

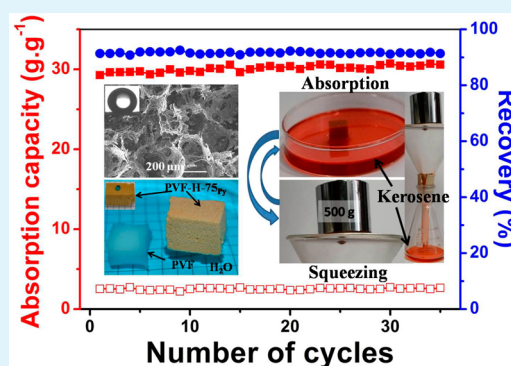
Evaluation of Hydrophobic Polyvinyl-Alcohol Formaldehyde Sponges As Absorbents for Oil Spill

Yanxiong Pan,^{†,‡} Kai Shi,[†] Chao Peng,[†] Weicai Wang,^{†,‡} Zhi Liu,[†] and Xiangling Ji^{*,†}[†]State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China[‡]State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, University of the Chinese Academy of Sciences, Changchun 130022, China

S Supporting Information

ABSTRACT: Macroporous materials are a class of absorbents used for oil spill cleanup. In this article, novel macroporous and hydrophobic polyvinyl formaldehyde (PVF-H) sponges were prepared by the reaction of stearoyl chloride with hydroxyl groups of hydrophilic PVF sponge at different temperatures. Attenuated total reflectance-infrared (ATR-IR) spectroscopy confirmed the successfully anchoring of hydrophobic stearoyl groups on the PVF networks. Scanning electron microscopy (SEM) images demonstrated that the as-prepared PVF-H had interconnected open-cell structures, and mercury intrusion porosimetry indicated that the average pore size ranged from 60 to 90 μm and porosity was greater than 94.8%. Such PVF-H sponges can absorb oil products effectively, such as toluene, *n*-hexane, kerosene, soybean oil, hydraulic oil, and crude oil up to 13.7 $\text{g}\cdot\text{g}^{-1}$ to 56.6 $\text{g}\cdot\text{g}^{-1}$, and this level of absorption was approximately 2–4 times higher than that absorbed by commercial polypropylene nonwoven mat. In low-viscosity oils, the samples can reach the saturated absorption amount only in 1 min, but in higher-viscosity oils, absorption equilibrium can be reached in 10 min. In a simulated oil slick system, these macroporous and hydrophobic sponges can still maintain high oil absorption capacities within the range of 14.4 $\text{g}\cdot\text{g}^{-1}$ to 57.6 $\text{g}\cdot\text{g}^{-1}$, whereas a relatively low absorption rate (approximately 20 min) indicated high absorption performance and excellent selectivity in the oil–water mixture. In addition, the absorbed oils were collected effectively only through a simple squeeze. The PVF-H sponges were subjected to 35 absorption–squeeze cycles and exhibited good reusability and 90% recovery for oils. The samples prepared at different temperatures differed in their absorption capacities to some extent. However, this new kind of macroporous and PVF-H sponges had excellent absorption performance on oil products.

KEYWORDS: hydrophobic sponge, macroporous absorbents, poly(vinyl alcohol)-formaldehyde, oil spill



INTRODUCTION

The frequent occurrence of oil spills seriously harm marine ecological and human living environments.¹ Various methods have been proposed for oil spill remediation, such as dispersants,^{2,3} solidifiers,⁴ absorbents,^{5–10} booms, skimmers, and controlled burning. Among current techniques, oil absorbent materials have particular potential because oil pollutants can be transformed from liquid to semisolid phase; collecting and removing oils from the spill site just by removing the absorbents are also possible.^{11,12}

Oil absorbents used in oil spill cleanup can be roughly divided into three major classes, namely, inorganic mineral products, organic natural products, and synthetic polymers. These materials have been widely investigated and applied in practice, but some shortcomings exist. Inorganic mineral products, such as silica,^{13,14} zeolites,^{15,16} and perlite,¹⁷ have low absorption capacity (less than 2 $\text{g}\cdot\text{g}^{-1}$). Organic natural products, such as wool fiber,¹⁸ rice straw,¹⁹ kapok fiber,²⁰ wood fiber, corn cob,²¹ and milkweed fiber,⁸ exhibit relatively high absorption performance, but instability occurs in aqueous

medium over time after oil absorption.^{18,19} Synthetic polymers, including rubber,²² polyacrylate,²³ and polyolefin²⁴ display high absorption amounts up to approximately 40 $\text{g}\cdot\text{g}^{-1}$, but the absorption rate is slow and regeneration after adsorption is difficult,^{23,24} which limit their application. Previously, novel absorbents with hydrophobic surfaces and interconnected macroporous structures based on different materials, have received attention because of their excellent absorption performance and additional functions. Some examples of these materials are carbon nanotube sponges,^{6,25,26} coated polyurethane foam,^{27,28} graphene sponge,^{29,30} nanocellulose aerogel,⁷ hydrophobic polyurethane foam,³¹ butyl rubber,^{4,32} electrospun fibers,^{10,33,34} and polydimethylsiloxane sponge.³⁵ These advanced materials exhibit high uptake capacity, rapid absorption kinetics, hydrophobicity, oleophilicity, floating before and after oil absorption, absorption selectivity, easy oil

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recovery from absorbents, and good reusability. Nevertheless, complicated reaction procedure, difficult scale-up, and high cost are limiting factors for the practical application of the above-mentioned materials. Thus, finding a novel material with advanced absorption performance is urgent.

