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Electrospinning using a Teflon-coated spinneret

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ABSTRACT

In this paper, we report for the first time the use of a Teflon-coated spinneret for electrospinning processes. Polyvinylpyrrolidone (PVP) and zein were explored as filament-forming polymers, and electrospinning undertaken using both Teflon-coated tubing and traditional stainless steel tubing as spinnerets. Scanning electron microscope observations demonstrated that both the PVP and zein nanofibers produced using the Teflon-coated spinneret are narrower than those from the stainless steel equivalent. Electrospinning using a Teflon-coated spinneret resulted in smaller interfacial drawing forces counteracting the electrical forces on the spinning fluids. The Teflon-coated material thus takes advantage of the electrical forces more efficaciously than the steel analog. A molecular mechanism rationalizing the influence of the spinneret surface on electrospinning is proposed.

1. Introduction

Electrospinning is a flexible and facile route for the preparation of nano- and microscale structures with potential applications in a variety of fields [1–5]. Typically, an electrospinning system comprises four major components: a high-voltage power supply, a collector, a fluid driving device and a spinneret [6–10]. A range of innovations have recently been introduced to the system; the most significant of which concern the spinneret. Novel processes developed as a result include coaxial, side-by-side and needleless electrospinning [1].

Electrospinning generates materials directly through the interaction of electrical energy with the fluids being processed. It is intuitive that the spinneret must have good conductivity to transfer charge effectively. Hence, almost all spinnerets are made of metal, and most of them comprise stainless steel tubing [11–13]. However, this neglects that fact that electrospinning can only commence when the electrical forces overcome the forces holding the liquid in the spinneret: the most important of the latter is probably surface tension. Very little attention has been paid to the interactions between the working fluid and the fluid-directing tubing. A spinneret composed of metal can effectively convey electrical energy to the fluids being spun, but its surface tension may also exert a negative influence during the spinning process and thereby affect the properties of the resultant nanofibers.

Here, for the first time to the best to our knowledge, we report the usage of a Teflon-coated spinneret for the electrospinning of polymer nanofibers. Both polyvinylpyrrolidone (PVP) and zein were explored as model polymers. PVP, a man-made polymer, has a wide variety of applications in medicine, pharmacy, and cosmetics *inter alia*. In electrospinning, PVP has been long used as a template for preparing functional nanofibers. Materials have been produced for use as drug-delivery systems, inorganic–organic composites, precursors for organic peroxide fibers and for the generation of liposomes [14,15]. Zein is a naturally occurring mixture of proteins with different molecular weights which is found in corn gluten meal. It is used in the manufacture of a variety of commercial products including coatings for food, excipients for pharmaceutics, and clothing. These applications arise from zein's favorable biodegradability, biocompatibility, low hydrophilicity, good elasticity and film-forming capabilities. Recently the electrospinning of zein into nanofibers has attracted attention, particularly in the biomedical field [16–18].

2. Experimental

2.1. Materials

Polyvinylpyrrolidone K60 (PVP, $\bar{M}_w = 3,60,000$) was purchased from the Shanghai Yunhong Pharmaceutical Aids and Technology Co., Ltd., Shanghai, China. Zein (purity 98%) was obtained

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from Aldrich (Milwaukee, WI, USA). N,N-Dimethylacetamide (DMAc), acetic acid and anhydrous ethanol were provided by the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals used were of analytical grade.

2.2. Electrospinning

The PVP working solution consisted of 10 g PVP in 100 mL of a solvent mixture comprising DMAc and ethanol (10:90, v/v). Zein solutions were prepared by dissolving 25 g zein in 100 mL of an ethanol/acetic acid mixture (60:40, v/v).

Two types of spinneret were employed. The first comprised a stainless steel tube, and the second stainless steel tubing with a Teflon-coated nozzle. A syringe pump (KDS200, Cole-Parmer, Vernon Hills, IL, USA) and a high-voltage power supply (ZGF 60 kV/2 mA, Shanghai Sute Corp., Shanghai, China) were used for electrospinning. The fibers produced were collected on aluminum foil at a distance of 20 cm. All electrospinning processes were carried out under ambient conditions (24 ± 2 °C with relative humidity $64 \pm 4\%$). After some initial optimization experiments, applied voltages for the electrospinning of PVP and zein were set at 10 kV and 15 kV, and the flow rates at 2.0 mL/h and 1.0 mL/h, respectively. The electrospinning process was recorded using a digital video recorder (PowerShot A490, Canon, Tokyo, Japan).

