Preparation of Polysulfone Microspheres with a Hollow Core/Porous Shell Structure and Their Application for Oil Spill Cleanup

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ABSTRACT: Polysulfone (PSF) microspheres with a hollow core/porous shell structure were prepared by a water-in-oil-in-water emulsion solvent evaporation method. The morphology of PSF could be controlled by variation of the surfactants, which included oleic acid, poly(vinyl pyrrolidone), and tween 80. The three kinds of prepared microspheres were developed as sorbents for the selective removal of oil from water. PSF microspheres with a hollow core/porous shell structure exhibited the best separation efficiency, which was 44.8 times higher than that of the pristine PSF powder. The oil-absorbed microspheres combined with unsinkability, appropriate size, and highly hydrophobic and superoleophilic properties could be quickly distributed and collected in seconds and exhibited recyclability. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

With increasing oil spill accidents, there is a growing demand for materials capable of removing various forms of oil spills from water. The existing absorbent materials used to achieve this goal include high-surface-area carbons, membranes, highly porous materials, and superhydrophobic and superoleophilic materials.[1–6] Among all those conventional materials, activated carbon is one of the most efficient materials because of its high surface area, abundant porosity, and sustainability.[7] However, its development has disadvantages, including difficulty in collection because of its small particle size, high regeneration temperatures, and low separation efficiency, which is caused by the coadsorption of water.[8] Some membranes show a high adsorption capacity, but they are unsuitable for the cleanup of large-area oil spills because of their poor distribution ability.[3] Therefore, there is still an urgent call for novel and efficient materials with appropriate sizes, high porosity, and superhydrophobic and superoleophilic properties. As a promising candidate, polysulfone (PSF) has superhydrophobic and superoleophilic properties. Our aim was to synthesize micrometer-sized PSF spheres with a hollow core/porous shell structure. Because of their low density, appropriate size, and high specific surface, such materials are useful in removing oil from water.

Hollow spherical materials have attracted a considerable amount of attention. Various synthetic approaches,[9–14] such as hard and soft colloidal templating, layer-by-layer deposition, template-free synthesis, and more recently, microfluidics and particle-stabilized emulsions, have been developed to fabricate them. Recently, tailor-made hollow spheres, including tin oxide nanoparticle microshells,[15] silica hollow spheres and microballons,[16] silica nanocages,[17] and poly(methyl methacrylate) microspheres with a hollow core/porous shell structure have been developed with these techniques.[18] As a convenient procedure, the emulsion solvent evaporation technique[19–22] has been reported extensively for the preparation of polymer microspheres. However, it has not been used to prepared porous microspheres.

In this study, we used the emulsion solvent evaporation technique to prepare PSF microspheres with a hollow core/porous shell structure, and the oil sorption and oil–water separation of the microspheres were evaluated.

EXPERIMENTAL

Materials

PSF was provided by Solvay Advanced Polymers. Poly(vinyl pyrrolidone) (PVP), poly(vinyl alcohol) (PVA), oleic acid (OA), tween 80, methylene chloride (DCM), and 1-methyl-2-pyrrolidone were all analytical-grade reagents (Beijing Chemical Co., Beijing, China). The other reagents were used as received without further purification. Deionized water was used throughout the experiment to prepare solution.
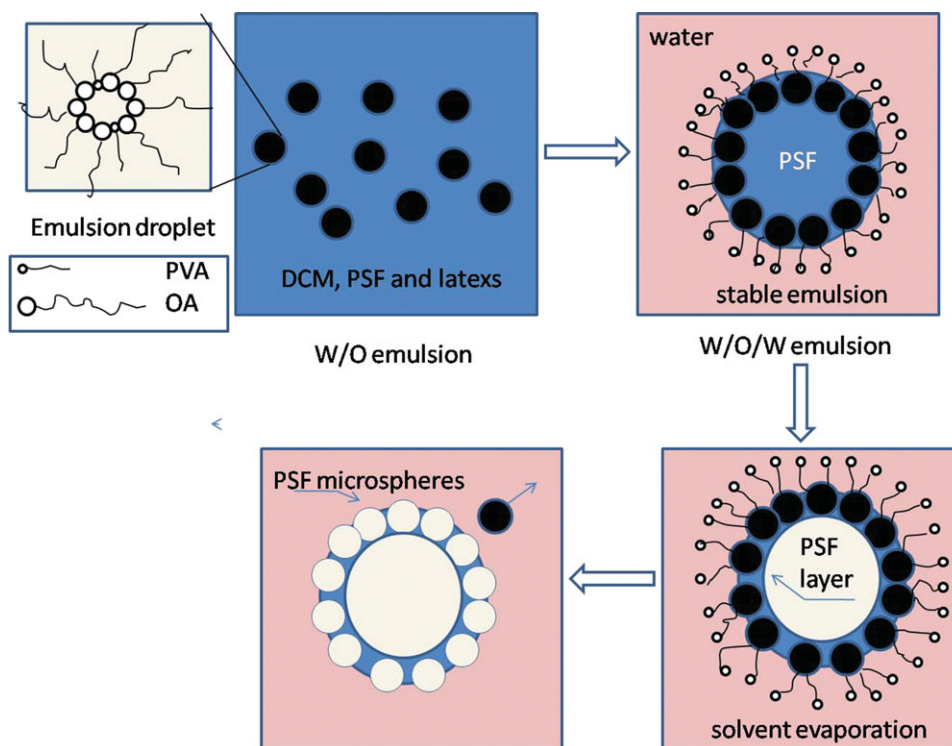
Scheme 1. Schematic illustration of PSF microsphere formation with a hollow core/porous shell structure (W/O = water in oil). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Preparation of Three Kinds of PSF Microspheres