Traditional hydrophilic poly(vinyl alcohol)-formaldehyde (PVF) sponges with macroporous structure exhibit good properties, such as open-cell structure, good mechanical property at low apparent density, high water uptake up to 15 g g⁻¹, and super softness at wet state. PVF sponges have been widely used as mops, surgical pads,³⁶ bandage pads,³⁷ and operative implants.³⁸ However, numerous isolated hydroxyl groups exist in hydrophilic PVF network because the hydroxyl groups in poly(vinyl alcohol) react with formaldehyde in pairs^{39,40} and restrict the usability of PVF in hydrophobic materials, such as absorbents of hydrocarbons, packaging materials, and building materials. However, isolated hydroxyl groups in PVF sponges allow further modification to obtain new functional materials with desired properties for practical applications. In this study, hydrophobic PVF (PVF-H) sponges are produced via heterogeneous phase reaction between stearoyl chloride and hydroxyl group in PVF. The optimum synthesis conditions for oil absorbents were determined, and the absorption performances in various oils were also investigated in detail.

EXPERIMENTAL SECTION

Materials and Regents. Poly(vinyl alcohol) (PVA) powder with a polymerization degree of 2000 and saponification degree of 99% was purchased from Shanxi Sanwei Group Co., Ltd., China. Triton X-100, glutaraldehyde, and stearic acid were obtained from Aladdin (Shanghai, China). Stearoyl chloride was prepared using conventional methods from literature.⁴¹ Formaldehyde and other organic solvents with different solubility parameters including *n*-hexane (7.24 (cal·cm⁻³)^{1/2}), cyclohexane (8.20 (cal·cm⁻³)^{1/2}), xylene (8.75 (cal·cm⁻³)^{1/2}), toluene (8.91 (cal·cm⁻³)^{1/2}), chloroform (9.21 (cal·cm⁻³)^{1/2}), dichloromethane (9.73 (cal·cm⁻³)^{1/2}), THF (9.52 (cal·cm⁻³)^{1/2}), 1,2-dichloroethane (9.80 (cal·cm⁻³)^{1/2}), *N,N*-dimethylacetamide (11.10 (cal·cm⁻³)^{1/2}), DMF (12.14 (cal·cm⁻³)^{1/2}), ethanol (12.70 (cal·cm⁻³)^{1/2}), methanol (14.50 (cal·cm⁻³)^{1/2}), glycol (16.50 (cal·cm⁻³)^{1/2}), and formamide (17.80 (cal·cm⁻³)^{1/2}) were purchased from Beijing Chemical Works and used as received. Kerosene (8.3 (cal·cm⁻³)^{1/2})⁴² and hydroaolic oil were purchased from China National Petroleum Corporation (CNPC); soybean oil (8.4 (cal·cm⁻³)^{1/2})⁴³ was regular cooking oil. Crude oil was obtained from PetroChina Jilin Oilfield Company.

Preparation of PVF Sponge. The preparation of PVF sponges has been reported in literature.⁴⁴ Typically, 50 g of PVA was dissolved in 450 g of deionized water by vigorous stirring with a magnetic stirring bar at 95 °C until completely dissolved. A PVA solution with a concentration of 10 wt % was obtained. Formaldehyde (10 mL) and Triton X-100 (1.5 g) were poured into 60 g of hot PVA solution with vigorous stirring. The liquid froth was obtained after 5 min, after which 30 mL of 50 wt % H₂SO₄ was poured into the froth at room temperature. The froth at maximum volume was poured into a mold and cured in an oven at 60 °C for 5 h. The raw sample was washed with water at least five times to remove the unused reactants. Finally, the sample was obtained after drying to constant weight at 60 °C. The PVF has an apparent density of 0.073 g·cm⁻³.

Preparation of Hydrophobic PVF (PVF-H) Sponges. The obtained pristine PVF was cut into small pieces with a dimension of 10 × 10 × 50 mm³ and immersed into the mixture of stearoyl chloride and acetonitrile in the presence of pyridine at different temperature (25, 50, and 75 °C) for 24 h. The as-prepared samples were washed thoroughly with toluene, dried in a vacuum oven at 50 °C, and designated as PVF-H-25_{py}, PVF-H-50_{py}, and PVF-H-75_{py} (the

numbers 25, 50, and 75 correspond to the reaction temperatures of 25, 50, and 75 °C, respectively).

Instruments and Characterization. Fourier-transform infrared (IR) spectrum was obtained on Bruker Vertex 70 spectrometer with attenuated total reflection (ATR) attachment. Scanning electron microscopy (SEM) images were observed using a field-emission environmental SEM (Micro FEI Philips XL-30-ESEM-FEG) operating at 15 kV. Water contact angle was observed using Krüss DSA 10-MK 2 drop shape analyzer at ambient temperature, using water as probe liquid (approximately 3 μL). Pore size and porosity were obtained by an automatic intrusion porosimeter (Autopore IV 9500, Micromeritics, U.S.A.). Viscosities of the oils were measured by MDJ-8S digital viscometer, and densities of the oils were measured by gravimetric method. The water contents of recovered oil from oil–water mixture were measured using a Mettler Toledo C20 coulometric Karl Fisher titrator.

Procedures of Oil Removal. Six types of oils, including toluene, *n*-hexane, kerosene, vegetable oil, hydraulic oil, and crude oil, were selected to examine the efficiency of the as-prepared macroporous PVF sponges. Physical constants of oils are listed in Table 1. Toluene

Table 1. Properties of Oils Used in Experiments

| oil type | viscosity (cp) (20 °C) | specific gravity (20 °C) | solubility param. ((cal·cm ⁻³) ^{1/2}) |
|------------------|------------------------|--------------------------|-------------------------------------------------------------|
| toluene | 0.29 | 0.87 | 8.91 |
| <i>n</i> -hexane | 0.33 | 0.66 | 7.24 |
| kerosene | 3 | 0.80 | 8.26 ²⁸ |
| soybean oil | 55 | 0.92 | 8.37 ²⁹ |
| hydraulic oil | 84 | 0.87 | |
| crude oil | 172 | 0.86 | |

represents the most common weak polar volatile organic compounds (VOCs), respectively, whereas *n*-hexane and kerosene is selected to represent low-viscosity oils, such as gasoline, diesel fuel, and light crude oil. Hydraulic and crude oils are satisfactory representatives of higher-viscosity oils. Soybean oil represents consumed regular cooking oil. All tests were performed at 25 °C, and the obtained PVF-H-25_{py}, PVF-H-50_{py}, and PVF-H-75_{py} sponges and commercial PP nonwoven mat were cut into a size of 10 × 10 × 5 mm³. The samples were weighted (*W*₀) and immersed into 200 mL oils, and the weight of absorbents was monitored as a function of time. The swollen sponges were removed from the oils at certain intervals, and their weights were determined at time *t* after draining for 0.5 min on stainless steel mesh. The absorption capacity (*Q*_{*t*}) at time *t* was calculated according to the following equation:

$$Q_t = (W_t - W_0) / W_0 \quad (1)$$

where *W*₀ is the dry sponge mass, and *W*_{*t*} is the total weight of wet sponge at time *t*. *Q*_{*s*} is the saturated absorption capacity; that is, the absorbents were immersed into the different oils for 30 min.

