged jet during its flight to the grounded target, which resulted in the disappearance of the beads. Additionally, the average diameters of the PVA fibres increased gradually from 165±4 to 263±8 nm as the concentrations of the PVA solution increased from 7 wt% to 12 wt%. This result agreed with the electrospinning results of PVA microfibres by Koski et al. [23].

Effect of Gas Flow Rate
In electrospinning, as the applied voltage increases, the droplet on the top of the capillary takes a conical shape called the Taylor cone [24]. If the higher voltages are applied, a jet is formed from the deformed droplet, which moves towards the collector and becomes narrower in the process [25]. Larsen et al. [24] used a coaxial gas jacket, a similar setup with gas-jet, to stabilize Taylor cones of a volatile solution and to induce particle-to-fibre transitions. Although varying the flow rate of solvent-saturated N2 in the range of 8-80 mL/min had no effect on the Taylor cone structure because of the low gas flow rates, the structures of the collected samples changed from particle to beaded fibres as the solvent-saturated N2 flow rate decreased from 80 mL/min to 8 mL/min [24]. Figure 2 shows the images of the capillary tip in the electrospinning and the gas-jet/electrospinning. In this study, when the higher gas flow rates of 2.5 L/min to 10 L/min were applied, the Taylor cone disappeared because of the higher stretching force of the gas jet.

Figure 3 shows the SEM image of electrospun PVA ultrafine fibres. Under this condition, the uniform PVA fibres with the average diameter of 210±7 nm could be obtained.

In order to evaluate the effect of the gas flow rate on the morphology of PVA fibres, a solution of 8 wt%
was gas-jet/electrospun at different gas flow rates. The SEM images of PVA fibres gas-jet/electrospun at the solution feeding rate of 1.1 mL/h under different gas flow rates are shown in Figures 1b and 4. When the gas flow rate was 2.5 L/min, the gas jet was not enough to volatilize water and the drawing action of the gas jet on the polymer fluid jet was not enough to stretch the jet. As a result, there were obviously interfibrillar bondings in the junction of PVA fibres and the average diameter of PVA fibres was the thickest (317±10 nm) among others. As the gas flow rate increased, the stretching force of the gas jet and the volatilization rate of water increased. Consequently, the degree of interfibrillar bondings remarkably decreased and smooth fibres were obtained when the gas flow rate was 7.5 L/min and above. Previous gas-jet/electrospinning results of poly(ether sulphone) (PES) showed that the average diameters of the PES fibres decreased as the gas flow rate increased from 5.0 L/min to 15.0 L/min [18]. Although the increase in gas flow rate resulted in the increase in volatilization rate of the solvent, the increase in volatilization rate of DMF was slightly higher because the solvent used in the gas-jet/electrospinning of PES solutions was DMF, a high boiling solvent (165°C). Thus, there was enough time to stretch the jet and the stretching action of the gas jet played an important role in that process. Therefore, the average diameters of the PES fibres decreased as the gas flow rate increased from 5.0 L/min to 15.0 L/min [18].

Figure 1. SEM images of PVA fibres gas-jet/electrospun from different concentrations: (a) 7 wt%; (b) 8 wt%; (c) 10 wt%; and (d) 12 wt%.
fibres decreased as the gas flow rate increased. In this study, the average diameters of the PVA fibres were decreased from 317±10 to 219±5 nm after an initial increase in the gas flow rate from 2.5 L/min to 7.5 L/min and then increased to 287±9 nm as the gas flow rate increased to 10.0 L/min. In the gas-jet/electrospinning of PVA aqueous solutions, the solvent was water. The boiling point of water is lower than that of DMF. The increase in volatilization rate of water is more than that of DMF when the gas flow rate is increased. As the gas flow rate increased from 2.5 L/min to 7.5 L/min, the drawing action of gas jet was dominant although the volatilization rate of water increased, which resulted in decreased average diameters of the PVA fibres. When the gas flow rate was 10.0 L/min, there was a little residual water in fibres before the fibres reached the collector. In other words, the factual stretching distance reduced and as a result, the average diameter of fibres increased.

