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Facile fabrication of durable superhydrophobic fabrics by silicon polyurethane membrane for oil/water separation

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ABSTRACT

Nowadays, oil contamination has become a major reason for water pollution, and presents a global environmental challenge. Although many efforts have been devoted to the fabrication of oil/water separation materials, their practical applications are still hindered by their weak durability, poor chemical tolerance, environmental resistance, and potential negative impact on health and the environment. To overcome these drawbacks, this work offers a facile method to fabricate the eco-friendly and durable oil/water separation membrane fabrics by alkaline hydrolysis and silicon polyurethane coating. The X-ray photoelectron spectroscopy, scanning electron microscopy, and atomic force microscopy results demonstrate that silicon polyurethane membrane could be coated onto the surface of hydrolyzed polyester fabric and form a micro-/nano-scaled hierarchical structure. Based on this, the modified fabric could have a stable superhydrophobic property with a water contact angle higher than 150°, even after repeated washing and mechanical abrasion 800 times, as well as chemical corrosion. Moreover, the modified fabrics show excellent oil/water separation efficiency of up to 99% for various types of oil–water mixture. Therefore, this durable, eco-friendly and cost-efficient superhydrophobic fabric has great potential in large-scale oil/water separation.

1. Introduction

Recently, due to the increasing amounts of industrial oily wastewater and the frequent oil-spill incidents, oily wastewater has attracted worldwide attention due to its negative impact on the environment and human health [1–3]. However, the present treatments for oily wastewater are still insufficient in universality, practicability, and adaptability for oil/water separation, owing to the weak durability, low separation efficiency, poor reusability, high operating costs, or complicated operation procedures. Thus, globally, it is highly urgent to develop efficient and long-lasting treatment methods for oily wastewater [4,5]. Superhydrophobic materials with high separation efficiency and outstanding durability are considered to be a brilliant solution for oil/water separation [6–12]. And this can be achieved by coating superhydrophobic substances onto the substrates.

Superhydrophobic coating, which has low-surface energy and can form hierarchical micro-/nano-structures on the surface of substrates, determines the separation efficiency of the whole materials [13,14]. Although fluorinated chemicals are widely used for micro-/nano-level particle surface modification due to their low surface energy [15,16], they may pose harm to organisms and the environment [17–22]. Therefore, researchers have shifted their attention to organic silicon, and regarding this, the general method is to create the required low surface energy by coating organic silicon onto the surface of the substrate [23–26]. For example, Ge *et al.* [27] dispersed a polydimethylsiloxane (PDMS) polymer in water to form a "PDMS-in-water" emulsion, which allows the construction of an intelligent self-healing and robust superhydrophobic coating on cotton fiber. The PDMS@cotton fabric exhibits high superhydrophobicity with a water contact angle (WCA) over 155°. After 10 times of abrasion, PDMS@cotton fabric lost its superhydrophobicity with the WCA decreasing to 132.21°. However, when the damaged cotton fabric was heated at 80 °C for 30 min, it exhibited restored superhydrophobicity with a WCA of 157.21°. Lahiri *et al.* [28] deposited an H_3BO_3-incorporated SiO_2-

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alkyl-silane coating onto the surface of woven cotton fabric, which was modified by PDMS. This modified fabric showed quite good stability. After suffering 30 abrasion cycles, its WCA was still stable, about 150°. Similar results have also been reported by Huang *et al.* [26] and Zhou *et al.* [29].

However, if the nanoparticles are just physically attached onto the surface of substrates, there could be stability issues as they may be easily stripped off from the substrates, resulting in non-durability of the materials [30–34]. Therefore, in recent years, the research in non-particle superhydrophobic coatings has focused on the use of chemical bonding to attach such coatings onto substrates. Huang *et al.* [22] prepared three poly(AA-HEA)-g-PDMS graft copolymers *via* traditional free radical polymerization. The coatings were stable against laundry tests and acid/alkali solutions immersion tests. After 50 abrasion cycles, its WCA on the abraded side was still stable, 148° ± 2°. Deng *et al.* [35] directly anchored hydrophobic/oleophilic polyhedral oligomeric silsesquioxane onto the surface of cotton fabric by a one-step dipping strategy to yield a robust hydrophobic oil/water separation membrane. The modified fabric became hydrophobic with the WCA higher than 142° and remained stable under UV irradiation, chemical corrosion, and washing conditions. Its WCA only show a slight decline from 142.2° to 140.1° after 180 abrasion cycles.

Textile, especially polyester fabrics, is one of the desirable substrates for oil/water separation materials [36–41], due to their obvious advantages in flexibility, mechanical stability, high adsorption capability, and low cost. Many strategies, such as sol–gel process [42], chemical vapor deposition [43], hydrothermal synthesis [44], layer-by-layer assembly [45], phase separation [46], electrospinning technique [47], plasma treatment [48], foam finishing[49], and coating [50–52] have been employed to fabricate superhydrophobic films on the surface of fabrics. For example, a superhydrophobic polyester textile was obtained by modifying pristine textile with PDMS and paraffin wax under 120 °C [53], and its WCA was still 143° after 800 times of abrasion.