The overall synthetic procedure is shown in Scheme 1. OA (0.1 g) was dissolved in 5 mL of DCM, and then, 0.3 mL of a PVA (0.1%) solution was poured into the DCM solution with stirring for 5 min at room temperature to form a preemulsion. The small internal aqueous droplets were surrounded by a mixture of surfactants, with PVA acting as a cosurfactant, which increased the efficiency of the interfacial activity between the oil and the aqueous phase. PSF (0.1 g) was dissolved in 1 mL of 1-methyl-2-pyrrolidone and was then slowly added to previous preemulsion solution. This system was stirred for 2 h at room temperature. During this period, PSF tended to diffuse in the emulsion droplets. After this system was slowly added to 50 mL of the PVA (0.1%) solution for 2 h at 35°C, the water-in-oil-in-water (W/O/W) emulsion was stabilized by the emulsion droplets and surfactants for the outer aqueous phase. With shrinkage of the PSF shell caused by solvent evaporation, a hollow core formed. At the same time, it propelled the emulsion droplets to disengage themselves automatically from the polymeric shell, leaving behind a porous polymer shell. The synthesized products were designated as PSF-1.

To determine the influence of different surfactants on the morphology of PSF, a set of experiments were performed with two other types of surfactants, PVP (PSF-2) and tween 80 (PSF-3), while the other synthetic parameters were kept constant.

Removal of the Oils from Water

The microspheres were scattered on a layer of oil on the water surface, and the microspheres absorbed the oil quickly. The oil-absorbed microspheres were then separated from the water

surface with a homemade net. The oil was removed from the surface of the microspheres by ultrasonic washing in ethanol for 10 min. After they were dried *in vacuo*, the microspheres were reused. The oil-absorption capacity of the microspheres was calculated by the formula as follows:

$$k = (m_2 - m_1)/m_1 \tag{1}$$

where k is the sorption capacity (g/g) and m_1 and m_2 are the weights of the microspheres before and after oil absorbance, respectively.

Characterization

The water contact angle (CA) measurements were performed with an optical video CA instrument (model OCA 40, Dataphysics Corporation, Germany) at room temperature. Before the measurements, the microspheres were placed on a slide and pressed into a flat film. A deionized water droplet or an oil droplet was used as the indicators. Scanning electron microscopy (SEM) images were obtained with an S4800 ESEM FEG scanning electron microscope (Japan's Hitachi Ltd, Japan) operated at 10 kV with energy-dispersive X-ray analysis attached to the scanning electron microscope. Fourier transform infrared (FTIR) spectra were obtained with a NEXUS-870 spectrophotometer (Nicolet Instrument Co., U.S.A.).

