Shellac nanofibers prepared using a modified coaxial electrospinning with a Triton X-100 solution as the sheath fluid

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Keywords: Modified coaxial electrospinning; Nanofibers; Shellac; Sheath solutions; Triton X-100

Abstract. The present study reports that a modified coaxial electrospinning process, which was successfully carried out to control the diameters of shellac fibers. With a Triton-X100 in ethanol as sheath working solution and shellac ethanol solution as a core electrospinnable fluid, the coaxial electrospinning processes can be conducted continuously and smoothly. Optical observations of the electrospinning process demonstrated that both a single-fluid and a coaxial process can be realized using the same apparatus. Field-emission scanning electron microscopy results demonstrated that the flow rate of sheath Triton X-100 solutions had a significant influence on the size of shellac fibers. As the sheath-to-core fluid flow rate ratio increased from 0 to 0.4, the shellac fibers' diameter decreased from 1.21 ± 0.41 μm to 0.19 ± 0.07 μm. The fibers' diameter (D, μm) has a clear linear relationship with the flow rate of sheath Triton X-100 solution (F): D = 1.08 - 2.25 F (R^2=0.9851).

Introduction

Electrospinning, as a simple and straightforward process for synthesizing one-dimensional nanofibers, is very popular due to its capability in creating nanomaterials costly and the wide potential applications of electrospun nanofibers [1]. This one-step facile process now has developed from using a single fluid, to two fluids (coaxial and side-by-side electrospinning), and to multiple fluids (multiple coaxial electrospinning) [2]. New types of nanofibers with well-defined complicated nanostructures, novel morphologies, varied shapes, and/or new functions have been broadly reported in literature [3]. However, very limited attention has been paid on controlling the size of electrospun nanofibers [4].

Over the past decade, the strategies taken to manipulate the simple and straightforward electrospinning process for obtaining polymer nanofibers with thinner diameters can be classified into three categories: i) manipulating process parameters (such as applied voltage, solution flow-rate, fibers collected distance and temperature); ii) adjusting the intrinsic properties of working solutions (such as surface tension, conductivity and viscosity); and iii) changing the ambient conditions or providing some assistant apparatuses, such as conducting the electrospinning process in a more humid closed chamber, in vacuum conditions and with an air-blow systems [5]. However, these methods are still far from being able to accurately predict the electrospun fiber diameter due to the complex electro-fluid-mechanical property of the electrospinning process and the filament-forming polymers often have a relatively narrow electrospinnable window [4].

New strategy that can produce high quality polymer nanofibers with predicted size stably and controllably is highly desired. Co-axial electrospinning, in which a concentric spinneret can accommodate two different liquids, is regarded as one of the most significant breakthroughs in this field [6,7]. During the traditional co-axial electrospinning process the sheath solution acts as a guide and surrounds the core material, and the viscosity of the sheath solution is required to overcome

interfacial tension between the two solutions to enable the formation of a compound Taylor cone and a subsequent fluid jet [8]. However, a modified co-axial electrospinning was recently reported, in which unspinnable solvents were able to used as sheath fluids.[6] This modified processes have been used to prepare ultra-fine structures from concentrated polymer solutions that were previously thought to be un-electrospinnable and to improve polymeric nanofibers' quality systematically [4,6].

Based on the above-mentioned knowledge and the exploitation of modified coaxial electrospinning, here we developed a new protocol for generating nanofiber with tunable diameters. Shellac, which was exploited as the model polymer here, is the purified product of the natural material Lac which is secreted by the small parasitic insect Kerria lacca on various host trees in South Eastern Asia. It found potential applications in agriculture, food products, and drug delivery systems as the only pharmaceutically used resin of animal origin [9].

Experimental

Materials Shellac (purity of 95% and wax free) was obtained from Shanghai Wanjiang Bio-Technology Co., Ltd. (Shanghai, China). Anhydrous ethanol and Triton X-100 were provided by Shanghai Guangjia Chemicals Co., Ltd. (Shanghai, China). All chemicals used were analytical grade.

Co-axial electrospinning Ethanal solution with a concentration of 10 $mg \cdot ml^{-1}$ was used as the shell working fluid. A solution containing 8.0 g shellac in 10 ml ethanol was exploited as the core fluid. Both the concentric spinneret and the electrospinning system were homemade. The electrospinning system comprised a ZDF-2000 power supply (Shanghai Sute Electrical Co., Ltd., Shanghai, China), two KDS 100 syringe pumps (Cole-Parmer®, Vernon Hills, IL, USA), the concentric spinneret and a cardboard wrapped with aluminum foil as fiber collector. Four different types of fibers were prepared under a fixed core fluid flow rate of 2.0 ml/h and a varied shell fluid flow rate, which was manipulated by the syringe pump (Table 1). The applied voltage and fiber-collected distance were fixed as 15 kV and 20 cm, respectively. The electrospinning processes was recorded using a digital camera (PowerShot A640, Canon, Japan) under a suitable magnifications.

Table 1. Parameters of the electrospinning processes and their products.