Another benefit of polyester fabrics is their high chemical activity. Alkaline hydrolysis is a common modification method to release active groups such as —COOH or —OH. Mazrouei-Sebdani *et al.* [54] manipulated the surface topography of polyester fibers by alkaline hydrolysis, and manufactured a superhydrophobic fabric by fluorocarbon coating. The modified fabric illustrated good tensile strength, abrasion resistance, and air permeability. Similarly, Han *et al.* [55] developed a superhydrophobic fabric by alkaline hydrolysis and surface coating with fluoropolymers. The newly fabric exhibited high water vapor and air permeability.

Based on the previous studies, in this work, we used a waterborne organosilicon and a polyester fabric to fabricate an on-particle and fluorine-free super-hydrophobic fabric for oil/water separation (see Fig. 1). The obtained superhydrophobic fabric realized effective filtration of oil from water, and was robust and durable, which exhibits brilliant prospects in treating oily wastewater.

2. Experimental

2.1. Materials

Isophorone diisocyanate (IPDA, AR) was supplied by Energy Chemical Co., Ltd. (China). Single-ended dihydroxy polydimethylsiloxane (2-PDMS, Tech) was supplied by Guangzhou Silok Polymer Co., Ltd. (China). Monohydroxy-terminated polydimethylsiloxane (HPDMS, Tech), trimethylolpropane (TMP, AR), 2,2-dimethylolbutanoic acid (DMBA, AR), 3-methoxy-1,2-propanediol (AR), triethylamine (TEA, AR), dibutyltin dilaurate (DBTDL, AR), *N*,*N*-dimethylformamide (AR), ethanol (AR), sodium hydroxide (NaOH, AR), hydrochloric acid (HCl, 37%, AR), *n*-hexane (AR), diiodomethane (AR), methylene blue, and Oil Red O were supplied by Aladdin Reagent Co., Ltd. (China). Polyurethane-based fabric and sandpaper (13 μm) were bought from local stores. 2-PDMS, HPDMS, DMBA, and TMP were dehydrated in a vacuum environ-

