JOURNAL OF Applied Polymer SCIENCE

Silicone Rubber/Polyvinylpyrrolidone Microfibers Produced by Coaxial Electrospinning

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ABSTRACT: Core-shell structured silicone microfibers were prepared by coaxial electrospinning using polyvinylpyrrolidone (PVP) as the shell and silicone rubber (SR) as the core. The electrospinnability of SR at three time windows was evaluated and the electrospinning process was optimized accordingly. A positive correlation was found between the fibrous morphology and the SR/PVP speed ratios. As the speed ratio increased, the composite fiber showed larger diameter and wider diameter distribution. For the fibers prepared at PVP/SR speed ratios of 1.7/2.5 and 3.5/2.5 (mL/h), the fibrous structure remained intact after immersion in water for 8 h. The pure SR microfiber could be made from the composite after immersion in water, which can be potentially used as stretchable and selectively permeable membranes for chemical protective applications and in plastics toughening. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: silicone rubber; fibers; coaxial electrospinning; microstructure; nanocomposites

Received 9 October 2011; accepted 29 March 2012; published online
DOI: 10.1002/app.37848

INTRODUCTION

Nano/microfibers have a number of amazing properties, such as very large surface area-to-volume ratio and high porosity with very small pore size.[1] Therefore, nano/microfibers can be promising materials for biomedical applications such as tissue templates, medical prostheses, artificial organ, drug delivery, and wound dressing. Electrospinning has been widely accepted as the simplest and least expensive means to fabricate ultrafine fibers.[2–4] The electrospinnability of polymer is limited by its molecular weight, viscosity, conductivity, and surface tension. Coaxial electrospinning increases the scope of polymers available for electrospinning[5] and has thus attracted growing attention in the recent decade.

In recent years, a number of studies have focused on improving the mechanical, physicochemical, and biological properties of polymers such as silicone rubber[6,7] and PDMS.[8] Silicone rubbers are widely used in tissue engineering[9] due to its high chemical inertness, high thermal stability, high oxidation resistance, and good mechanical properties (ductility >500%, tensile strength >1 MPa). Although considerable research has been performed on the elastomer-based fibers by traditional uniaxial electrospinning, to our knowledge there is few report on the silicone rubber (SR) superfine fiber prepared by electrospinning. There are a number of difficulties for generating ultrafine elastomer-based fibers by electrospinning. For example, the SR electrospun solution has high viscosity, low molecular weight, and poor conductivity, which are unfavorable for the formation of solution jetting. Besides, the viscosity of the SR solution varies dynamically during curing. In addition, upon reaching the collector the elastomer fibers can elastically recoil and the electrostatic force disappears.

In this work, we report the synthesis of SR based microfiber through coaxial electrospinning. During the coaxial electrospinning process, polyvinylpyrrolidone (PVP) dissolved in a facilitating solvent was used as the shell spinning solution to entrain the SR solution, leaving behind the silicone rubber as the core material. PVP was selected as the shell material since it showed high electrospinnability and is soluble in water. The pure silicone rubber microfibers were fabricated after the composite fibers (PVP/silicone rubber) were immersed in water to dissolve the shell material.

EXPERIMENTAL

Preparation of Spinning Solutions

PVP (M_w = 1,300,000) was purchased from Alladin Biochemistry, Silicone rubber base (SF-657 Addition-type, fine fluidity,

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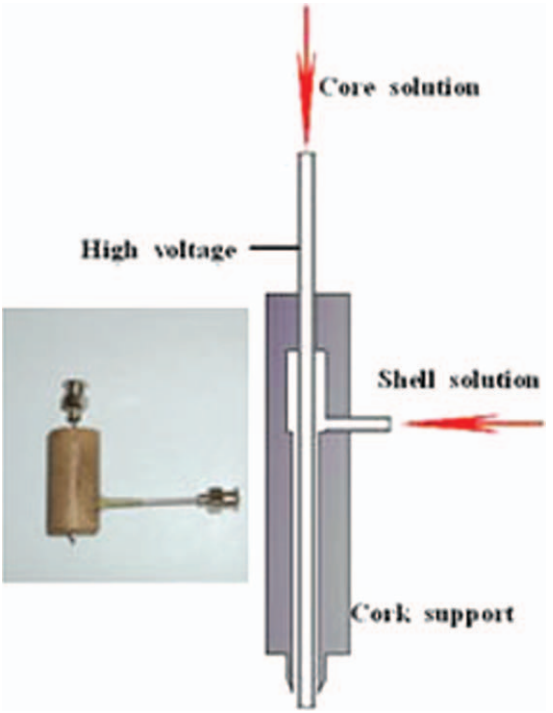