No.	Process	Flow rate ratio	Morphology [b]	Diameter [c] (μm)
F1	Single	0	Linear	1.21 ± 0.41
F2		0.1	Linear	0.89 ± 0.11
F3	Coaxial [a]	0.2	Linear	0.58 ± 0.09
F4		0.4	Spindle-on-a-string	0.19 ± 0.07

Note:

[a] Coaxial electrospinning with a fixed core flow rate of 2.0 mL/h.

[b] 'Linear' morphology refers to fibers without beads or spindle.

[c] Expressed as the mean ± SD of over 100 fiber diameter measurements.

Characterization The surface morphology of electrospun fibers was observed using a JSM-5600LV scanning electron microscope (SEM, Japan Electron Optics Laboratory Co. Ltd.). Prior to the examination, the samples were platinum sputter-coated under nitrogen atmosphere to render them electrically conductive. The average fiber size was estimated through measuring diameters of fibers at over 100 places from SEM images using ImageJ software (National Institutes of Health, USA).

Results and discussion

Typically an electrospinning system consists of four components (Fig. 1a): a high-voltage power supply, a collector, a pump and a spinneret. Some modifications to the system involve the use of alternative collectors or the usage of auxiliary apparatus to facilitate the fabrication process.

However, more significant modifications to electrospinning always concern the spinneret, by which different processes have been developed, such as coaxial electrospinning, side-by-side and needleless electrospinning [10-12]. The homemade concentric spinneret exploited here is shown in Fig. 1b. The upper surface of the core capillary was slightly projected out 1.0 mm from the tip of the sheath capillary. This differed from conventional coaxial spinnerets, in which the tips of the inner and the outer capillary were often co-planar.

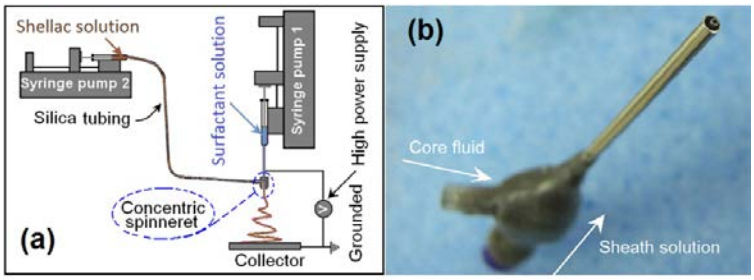

Fig. 1. Modified co-axial electrospinning with surfactant solution as a sheath fluid for preparing shellac fibers: (a) A schematic diagram shows the components of the coaxial electrospinning system, (b) A digital picture of the homemade concentric spinneret.

The arrangement of apparatuses in the coaxial system is shown in Fig. 2a. When the sheath fluid was closed, the coaxial process was transferred into a single-fluid process of the core shellac solution (Fig. 2b and c). Shellac fibers F1 were prepared through this approach. When the sheath fluid was turned on and driven in a certain flow rate, the process was a modified co-axial one, which are shown in Figure 2b and c for the preparation of shellac fibers F2.

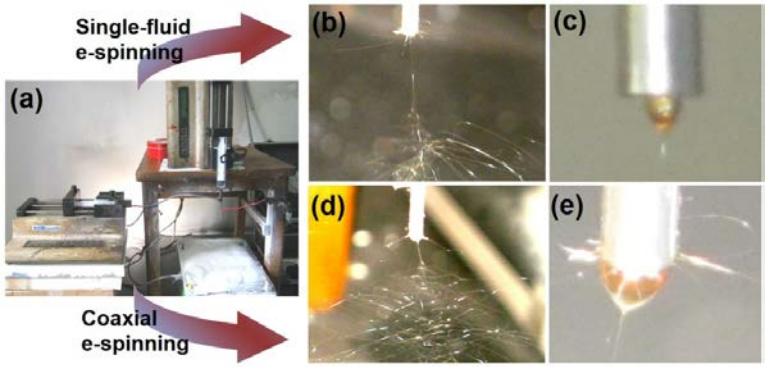

Fig. 2. Implementation of the electrospinning (e-spinning) processes. (a) A digital picture showing the arrangement of apparatuses; (b) A typical single-fluid electrospinning process of the core shellac solution; (c) A digital picture of the Taylor cone during the single-fluid electrospinning; (d) A typical coaxial electrospinning process for the preparation of shellac fibers F2; (c) A digital picture of the compound Taylor cone. The applied voltage was fixed at 15 kV and the tip-to-collector distance was 20 cm.

Regardless of double or single working fluids, both of them similarly experienced the subsequent three steps before the collection of solid shellac fibers. The first step is the formation of Taylor cone, as shown in Fig. 2c and 2e. The second step is the emission of the straight fluid jets, which were ejaculated out from the Taylor cone when the applied voltages were elevated to a certain value. Compared with the straight fluid jet of the single-fluid electrospinning in Fig. 2b, the straight fluid jet of the coaxial process in Fig. 2c is obviously shorter. This phenomenon reflects that the sheath surfactant solution facilitated the initiation of bending and whipping process, and which in turn promoted the drawing of fluid jets to create finer shellac fibers. The third step is the bending and whipping of fluid jets in the instable region, which should be responsible for the formation of fibers through solidification and thinning.