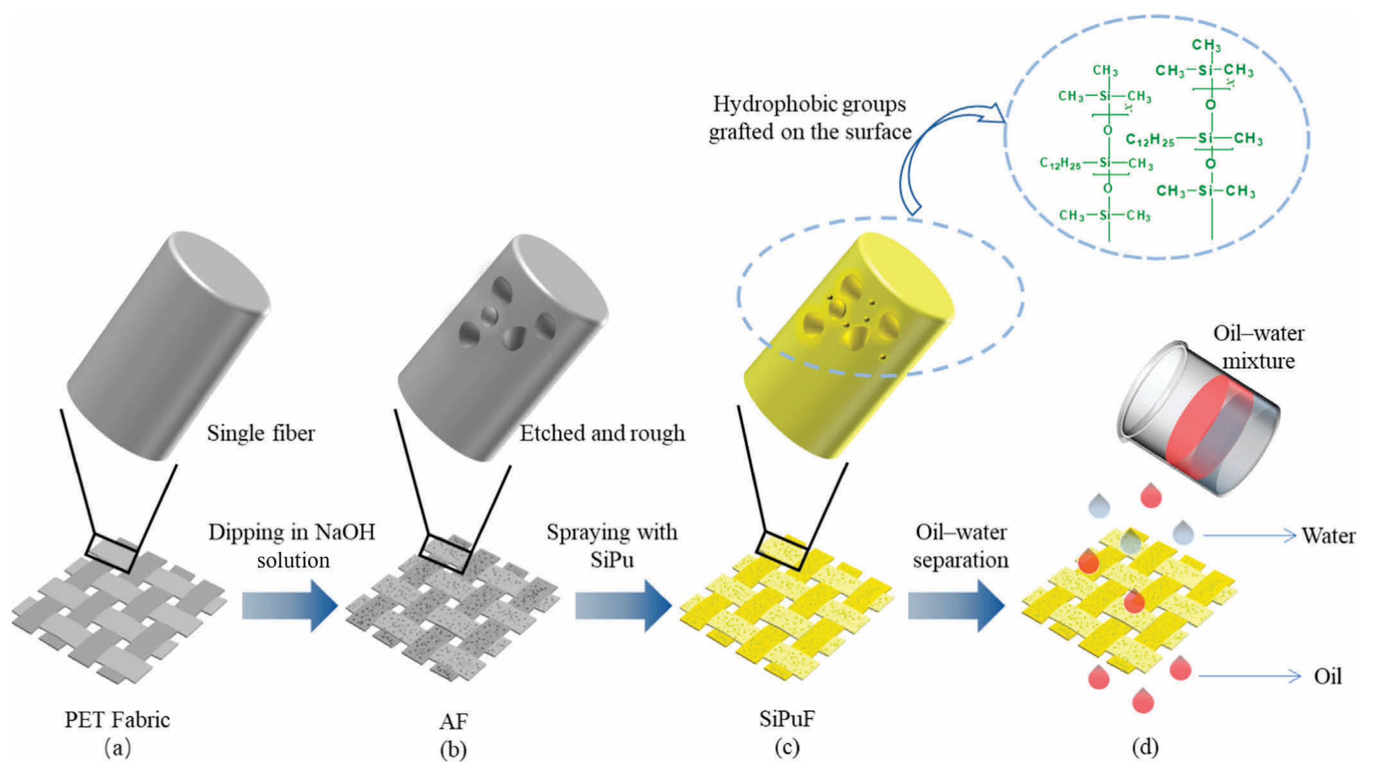


Fig. 1. Schematic representation of the superhydrophobic polyester fabric: (a) polyester (PET) fabric weaved by smooth fiber, (b) PET fabric etched by NaOH solution, (c) roughened PET fabric coated by organosilicon polyurethane, (d) application of SiPuF on the separation of oil–water mixture.

ment at 110 °C. The activated molecular sieves were stored in DMF for 48 h to dehydrate.

2.2. Synthesis of waterborne organosilicon polyurethane (SiPu)

The synthesis route of the waterborne organosilicon polyurethane (SiPu) was illustrated in Fig. 2. Firstly, 47.22 g of 2-PDMS, 3.12 g of DMBA, 0.62 g of TMP, and 0.27 g of 3-methoxy-1,2-propanediol were mixed well at 50 °C for 30 min in a 500 ml four-necked flask equipped with a thermometer, a mechanical stirrer, and a condenser. After mixing evenly, 11.12 g of IPDA and 30.00 g of DMF were added to the flask followed by the addition of 3 or 4 drops of DBTDL as a catalyst. The reaction was continued for 3 h at 80 °C until the content of —NCO reached the theoretical value. Subsequently, after the addition of HPDMS as a capping agent, the reaction was continued at 80 °C for 6 h until the residual —NCO groups reacted completely. Then, the polyurethane prepolymer (Fig. 2) was cooled to 50 °C and neutralized by 1.70 g of TEA for about 30 min with stirring at 1000 r·min^{-1}. Thereafter, the prepolymer was poured into distilled water and dispersed by stirring at 3000 r·min^{-1} for 30 min at room temperature to obtain a bluish waterborne SiPu emulsion with 30% content of the solid. The product was tested by FT-IR (Fig. S1 in Supplementary Material).