Figure 1. Schematic of the coaxial electrospinning setup. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

addition polymerization, curing at room, or low temperature) was purchased from Guangdong BioMax Si&F New Material, China. The shell solution was prepared by dissolving different amounts of PVP in ethanol solution with sufficient stirring at the room temperature. The core solution was prepared from 1:1 v/v silicone rubber base and curing reagent sufficiently blended at room temperature.

Coaxial Electrospinning

Figure 1 shows the basic experimental setup for coaxial electrospinning. The spinneret apparatus consisted of the inner needle (inner diameter: 0.41 mm, outer diameter: 1.01 mm) and the outer needle (inner diameter: 1.6 mm) coaxially aligned. Two syringe pumps (WZS-50F6, Zhejiang University, China) were used to deliver the core and shell solutions through the inner and outer needles under controlled feeding rates. A high voltage DC power supply (DW-P503-4ACDE, Tianjin Dongwen, China) was used to generate a maximum 50 kV voltage. The distance between the collector and the needle tip was 12 cm. The ultrafine fibers were collected as randomly overlaid mats on electrically grounded plate wrapped with aluminum foil.

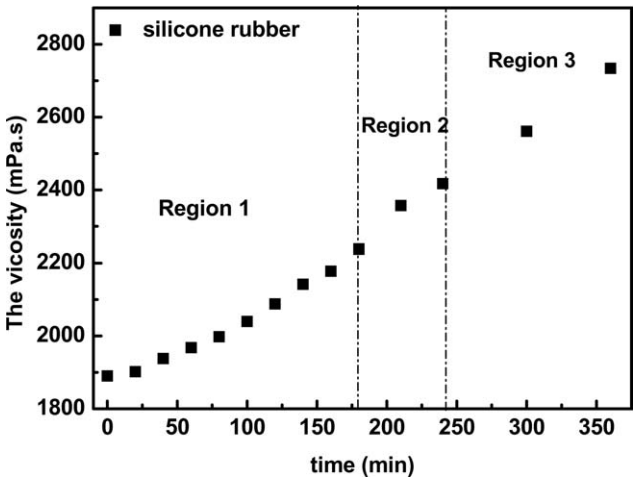

Figure 2. Dynamic variation of viscosity.

Characterization

The fiber morphology was observed using a digital vacuum scanning electron microscope (JSM-5900, Japan Electron Optical Laboratory) at 15 kV accelerating voltage. Samples for SEM observations were sputter coated with gold before observation. The diameter of the electrospun microfibers was measured with the image visualization software Image-J 1.34. Average fiber diameter and diameter distribution were determined by measuring about 100 random fibers from the SEM images. The shear viscosities of the solutions of different speed ratios were measured in a shear rate range of 5–500 s^{-1} using a Haake Viscometer (Brookfield DV□).

RESULTS AND DISCUSSION

Time-Dependent Electrospinnability

The variation in fibrous morphology and electrospinnability with time after the addition of the curing agent (which has the same weight as silicone base) to silicone base suggested that significant rheological changes in solution occurred during electrospinning. Therefore, the variation in viscosity of the silicone rubber during curing was monitored to determine time window of optimum electrospinnability. The viscoelastic changes observed in Figure 2 suggested that the viscosity was correlated positively with time. The viscosity increased from 1890 to 2734 mPa s as time elapsed from 0 min to 360 min.