The volume swelling ratio (*Q*_{*v*}) of as-prepared samples in various organic solvents with various solubility parameters was also calculated from the saturated absorption capacity and defined as follows:

$$Q_v = (W_s / \rho_s + W_0 / \rho_0) / (W_0 / \rho_0) \quad (2)$$

where *W*_{*s*} is the weight of absorbed organic solvents at saturated state of samples in various organic solvents, and ρ_s and ρ_0 are the apparent densities of the organic solvent and the dried sample, respectively.

Absorption Selectivity and Reusability. The procedures for oil removal from tap water by absorbents were obtained from literature.^{8,45} To emphasize excellent oil adsorption selectivity of our materials in the aqueous medium, just a small amount of oil was poured into a beaker to obtain a layer approximately 1.5 mm above the water. Subsequently, the samples were placed on the surface of oil–water mixture, and the weight of the sponges was monitored as a

function of time. The absorption capacities of absorbents in different oil–water mixture were calculated from eq 1.

Reusability test was carried out by simple squeezing, and the absorbed oils were collected from sponges. The recovery (R) of oil was calculated as follows:

$$R = W_{re}/(W_e - W_0) \times 100 \quad (3)$$

where W_{re} is the weight of collected oil, W_0 is the dry weight of sponge, and W_e is the swollen sample mass at absorption equilibrium state. The squeezing experiments were performed for 35 cycles for each sample.

RESULTS AND DISCUSSION

Characterization of Macroporous and Hydrophobic PVF Sponges and PP Nonwoven Mat. Figure 1 shows the

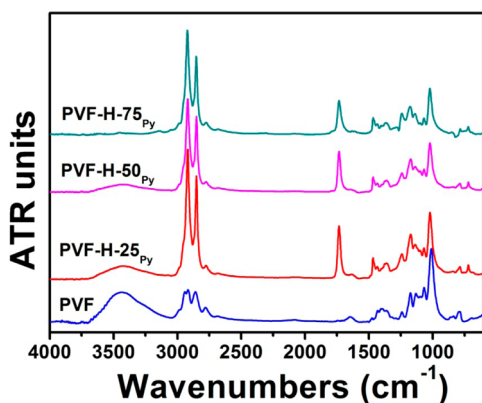


Figure 1. FTIR spectra of PVF, PVF-H-25_{Py} (25 °C), PVF-H-50_{Py} (50 °C), and PVF-H-75_{Py} (75 °C).

ATR-IR spectra of PVF, PVF-H-25_{Py}, PVF-H-50_{Py}, and PVF-H-75_{Py}. The broad absorption in the range 3200 to 3600 cm^{-1} and the peak at 2843 to 2943 cm^{-1} in the PVF are attributed to the O–H stretching vibration and C–H strength vibration of the alkyl chain, respectively. After hydrophobic modification using stearoyl chloride in the presence of pyridine at 25 °C, the PVF-H-25_{Py} showed an obviously reduced intensity in the range 3200 to 3600 cm^{-1} and the appearance of prominent new peaks at 1734 and 721 cm^{-1} , which are attributed to carbonyl stretching and rocking vibrations of the alkyl chain from octadecyl chains, respectively. These changes indicate the successful substitution with hydrophobic stearoyl groups on the PVF. The peaks at 2843 to 2943, 1734, and 721 cm^{-1} increases with increasing reaction temperature from 25 to 75 °C. Meanwhile, the O–H stretching vibration decreases dramatically with reaction temperature, implying that a sponge with a high degree of substitution can be produced at high reaction temperature. The O–H stretching vibration eventually disappeared completely at 75 °C, and PVF-H-75_{Py}, which shows complete substitution of stearoyl groups in PVF, was obtained.

Figure 2 shows the pore size distribution of the PVFs before and after hydrophobic modification. PVF and PVF-H-25_{Py} showed a similar average pore size of 60.4 μm , whereas PVF-H-50_{Py} and PVF-H-75_{Py} showed a pore size of 90.8 μm . The porosities of PVF, PVF-H-25_{Py}, PVF-H-50_{Py}, and PVF-H-75_{Py} are 95.0%, 94.5%, 90.5%, and 91.7%, respectively. For comparison, the commercial PP nonwoven mat was tested. The average pore size and porosity of commercial PP nonwoven mat are 45.3 μm and 88.9%, respectively. Figure 3

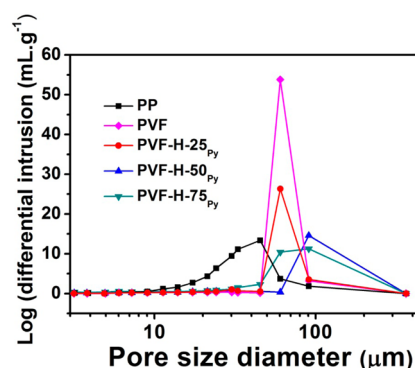


Figure 2. Pore size distributions of PVF, PVF-H-25_{Py}, PVF-H-50_{Py}, PVF-H-75_{Py} and PP nonwoven mat.

presents low-magnification SEM images of the sponges. As shown in Figure 3a, the pristine hydrophilic PVF has an interconnected open-cell structure with an average diameter of 51.9 μm . These structural characters offer rapid penetration and diffusion of reagent and react with the residue hydroxyl groups of the PVF network. In Figure 3b and c, after hydrophobic modification, PVF-H-25_{Py} and PVF-H-75_{Py} maintain the interconnected pore structure but with larger pores in accordance with data in Figure 2. The hydrophobic modification increase the pore size and distribution to some extent, but PVF-H sponges maintain high porosity greater than 90%, which will facilitate rapid absorption and high capacity for organic solvents. Figure 3d shows a PP nonwoven mat with fiber assemblies and porous and cloth-like structure. The diameter of fibers is in the range 1.0 to 15.0 μm and the bulk density of PP is approximately 0.110 $\text{g}\cdot\text{g}^{-1}$.