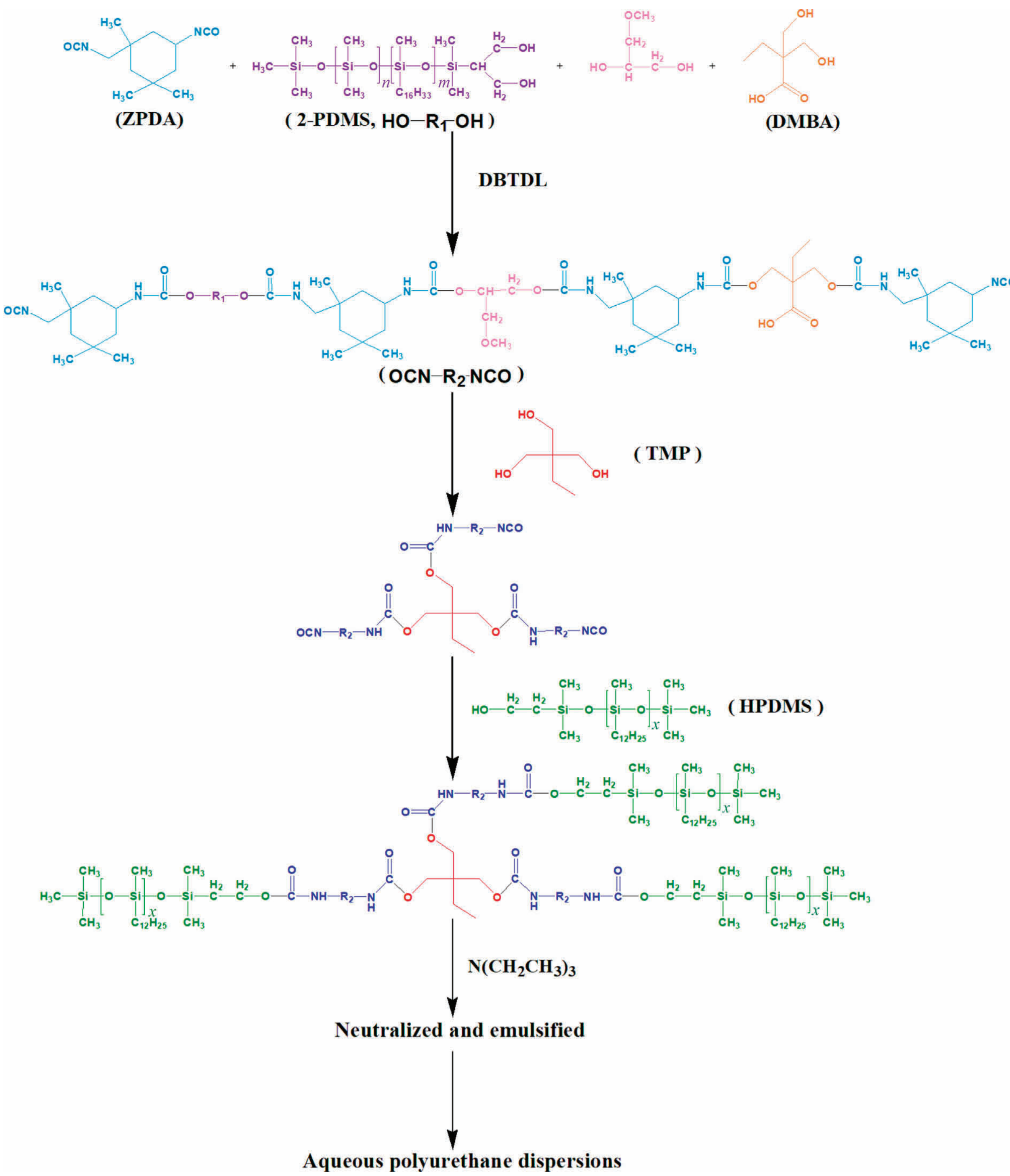


Fig. 2. Synthesis of waterborne organosilicon polyurethane (SiPu).

2.3. Fabrication of SiPu-modified fabric (SiPuF)

The fabrication process was depicted in Fig. 1 and the details were as follows. The fabric (5 cm × 5 cm) was soaked in sodium hydroxide solution (3 mol·L^{-1}) for 60 min at 90 °C, and then rinsed with deionized water until its pH value reached 7. After that, the alkali-treated polyester fabric (AF) was dried at room temperature, sprayed with the waterborne organosilicon polyurethane, and dried at 170 °C.

2.4. Sample surface characterization

The surface chemical composition of the samples was detected by an X-ray photoelectron spectrometer (XPS, Thermo ESCALAB 250 Xi, USA). The surface morphology was characterized by a scanning electron microscope (SEM, JEOL JSM-7001F, Japan). The surface architecture and roughness of the fiber were observed by atomic force microscopy (AFM, Dimension Fast Scan, Germany).

2.5. Durability and stability evaluation of the modified fabric

The tensile properties were tested using a universal tensile testing machine at room temperature with a tensile rate of 5 mm·min^{-1}. At least five measurements for each sample (4 cm × 2 cm) were conducted.

The abrasion resistance of the SiPuF sample was evaluated by placing it on top of sandpaper (13 μm), pressing a 100 g weight on it, and the sample was moved in one direction with a distance of 10 cm for one cycle [22]. Next, the washing stability of the sample was evaluated by washing it in 150 ml of an aqueous solution, which contained 0.15% (mass) of soap powder, under stirring at 40 r·min^{-1}. One laundering cycle lasted for 45 min, and then the treated fabric was rinsed with deionized water to remove the detergent and dried at 80 °C [22]. Besides, the chemical stability of the modified fabric was evaluated by immersing it in a hydrochloric acid solution (pH = 1–2), a sodium hydroxide solution (pH = 12–13), water, and organic solvents (*n*-hexane and ethanol), respectively. After 24 h of immersion, the fabric was completely washed with deionized water and dried at room temperature.

Static water contact angle (WCA) measurements were carried out at room temperature. 4 μl of deionized water was dropped onto the surface of the fabric for each test. The WCA was recorded automatically by the equipment (JC2000A, Shanghai Zhongchen Powereach, China) after 15 s of droplet deposition. For each sample, at least five tests at different spots were carried out.

2.6. Oil/water separation experiments

A series of gravity-driven oil/water separation experiments were carried out using SiPuF, which was fixed between two glass tubes. Oil Red O and methyl blue were used to color the oil and water respectively for better observation. The separation volume oil/water mixture (oil phase = 1:1) was 30 ml per cycle. The separation efficiency (η, %) was evaluated by calculating the oil rejection coefficient according to Eq. (1) [56]:

$$\eta = \frac{m_1}{m_0} \times 100\% \tag{1}$$

In Eq. (1), m_0 and m_1 are the mass of the water before and after oil/water separation, respectively. The permeate flux (J, L·m^{-2}·h^{-1}) was calculated according to Eq. (2) [35], where V is the permeate volume, A is the active area, and t is the permeate time (h).

$$J = \frac{V}{At} \tag{2}$$

To evaluate the oil adsorption capacity, the modified fabric was immersed in various types of oil, after achieving saturation, the fabric was taken out rapidly (to avoid evaporation) and weighed quickly. The mass gain (%) of the modified fabric was used to reflect the oil adsorption capacity [57], which was calculated according to Eq. (3) [35]:

$$\text{Mass gain} = \frac{m_3 - m_2}{m_2} \times 100\% \tag{3}$$

where m_2 and m_3 are the masses of the modified fabric before and after adsorption, respectively.