RESULTS AND DISCUSSION

Characterization of the PSF Microspheres

The morphology of the PSF microspheres fabricated by the W/O/W method was investigated by SEM. Figure 1(a) displays the
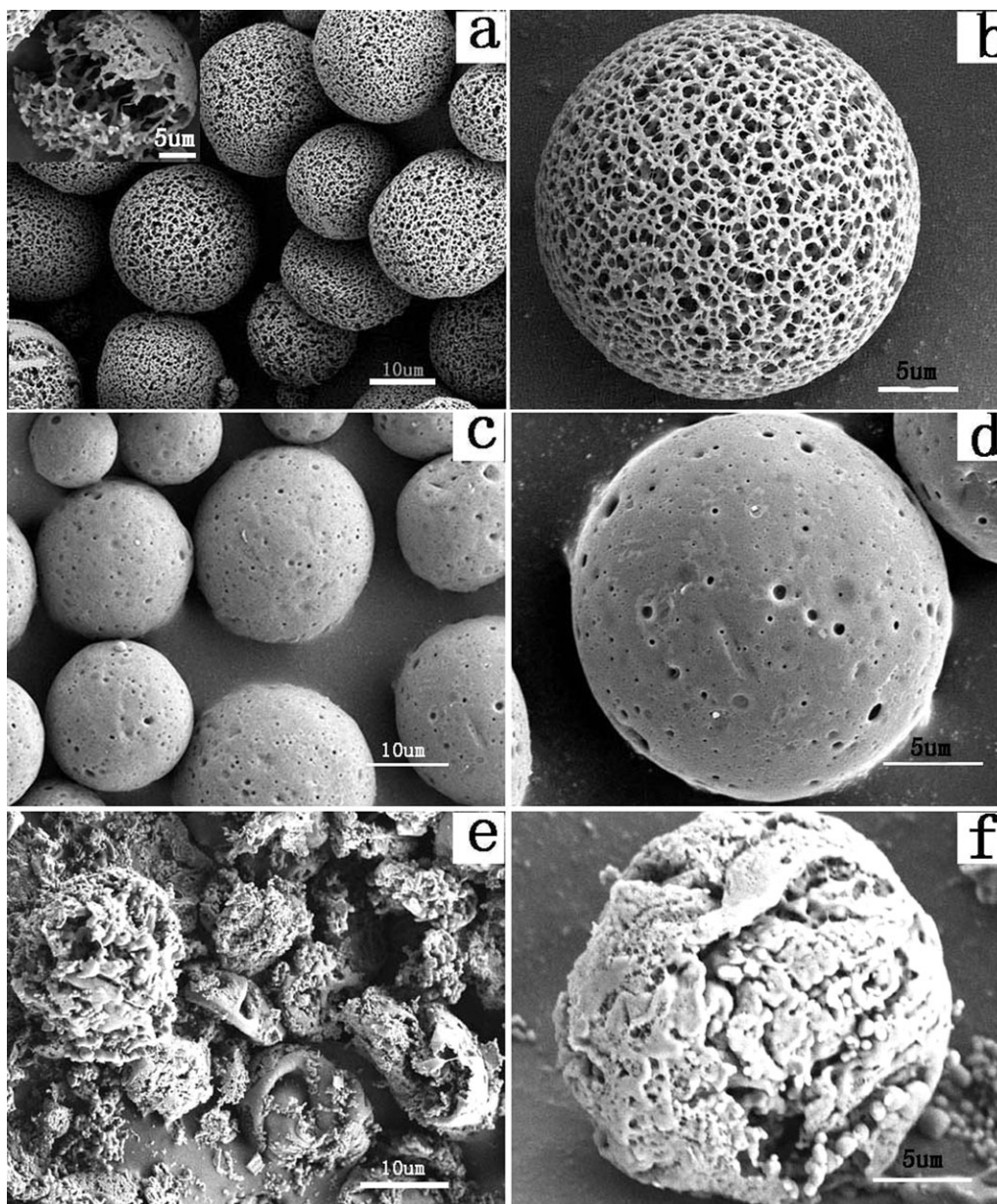
Figure 1. PSF microspheres fabricated by W/O/W: (a) SEM (inset: a broken capsule) and (b) larger scale SEM images of PSF-1, (c) SEM and (d) larger scale SEM images of PSF-2, and (e) SEM and (f) larger scale SEM images of the PSF-3.

SEM image of the PSF microspheres (PSF-1) with OA as surfactant; this indicated clearly that the products were monodisperse microspheres with an average diameter of 25 μm. In addition, the PSF microspheres possessed not only interconnected pores but also a hollow core structure, as shown in the broken microspheres in the inset in Figure 1(a). The larger scale SEM image [Figure 1(b)] showed that the shell of microspheres was porous, with diameters in the range 1–3 μm on the surface. Therefore, the as-prepared microstructures could be generally classified as microspheres with a hollow core/porous shell structure.