Wettability or water-repellency of substrates is greatly affected by the surface composition and the surface topography of substrates,⁴⁶ especially for porous substrates with open-cell structure.⁴⁷ As shown in the inset of Figure 3a-2, the pristine PVF sample has a hydrophilic surface, and the water droplet penetrated into the pores completely within 20 s. Thus, the static contact angle cannot be obtained. On the contrary, the water droplet was not absorbed by PVF-H-25_{Py}, PVF-H-50_{Py}, PVF-H-75_{Py}, and PP, and remained on the surface of the above samples for a long time. The water contact angles of PVF-H-25_{Py}, PVF-H-50_{Py}, PVF-H-75_{Py}, and PP are $131^\circ \pm 0.5^\circ$, $133^\circ \pm 1.1^\circ$, $138^\circ \pm 1.5^\circ$, and $141^\circ \pm 0.7^\circ$, respectively. Obviously, the PVF-H-75_{Py} and PP nonwoven mat show remarkably higher water contact angle than PVF-H-25_{Py} and PVF-H-50_{Py}, demonstrating that hydrophobicity of modified samples increased with modified temperature. The high contact angle of hydrophobic sponges is due to the rough surface and immobilization of hydrophobic long-alkyl chain on the surfaces, which effectively enhanced the hydrophobicity of sponges. Figure 4a illustrated the structural change from hydrophilic to hydrophobic. PVF-H sponges can float on the water as shown in Figure 4b, but pristine PVF sank into the water. Interestingly, the droplets with low surface tension such as kerosene and crude oil would penetrate into the PVF-H sponge very quickly whereas those with higher surface tension such as water and glycol were “standing” on the surface (Figure 4c).

Oil Absorption Performance. Oil absorption kinetics and absorption capacity are two very important parameters that characterize the quality of absorbents. The absorbents with interconnected pore structure could be rapidly penetrated by suitable solvents, and absorption equilibrium can be reached

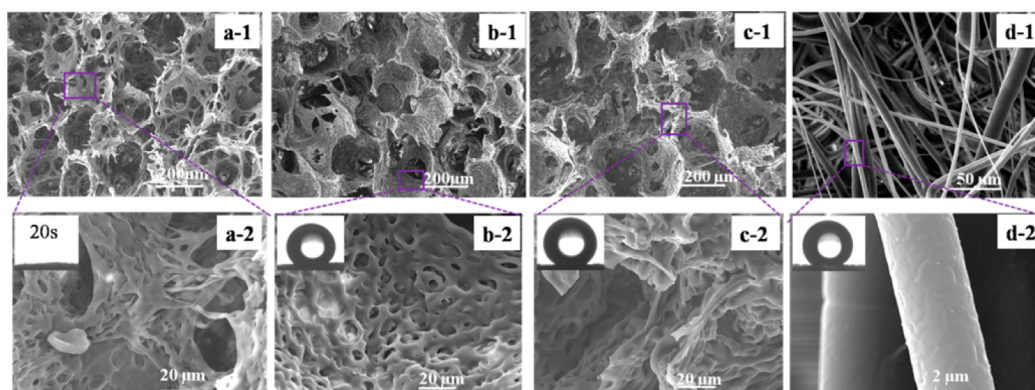


Figure 3. SEM images of PVF samples and PP nonwoven mat, (a-1) pristine PVF, (a-2) enlarged view of local (a-1); (b-1) PVF-H-25_{py}, (b-2) enlarged view of local (b-1); (c-1) PVF-H-75_{py}, (c-2) enlarged view of local (c-1); (d-1) PP nonwoven mat, (d-2) enlarged view of local (d-1); insets in a-2, b-2, c-2, d-2 corresponding to pictures taken during water contact angle measurement.

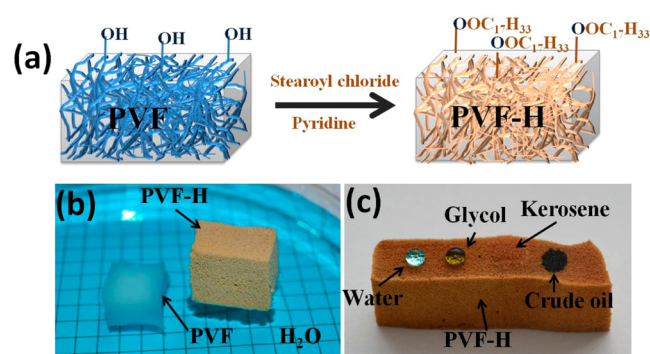


Figure 4. (a) Hydrophobic PVF was obtained by reaction of stearoyl chloride with hydroxyl groups of hydrophilic PVF samples at different temperature. (b) PVF-H-75_{py} floated on water while pristine PVF sank into water. (c) Water and glycol droplets kept stay on PVF-H-75_{py} sponge, whereas kerosene and crude oil droplets were absorbed by PVF-H-75_{py} quickly.

within a short time.^{48,49} Figure 5a-f shows the absorption kinetics of the sponges in various oil media. In low-viscosity oils, such as toluene, *n*-hexane, and kerosene, the sponges can reach absorption equilibrium within 1 min (See the Supporting Information, Movie 1). In oils of higher-viscosity, such as soybean oil, hydraulic oil, and crude oil, at least 10 min is required to reach absorption equilibrium. In low-viscosity oil products, the oil molecules move quicker and can diffuse into the pore channels of sponge in a shorter time, which also leads to the solvation of the polymer network simultaneously. Thus, this absorption process is dominated by the diffusion step. However, for higher-viscosity oils, the slow diffusion of oil molecules leads to slow solvation of the network and swelling, indicating that reaching equilibrium would take a long time. The original hydrophilic PVF and PP nonwoven mats have almost no volume expansion after oil absorption, indicating that the oil molecules only filled the pore channels of these samples almost without solvation of polymer networks.