2.3. Characterization

The morphology of the nanofiber mats was assessed using an S-4800 field emission scanning electron microscope (FESEM; Hitachi, Tokyo, Japan). Prior to examination, samples were gold sputter-coated under a nitrogen atmosphere to render them electrically conductive. The average fiber diameter was determined by measuring their diameters in FESEM images at more than 100 different places using the Image J software (National Institutes of Health, Bethesda, MD, USA).

An electronic balance (AL204, Mettler Toledo, Shanghai, China) and a DSA100 drop shape analysis instrument (Krüss GmbH, Hamburg, Germany) were used to explore the interfacial tensions between the polymer solutions and nozzles of the spinnerets.

3. Results and discussion

3.1. Teflon-coated spinneret

Teflon-coated spinnerets were prepared simply by inserting a stainless steel tube (length 46 mm, outer diameter 1.0 mm and inner diameter 0.82 mm) into a Teflon tube (inner diameter 1.0 mm, length 10 mm). This is depicted in Fig. 1a. For comparison, spinnerets comprising only stainless steel were prepared from stainless steel capillary (having an outer and inner diameters of 1.36 mm and 1.00 mm, respectively) with a length of 50 mm (Fig. 1a). All the stainless steel tubes were made of 06Cr19Ni10 (GB24511 in China) austenitic stainless steel, comprising steel, C ($\leq$0.07%), Cr (17.00–19.00%), Ni (8.00–10.00%), Mn ($\leq$2.00%), Si ($\leq$1.00%) and traces of S and P. A digital image of the arrangement of apparatus for conducting the electrospinning process is shown in Fig. 1b. A syringe pump was used to drive the fluid and an alligator clip to connect the spinneret (the non-coated part of the Teflon-coated spinneret) to the high voltage power supply.

A typical fluid jet traveling process is illustrated in Fig. 1c and d for the electrospinning of PVP at 10 kV. With both the Teflon-coated (Fig. 1c) and steel (Fig. 1d) spinnerets a straight thinning jet is emitted from the Taylor cone, and is then followed by a bending and whipping instability region with loops of increasing size. However, there are three obvious differences between the processes observed with the two spinnerets: (1) the Taylor cone is indented in Fig. 1c but can be clearly distinguished in the inset of Fig. 1d; (2) the thinning straight jet in Fig. 1c is shorter than that in Fig. 1d; (3) some fibers are draped on the stainless steel spinneret in Fig. 1d but very few on the Teflon-coated spinneret in Fig. 1c. These differences suggest that the electrical energy might exert more efficacious drawing on the PVP solutions when the Teflon-coated spinneret is exploited.

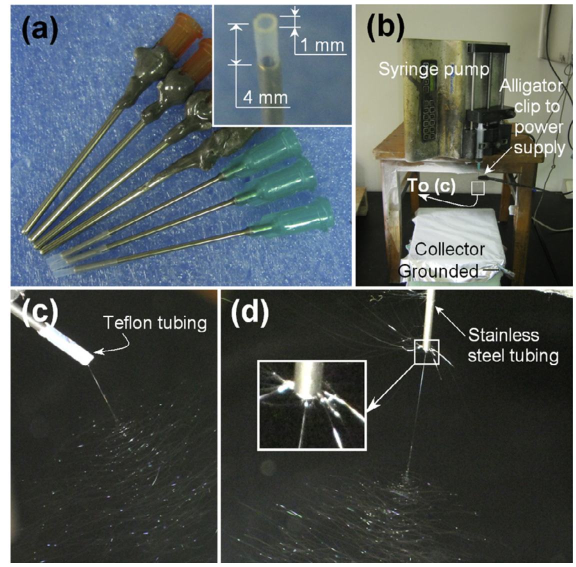

Fig. 1. Digital images of the electrospinning processes: (a) the two spinnerets; the inset shows the dimensions of the Teflon coating; (b) the electrospinning apparatus; (c) the fluid jet of a PVP solution using a Teflon-coated spinneret; (d) the fluid jet of a PVP solution using a traditional stainless steel spinneret. Electrospinning was undertaken at 10 kV.