It is well known that the hydrophilic lypophilic balance (HLB) number of a surfactant influences the emulsion stability. We tried to investigate the effects of the HLB numbers on the formation of the microspheres. When PVP with a higher HLB number was used as a surfactant, the PSF microspheres (PSF-2) had a smooth surface with few pores, as shown by a comparison of Figure 1(c) with Figure 1(a). Moreover, the average pore diameters decreased to about 900 nm [see Figure 1(d)]. When tween 80 with the highest HLB number was used as surfactant, only a few PSF microspheres (PSF-3) were obtained [Figure 1(e)], and the surface of the microspheres was rugged [Figure 1(f)]. A similar phenomenon was reported in the preparation of poly(lactic-co-glycolic acid) microspheres.[23] The type of surfactant determined the surface porosity. The hollow core structure may have been due to the stability of the surfactant. Nihant et al.[24] found that the internal structure of microparticles could be changed from a multive-sicular to a matrixlike structure, depending on the stability of surfactant. It was
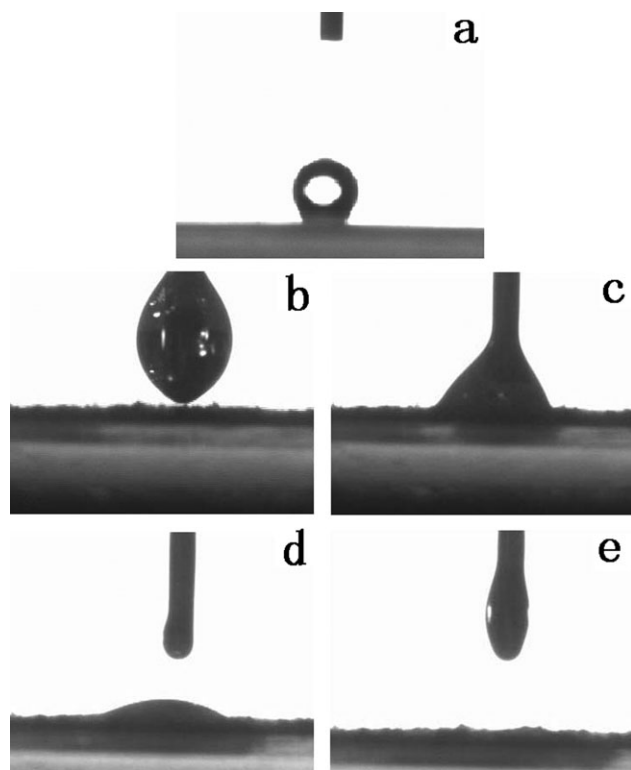
Figure 2. (a) Optical image of a water droplet placed on a bed of PSF-1 and (b–e) video snapshots of the wetting of an oil droplet on the bed of the PSF-1.

obvious that the surfactants with different HLB numbers had significant effects on the morphology. In this study, a low-HLB-number surfactant (OA) contributed to the generation of PSF microspheres with a hollow core/porous shell structure. In addition, our experiments showed that the effects of the temperature on the morphology were relatively small.

Removal of the Oils from Water

According to the previous results, PSF microspheres were achieved that could have had higher absorption capacities because of their relatively uniform interconnected pore shell and hollow core structure. Zhu et al.[1] found that a high porosity and appropriate void size of the sorbent were keys for a high absorption capacity. Thus, these microspheres could be applied for the removal of oil from the water surface.

The CA measurements, which implied potential application in oil–water separation, showed that the microspheres displayed highly hydrophobic and superoleophilic properties. The apparent CA of a water drop on the bed of PSF-1 was about 158° [Figure 2(a)]; this confirmed the high hydrophobicity. In contrast, a drop of motor oil quickly spread on the bed of the highly hydrophobic microspheres; this indicated superoleophilic properties, and the wetting time for an oil droplet added to the microspheres was found to be 4 s, as evidenced by the dynamic CA measurements [Figure 2(b–e)].

Because of the highly hydrophobic and superoleophilic properties, the microspheres exhibited a property called *selective absorbance*. When brought into contact with a layer of motor oil on a water surface, the PSF-1 quickly absorbed the oil while repelling the water, as shown in Figure 3. The PSF-1 floated over the water surface before and after the oil sorption [the inset in Figure 3(b)] because of its hollow core/pore shell structure, which was helpful for oil sorption and removal from the spilled area. More interesting, the oil-absorbed microspheres could be readily moved with a net.