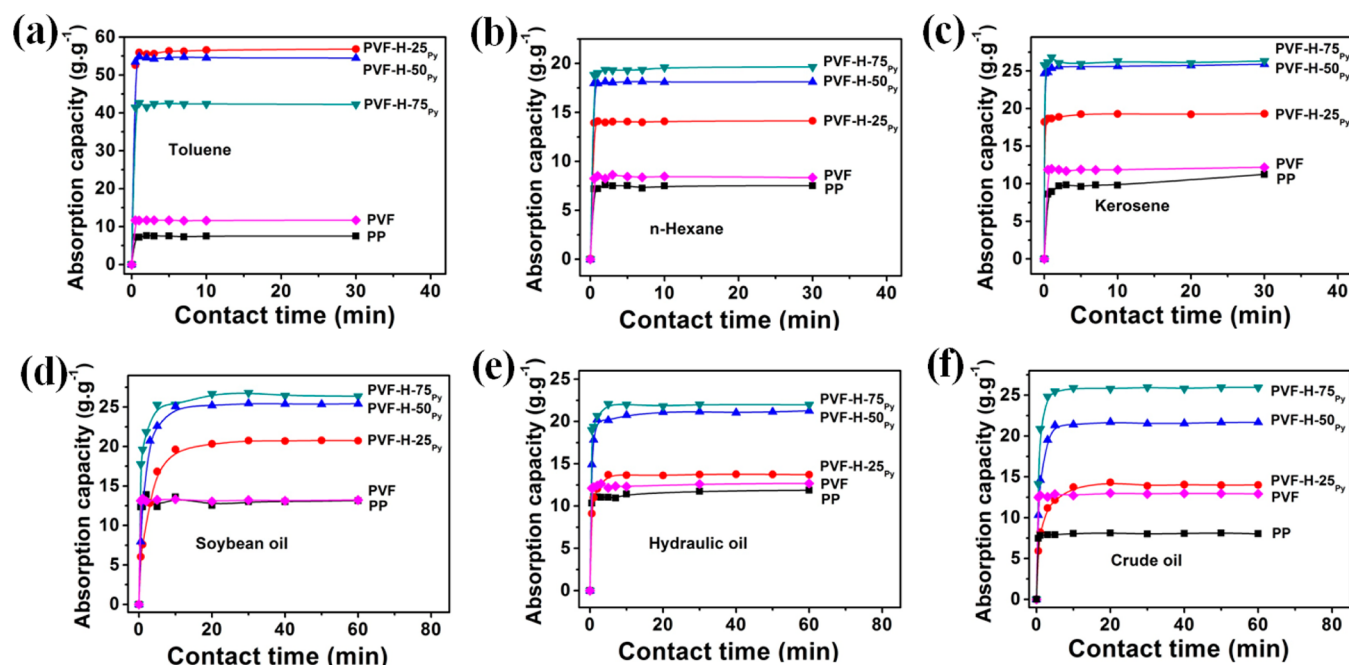


Figure 5. Absorption kinetic curves of sponges in (a) toluene; (b) *n*-hexane, (c) kerosene; (d) soybean oil; (e) hydraulic oil; (f) crude oil media.

The absorbents were immersed into the different oils for 30 min, and the saturated absorption capacity is obtained, as shown in Figure 6. The absorption capacities of PP nonwoven

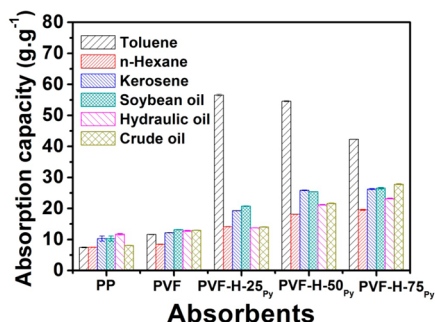


Figure 6. Saturated absorption capacity of absorbents in various oils.

mat in toluene, *n*-hexane, kerosene, soybean oil, hydraulic oil, and crude oil, are 7.4, 7.5, 10.3, 13.2, 11.7, and 8.1 g.g⁻¹, respectively, whereas those of pristine PVF are 11.6, 8.4, 12.2, 13.1, 12.8, and 12.9 g.g⁻¹, respectively. The PVF-H sponges, such as 1 g of PVF-H-25_{Py}, absorb 56.6 g of toluene, 14.1 g of *n*-hexane, 19.3 g of kerosene, 20.7 g of soybean oil, 13.7 g of hydraulic oil, and 14.0 g of crude oil. Obviously, hydrophobic modification improves the absorption capacity of sponges in different oil products. However, PVF-H sponges prepared at higher temperatures have higher absorption capacity for oils. For example, Q_s of PVF-H-50_{Py} in toluene, *n*-hexane, kerosene, soybean oil, hydraulic oil, and crude oil are 54.6, 18.1, 25.8, 25.4, 21.1, and 21.6 g.g⁻¹, whereas those of PVF-H-75_{Py} are 42.3, 19.5, 29.4, 26.5, 22.0, and 25.9 g.g⁻¹, respectively. The above-mentioned results are approximately 2–4 times higher than those of PP nonwoven mat and original PVF sponge.

