Facile and Scalable Fabrication of Porous Polystyrene Fibers for Oil Removal by Centrifugal Spinning

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Supporting Information

ABSTRACT: The demand for an efficient oil sorbent with high sorption capacity, low cost, scalable fabrication, and high selectivity for the cleanup of spreading oil on water is increasingly urgent due to the frequent occurrence of oil spill accidents in seawater all over the world. In this study, porous polystyrene (PS) fibers with high hydrophobicity and superoleophilicity were directly fabricated by a centrifugal spinning method (CS). The effect of solvents, tetrahydrofuran (THF), and dimethylformamide (DMF) on the morphology and porous structure of the polystyrene fibers was evaluated by using scanning electron microscopy and nitrogen adsorption–desorption experiments. The formation mechanism for the porous structure on the fibers was also evaluated. The oil sorption capacities of the PS fibers for silicon oil, pump oil, and vegetable oil were investigated. The highest oil sorption capacity was found in PS fibers fabricated from PS solution with a THF/DMF weight ratio of 1/3, which exhibited the highest specific surface area, pore volume, and porosity. The high productivity and highly porous structure of PS fibers indicate that CS is a promising method to fabricate porous fibers for the cleanup of oil spills.

INTRODUCTION

Oil spill accidents that occur during the process of oil being explored, transported, stored, and used have attracted more and more attention due to the significant and serious damage caused by oil spills to the ecology of the environment and human well-being. 1,2 With an increasing level of attention focused on the preservation of the environment, researchers have developed a plethora of materials to concentrate and transform liquid oil to a semisolid or solid phase, which can then be easily removed from the location of the oil spill. Recently, many kinds of oil sorbents have been developed, such as boron-nitride nanosheets, 3 carbon-nanotube 4 and graphene oxide, 5 which exhibit excellent oil sorption performance compared with conventional fibers. 6–11

Polystyrene (PS), a common and inexpensive thermoplastic polymer with low surface energy due to its CH group, has been widely used to fabricate artificially hydrophobic fibers via electrospinning for oily water treatment. Wu et al. and Lin et al. fabricated nanoporous polystyrene fibers using electrospinning for oil sorption. 12,13 An electrospun polystyrene nanofiber membrane with superhydrophobicity and superoleophilicity properties was prepared by Lee et al. for the separation of an immiscible low viscous oil/water mixture. 14 A macroporous fibrous mat with ultrahigh oil adsorption capability has also been developed by Chen and co-worker. 15 While electrospinning is a simple and convenient technique, the electrospinning technique still suffers from several limitations, such as low productivity and the requirement of applying a high electric field. 16,17 Centrifugal spinning (CS) (sometimes called force spinning or rotary jet-spinning) is an emerging nanofiber fabrication process that overcomes many of the disadvantages associated with electrospinning. 18,19 In this process, polymer jets are generated and then are elongated
to form fibers due to centrifugal forces regardless of high voltage, enabling the formation of micro/nanofibers from both conductive and nonconductive polymer solutions. Furthermore, CS has much higher productivity compared with electrospinning, which is essential for practical application.20,21

Recently, CS has been used to produce fibers from various polymers, such as polycaprolactone (PCL),22 polyacrylonitrile,23 poly(acrylic acid),24 chitin,25 poly(vinylpyrrolidone),26 and polyamide.27 In the CS process, several processing parameters, e.g., the polymer concentration, the rotational speed, and solvents will affect the properties of the final fibers. Among these, the solvents have been shown to have a direct influence on the morphology and properties of fibers. A finding reported by Golecki et al. showed that the morphology and diameter of the polylactic acid (PLA) fibers were greatly influenced by the evaporation rate of solvents from the polymer solution.28 Obregon et al. reported that the concentration of dimethylformamide (DMF) in the tetrahydrofuran (THF)/polycaprolactone (PCL) solution affected the formation of beads and the thermal properties of PCL fibers.29 Hou et al. demonstrated that ethyl cellulose/poly(vinylpyrrolidone) fibers with different porous structures were obtained by control the ethanol/water ratios.30

CS was also used to prepare superhydrophobic polystyrene/ 
SiO2 composite microfibers.31 However, the effect of solvent on the morphology and the porosity of PS fibers was not evaluated. Furthermore, the oil adsorption capacity of centrifugally spun PS fibers was not studied. In this study, we introduce a scalable and facile strategy to fabricate hydrophobic and oleophilic PS fibers by CS. The morphology and porosity of the fibers can be manipulated by controlling the solvent composition (THF and DMF). The oil sorption capacity of the obtained fibers was investigated using three different kinds of oils. The mechanical properties of the as-spun PS fibrous mats were characterized using a tensile testing system.