3. Results and Discussion

3.1. Material design and processing

In this paper, the organosilicon polyurethane and polyester fabric were used to prepare a stable and durable superhydrophobic membrane. Specifically, for polyester fabric, —COOH or —OH groups can be generated after alkali hydrolysis [58,59]. Organosilicon polyurethane, which is fluorine-free with low surface energy, has the —NH or —COOH groups [22]. Therefore, when AF is coated by the SiPu membrane and heated at 170 °C, the covalent bonds between them are formed, which ensure the tight attachment of coating on the fabric surface and give excellent mechanical, abrasive and corrosion-resistant properties to SiPuF.

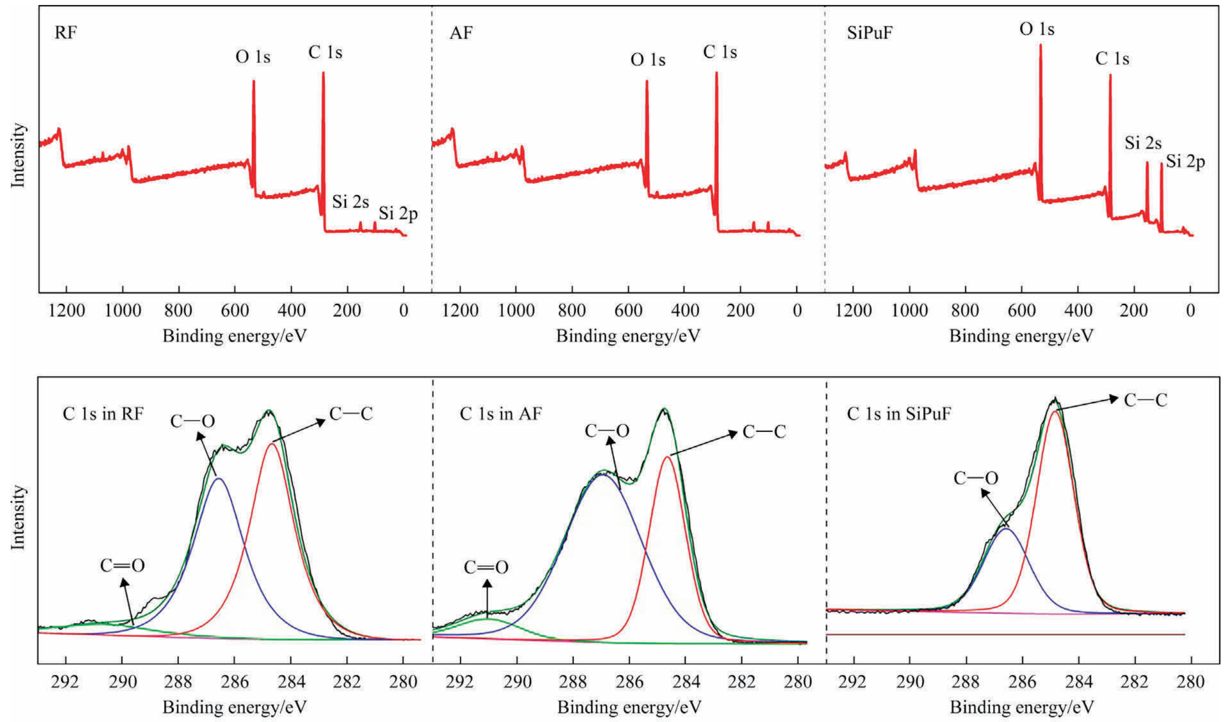
While formers preferred using linear-chain dihydroxyl polydimethylsiloxane to prepare organosilicon polyurethane [22,60], in this paper, a branched-chain dihydroxy 2-PDMS was chosen. This is because that ordinary dihydroxysilicon has two hydroxyl groups at both ends of organic silicon, and thus when reacting with polyurethane, the organicsilicon chains are embedded in the main chains, leading to high surface energy and poor hydrophobicity. Therefore, 2-PDMS, which only has one single-ended dihydroxy, was selected to ensure that organosilicon locates on the branched chains after reaction with polyurethane (see Fig. 1). Moreover, after coating and heating, siloxane blocks can self-assemble to produce protrusion structures on the fiber surface, which provided nano-scaled roughness and enhanced the hydrophobicity of SiPuF further.

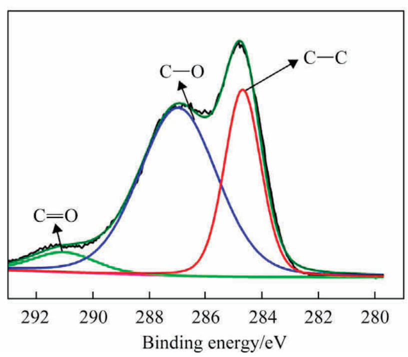
Besides, HPDMS was used as the capping agent instead of water, because its low surface energy could make it extend outward and self-enrich on the coating surface. This design ensures that there is a large amount of siloxane chains on the outer surface of the coating, so that the surface energy of the system is reduced to lead to water repellency.