Absorption Selectivity for Oil Slick. Oil absorption selectivity in aqueous medium is a key factor to evaluate the

applicability of an absorbent for oil spill cleanup. Generally, materials with hydrophobic and oleophilic surfaces can be wetted selectively by the oils while repelling water.⁵⁰ As-prepared sponges and PP nonwoven mat were placed on the surface of water–oil mixture to investigate oil absorption selectivity and absorption kinetics in the water–oil mixture. Figure 7a–c shows that for a low-viscosity oil–water mixture such as toluene, *n*-hexane, and kerosene, the absorption kinetics is similar to pure oil medium and saturated absorption capacity can be reached within 1 min. As shown in Figure 8a, b, the kerosene on water could be rapidly removed once the PVF-H-75_{Py} was placed on the surface of kerosene–water mixture (See the Supporting Information, Movie 2). However, as shown in Figure 7d–f, for a higher-viscosity oil–water mixture including soybean oil, hydraulic oil, and crude oil, absorption equilibrium can be reached in 20 min because of the slow diffusion of oil molecules in the polymeric networks.⁸

Hydrophobic PVF-H sponges with low apparent density have high buoyancy, and thus, the samples could keep floating on the surface of oil–water mixture before and after absorption (Figure 8b), which facilitate removal of oil pollutants from the spill area (Figure 8c). The absorption kinetic curve of pristine hydrophilic PVF in the oil–water mixture (kerosene, soybean oil, hydraulic oil, and crude oil) can be divided into the following two stages, saturation by upper oil layer within a short time, and repulsion of absorbed oil from the PVF network and substitution by water with increased time. This conjecture is confirmed by the fact that the PVF eventually sinks into the water over time and the saturated absorption capacity with water is approximately 17 g.g⁻¹, which is close to the maximum absorption capacity in pure water (See Figure S1 and Figure S2 in the Supporting Information). This finding indicated that the hydrophilic PVF sponges cannot be used as oil absorbents.

The saturated absorption capacities of PP nonwoven mat, PVF-H-25_{Py}, PVF-H-50_{Py}, and PVF-H-75_{Py} in the oil–water mixture are plotted in Figure 9. The absorption capacities of PP

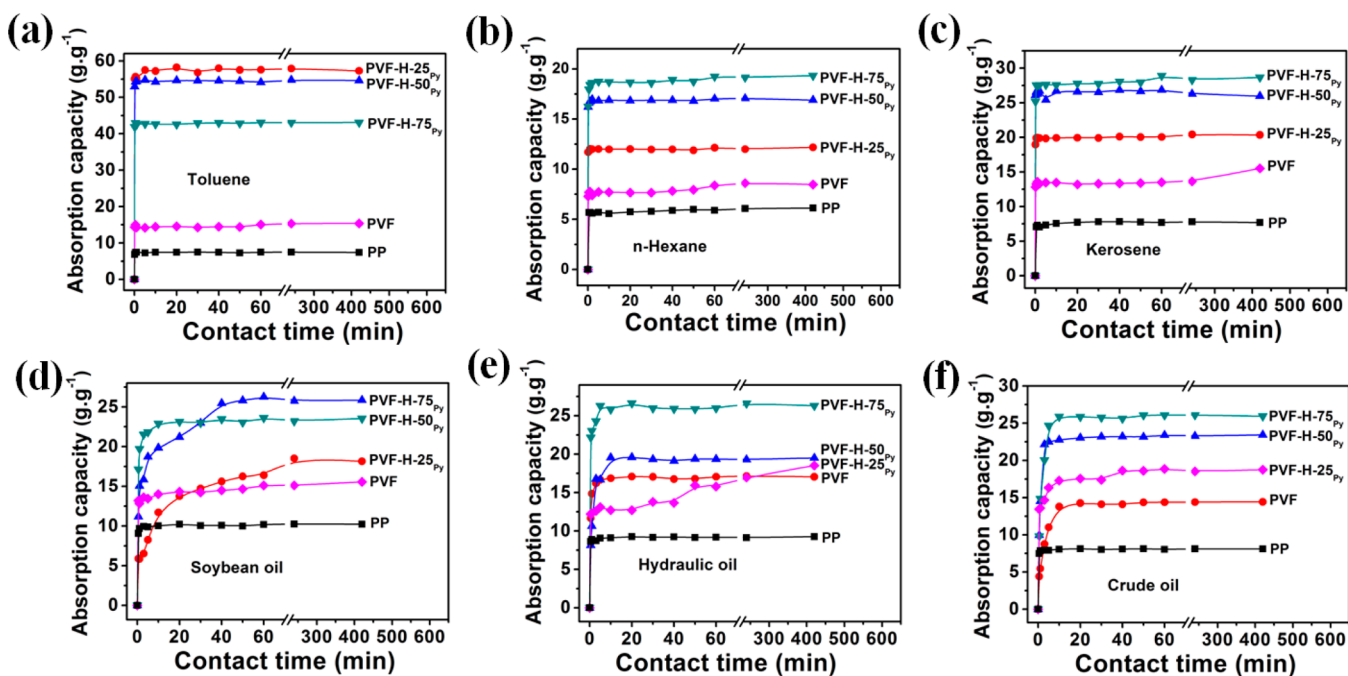


Figure 7. Absorption kinetic curves of sponges in various oil–water mixtures: (a) toluene–water mixture; (b) *n*-hexane–water mixture; (c) kerosene–water mixture; (d) soybean oil–water mixture; (e) hydraulic oil–mixture; (f) crude oil–water mixture.