■ EXPERIMENTAL SECTION

Materials. Polystyrene pellets ($M_w = 252,000$ g mol$^{-1}$) and tetrahydrofuran were purchased from Wako Co. (Japan). Dimethylformamide was supplied by Nacalai Tesque Co. (Japan). Silicone oil (ASO-100) was obtained from As One Co. (Japan). Pump oil (Neovac MR-200) was brought from Moresco Co. Vegetable oil was purchased from Nisshin OilliO Group, Ltd. (Japan). Oil cleaning paper was purchased from Kohnan Co. (Japan). All of the materials listed above were used without further purification.

Preparation of Polymer Solution and the Centrifugal Spinning Process. To prepare the solutions for the CS process, PS pellets were dissolved in solvent mixtures of THF and DMF at different weight ratios (4/0, 3/1, 1/1, 1/3, 0/4), which was followed by mixing for 30 min using a planetary centrifugal mixer (ARE-310, Thinky Co., Japan) at 2000 rpm and then degassing at 2200 rpm for 1.5 min. The solutions were kept in a constant-temperature shaker (MMS-1, Eyela Co., Japan) at 25 °C to obtain homogeneous solutions. The PS solutions were spun using a CS system of our own design (Figure 1). The CS system was made by modifying a centrifuge (Tomy MC 150, Tomy Geiko Co., Japan). The CS system consisted of a 32 mm needle-based spinneret equipped with blunt needles with an inner diameter of 160 μm and a shaft length of 5 mm, which was rotated by an AC motor at speeds of 15,000 rpm. The feed rate for the polymer solution was controlled to be 100 mL h$^{-1}$ by a syringe pump (KDS-100, KD Scientific Inc.). The relative humidity and temperature were monitored by a hygrothermograph placed inside the CS chamber and maintained at constant values of 50 ± 5% and 25 ± 2 °C, respectively.

Characterization. The viscosity of each PS solution and oil used for the oil sorption test was measured by a vibronic viscometer (SV-1A, A&D Co., Japan) at 25 °C; each sample was examined at least three times. The cloud points for the H2O/(THF/DMF)/PS system were measured at a temperature of 25 °C. PS solutions with varying concentrations (10, 15, 22, 30 wt %) were prepared by dissolving the polymer in binary solvent systems using different THF/DMF weight ratios. The as-prepared homogeneous solution was titrated using deionized water as a nonsolvent. The titration process was started by adding one droplet of water onto the polymer solution under stirring and continued by adding more droplets of water after a clear solution was obtained. The occurrence of the turbid point was regarded as

![Figure 1](image-url)
the onset of the cloud point. The polymer solution composition and the amount of used water were recorded and plotted in a ternary phase diagram, which was used to represent the binodal curves.

The morphology and cross section of the as-spun fibers were examined by field-emission scanning electron microscopy (FE-SEM) (JEOL-7600, JEOL Ltd., Japan). The fibers were collected on the SEM sample base and then sputter-coated with a 30 nm thick layer of palladium before being measured with FE-SEM at an accelerating voltage of 5 kV. The diameters of the fibers were obtained from SEM images for 200 fibers using image processing software (ImageJ).

The nitrogen adsorption−desorption isotherms for the PS fibers were carried out using an automatic surface area and porosimetry analyzer (TriStar II 3020 Micromeritics; distributed by Shimazu Co., Japan). The mass of each sample was approximately 0.3 g. The specific surface area of the as-spun fibrous mats was calculated using the Brunauer−Emmett−Teller method. The detailed pore size distribution and total pore volume for the relevant PS fibrous mats were obtained from the desorption branch using the Barrett−Joyner−Halenda method.