3.2. Fabrication and formation mechanism of SiPuF

Fig. 3 presents the XPS spectra of the samples. It was found that only C and O elements were detected from raw fabric (RF) and AF, while C, O and Si elements were observed from SiPuF. The survey spectrum implied that RF consisted of elements C and O. Based on this, we concluded that SiPu was successfully grafted onto the fabric surface.

Furthermore, the high-resolution XPS C 1s and Si 2p spectra of RF, AF, and SiPuF were analyzed. The C 1s spectrum of RF can be curve-fitted into typical characteristic peaks of C═O, C—O, and C—C with binding energies of 291, 286.9, and 284.6 eV, respectively. However, the peak of C═O increased firstly for AF because hydroxyl ions from aqueous sodium hydroxide attacked the electron-deficient carbonyl carbons of the polyester to form intermediate anions, and then decreased for SiPuF due to the coverage of cured SiPu on the fibers [55]. The Si 2p stemming from SiPuF can





Sample	Atomic/%		
	C	O	Si
RT	59.57	40.43	0
AT	56.03	43.97	0
SiPuF	36.14	47.81	16.05

Fig. 3. XPS results for RF, AF, and SiPuF.

be curve-fitted into Si—C and Si—O—Si peaks. The result indicates that cured SiPuF has been incorporated onto the surface of the fabric.

3.3. Surface morphology of the modified fabric

SEM images (Fig. 4(a)–(c)) show clear differences in surface morphology among RF, AF, and SiPuF. The micro-surface structures of RF, AF and SiPuF were also examined by atomic force microscopy (AFM).

The surface of RF (Fig. 4(a)) was clean and smooth, whereas the surface of AF showed many cracks and grooves (Fig. 4(b)), demonstrating inherent roughness on the microscale. As shown in Fig. 3 (d), RF with an average roughness of 4.125 nm exhibited a relatively smooth surface, and the root-mean-square roughness (RMS) was 5.755 nm. Different from that of RF, the microstructure of AF contained lots of mountainous protrusions and "craters", leading to an increase in average roughness to 37.967 nm with an RMS of 50.600 nm. The formation of craters was caused by alkaline hydrolysis on the ester bonds of polyester fabric [55].

As shown in Fig. 3(c) and (f), compared with AF, some "craters" disappeared on the surface of SiPuF. The average roughness was only decreased to 31.167 nm and the RMS was 47.167 nm. This indicates the SiPu membrane was formed on the surface of fibers. However, nanoscale bumps were obviously discernible on SiPu fibers, which provided nanoscale roughness to complement the inherent micro-scale roughness of the AF surface. Regarding this, SiPu adhered to the surface of the fabric and after heat treatment, SiPu shrank to form microsphere-like adhesion on the surface of the fabric, so as to improve the surface nano-scaled roughness of the fabric [56,61].

3.4. Durability evaluation of the modified fabric

For practical applications, the modified hydrophobic surfaces should be capable of maintaining adequate water-repelling ability after different physical and chemical attacks [62]. Therefore, the mechanical properties, abrasion resistance, and washing stability of the modified fabric were evaluated.

The representative strain–stress curves under uniaxial tension for RF, AF, and SiPuF were shown in Fig. 5(b). In comparison with RF (36.177 ± 2.584) MPa, the tensile strength of AF was reduced to (29.164 ± 1.498) MPa. The reason was that alkali treatment hydrolyzed the fiber surface and destroyed its original structure. The craters, which were formed on the surfaces of fiber, seemed to affect tensile strength, because the tensile strength was consid-

