PAN/PS electrospun fibers for oil spill cleanup

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Abstract. A high-capacity oil sorbent was fabricated by electrospinning using PS/PAN blend. Morphology, contact angle and oil adsorption of PAN/PS fiber and PP nonwoven fabric were studied. It was found that the PAN/PS fiber had a smaller diameter than PP, and the maximum sorption capacities of the PAN/PS sorbent for pump oil, peanut oil, diesel, and gasoline were 194.85, 131.7, 66.75, and 43.38 g/g, which were far higher than those of PP. The sorbent PS/PAN fiber showed a contact angle of water 144.32° and diesel oil 0°. The sorption kinetics of PAN/PS and PP sorbent were also investigated. Compared with the commercial PP fabric, the PAN/PS fiber seems to have the ability to be used in oil-spill cleanup application.

Keywords: electrospinning; PS/PAN; fiber; sorption capacity

1. Introduction
In recent years, with the frequent occurrence of oil spills during oil exploration, transportation and processing, oil absorption materials have attracted extensive attention because of their efficient, economical and easy recovery of oil. Currently, oil adsorption materials can be divided into three categories [1]: inorganic products, organic natural products and organic synthetic products. Among them, organic synthetic products are considered to be potential sorbents for oil spill cleanup for their oleophilic and hydrophobic properties, low cost, and high buoyancy. However, the oil sorption capacities of these sorbents are relatively low, which has limited the application. An ideal sorbent should have high oil sorption capacity, fast uptake capacity, high oil/water selectivity and ready availability. Electrospinning is a method for efficiently producing micro- and nanofibers. There have been some works about polystyrene (PS) fiber [1, 2], which shows high oil sorption capacities. However, PS fiber can be dissolved in gasoline because of its non-polarity. In addition, PS fiber has a poor mechanical behavior and can be dispersed in oil after oil adsorption. PAN [3] fiber has been...
widely used in industry because of its good conductivity, solvent resistance and high strength. However, PAN fiber shows very poor interaction with non-polarity solvents. To solve the problems of PS fiber, PAN/PS sorbents were fabricated by electrospinning using PS/PAN blend.

2. Experiments

2.1 Materials
Polystyrene (PS), analytical grade, with molecular weight of Mw = 250,000 g/mol was purchased from Energy Chemical. Polyacrylonitrile (PAN), industrial grade, with molecular weight of Mw = 80,000 g/mol was purchased from Beijing Yili Fine Chemicals Co, Ltd. N, N-dimethylformamide (DMF) was purchased from Shanghai Chemical Reagents Co., Ltd., China. The oils used for absorption were vacuum pump oil (Beijing Si Fang special oil factory), peanut oil (Shandong Lu Hua Group Co., Ltd.), diesel and gasoline oil (Shandong Qingdao SINOPEC Co., Ltd.). The oil properties investigated are listed in Table 1. The nonwoven polypropylene (PP) was obtained from Shanxi Changqing Oilfield.

2.2 Method
A mixture of PAN (Mw=80000, China) and PS (Mw=250000, USA) was dissolved in DMF by stirring for 4 h to form 18wt% solution. PAN/PS with mass ratio of 1/1 was named as P1. The mixed solution was defoamed standing. All the electrospun fibers were prepared at 25 kV in a relative humidity of 40% at 30 °C, at a flow rate of 0.1 mm/s and with the distance between the tip and the collector fixed of 10 cm.

2.3 Characterization
The morphologies of the electrospun fiber and PP nonwoven fabric were examined by field emission scanning electron microscopy (S-4800, Hitachi Ltd., Japan).

Contact angles of electrospun fiber and PP nonwoven fabric were measured in a contact-angle system (SL200B, Kino Inc, USA) at 25 °C. The average contact angle of water and oil was obtained by measuring at three different positions of the same sample.