The thermal properties of the PS fibers were investigated using a differential scanning calorimeter (DSC) (TA Q200, TA Instruments Japan Inc., Tokyo, Japan) with a heating program. The sample was heated at 10 °C min−1 from −10 to 300 °C under a nitrogen atmosphere with a gas flow rate of 50 μL·h−1. Each sample was measured at least three times.

The contact angle measurements were conducted using a Phoenix 300 contact-angle system (Kromtek Co., Malaysia) at 20 °C and were further measured using Image software. Five microliters of deionized water and silicone oil droplets were dropped onto the surface of the fibrous mats, respectively. The average water contact angle value was obtained by measuring at least eight different locations across the same sample surface.

The mechanical properties of the PS fibrous mats were investigated using a universal tensile testing machine (TENSILON RTF−1210, A&D Co., Japan) (gauge length: 10 mm, crosshead speed: 1 mm s−1, load cell: 100 N). A paper window frame size of 20 × 35 mm2, with a window size of 4 × 25 mm2, was used as a mount for tensile testing. Sections of the fibrous mat were cut out in the form of miniaturized dog bone-shaped specimens (type SB in BS ISO 527: 2012) using a cutting blade. Then, the specimens were mounted onto the frame and fixed using double-sided tape. The loading direction for the samples in the testing machine was parallel to the circumferential fiber collection direction. The thickness of the testing sample was measured using a micrometer screw gauge (Mitutoyo 406-250, Mitutoyo, Japan). Tensile tests were performed in an atmosphere with temperature and humidity of 20 ± 2 °C and 30 ± 5% RH, respectively. At least five specimens for each fibrous mat were tested.

The density and porosity of fibrous membranes were calculated using the following equations

\[
D = \frac{m}{t \times A} 
\]

(1)

\[
P = \left(1 - \frac{m}{t \times A \times \rho}\right) \times 100\%
\]

(2)

where \(D\) and \(P\) are the density and porosity of the relevant fibrous membrane, respectively. \(m, t,\) and \(A\) are the mass, thickness, and area of the measured membrane, respectively. \(\rho\) is the density of polymer raw material and the density of PS is 1.09 g cm−3.

Oil Sorption Test. The following procedure was utilized to determine the maximum oil sorption capacity for the porous fibers: The PS samples were cut into specimens (2 × 2 cm2) with an approximate weight of 10 mg. The testing specimen was placed in a glass beaker filled with 100 mL of oil. After 60 min, the wet sorbents were removed from the oil container using a nipper and drained for 10 s. The oil sorption capacities for the PS fibers were calculated using the following equation:

\[
\text{Oil Sorption Capacity} = \frac{m_{\text{after}} - m_{\text{before}}}{m_{\text{before}}} \times 100\%
\]

Figure 2. FE-SEM images of PS fibers prepared from PS/THF solutions with varying PS concentration of (a) 16 wt %, (b) 18 wt %, (c) 20 wt %, and (d) 22 wt %. CS condition: rotational speed, 15 000 rpm; needle inner diameter, 160 μm; collection distance, 10 cm.
RESULTS AND DISCUSSION

Morphologies and Porous Structures of As-Spun Fibers. In the CS process, the morphology of the fibers is influenced by several factors, such as solution properties (concentration-viscosity, the evaporation rate of solvents) and process parameters (rotational speed, needle size, collector distance). In the first step, the optimum parameters for the fabrication of PS fibers were studied using PS solution in THF. A PS solution in THF with a concentration of 16, 18, 20, and 22 wt % was spun at a rotational speed of 15 000 rpm using needles with inner diameters of 160 μm and a collection distance of 10 cm. The SEM images of the PS fibers prepared from these relevant solutions are shown in Figure 2. As shown in Figure 2, bead-free fibers were observed at PS concentrations of up to 22 wt % but beaded fibers were obtained at lower PS concentration. The appearance of beads on fibrous webs produced from low-concentration polymer solutions is attributed to the occurrence of Rayleigh instability during the CS process, which has been studied in previous reports. The effect of solvents on the porous structure of the PS fibers was evaluated by changing the weight ratio of THF and DMF using a polymer concentration of 22 wt %.