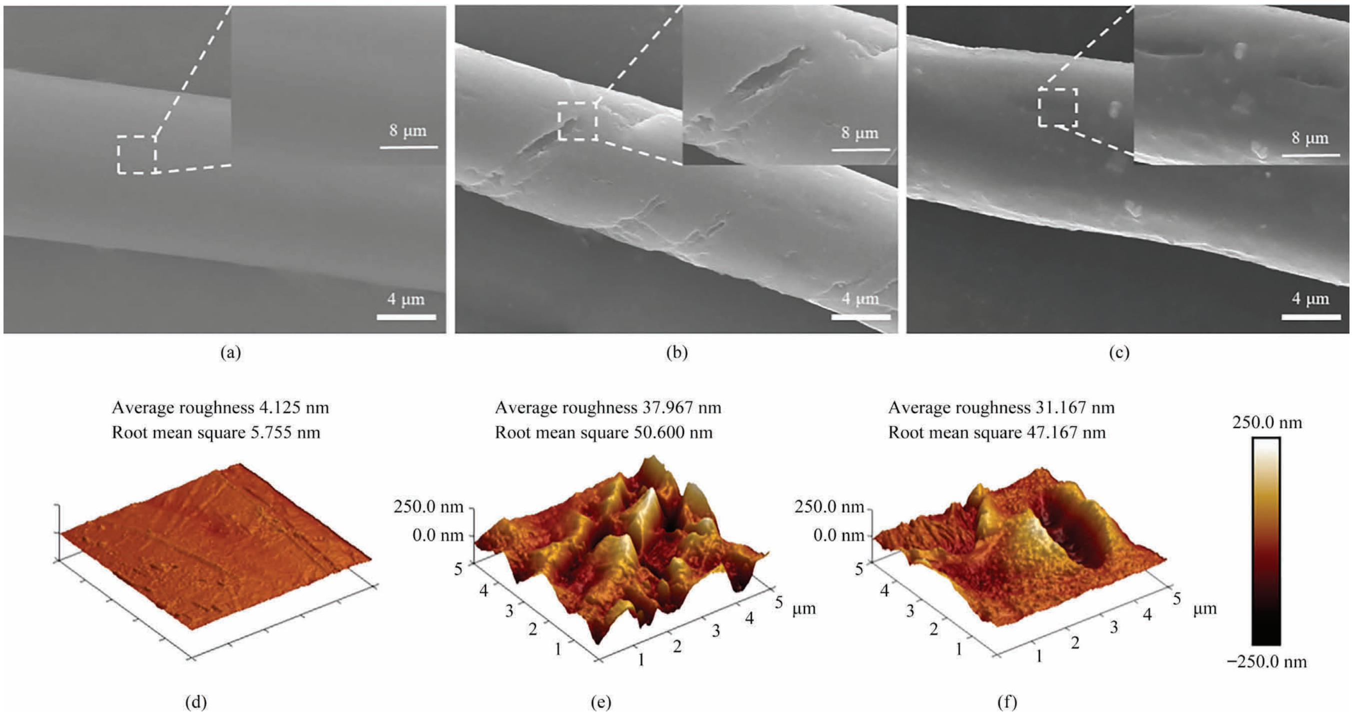


Fig. 4. SEM images of RF, AF, and SiPuF ((a), (b), and (c), respectively) and AFM images ((c), (d), and (e), respectively), which changed from smooth to micro-scale roughness, and micro-/nano-scale roughness.

erably affected by weak points [54,55]. However, the tensile strength of SiPuF was (39.360 ± 2.752) MPa, higher than those of RF and AF. These enhanced mechanical properties should be attributable to a complete and compact surface of the silicon polyurethane coating [53].

As shown in Fig. 5(a), the WAC of the modified fabric was 154°, and its water sliding angle (WSC) was 8°. The material has excellent superhydrophobic properties. Besides, a liner sandpaper abrasion test was carried out. As depicted in Fig. 5(c), the WAC of the modified fabric only showed a slight decline from 154° to 152.3° even after 800 cycles of liner sandpaper abrasion, demonstrating the excellent abrasion resistance. Such outstanding mechanical durability of the modified fabric can be attributed to the durable roughness resulting from the AF structure itself, and the complete and compact superhydrophobic surface of the silicon polyurethane coating [53]. As can be seen from the SEM images of the morphology in Fig. 5(c), the coating on the fiber surface was still not damaged and the fiber surface still has a certain micro- and nanostructure after 800 cycles of liner sandpaper abrasion test.

Fig. 5(d) indicated that the values of the modified fabric were 156.3°, 152.1°, 150.4°, 156.6°, and 156.9°, respectively after immersion in *n*-hexane, ethanol, hydrochloric acid, water, and sodium hydroxide solutions for 24 h. Migration of low-surface-energy molecular chains to the outmost surface has already been reported. The results can be explained by the superb chemical stability of PDMS that tightly wrapped around the fibers [63]. This shows that the fabric has good chemical durability, which is beneficial for practical application.

The washing stability of the modified fabric was also tested (Fig. 5(e)). Washing for 50 cycles did not apparently change the WCA and surface hydrophobicity of the modified fabric, suggesting the fabric possessed excellent washing resistance. Regarding this, dehydration occurred between the OH groups on the surface of AF and SiPu, allowing hydrophobic SiPu to be successfully bonded onto the fabric surface [35,61].

In this work, alkali-etching gave the fabric a microscale structure, and the silicon polyurethane brought hierarchical structures and lowered surface energy by reacting with —OH groups on the surface of AF. These factors lead to the robust superhydrophobic properties of the modified polyester fabric [64,65].

3.5. Oil/water separation property of the modified fabric

Considering its strong anti-wettability, SiPuF was promising to separate oil and water through adsorption and separation. Fig. 6(a) and Video S1 illustrate the adsorption processes of chloroform (oily sample, colored by Oil Red O) in water. Several droplets of colored chloroform were put into the bottom of the water (colored by methylene blue), and then SiPuF was in contact with oil droplets in the water. The oily droplets were completely absorbed by SiPuF within a few seconds underwater, and SiPuF was completely taken out from the bottom of the water without carrying water.

To evaluate the oil adsorption capacity, the mass gain of the modified fabric for various oily samples was measured. As shown in Fig. 6(b), the mass gain of modified fabric was at least about twice, and reached 4.5 times its own mass after the adsorption of diiodomethane. These results illustrated the excellent oil adsorption capacity of SiPuF.