Therefore, the optimal gas flow rate was 7.5 L/min under this condition and the average diameter of PVA ultrafine fibres under this gas flow rate was 219±5 nm. Although the PVA solution feeding rate of the gas-jet/electrospinning increased to 5.5 times as that of the electrospinning, the average diameter of the gas-jet/electrospun PVA fibres was almost the same as the average diameter of the electrospun fibres.

**Effect of Feeding Rate**

A series of experiments were carried out in which the feeding rate was varied from 1.1 mL/h to 3.3 mL/h, while the PVA concentration was 8 wt% and the gas flow rate was 7.5 L/min. The experimental results are shown in Figure 1a and Figure 5. At lower solution feeding rate of 1.1 mL/h, the PVA fibres had a uniform morphology and no bead defect was observed. As the solution feeding rate increased to 2.2 mL/h, the morphology of fibres showed no obvious change. However, when the solution feeding rate was 3.3 mL/h, the beaded fibres appeared. Ojha et al. [26] and Jalili et al. [27] found that the beaded fibres would appear when the feeding rate exceeds the rate...
of removal at a fixed electric field during the electrospinning. Similarly, when the feeding rate was 3.3 mL/h, the feeding rate exceeded the rate of removal during the gas-jet/electrospinning process. Therefore, the production rate of the gas-jet/electrospinning of PVA solution was 2.2 mL/h under this condition. And the average diameters of PVA fibres increased from 219±5 to 251±8 nm with the increase in feeding rate from 1.1 mL/h to 3.3 mL/h.

**Gas/jet Assisted Production Rate of PVA Ultrafine Fibres**

To study the production rate of the PVA gas-jet/electrospinning, the production rate of the single nozzle electrospinning was investigated under the same operating parameters except the gas flow rate. During the single nozzle electrospinning process, the maximum production rate was 0.2 mL/h (Figure 3). When the solution feeding rate exceeded 0.2 mL/h, such as 0.3 mL/h, a droplet of solution dripped from the end of the nozzle. On the basis of the above-mentioned results, it could be concluded that the PVA production rate of the gas-jet/electrospinning increased to 11 times that of the single nozzle electrospinning. In addition, the average diameter of the electrospun PVA fibres was 210±7 nm, while that of the PVA fibres
Figure 5. SEM images of PVA fibres gas-jet/electrospun at different solution feeding rates: (a) 2.2 mL/h; and (b) 3.3 mL/h with solution concentration of 8 wt%.

gas-jet/electrospun at the solution feeding rate of 2.2 mL/h was 231±7 nm. The difference between the electrospun fibres and the gas-jet/electrospun fibres was small. Compared with the multiple nozzles electrospinning, the gas-jet/electrospinning showed higher efficiency, and besides the gas-jet/electrospinning apparatus was relatively simple.

CONCLUSION

The gas-jet/electrospinning provided a simple method for preparing the PVA ultrafine fibres. In the spinning process, the process parameters such as the concentration of the polymer solution, the gas flow rate, and the feeding rate played an important role. As a result, a small number of beads existed in the PVA fibres mats when the solution concentration was 7 wt%. As the concentration was further increased, the beads disappeared. When the concentration of the PVA aqueous dope was increased from 7 wt% to 12 wt%, the average diameters of PVA fibres increased gradually from 165±4 to 263±8 nm. In addition, the average diameters of these ultrafine fibres were decreased from 317±10 to 219±5 nm after an initial increase in the gas flow rate from 2.5 L/min to 7.5 L/min and then increased to 287±9 nm as the gas flow rate increased to 10.0 L/min. The average diameters of PVA fibres increased with the increase in the feeding rate. Uniform PVA ultrafine fibres with an average diameter of about 220 nm were prepared by the gas-jet/electrospinning with the following optimal process parameters: the concentration was 8 wt%, the applied voltage was 25 kV, the gas flow was 7.5 L/min, the inner diameter of the inner capillary was 0.24 mm, the tip-collector distance was 25 cm and the solution feeding rate was 1.1 mL/h. The production rate of the PVA ultrafine fibres by the gas-jet/electrospinning was 11 times that of the conventional electrospinning.

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