The relationship between viscosity and the diameter of electrospun fiber has been reported by many researchers. In view of the dynamic viscoelastic changes, we investigated the electrospinnability at three time windows at a constant SR/PVP speed ratio of 1.7/2.5 (mL/h). The observations are shown in Table I

Table I. The Electrospinning Process in Different Time Windows

Time	Average viscosity (mPa s)	Elctrospinnability	Electrospinning process
0–180 min	2064 ± 174	Excellent (uniform fiber)	Easy for electrospinning
180–240 min	2328 ± 90	Good (uniform fiber with a few droplets)	Coaxial nozzle frequent blocks
240–400 min	2576 ± 159	Poor (fiber with beads and droplets)	Both coaxial nozzle and tube frequently block

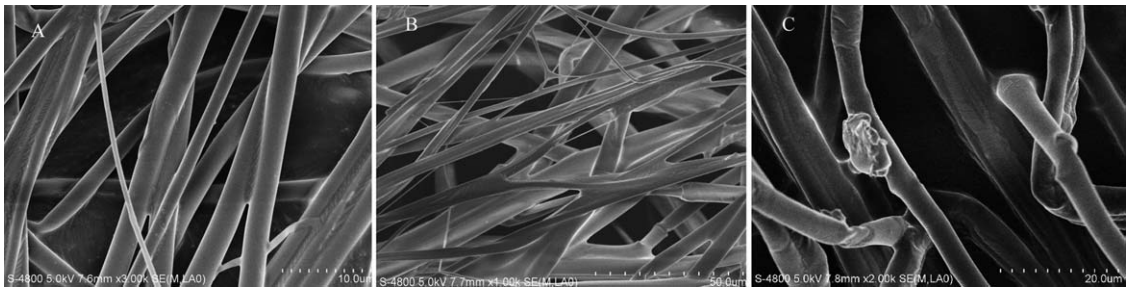

Figure 3. SEM images of electrospun structures at different time windows: (A) 0–180 min; (B) 180–240 min; (C) 240–400 min.

and Figure 3: In the first time window (0–180 min), the fibrous morphology was stable, uniform and free of droplets. In the second time window (180–240 min), the spun fiber exhibited nonuniform structure with a few bead fibers. In the third time window (240–400 min), the spun fiber showed nonuniform structures with a considerable amount of beads embedded. Additionally, the solutions easily blocked the tubes and the coaxial nozzle during electrospinning process during the second and third time windows. Therefore, the electrospinning process should be carried out during the first time window.

Morphology and Structure of SR/PVP Composite Fibers

The morphology of the coaxial electrospun fibers is also controlled by the materials parameters and process parameters, including electrospinning solution concentration, applied voltage, distance, and feeding rate.[10] The speed ratio of SR/PVP

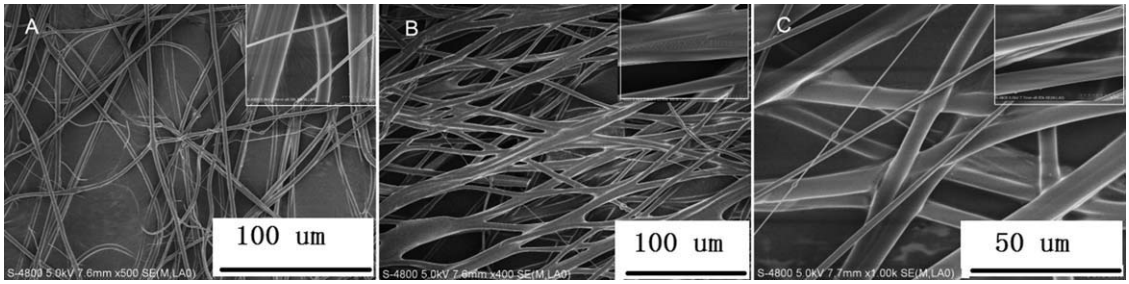

Figure 4. SEM images of electrospun structures from solutions with different SR/PVP speed (mL/h) ratios: (A) 1.1/2.5; (B) 1.7/2.5; (C) 3.5/2.5.