Figure 3 shows the FE-SEM images of fibers prepared from 22 wt % PS solutions with varying THF/DMF weight ratios of 4/0, 3/1, 1/1, 1/3, and 0/4. It can be seen that the fibers prepared from different solvent mixtures have distinct interior structures and surface morphologies. A structure with a noncircular cross section and densely packed porous structure on the surface was found for the fibers produced from PS/THF solution, as observed in Figure 3a,b.

With increasing DMF content in the solvent mixtures, significant differences in terms of morphology and structure of the fibers were observed. It can be seen that the cross section was circular and that a porous interior structure was obtained, as shown in Figure 3. When mixture solvents with a THF/DMF ratio of 3/1 were used, a groove structure was observed on the surface of the fibers instead of a porous surface (Figure 3c,d). Additionally, two kinds of surface structures were found for the fiber prepared with a THF/DMF ratio of 1/1, including wrinkles and a porous surface with holes inside the fibers (Figure 3e,f). With further increase in the DMF in the solvent mixture (THF/DMF = 1/3), the fiber became smoother with densely packed small holes in the surface. Furthermore, a highly porous structure with large voids near the surface was obtained (Figure 3g,h). When only DMF was used, the structure of the fibers showed a completely circular cross section and the surface became smooth. The porous structure inside the fibers also became more uniform and denser (Figure 3i,j).

Mechanism of Porous Structure Formation on Fibers. During the CS process, the evaporation of the solvent from the liquid jet leads to the rapid solidification of the polymer from the solution. In addition to the simple drying process, the formation process of the porous morphologies induced by water vapor condensation can be divided into three steps, as shown in Figure 4a. At first, the process of solvent evaporation absorbs heat from the environment, leading to the condensation of the surrounding water vapor. In the second step, the breath figure and phase separation processes induce the generation of voids and the subsequent stretching of the polymer jet under centrifugal forces. In the final step, solvents further evaporate, leading to the solidification of fibers with fixed morphology and structure. As illustrated in Figure 4a, the amount of water determines the surface features of the fibers.

The formation of surface grooves and inner pores for the PS fiber can be attributed to the breath figure and/or phase separation process that occurs during centrifugal spinning. After condensing from the vapor, the water droplets immediately permeate into the solution jets and merge with the solvents. Because water is a nonsolvent for PS, phase separation can occur depending on the solvent system, called vapor-induced phase separation (VIPS). This process

\[ Q = \frac{m_w - m_0}{m_0} \]  

where \( Q \) (g g\(^{-1}\)) is the maximum oil sorption capacity, \( m_w \) is the total mass of the wet fibers after draining for 10 s, and \( m_0 \) is the mass of the fibers before the adsorption test. The oil adsorption capacity of each sample was measured at least three times. All of the oil sorption measurements were carried out at 25 °C. The oil sorption test was set up following published reports.
separates the polymer jet into polymer-rich regions and water/solvent-rich regions. Consequently, the polymer-rich regions turn into fiber and water/solvent-rich regions turn into pores. Combining this phase behavior with the CS process, the formation mechanism of a porous structure on the nanofiber surface can be attributed to the breath figure process. While a proportion of these droplets can penetrate the solution jet to induce a porous structure in the interior, the remaining droplets on the surface of the jet evaporate and generate holes on the fiber surface.

The SEM images in Figure 3 confirm the importance of the breath figure and VIPS in forming the surface structure and inner pores of the PS fibers. Therefore, a phase diagram was drawn to depict the phase behavior for the PS solutions during the CS process. As illustrated in Figure 4b, the ternary diagram is separated into two zones by binodal curves. The solution jet is homogeneous upon being extruded from the spinneret (Zone I). With the volatilization of THF and the subsequent permeation of water into the solution jet, the proportion of the four components (THF, DMF, water, and PS) in the jet is dynamically tuned to follow the path shown by the arrows. After crossing the binodal curve, the solution jet starts to enter Zone II, where it becomes opaque and separates into a multiphase due to thermodynamic instability.

