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Fabrication of polystyrene fibers with tunable co-axial hollow tubing structure for oil spill cleanup

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ABSTRACT

Hollow tubing polystyrene (PS) fibers (HFs) with porous shell were successfully fabricated through co-axial electrospinning and selectively dissolving and removing polyvinyl pyrrolidone (PVP) core of the co-axial PS/PVP fibers using C_2H_5OH at room temperature. The size of co-axial hollow tubing structure (CHTS) and the thickness of shell can be controlled by varying the feed rate ratio of the core solution to the shell solution. The oil-sorption results show that the oil-sorption capacity increases with the increasing of the size of CHTS in the HFs, and the HFs have higher oil-sorption capacities than the porous PS fibers (PFs) without CHTS. It is noticeable that the diesel sorption capacity (66 g/g) of the HFs is approximately 1.74 times as much as that (38 g/g) of the PFs. The motor oil sorption capacity (147 g/g) of the HFs is approximately 1.55 times as much as that (95 g/g) of the PFs. It is suggested that the HFs have a better oil-sorption performance than the PFs, especially for the low viscosity oil, which is contributed to large CHTS and high porosity.

1. Introduction

Oil spill accidents which frequently occur during the process of oil transportation and utilization have caused serious environmental pollution and a negative impact on the production and life of human beings [1,2]. Therefore, oil spill cleanup has become an urgent problem to solve. Now, the effective methods for oil spill cleanup involve mechanical extraction, in situ burning, and bioremediation [3–5]. Mechanical extraction by sorbent is more popular for it can concentrate and transform liquid oil to a semisolid or solid phase, and then transfer it from the pollution area in a quick, easy and environment-friendly way [6].

The oil sorbent materials can be divided into three categories: organic synthetic sorbent, inorganic mineral product, and organic natural material [7–9]. A sorbent material with excellent performance for oil spill cleanup should include oleophilicity and hydrophobicity, high oil-sorption capacity, good oil/water selectivity, high buoyancy, and enough strength [10–12]. Non-woven polypropylene (PP) fibers as commercial synthetic organic sorbent have been widely used in oil spill cleanup due to their oleophilicity and hydrophobicity, good oil/water selectivity and fabrication on a large scale [13]. It is believed that the oil-sorption capacity of the fibrous sorbent is related to the voids not only among fibers but also in the interior of fibers [14,15]. However, large diameter (about 30 μm) and solid structure of the PP fibers result in low voids among or in the fibers and low oil-sorption capacity which limits their development in the future [16].

The porous polystyrene fibers (PFs) as another potential oil sorbent produced by electrospinning have small diameters from nanoscale to a few microns [1,17] and their oil-sorption capacity and oil-water selectivity have been greatly increased compared to the conventional PP fibers [18,19]. Though the electrospun PS fibers have porous structure, the interior pores are too small to enter for the spilled oil due to high viscosity [19–21]. Therefore, it is necessary that large co-axial hollow structure with diameters from a few hundred nanometers to micrometer are produced in the PS fibers so that they can offer enough room to get into for oil. Large co-axial hollow tubing structure (CHTS) can be easily produced in the inorganic fibers fabricated via co-axial electrospinning by selectively removing organic or polymer core material by calcination [22,23]. However, the fabrication of hollow tubing PS fibers (HFs) by co-axial electrospinning still remains a challenge for the polymer core can not be removed by calcination because of the thermal instability of linear PS shell, and is also difficult to be removed by the organic solvent due to oil-dissolving character of linear PS.

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Table 1
The oil properties at room temperature.

Oils	Viscosity (mPa s)	Density (g/cm^3)
Motor oil	275	0.846
Peanut oil	75	0.925
Soybean oil	56	0.915
Diesel	4	0.833

Here, a novel route to fabricate HFs with porous shell is developed, and the size of CHTS in the HFs can be up to micrometer. Firstly, the co-axial PS/PVP fibers are fabricated via co-axial electrospinning of the PVP core solution and the PS shell solution using N,N-dimethylformamide (DMF) as solvent. After selectively dissolving and removing the PVP core by C_2H_5OH at room temperature, the HFs are successfully obtained. It is crucial that the PVP is creatively selected as core material due to its amphipathicity and has good dissolvability not only in oil-dissolving solvents such as DMF but also in water-dissolving solvents such as C_2H_5OH in which the PS shell does not be dissolved at room temperature. The effect of the feed rate ratio of the core solution to the shell solution on the CHTS size and the shell thickness, the influence of the CHTS size and the oil viscosity on the oil-sorption capacities of the HFs, oil retention capacity and oil-water separation property are respectively evaluated.