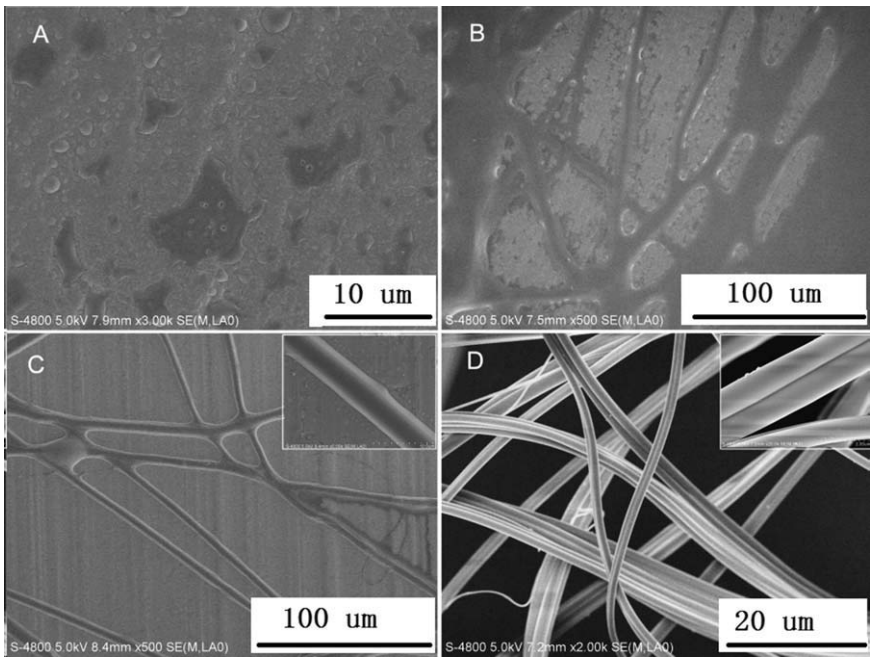

Figure 5. SEM images of SR/PVP composite fibers prepared at different SR/PVP speed (mL/h) ratios after immersion in water at room temperature: (A) 0.9/2.5, immersion 2 h; (B) 1.1/2.5, immersion 2 h; (C) 1.7/2.5, immersion >8 h; (D) 3.5/2.5, immersion >8 h.

represents the electrospinning solution concentration and feeding rate, which are important parameters in the present study that affect the fiber structure. The morphology of the core-shell microfibers are shown in the SEM micrographs in Figure 4. The morphology was influenced by the SR/PVP speed ratio. When the speed ratio was 1.7/2.5 (mL/h), the diameter of the obtained fiber ranged from 1.25 to 3.64 μm (average diameter 2.76 μm). When the speed ratio increased to 2.5/2.5 (mL/h), the fiber diameter ranged from 3.77 to 6.22 μm (average diameter 4.69 μm). When the speed ratio increased to 3.5/2.5 (mL/h), the fiber diameter ranged from 1.00 to 10.20 μm (average diameter 5.72 μm). The average fiber diameter gradually increased as the speed ratio increased for all tested samples. Apparently, the distribution of fiber diameter became wider at higher speed ratio, possibly because the higher concentration of SR in the electrospun solution further decreased the conductivity and viscosity of the electrospun solution. Bian et al. also reported the difficulties in forming SR fiber due to its low conductivity and viscosity[11] and only beads and droplets were obtained. Recently, Angammana and Jayaram reported a novel method for electrospinning insulating materials by using ion liquid with high electrical conductivity.[12] The above result suggests the possibility of electrospinning insulating materials by coaxial electrospinning.

Integrity of Fiber in Water

The pure SR fiber could be prepared by immersion of the composite fiber in water. Thus, it is of practical interest to study the effect of speed ratio on the integrity of the microfibrous structure in water. As shown in Figure 5, the membranes prepared at 0/2.5 and 1.1/2.5 (mL/h) SR/PVP speed ratios lost their initial fibrous structure after immersion in water for 2 h. The membranes prepared at 1.7/2.5 and 3.5/2.5 (mL/h) SR/PVP speed ratios maintained their fibrous structure in water for more than 8 h, demonstrating that pure SR microfiber can be successfully prepared by coaxial electrospinning. Note that "hydrophobic interactions" exist between SR fibers in water. The SR fibers packed in parallel to decrease the hydrophobic surface area, thus lowering the system energy.

CONCLUSIONS

This study showed that SR/PVP composite fiber can be prepared by coaxial electrospinning and pure silicone rubber fibers could be obtained by dissolving the PVP shell layer of the composite fiber. The spinnability was time-dependent due to the variation of viscosity of silicone rubber during curing. Considering the dynamic variation of spinnability, the electrospinning process should be carried out in the time window of 0–3 h. The average fiber diameter increased gradually with rising SR concentration in the composite fiber. The fibers prepared at SR/PVP speed ratio of 1.7/2.5 and 3.5/2.5 (mL/h) retained fibrous structure after immersion in water for 8 h and showed excellent integrity.

ACKNOWLEDGMENTS

This work was supported by the Key Program of the National Natural Science Foundation of China (No. 20936002).

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