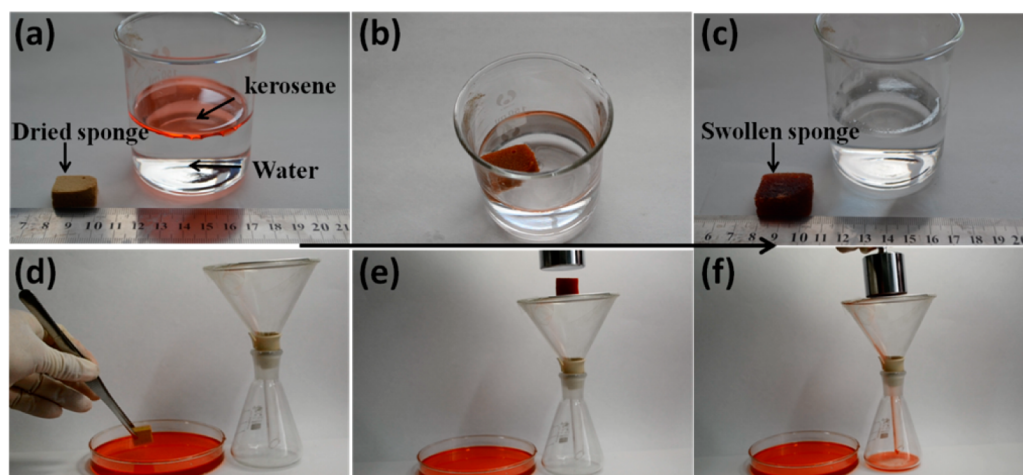


Figure 8. Snapshots show the PVF-H-75_{py} sponge for the absorption and recovery of kerosene from aqueous medium, (a–c) absorption of 4 mL kerosene from static aqueous medium; (d–f) absorption and recovery kerosene from kerosene medium.

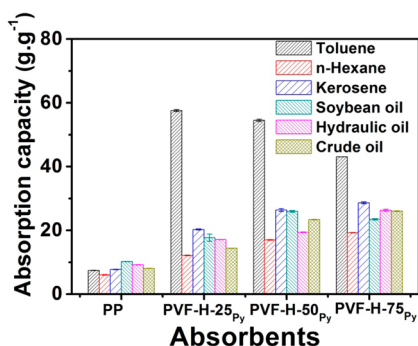


Figure 9. Saturated absorption capacity of absorbents in various oil–water mixtures.

nonwoven mat in toluene, *n*-hexane, kerosene, soybean oil, hydraulic oil, and crude oil with water mixture were 7.4, 6.0, 7.7, 10.2, 9.2, and 8.1 g·g⁻¹, respectively, which were slightly lower than the corresponding values in pure oil medium. The absorption capacities of PVF-H-25_{py} were 57.6, 12.1, 20.3, 17.7, 17.1, and 14.4 g·g⁻¹, respectively. The Q_s of PVF-H-75_{py} in toluene, *n*-hexane, kerosene, soybean oil, hydraulic oil, and crude oil were 43.1, 19.2, 28.6, 23.4, 26.3, and 26.0 g·g⁻¹, respectively. PVF-H-75_{py} had the highest absorption capacity in the oil–water mixture, which was similar to the results obtained from pure oil medium. The sample obtained at high reaction temperature exhibited high absorption capacities, except in toluene. The water content of recovered kerosene was measured using Coulometric Karl Fischer titration and it is 83.2 ppm (mg/L) (average value for three times), which confirms that little water is absorbed during the test, indicating the excellent oil absorption selectivity; that is, the existence of water had nearly no influence on the absorption performance of the sample.

Generally, the absorption rate of polymer absorbents is mainly determined by pore size, channel structure, and surface property. The absorption capacity is affected by pore size and solvation degree of the cross-linking network. The solvation degree is related to the cross-linking degree of absorbents and the difference of solubility parameters between polymer network and the solvents. The cross-linked polymer exhibits maximum volume swelling ratio in the solvent, but only when the solubility parameters of polymer and those of the solvent

are equal. As shown in Figure 10, the maximum volume swelling of PVF-H-25_{py}, PVF-H-50_{py}, and PVF-H-75_{py} could be

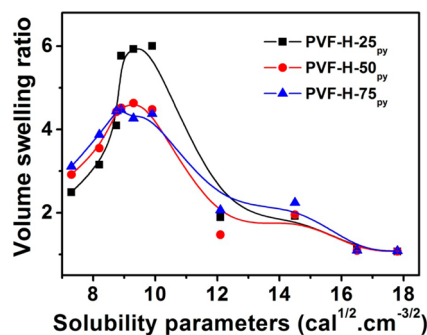


Figure 10. Variation of volume swelling ratio with solubility parameters of various organic solvents.

observed in THF, chloroform, and paraxylene, respectively. The fitted values of 9.45, 9.26, and 8.80 (cal·cm⁻³)^{1/2} can be regarded as the solubility parameters of PVF-H-25_{py}, PVF-H-50_{py}, and PVF-H-75_{py}, respectively. The solubility parameter of hydrophobic sponge decreases with the reaction temperature because highly substituted sponge can be obtained at high temperature, and the hydrophobicity of sponges increased. PVF-H sponge prepared at high temperature, such as PVF-H-75_{py}, showed the highest volume swelling ratio and absorption capacity in solvents/oils with solubility parameters less than 8.80 (cal·cm⁻³)^{1/2} due to the closer solubility parameters between PVF-H-75_{py} and these oils. In addition, high Q_s of PVF-H is also related to its open-cell structure, high porosity.

Reusability. PVF-H-75_{py} had excellent absorption performance in the oil and oil–water mixture. The reusability of PVF-H-75_{py} in various oils is shown in Figure 11a–f. The average Q_s in toluene, *n*-hexane, kerosene, soybean oil, hydraulic oil, and crude oil were 45.0, 19.6, 30.1, 27.4, 22.5, and 26.6 g·g⁻¹, respectively, which were slightly higher than that in the pure oil media. The oils that PVF-H-75_{py} absorbed are removed easily through simple squeezing (see the Supporting Information, Movie 1), and average recoveries for toluene, *n*-hexane, kerosene, soybean oil, hydraulic oil, and crude oil are 92.6%, 94.8%, 91.6%, 87.0%, 87.6%, and 84.1%, respectively (Figure 12). The recoveries of commercial absorbent PP nonwoven