As represented in Figure 4b, PS/THF solution requires the highest amount of water to enter the phase separation zone. Therefore, phase separation did not occur when PS/THF was used. Because this polymer solution has the highest evaporation rate among the used solvent mixtures, the highest amount of condensed water was found in the surface of its fibers, leading to the occurrence of the breath figure process, as demonstrated in Figure 4a. As a result, there was a dense cross-sectional structure inside the fiber and a rough surface, as found in Figure 3a,b.

When THF/DMF solvent mixtures are used, the formation of a grooved surface and porous interior structure is assigned to both the breath figure and phase separation process because the composition path easily crosses into the phase separation zone (Figure 4b). As shown in Figure 4a, when a THF/DMF weight ratio of 3/1 was used, the phase separation leads to a bigger hole compared to that of the PS/THF solution. With further stretching by the centrifugal force, the hole became the groove. Further, because of the low boiling point of DMF, fewer droplets were formed at a THF/DMF weight ratio of 1/3, resulting in small holes at the fiber surface, and large voids inside the fibers were obtained by the phase separation process. Interestingly, both a grooved structure and holes inside the fiber were obtained when the THF/DMF ratio was 1/1. Because of the difference in the evaporation rate between THF and DMF, the polymer jet was divided into a THF-rich phase and DMF-rich phase during the spinning process. As a result, both structures for the grooves and holes were obtained.

Because DMF evaporates even slower than water, the polymer jet formed from PS/DMF solution still retained its liquid form and could be stretched by centrifugal force. Consequently, the holes on the jet surface and inside the fibers are filled with polymer flow; as such, smooth fibers with a uniform and dense porous structure were observed, in accordance with the SEM images in Figure 3i,j.

Fiber Diameter and Porosity of Fibers. The effect of solvent composition on the diameter of the fibers was also investigated, as illustrated in Table 1. The detail fiber diameter distributions can be found in Figure S1. It can be seen that the fibers fabricated from PS/THF solution (4.46 μm) were larger than the fibers made from PS/DMF solution (4.21 μm) even though PS/THF solution exhibits a lower viscosity than that of PS/DMF solution. This finding is due to the higher vapor pressure of THF, which leads to a higher solidification rate for the polymer jet, reducing the elongation process for the polymer jet during the spinning process.²⁻ It should be noted that the fibers produced from mixtures of solvents exhibited a larger diameter than the fibers prepared from a single solvent. As reported by Golecki et al., PLA fibers produced from solvent mixtures having a lower evaporation rate were smaller.

Table 1. Fiber Diameter, Pore Volume, and Specific Surface Area of Centrifugally Spun PS Fibers

| samples               | solution viscosity (mPa s) | fiber diameters (μm) | BET surface area (m² g⁻¹) | BJH pore volume (cm³ g⁻¹) | density (mg cm⁻³) | porosity (%) |
|-----------------------|---------------------------|---------------------|---------------------------|--------------------------|-------------------|--------------|
| PS/THF                | 110 ± 2                   | 4.46 ± 2.74         | 0.42                      | 0.004                    | 188.9 ± 12.7      | 82.67 ± 1.17  |
| PS/(THF/DMF = 3/1)    | 127 ± 2                   | 5.11 ± 3.39         | 0.69                      | 0.004                    | 121.1 ± 6.1       | 88.89 ± 0.56  |
| PS/(THF/DMF = 1/1)    | 132 ± 2                   | 5.51 ± 2.98         | 6.30                      | 0.027                    | 120.9 ± 2.0       | 88.90 ± 0.19  |
| PS/(THF/DMF = 1/3)    | 144 ± 2                   | 6.00 ± 3.41         | 13.65                     | 0.075                    | 101.4 ± 8.0       | 90.70 ± 0.73  |
| PS/DMF                | 153 ± 2                   | 4.21 ± 3.03         | 12.12                     | 0.050                    | 120.7 ± 7.8       | 88.92 ± 0.72  |
than those fabricated from a high evaporation rate solvent mixture. However, in this study, the opposite trend was observed when the solvent composition was changed. This trend would be attributed to the solvent/nonsolvent exchange that occurs during the spinning process. The high evaporation rate of THF leads to the formation of a skin layer, and the solvent/nonsolvent exchange on the polymer jet surface leads to the higher solidification rate of the polymer jet surface, preventing the attenuation of the polymer jet and causing an incremental change in the diameter of the obtained PS fibers.