3.2. Comparison of nanofibers with different spinnerets

The morphologies of the electrospun PVP nanofibers are given in Fig. 2. The fibers prepared with both spinnerets have linear morphologies without any visible “bead-on-a-string” phenomena. This is a result of the good electrospinnability of the PVP solutions. However, there are still stark differences between the fiber sets. The nanofibers prepared with a traditional stainless steel spinneret have an average diameter of 870 ± 140 nm (Fig. 2a–c), somewhat larger than those generated using a Teflon-coated spinneret (average diameter: 540 ± 110 nm; Fig. 2d–e). The former set of fibers also exhibits more curvature than the latter. These results indicate that the PVP solutions undergo more effective drawing by the electrical forces, resulting in straighter and narrower nanofibers when a Teflon-coated spinneret was exploited.

Similar results were obtained when zein solutions were explored. The zein nanofibers generated with a traditional stainless steel spinneret have an average diameter of 350 ± 190 nm (Fig. 3a–c), larger than those from a Teflon-coated spinneret which have an average diameter of 270 ± 130 nm (Fig. 3d and e). Both sets of fibers are observed to have a few spindles in them owing to the relatively low concentration of zein in the spinning solutions.

3.3. Mechanisms by which the Teflon-coated spinneret can facilitate electrospinning

To investigate the influence of the spinneret composition on the electrospinning process, experiments were carried out to discern the differences between the Teflon-coated and stainless steel tubes when they were used to dispense polymer solutions. A flow rate of 1.0 mL/h was used to dispense the PVP working solution from each spinneret with no voltage applied, and an electronic balance

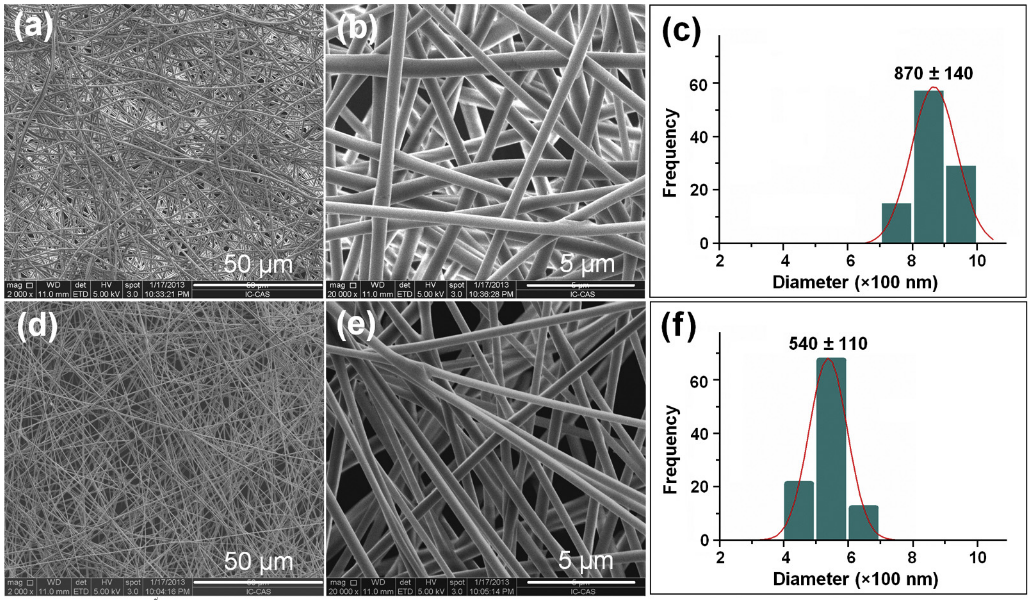

Fig. 2. FESEM images of PVP nanofibers prepared using a traditional (a–c) and a Teflon-coated spinneret (d–f).

employed to receive the falling droplets. This experiment is illustrated in Fig. 4a. Six independent experiments were performed. The average number of droplets dispensed in one hour were 57 (Teflon-coated) and 51 (stainless steel); the average droplet weights were 0.016 ± 0.001 and 0.018 ± 0.001 g ($n > 150$), respectively. Although both the Teflon and stainless steel tubing have the same inner diameter of 1.0 mm, the droplets from the steel tubing (Fig. 4b) were larger and heavier than those from the Teflon tubing (Fig. 4c). A further experiment was performed to determine the contact angles of the PVP solution on a Teflon and a stainless steel plate. The results are shown in Fig. 4d and e. A contact angle of $81 \pm 6°$ is observed on a Teflon plate, significantly larger than the $34 \pm 4°$ seen on the steel plate ($n = 6$). This indicates that the interfacial tension between the Teflon and PVP solution was smaller than that between the solution and steel.