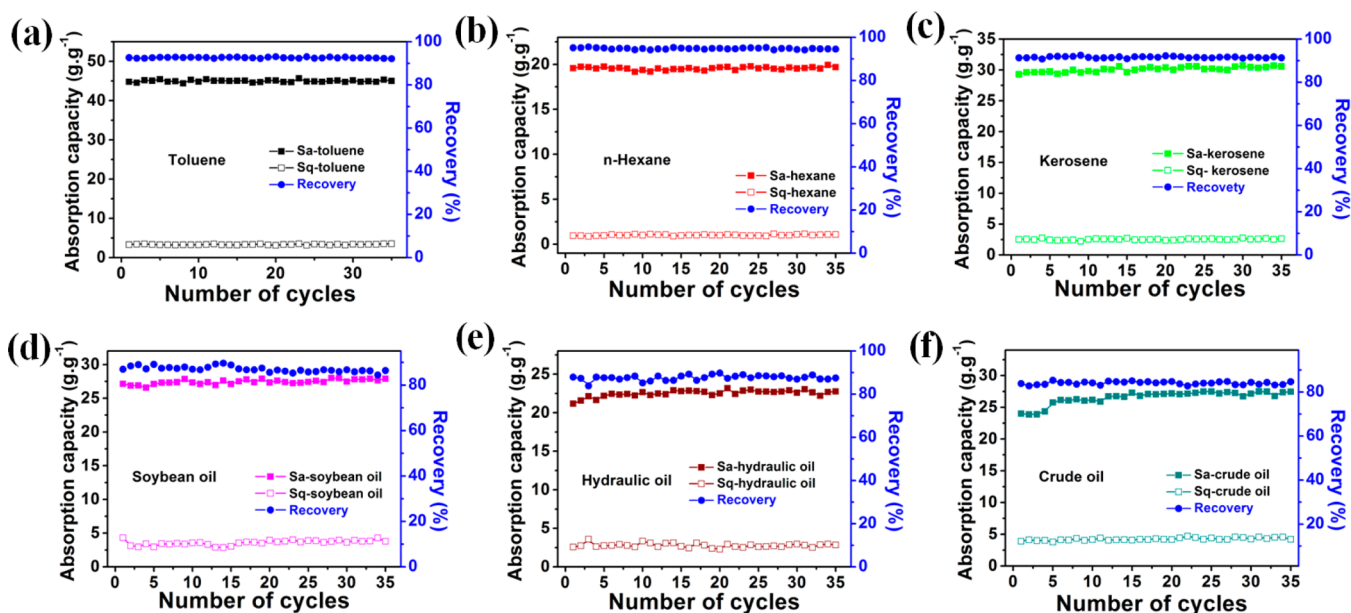


Figure 11. Repeated absorption capacity (Sa-), residual amount (Sq-) and recovery of PVF-H-75_{py} in (a) toluene, (b) *n*-hexane, (c) kerosene, (d) soybean oil, (e) hydraulic oil, and (f) crude oil with cycle number.

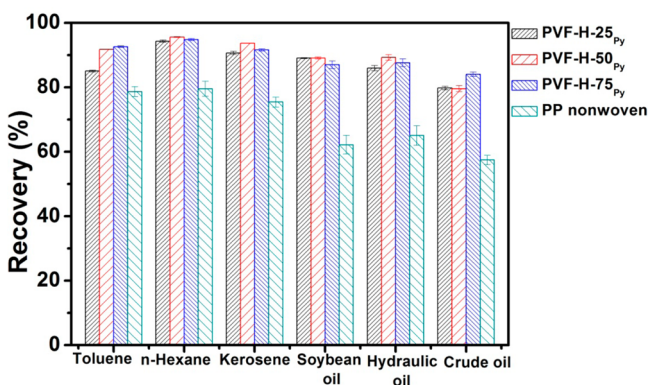


Figure 12. Recovery of PVF-H-25_{py}, PVF-H-50_{py}, PVF-H-75_{py}, and PP nonwoven mat in various oils.

mat for toluene, *n*-hexane, kerosene, soybean oil, hydraulic oil, and crude oil were 78.7%, 79.6%, 75.4%, 62.2%, 65.0%, and 57.4%, respectively. Thirty-five absorption–squeeze cycles confirmed that the recoveries and absorption capacities for oils almost maintained constant values. The excellent reusability and recovery are attributed to the good mechanical properties, open-cell structure, and high swelling in oils. In addition, the squeezed PVF-H-75_{py} could reach saturated absorption quickly once in contact with oils, regardless of the kind of oils. Theoretically, the recovery amounts of 1 kg of as-prepared PVF-H-75_{py} sponge subjected to 100 absorption–squeeze cycles can collect 4167 kg of toluene, 1856 kg of *n*-hexane, 2757 kg of kerosene, 2383 kg of soybean oil, 1971 kg of hydraulic oil, and 2237 kg of crude oil, indicating that PVF-H-75_{py} is an efficient oil absorbent that can be used in practical applications for oil spill cleanup.

CONCLUSIONS

Novel macroporous and hydrophobic PVF sponges were prepared successfully via a simple reaction of stearyl chloride with hydroxyl groups of hydrophilic PVF samples at different

temperatures. Solubility parameter measurement showed that increasing the reaction temperature results in a hydrophobic sponge. As-prepared PVF-H sponges exhibited rapid absorption kinetics in minute order even if used for absorbing higher-viscosity oils, such as soybean oil, hydraulic oil, and crude oil. These sponges present high saturated absorption capacities up to 10s of g·g⁻¹, which are approximately 2–4 times higher than that of commercial PP nonwoven mat. Using an oil–water mixture as a simulated oil slick system, these macroporous and hydrophobic sponges also showed high oil absorption capacities and excellent selectivity. The absorbed oil can be collected only through simple squeezing, and the oil recovery can reach up to 94.8%. Interconnected macroporous open-cell structure, good mechanical property, and hydrophobic surface contribute to excellent performance. This novel kind of sponges is an ideal candidate for absorbing oil spill cleanup because of the above-mentioned characters.

ASSOCIATED CONTENT

Supporting Information

Sink processes of pristine hydrophilic PVF in the kerosene–water mixture (Figure S1) and hydraulic oil–water mixture (Figure S2). Movie 1: Kerosene removal process. Movie 2: Kerosene removal from the kerosene–water mixture. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

AUTHOR INFORMATION

Corresponding Author

*Email: xlji@ciac.ac.cn.

Notes

The authors declare no competing financial interest.

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