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Highly porous fibers prepared by centrifugal spinning

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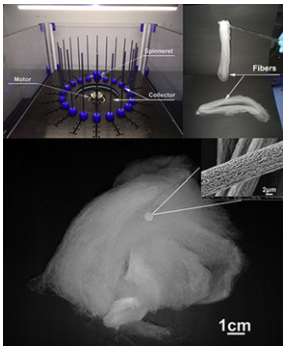
HIGHLIGHTS

- Porous EC/PVP fibers were fabricated by centrifugal spinning while nonporous fibers were obtained in electrospinning.
- The porous EC/PVP fibers showed great high specific surface area and contact angle.
- The mechanism was established to clarify the morphology change between centrifugal-spun fibers and electrospun fibers.
- The centrifugal spinning is meaningful for the rapid and large-scale fabrication of porous fibers.

GRAPHICAL ABSTRACT



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ABSTRACT

Ethyl cellulose (EC)/polyvinyl pyrrolidone (PVP) fibers with micro- and nano-porous throughout structures are fabricated by centrifugal spinning a binary solvent system of ethanol and water. A combination of different parameters including EC/PVP ratios, ethanol/water ratios and rheological properties are investigated to demonstrate pore formation. The specific surface area of EC/PVP fibers increases more than 11 times when the binary solvent contains 30% water. However, fibers with porous structure cannot be obtained in electrospinning process under the same solution and ambient conditions. The result indicates that the spinning method greatly influences the diameter and solvent evaporation of the jets, and as a consequence, fiber morphology varies in the two spinning processes.

1. Introduction

Due to the large specific surface area, micro- and nano-porous fibers have multiple applications in biomaterials [1–4], energy [5] and filtration [6]. Among these, biomaterials have attracted great scientific and technological interests. As one of the most commonly used cellulose derivatives, EC has been widely employed in drug release [7–10] and packaging [11] for the biocompatible, nonbiodegradable and eco-friendly properties. Besides, EC exhibits excellent plasticity, good solubility in organic solvents, high mechanical intensity, good heat-resistance, cold-resistance and stability [12,13]. However, EC fibers with micro- and nano- porous structures, which could have potential applications, have been hardly ever reported. Researchers have reported several methods to fabricate porous fibers by using self-assembly [14], phase separation [15] and electrospinning [16]. Among these techniques, electrospinning is the most popular method. According to some reports, EC fibers fabricated in electrospinning process are mostly of smooth surface morphology [17–19]. Park et al. [20] reported porous EC fibers fabricated with electrospinning, though only a few of pores on the surface. Besides, high voltage, sensitive to dielectric constant, and low fiber yield limit the application of electrospinning [21]. Thus, methods for rapid manufacturing micro- and nano-porous EC fibers are of great interest.

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In recent years, centrifugal spinning, a novel technique for generating micro- to nano-fibers, has successfully overcome the obstacles that electrospinning encounters [22–25]. This method utilizes centrifugal force to draw polymer jets into fibers instead of electrostatic force, so that both nonconductive and conductive polymers can be spun in solutions or in melts [26]. One of the important features of centrifugal spinning process is its high production rate. With two nozzles, the average production rate of a simple centrifugal spinning instrument is around 50 g/h, which is at least two orders of magnitude higher than a lab-scale electrospinning process(0.1–1.0 g/h) [24,27–29]. Although the production rate of melt blown is higher than centrifugal spinning [30], the melt blown has limited material choices and the materials must be spun in melts.

In 1991, a patent disclosed a rotating spinning centrifuge that can fabricate polymer fibers in molten or liquid state [31]. After that, some research groups attempted to employ different spinneret shape to improve the quality of the spun fibers, while the fiber diameter produced by this method was still much thicker than that produced by electrospinning [32,33]. In 2010, Oya et al. [34] used a centrifugal spinning to produce carbon nanomaterials, and then centrifugal spinning has drawn wide attention again. Lozano et al. [25] well developed this technology and named it Forcespinning, which means materials that are hard to fabricate by electrospinning or other methods can be successfully forcespun into micro- to nanometer range fibers. By now, the centrifugal spinning has been successfully used to fabricate micro- and nano-fibers of polymers [26,35–38], ceramics [39–42] and protein [43]. Besides, centrifugal spinning develops some special superiorities in manufacturing amylose rich starch-based fibers compared with electrospinning [44]. In addition, the centrifugal-spun material is more suitable for tissue engineering applications, for the 3D fluffy structure [45].