It is axiomatic that the electrospinning process is governed by a balance between the electrical force and the surface tension of the liquid being spun. When the electrical forces are sufficiently large to overcome the fluid-restraining forces of surface tension, a Taylor cone is formed and a thinning straight jet emitted from it to initiate electrospinning [1]. The literature emphasizes the influence of the surface tension between the liquid being processed and the atmosphere, but overlooks the interfacial interactions between this liquid and the nozzle of the spinneret. The latter must also play an important role in drawing the liquid back into the tube and countering the electrical forces. Here, the interfacial tension with the Teflon-coated tubing was found to be smaller than that with steel tubing, and hence the former led to more effective electrospinning.

There is a critical applied voltage for the preparation of nanofibers from a polymer solution, above which the electrospinning process can commence. Further increases in the applied voltage make the Taylor cone increasingly small until it is indented in the spinneret [19]. When Teflon-coated tubing is used as a spinneret nozzle, there is a smaller interfacial force, meaning that a

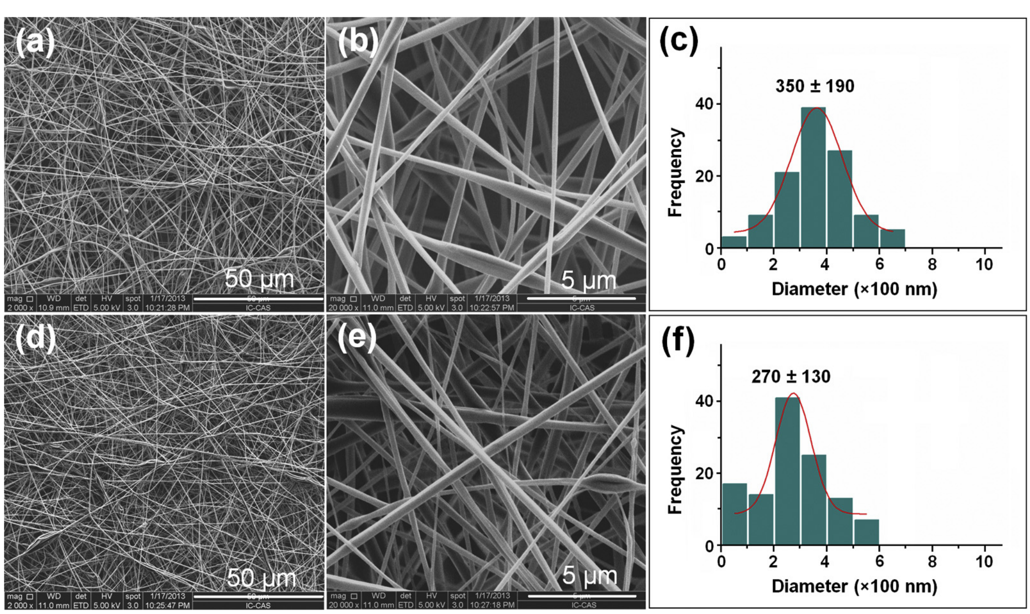

Fig. 3. FESEM images of zein nanofibers prepared with a traditional (a–c) and a Teflon-coated (d–f).spinneret.