The effect of solvent on the morphology and structure was further evaluated by carrying out nitrogen adsorption–desorption isotherms for the PS fibers fabricated from five different solvent weight ratios, as represented in Figure 5a. It can be seen from Figure 5a that all samples show type IVa isotherms in the classification of vapor adsorption isotherms combining proposals from IUPAC, which confirms the presence of a porous structure within the samples. The effect of the solvent on the Brunauer–Emmett–Teller (BET) surface area and pore volume of the as-prepared samples is shown in Figure 5b. The detailed BET surface area and Barrett–Joyner–Halenda (BJH) pore volume for the relevant PS fibers are presented in Table 1. The results shown in Figure 5 and Table 1 indicate that the solvent composition strongly affected the surface area and porosity of the obtained PS fibers. Overall, the presence of DMF in the mixture leads to a higher BET surface area and pore volume for the final PS fibers. The PS fibers prepared from PS/THF solution, which have only a porous structure on the surface, exhibited the lowest specific surface area and pore volume, with values of 0.42 m² g⁻¹ and 0.004 cm³ g⁻¹, respectively. Additionally, the PS fibers fabricated from PS/DMF solution showed a significantly higher specific surface area and pore volume, which reached 12.12 m² g⁻¹ and 0.050 cm³ g⁻¹, respectively. The highest specific surface area and pore volume, with values of 13.65 m² g⁻¹ and 0.075 cm³ g⁻¹, respectively, were found in the fibers prepared from the PS/(THF/DMF = 1/3) solution; these values are 32.5- and 18.8-fold, respectively, higher than the same values of the sample made from PS/THF solution. It should be noted that BJH measurement in this study is applicable for the voids with a pore size smaller than 300 nm. Therefore, the BJH results for the PS/(THF/DMF = 3/1) and PS/(THF/DMF = 1/1) samples showed low values even though they exhibited highly porous structures. The density and porosity of as-prepared fibrous mats were evaluated to address the drawback of BJH measurement, as shown in Table 1. The PS/(THF/DMF = 1/3) sample exhibited the lowest density and the highest porosity, with values of 101.4 ± 8.0 mg cm⁻³ and 90.70 ± 0.73%, respectively. Meanwhile, the PS fibers prepared from PS/THF solution showed the highest density of 188.9 ± 12.7 mg cm⁻³ and the lowest porosity of 82.67 ± 1.17%. Furthermore, the PS fibers prepared from PS/(THF/DMF = 3/1), PS/(THF/DMF = 1/1) and PS/DMF solutions showed approximately the same density and porosity. These results corresponded to the obtained SEM images shown in Figure 3. These results also confirmed that the porous structure formation mechanism was different when the solvents used were THF and DMF, as discussed above.

**Wettability of As-Prepared Fibrous Mats.** The wettability of as-spun fibrous mats was characterized by using a Phoenix 300 contact-angle system, as shown in Figure 6. The as-prepared PS fibers exhibited high hydrophobicity with a water contact angle of over 140°. The high hydrophobicity of the PS fibrous webs was assigned to their low surface energy caused by the presence of CH groups in their chemical structure and the micro-nano hierarchical structures caused by the CS process. As seen in Figure 6, the used solvents show a small influence on the wettability of the PS fibrous membranes by changing the surface morphology of the final fibers. The highest water contact angle of 148.3 ± 2.5° was found in the fibrous web produced from a solution of PS/(THF/DMF = 3/1), which is attributed to the high roughness surface caused by the grooves on the surface of the fibers. Additionally, the fibrous mat prepared from PS/DMF solution, which shows the smoothest surface structure, has the lowest water contact angle of 142.3 ± 2.8°. In contrast, when the

Figure 5. (a) Nitrogen adsorption–desorption isotherms and (b) BET surface area and BJH pore volume of the PS fibers fabricated from 22 wt % PS solution with different weight ratios of THF/DMF.