Figure 4(a) shows the oil-adsorption capacities, as calculated by eq. (1), of the pristine PSF powder, PSF-1, PSF-2, and PFS-3. The sorption capacity of the pristine PSF powder was 0.75 g/g. For the PSF-2 and PSF-3, the absorption capacities were higher. It should be noted that the sorption capacity of PSF-1 was 33.6 g/g. This was 44.8 times that of the pristine PSF powder. The previous results indicate that the hollow core/pore shell structure was favorable for the improvement in the oil–water separation. After absorbance, the PSF-1 could be regenerated by ultrasonic washing in ethanol for 10 min. The recyclability of PSF-1 is shown in Figure 4(b). After three cycles, the PSF-1 could selectively absorb motor oil up to 14.2 times that of the particles' weight.

Oil Sorption Mechanisms

The mechanism of oil sorption by absorbent materials can be adsorption, absorption, capillary action, or a combination of these.[25] Therefore, for porous absorbent materials, many parameters, such as the material properties (surface configuration, lipophilicity, special surface area, density, etc.), oil properties (special gravity and viscosity), pore structure in absorbent materials (porosity, pore sizes, pore shape, etc.), and interaction between the oil and absorbent materials affect the oil sorption capacity.

Nevertheless, for PSF-1, we propose there were two important parameters for determining the oil sorption capacity. The first
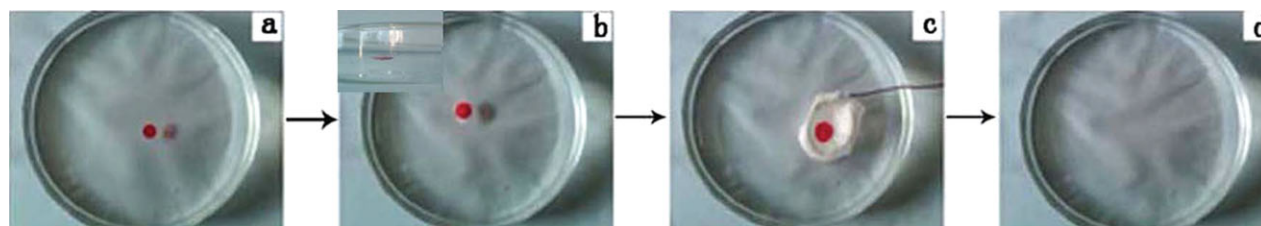

Figure 3. Removal of motor oil from the water surface (the motor oil was labeled by a dye for clarity): (a) a mixture of motor oil and water, (b) addition of the PSF-1 sample into a mixture of motor oil and water (inset: side view), (c) the oil-saturated microspheres were moved away with a net, and (d) pure water. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
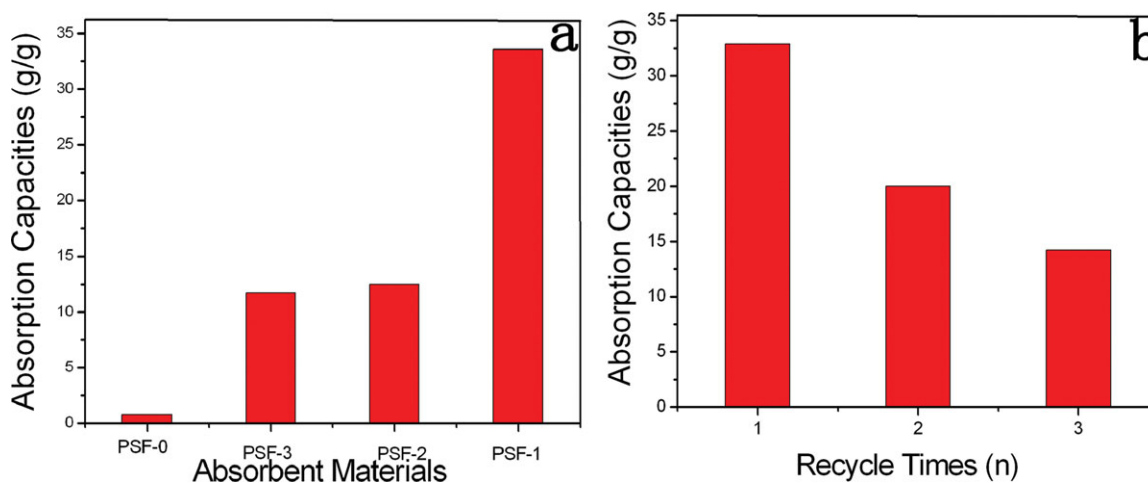
Figure 4. Adsorption capacity (a) of the oils from the water surface over various samples (the pristine PSF powder was denoted by PSF-0) and (b) after water–oil separation for three cycles (PSF-1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