The parameters of centrifugal spinning process greatly influence fiber morphology and diameter such as rotational speed, concentration, evaporation rate (for solutions), temperature (for melts), and collection distance. For solution spinning, concentration and rotational speed are considered as the main factors among the aforementioned parameters. The lower the concentration, the thinner the fibers and the narrower the fiber diameter distribution, while the rotational speed has a subtle effect on fiber diameter [46]. However, nozzles of the spinneret are easily clogged up due to the high viscosity or the small needle size. Chen et al. [47] reported a nozzle-less centrifugal spinning method which solved the problem and also improved the production rate. Compared with electrospun fibers, the larger fiber diameter and fiber diameter distribution of centrifugal-spun fibers have limited its development in fine chemicals, but the feature combined with 3D fluffy fiber assembly appeals to biomaterials [48]. Therefore, centrifugal spinning have great advantages in generating micro- and nano-fibers. So far, there is few reports on the micro- and nano-porous fibers fabricated by centrifugal spinning without further treatments. Although Ren et al. [37] reported the porous PLLA fibers fabricated by centrifugal spinning, the porous structure was developed after surface etching treatment.

In this study, the throughout porous EC/PVP fibers are prepared by centrifugal spinning a binary solvent system without further treatments. Structure and characterizations are investigated by changing polymer and solvent ratios and controlling processing parameters. The morphology, viscosity, specific surface area and contact angle (CA) are measured. Meanwhile, the formation mechanism for different structures between centrifugal-spun fibers and electrospun fibers which are fabricated under the same solution and ambient conditions is discussed.

2. Materials and methods

2.1. Materials

Ethyl cellulose (EC, 18–22 mPa·s) and Polyvinyl pyrrolidone (PVP, M_W = 1,300,000) purchased from Aladdin (Shanghai, China) were used without further purification. Ethanol (Aladdin, China) and water were selected as the solvent to dissolve EC and PVP polymers [18,49,50].

2.2. Synthesis of EC/PVP solutions

EC and PVP were dissolved in ethanol and water for 10 h to prepare a mass-volume concentration of 15% uniform polymer solution for centrifugal spinning. A range of EC/PVP polymer mass ratios was studied, which included 10%/90%, 30%/70%, 50%/50%, 70%/30%, and 90%/10%, and the ethanol/water were varied at 70%/30%, 80%/20% and 90%/10% volume ratio. To get a full spectrum of solution properties which helped the study of inducing porous fibers, the viscosity of the solution mixture was measured at room temperature after the degassing procedure.

2.3. Centrifugal spinning process

The centrifugal spinning setup is shown in Fig. 1, including motor, spinneret and collector. The spinneret is fixed on a shaft which is controlled by the motor. In this study, the rotational speed of the spinneret was controlled at 3500 rpm. The distance between the spinneret orifice and the rod collector was 12 cm.

2.4. Electrospinning process

The schematic diagram of electrospinning system is shown in Fig. 2, including high voltage power supply, needle (25 G), syringe (1 mL), and collector with aluminum foil. The tip-to-collector distance was set at 12 cm. The high voltage provided by the power supply was adjusted at 7 kV.

2.5. Fibers characterization

The morphology of fibers was characterized by FE-SEM and TEM. The centrifugal-spun fibers and electrospun fibers were examined on a ZEISS type-ULTRA55 scanning electron microscope and a JEM-2100 transmission electron microscope. Image Pro Plus 6.0 was used to measure the diameters of the fibers. The average fiber diameter and distributions were determined from 100 random fibers.

Physica MCR 301 rheometer was used to obtain the rheological properties of the solution. The used geometry was cone-plate (50 mm diameter; 0.341 mm gap). Viscosity data were collected at the shear rate ranging from 0.1 to 100 s^{-1} at 20 °C.

Micromeritics ASAP 2020HD88 was used to analyze the specific surface area of the samples. The samples were degassed at 80 °C for 24 h prior to the measurement in order to remove adsorbed impurities and moisture.

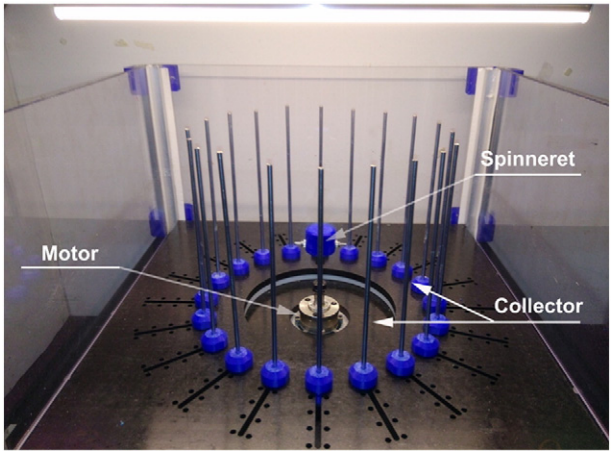

Fig. 1. Centrifugal spinning system.