Figure 6. Water contact angle of PS fibrous mats fabricated from a 22 wt % PS solution with varying weight ratios of THF/DMF.
oil droplet was placed onto the PS fibrous mats, the oil droplet immediately spread onto the mats, and the obtained oil contact angle was $0^\circ$, indicating that the PS fibers are superoleophilic (see Supporting Information Video S1). Within the superfast oil sorption rate and neglectable water sorption because of their high hydrophobicity, the PS fibrous mats show that they are good candidates for application to oil sorption.

**Oil Sorption Capacity.** For fibrous sorbents, the absorbed oil is mainly distributed over the fiber surface and trapped in the interconnected void between the fibers; this process is driven by a capillary force to reduce the surface free energy of the fibers. With porous structures, the oil adsorption performance can be further enhanced. The oil sorption test was carried out using three different kinds of oils: silicon oil, pump oil, and vegetable oil. The detailed physical properties for these oils can be found in the Supporting Information Table S1.

Figure 7 shows the maximum oil sorption capacity of centrifugally spun PS fibrous mats obtained from five different solvents mixtures and oil cleaning paper. It can be seen that the fibers prepared from PS solution with a THF/DMF ratio of 1/3 exhibited the highest oil sorption capacity, with oil sorption rates for silicone oil, pump oil, and vegetable oil of 47.7, 49.8, and 46.3 g g$^{-1}$, respectively, which are approximately 5 times higher than the oil sorption capacities of oil cleaning paper when tested with these oils. Although the PS fibers produced from PS/(THF/DMF = 1/3) solution are the thickest fibers, the highest porosity and the large holes inside the fibers located near to the surface of the fibers provide voids to effectively trap oils, explaining why this sorbent shows the best oil adsorption capacity. In contrast, the PS fibers made from PS/THF solution, which have a lowest porosity with a solid interior structure, show the lowest oil adsorption efficiencies of 32.2, 34.2 and 29.6 for silicon oil, pump oil and vegetable oil, respectively, even though these fibers are relatively small with the fiber diameter of 4.46 ± 2.74 μm. Further, with the same porosity, the PS/(THF/DMF = 3/1), PS/(THF/DMF = 1/1) and PS/DMF fibrous mats exhibited approximately the same oil sorption performance.

Taking a detailed look at the data, the sorption capacity among four kinds of oils decreases in the following order: pump oil > silicon oil > vegetable oil. Similarly, the adsorption performance of the other samples shows the same trend for the above three kinds of oils. The different sorption capabilities for these three different kinds of oils can be attributed to the viscosity of the oil used.12,15 The incremental change in the viscosity of the oil used leads to better adhesion of highly viscous oils to the fiber surface, which reduces the desorption rate. As a result, the adsorption capacity increases for oils with higher viscosity.

The comparison with other PS fibrous mats reported for oil sorption in Supporting Information Table S2 indicates that the oil sorption capacity of centrifugally spun porous PS fibers is lower than that of porous PS fibers fabricated by the electrospinning method. This difference is mainly due to the higher fiber diameter of centrifugally spun fibers, which leads to the formation of a large interconnected void between the fibers and causes lower oil sorption performance. However, the production yield of the CS process in this study is much higher than that of the electrospinning process, reaching approximately 22 g h$^{-1}$. The results indicate that CS is a promising method for the large scale fabrication of PS porous fibers.

**Mechanical Properties and Thermal Properties.** In practical applications, the mechanical properties of porous PS fibrous mats should be strong enough to withstand the weight of oil and the impact of removal. The tensile strength of the centrifugally spun porous PS fibrous membrane was tested, and the typical stress–strain curves are shown in Figure 8a. The maximum tensile stress and the elongation at maximum tensile

Figure 7. Maximum oil sorption capacities for the porous fibrous sorbents of different oils for PS fibers fabricated from 22 wt % PS solution with different weight ratios of THF/DMF. The reference is oil cleaning paper.