2. Materials and methods

2.1. Materials

Polystyrene (PS, M_w = 220,000, M_w/M_n = 2.41) was purchased from Yanshan Petrochemical Corporation, China. Polyvinyl pyrrolidone K-30 (PVP K-30) (M_w = 40000, 27.0 ≤ K ≤ 32.4) and analytically pure anhydrous ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd., China. N,N-Dimethylformamide (DMF) was purchased from Kemiou Chemical Reagents Researching Center, China. The oils used for sorption were motor oil (Exxon Mobil, USA), diesel (CNPC, China), peanut oil (Shandong Luhua Group Co., Ltd., China), and soybean oil (Standard Foods China Co., Ltd., China). The oil properties are listed in Table 1.

2.2. Preparation of hollow tubing PS fibers

The 20 wt% PS solution and the 30 wt% PVP solution were prepared by dissolving PS and PVP in DMF, respectively. The schematic of the co-axial electrospinning setup used in this study was shown in Fig. 1A, which was produced by Beijing Kangsente Technology Co., Ltd., China. A stainless steel plate covered with a sheet of aluminum foil was employed as a collector. The collection distance between the needle tip and the collector was 20 cm and the voltage was controlled between 14 kV and 16 kV. The diameters of inner and outer syringe needles of the co-axial nozzle were 0.8 mm and 1.5 mm, respectively. The fibers were prepared in a relative humidity of 40% at 30 °C. The PVP core and PS shell solutions were simultaneously fed into the co-axial nozzle and the co-axial PS/PVP fibers were formed on the collector (Fig. 1B). To obtain different co-axial PS/PVP fibers, the feed rate ratios of the core solution to the shell solution were varied by utilizing two syringe pumps at the total solution feed rate of 3 mL/h, and were respectively 1:1, 1:4, 1:8, and 1:16.

The co-axial PS/PVP fibers were soaked in C_2H_5OH for about 30 min at room temperature, and then washed by distilled H_2O/C_2H_5OH (1:1) solution for three times by ultrasonic for 10 min. Finally, the products were dried at 70 °C for 24 h in the oven. The obtained HFs (Fig. 1C) from various feed rate ratios (1:1, 1:4, 1:8, and 1:16) of the core solution to the shell solution were labelled as HFs-1:1, HFs-1:4, HFs-1:8, and HFs-1:16. The HFs-1:2, HFs-1:6 (Fig. S1). The porous PS fibers (PFs) without co-axial hollow structure as reference sample were also prepared by electrospinning 20 wt% PS solution at the feed rate of 3 mL/h in a relative humidity of 40% at 30 °C using the single hole nozzle with diameter of 0.8 mm. The collection distance between the needle tip and the collector and the voltage were the same as those of HFs.

2.3. Oil-sorption measurement

The oil sorption measurements were carried out at room temperature. 0.1 g of the HF sorbent was put into 30 mL oil in the beaker of 100 mL. 60 min later, the wet sorbent taken out of the beaker was naturally drained for 3 min, and then weighted. For each sample, the measurement was repeated three times. The average value and the standard deviation were calculated.

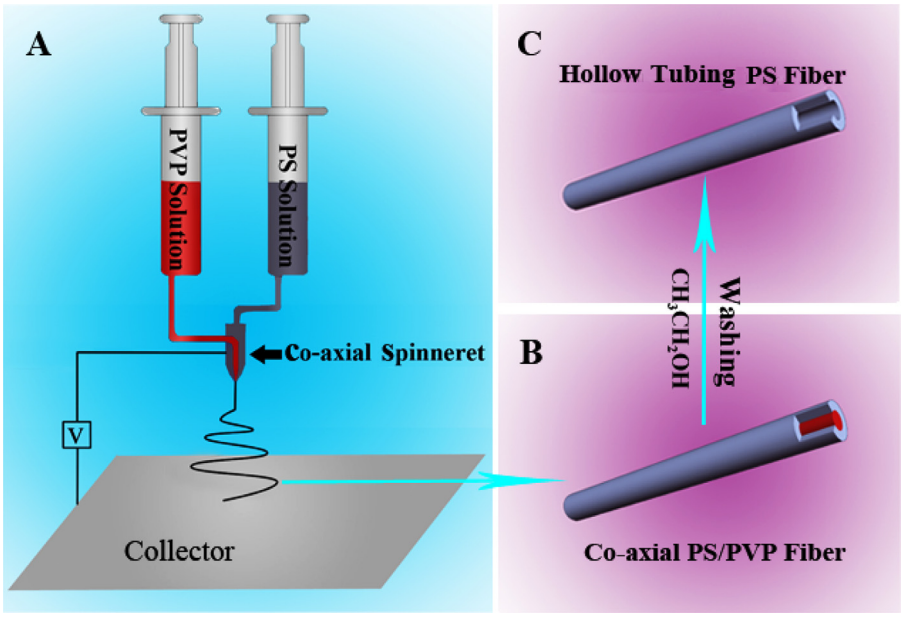

Fig. 1. Schematic representation of the synthesis procedure for HF by the co-axial electrospinning.