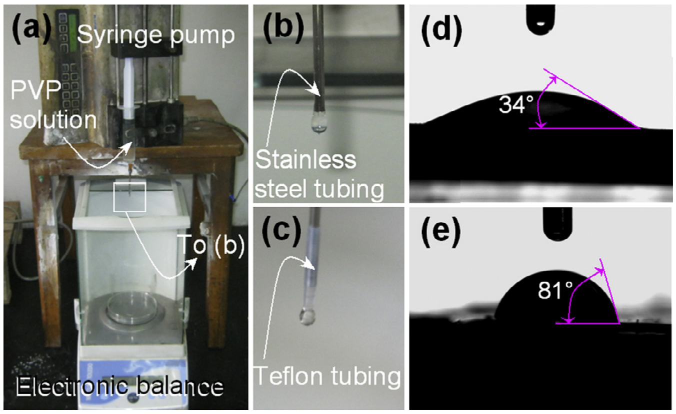

Fig. 4. Experiments to investigate the influence of spinneret composition on the electrospinning process. (a) The apparatus used to study droplet size and weight; (b) droplets of fluid from the stainless steel tubing; (c) droplets of fluid from the Teflon-coated tubing; (d) the contact angle of a PVP solution on a stainless steel plate; (e) the contact angle of a PVP solution on a Teflon plate.

lower electric field threshold is required to commence electrospinning. Thus, usage of the same voltage results in an obvious Taylor cone with a steel spinneret (see Fig. 1d) but a Taylor cone smaller than normal or even indented within the Teflon-coated nozzle as in Fig. 1c.

The interfacial tension between the spinning solution and Teflon-coated spinneret (F_{iT}) is lower than with a stainless steel nozzle (F_{is}). This is expected to result from interactions with both the solvent and polymer solutes. A schematic is given in Fig. 5. An electrospinning process is traditionally deemed to a balance between the electrostatic field force (E) and surface tension (γ). When a Teflon-coated spinneret is used, the abundant electron density of fluorine on the Teflon surface causes it to repel the working solutions because of the electronegative oxygen atoms present in both the PVP and zein molecules, suggesting a smaller interfacial tension. However, when a stainless steel tube is employed, the electropositive nature of the metal atoms makes them attract the working solvent and also the solutes *via* their electronegative atoms. This attraction makes the working solution sprawl on the stainless steel surface. This not only increases the forces acting counter to the electrical drawing, but also makes it easier for the electrospun fibers to become attached to the spinneret, as shown in Fig. 1d.

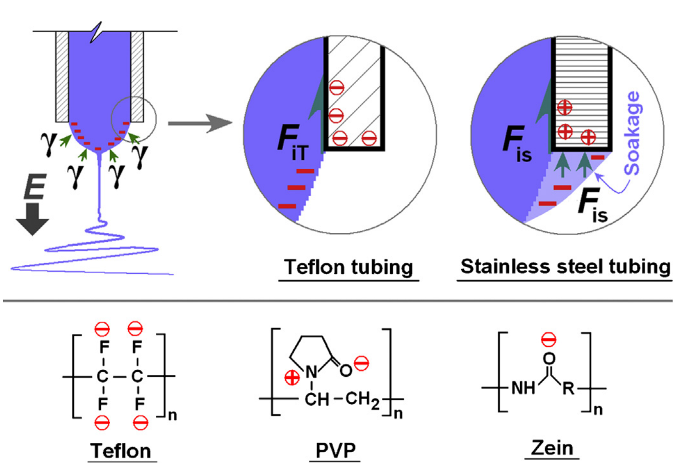

Fig. 5. The influence of spinneret composition on the electrospinning process.

4. Conclusion

This study demonstrated that coating the tip of a metal spinneret with a Teflon sheath can result in enhanced electrospinning. Under the same conditions, PVP nanofibers prepared using a Teflon-coated spinneret had similar linear morphologies to those generated with a traditional stainless steel spinneret, but the former had reduced diameters (540 ± 110 nm *cf.* 870 ± 140 nm respectively). Similarly, zein nanofibers from both a Teflon-coated and stainless steel spinneret had the same spindle-on-a-string morphologies but also had different diameters: 350 ± 190 nm and 270 ± 130 nm, respectively. With the usage of a Teflon-coated spinneret it appears that the electrical forces could be exploited more effectively in drawing the working fluid to generate finer nanofibers. The interfacial tensions between the working fluids and spinnerets were found to have a negative influence on electrospinning and on the as-prepared fibers. It is suggested that electrospinning with a Teflon-coated spinneret results in smaller interfacial spinneret/solution interactions countering the influence of the electrical forces on the spinning fluids. Thus, the coated spinneret exploits the electrical forces more effectively than a traditional steel spinneret.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apsusc.2013.08.030.

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