Figure 8. (a) Stress–strain curves and (b) tensile properties of centrifugally spun PS fibrous mats fabricated from 22 wt % PS solution with different weight ratios of THF/DMF.
stress obtained from the curves are summarized in Figure 8b. When the applied force increased, the porous PS fibrous mats cracked. The fiber mats made from PS/THF solution, which have the highest density, demonstrate the highest tensile strength of 0.52 ± 0.08 MPa and elongation as maximum stress of 3.7 ± 0.7%. Further, the fibers prepared from PS/(THF/DMF = 1/3) solution exhibit the lowest mechanical property values, with a tensile strength of 0.28 ± 0.06 MPa and elongation at a maximum stress of 6.2 ± 0.6%. This result is due to the lowest density and highly porous structure of the sample. The tensile strength of the PS fibers in this study was close to that reported for electrospun porous and nonporous PS fibrous mats in previously published studies.38,39 With the tensile strength ranging from approximately 0.3 MPa to over 0.5 MPa, it is assumed that the as-spun PS fibers can meet the requirement of mechanical strength for the application of oil–water separation.39

To investigate the effect of solvent composition on the thermal properties of the PS fibers, differential scanning calorimetry (DSC) was used. The DSC heating scans of the as-spun PS fibers fabricated prepared from 22 wt% PS solutions with different weight ratios of THF/DMF are shown in Figure S2. It can be seen that DSC thermograms of centrifugally spun PS fibers are typical of those expected for the amorphous PS with the appearance of glass-transition temperature (Tg) around 90 °C. Therefore, this study evaluated the effect of solvent composition on the glass-transition temperature of PS fibers. As shown in Table S3, the Tg of PS fibers was higher than that of PS bulk, indicating that the centrifugal force could lead to a higher arrangement of polymer chain inside the fibers. The Tg of PS fibers increased when the solvent mixtures having higher DMF fraction were used. The low evaporation rate of DMF caused a lower solidification rate of polymer jet, leading to further stretching of polymer chains during the centrifugal spinning process, resulting in the higher Tg of the final PS fibers.

CONCLUSIONS

We have successfully prepared porous PS fibers with a production yield of up to 22 g h⁻¹ by directly centrifugally spinning the PS solution with different THF/DMF weight ratios. The morphology and interior structure of the fibers can be controlled by changing the solvent composition. The differences in the morphologies and porous structures of the PS fibers are due to the occurrence of a breath figure and vapor-induced phase separation during the CS process. High sorption capacities of 47.7, 49.8, and 46.3 g g⁻¹ for silicone oil, pump oil, and vegetable oil, respectively, were found in the PS fibers fabricated from PS solution with a THF/DMF weight ratio of 1/3. The tensile strength of the PS fibrous membrane can reach over 0.5 MPa, which can meet the requirement of mechanical strength for the cleanup of an oil spill event. However, the PS fibers are still relatively thick, which limits their oil sorption performance. Therefore, the centrifugal spinning parameters need to be further studied to reduce the diameter and increase the porous volume of the PS fibers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02091.

Physical properties of the oils studied at the room temperature; comparison of production yield and oil sorption capacity of various porous PS fibers fabricated by electrospinning and centrifugal spinning; differential scanning calorimetry thermograms of PS fibers prepared from 22 wt % PS solutions with different weight ratios of THF/DMF; the glass-transition temperatures of PS bulk and PS fibers fabricated from 22 wt % PS solution with different weight ratios of THF/DMF; (PDF) Fast oil sorption rate of the PS fibrous membrane fabricated from the PS/(THF/DMF = 1/3) solution (Video S1) (AVI)

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H.N.D. designed the experiments; H.N.D., D.K.N., P.P.V., and K.H. performed the experiments and collected and analyzed the data. H.N.D., K.K., N.T., W.S., and D.P.H. discussed the research results; H.N.D. wrote the original draft and K.K. and N.T. reviewed and edited the manuscript.

Notes

The authors declare no competing financial interest.

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