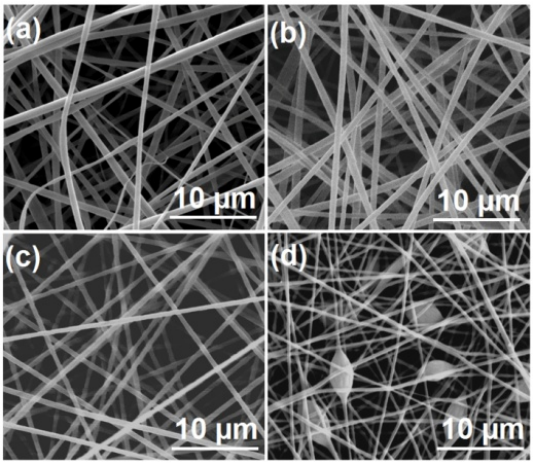

Fig. 3. FESEM images of the as-prepared shellac fibers: (a) F1; (b) F2; (c) F3 and (d) F4.

The SEM morphology of as-prepared shellac fibers F1 to F4 are shown in Fig. 3. All the fibers showed a straight linear with smooth surface. These fibers deposited homogeneously without any beads or spindles found in them except fibers F4 (Fig. 3d). The core fluid of shellac solution in ethanol had good electrospinnability. Although the fibers F1 prepared using the single-fluid electrospinning were linear, but they had an average diameter of 1.21 ± 0.41 μm (Fig. 4a). In sharp contrast, shellac fibers F2 and F3, prepared using the modified coaxial electrospinning with a sheath fluid flow rates of 0.2 and 0.4 ml·h, had an average diameters of 0.89 ± 0.11 μm (Fig. 4b) and 0.58 ± 0.09 μm (Fig. 4c), respectively. They not only had a fine fibers' diameters but also had a more uniform diameter distribution. However, when an excessive sheath fluid was exploited, the spindles-on-a-string morphology occurred, as exhibited in Figure 3d for fibers F4, although their diameters were further reduced to 0.19 ± 0.07 μm (Fig. 4d).

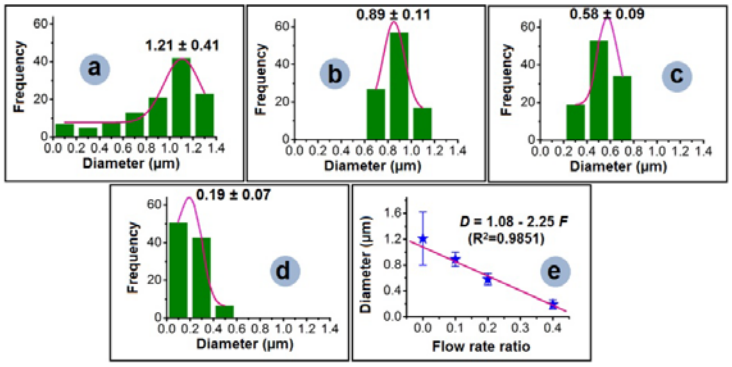

Fig. 4. The influence of sheath Triton X-100 solution flow rate on the size of shellac fibers: (a) F1; (b) F2; (c)F3; (d) F4; (e) the relationships between the fibers' diameter (*D*, μm) and the flow rate of sheath Triton X-100 solution (*F*).

A comparison of fibers F2 and F3 in Fig. 3b and 3c gives an obvious hint that the shellac fibers' size changed with the variation of sheath fluid flow rate. A linear regression of the shellac fibers' diameter (*D*, μm) and the flow rate of sheath Triton X-100 solution (*F*) is shown in Fig. 4e. The linear equation $D = 1.08 - 2.25\ F$ has a correlation coefficient of R^2=0.9851. Thus based on the coaxial process and the exploitation of surfactant as sheath fluid, the polymeric nanofibers' diameters can be manipulated and predicted.

Conclusions

A modified co-axial electrospinning was investigated, in which a surfactant solution containing Triton X-100 were exploited as the sheath working fluid to facilitate the nanofabrication of polymeric nanofibers. Under a reasonable selection of the sheath-to-core flow rate ratio, the coaxial

electrospinning process could be run continuously and smoothly. Compared with the shellac fibers from the single-fluid electrospinning, those from the coaxial process possessed a higher quality in terms of fibers' diameters and their size distributions. The fibers' diameter (D, μm) has an obvious linear relationship with the flow rate of sheath Triton X-100 solution (F) as D = 1.08 - 2.25 F (R^2=0.9851). It is concluded that modified co-axial electrospinning with a surfactant solution as a sheath fluid comprises a facile process for producing high quality polymeric nanofibers.

Acknowledgement

This work is supported by the Training Project for Excellent Young and Middle-aged Backbone teachers of Higher Schools in Guangxi province, the National Science Foundation of China (No. 51373101), the Natural Science Foundation of Shanghai (Nos. 13ZR1428900), the Key Project of the Shanghai Municipal Education Commission (No.13ZZ113) and the College Student Innovation Project (Grants SH201510252167 & 201510252053).

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