2.4 Oil absorption
Approximately 0.15 g of oil sorbent was dropped into a glass beaker filled with 100 mL of oil. After 60 min of sorption, the wet sorbent was drained for 60 s. The oil sorption capacities for the sorbents were obtained with the following equation [4]:

\[
Q = \frac{m - m_0}{m_0},
\]

where Q is the oil sorption capacity (g/g), m is the total mass of wet sorbent after the oil was drained for 60 s, and m_0 is the mass of the sorbent before sorption (g). Each sample with a same sorption time was measured three times independently, and the average value and standard deviation were calculated. All of the oil sorption measurements were conducted at 20 °C.
3. Results and discussion

3.1 Surface morphology of the sorbents

The morphologies of P1 and PP sorbents are illustrated in figure 1. As shown in Figure 1a and c, the P1 sorbent has diameters of 1.2-2.7 \( \mu \)m, while the diameters of PP are in the range of 10-15 \( \mu \)m. The P1 sorbent has a smaller diameter, contributing to a higher specific surface area and porosity [5], which is conducive to oil sorption. In addition, Figure 1b and 1d show that the surface of P1 sorbent is rougher than that of PP, which is helpful for the adhesion of oil on its surface. Thus, the P1 fiber has a smaller diameter and rougher surface, which will contribute to a higher oil sorption capacity than PP.

![Figure 1](image1.png)

**Figure 1.** (a,c) Low and (b,d) high SEM images magnification of P1 and PP sorbents.

3.2 The wettability of the sorbents

![Figure 2](image2.png)

**Figure 2.** Contact angle photos of (a) Water and (b) diesel oil droplet on the P1 sample with a contact angle of 144.32° and 0°

The wettability of electrospinning fiber was measured by the contact angle of water and diesel oil droplet, as shown in Figure 2. It shows that the water and diesel oil contact angles on P1 sample are 144.32° and 0°, respectively. The wettability of liquid droplet on a surface is determined by two
aspects\textsuperscript{[6]}: chemical composition and surface roughness. P1 sorbent consists of PAN and PS, all known as hydrophobic materials. Electrospinning is an efficient method producing fibers with diameters on micro- and nano-scales. Thus, the sorbent P1 have smaller diameter and rougher structures consistent with SEM photos that showed excellent hydrophobicity and oleophilicity.

### 3.3 Oil absorption and oil sorption mechanisms

| Oil               | Viscosity (mPa s\textsuperscript{-1}) | Density (g cm\textsuperscript{-1}) |
|-------------------|----------------------------------------|-----------------------------------|
| Vacuum pump oil   | 162.3                                   | 0.8566                             |
| Peanut oil        | 78.45                                   | 0.9151                             |
| Diesel oil        | 4.75                                    | 0.8449                             |
| Gasoline          | 0.3                                     | 0.7724                             |

![Figure 3. Maximum sorption capacities of P1 and PP for various oils](image-url)
Oil absorption and oil sorption mechanism are the most important parameters in oil recovery. Figure 3 shows the oil sorption capacities of P1 and PP sorbents. The high sorption capacity of PAN/PS fiber is the combined result of oleophilicity that caused by lower surface tension, smaller diameter and linear grooves, which increase the specific surface area [7].

As can be seen in Figure 4, as absorption time increases, the sorbents’ adsorption of the four oils increase rapidly, then slow down, and finally stabilize. At the initial stage of oil sorption, as to oleophilic interaction and the surface capillary force, the oil will be adsorbed on the surface. Then as to van der Waals forces, the oil can be adsorbed into inner fiber voids. Specific surface area of the fibers produced by void fractions, as well as linear grooves would predominantly affect the sorption capacity [8]. Oil sorption capacity is a combination of oil properties and fiber properties. With the increase of oil viscosity, the oil can more likely adhere to the surface of the fibers [8]. As shown in Table1, the oils arranged by their viscosity are pump oil >peanut oil >diesel oil>gasoline, which is consistent with the oil sorption capacities of the fibers. In addition, high viscosity can also inhibit the oil from entering the interior of the fibers, so the sorption capacity of pump oil is the highest, but is balanced by the lowest sorption rate.

**Conclusion**

PAN/PS fiber is hydrophobic and oleophilic and has a high oil sorption capacity. PAN/PS fiber has high oil sorption capacity and short balance time, which make it suitable to be used in oil spill cleanup.

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