one was an external factor, that is, the pore structure. The other key factor was the intrinsic factor, that is, the interaction between the oil and PSF microspheres. The hollow core/porous shell structure, with diameters in the range 1–3 μm, provided large amounts of storage volume for motor oil and acted as an oil reservoir; this was important for the highest absorption capacity of the PSF-1 [Figure 5(a)].

The curve 1 in Figure 5(b) reveals bands at 1321 and 1188 cm^{-1}, which were attributed to the symmetric and asymmetric stretching vibrations of S=O bonds in the PSF backbone. The band corresponding to the stretching vibrations of the C—O—C structures appeared around 1264 cm^{-1}. In addition, the sharp bands at 1620, 1562, and 1403 cm^{-1} were attributed to the benzene ring. The characteristic peaks of motor oil are shown in curve 2 [Figure 5(b)] and remained unchanged in curve 3. However, the characteristic peaks [v(S=O), v(C—O—C)] of PSF shifted slightly [curve 3 in Figure 5(b)]. The band for the

benzene ring at 1562 cm^{-1} disappeared. A new band was observed at 964 cm^{-1}. These changes in the FTIR spectra indicated interaction between the PSF microspheres and motor oil.

These results indicate that the hollow core/porous shell structure with diameters in the range 1–3 μm and the interactions were the keys to gaining higher absorption capacities.

CONCLUSIONS

In summary, we presented a W/O/W emulsion solvent evaporation method for preparing PSF microspheres with a hollow core/porous shell structure. The PSF microspheres synthesized in the presence of OA exhibited the best separation efficiency, which was 44.8 times higher than that of the pristine PSF powder. The microspheres showed unsinkability, appropriate size, and recyclability, all of which are of importance in practical applications.
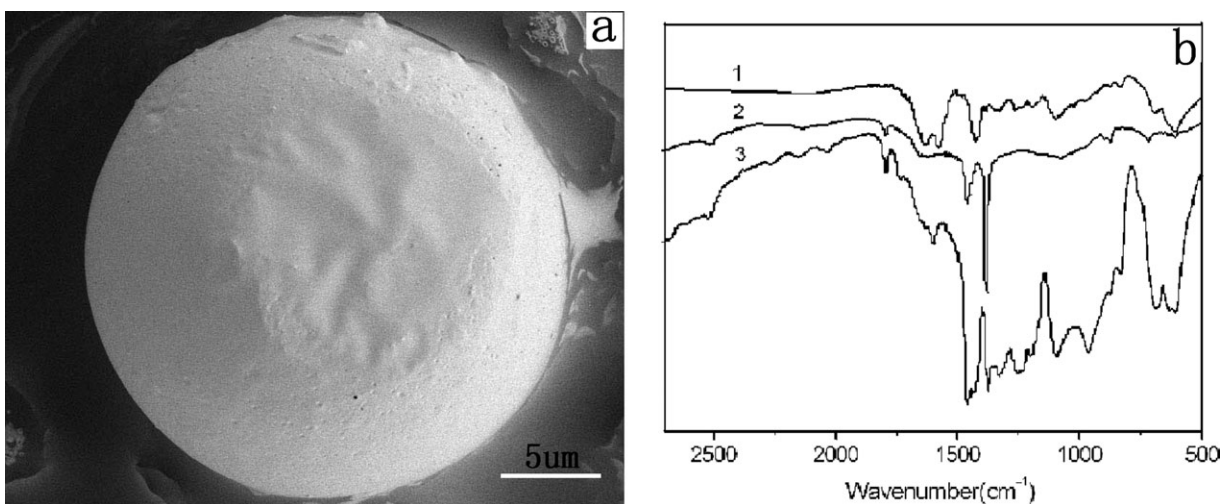

Figure 5. (a) SEM image of PSF-1 after the sorption of motor oil and (b) FTIR spectra of (1) PSF-1, (2) motor oil, and (3) oil-absorbed microspheres.

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