Besides, the modified fabric can be a good candidate to be used as the selective filter membrane for the separation of different oil/water mixtures, owing to its good oleophilicity and porous structure. As shown in Fig. 7(a) and Video S2, SiPuF was fixed between two glass tubes. When chloroform (oily sample, dyed by Oil Red O)/water mixture was poured onto the surface of the modified fabric, the oil phase sank into the lower layer due to the gravity force, and then immediately permeated through without any external

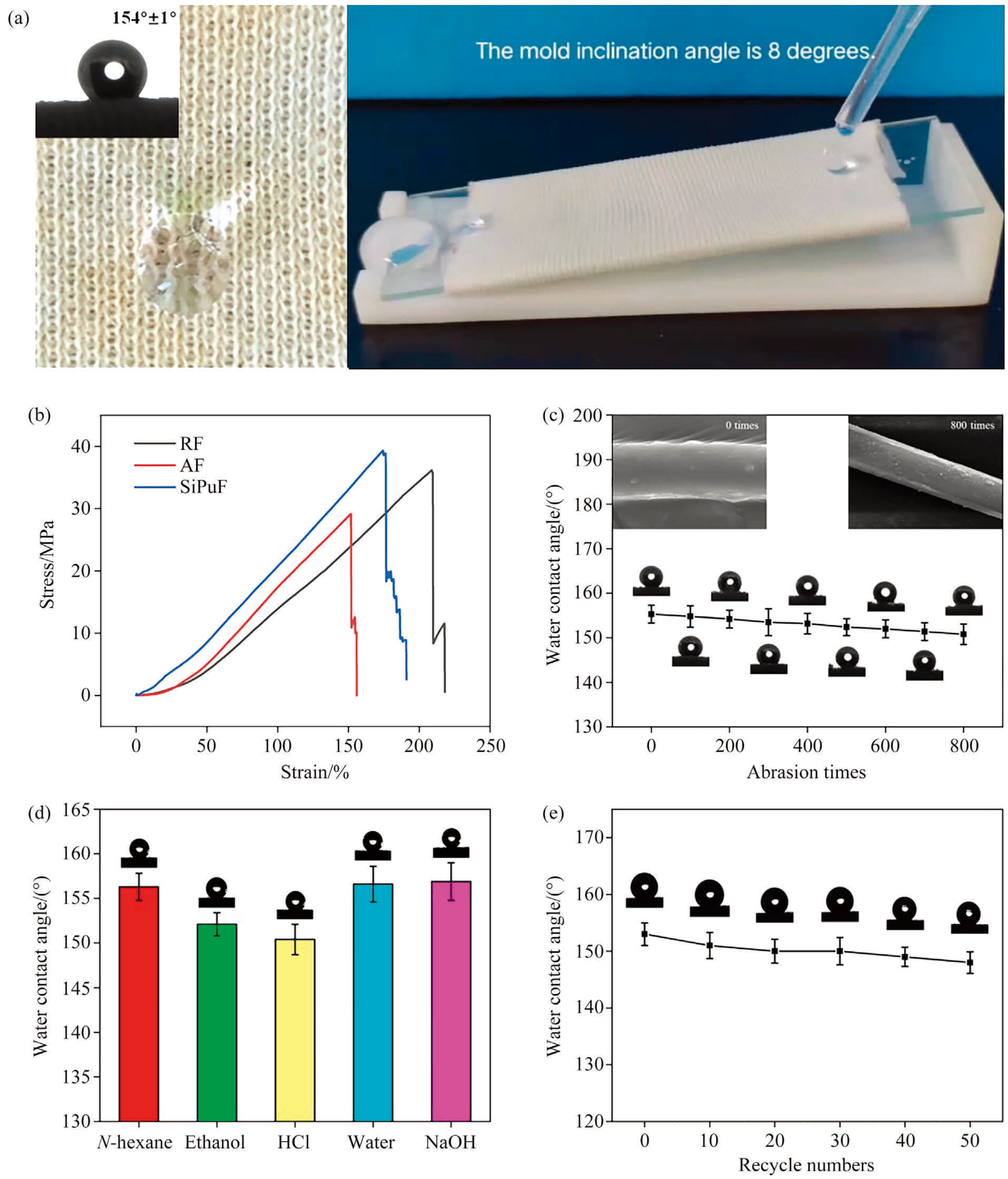


Fig. 5. Property of SiPuF: (a) water contact angle and water sliding angle, (b) stretching ability, (c) wear-proof property, (d) chemical erode resistant property, and (e) washing stability.

driven force, while the water was still retained above the fabric because of its hydrophobicity.

Permeate flux is an indispensable parameter to evaluate oil/water separation in industrial applications. Therefore, the permeate fluxes of various oil/water mixtures were investigated. As shown in Fig. 7(b), the permeate fluxes were all over 15000 $L\cdot m^{-2}\cdot h^{-1}$ for different oily samples, and reached 20000 $L\cdot m^{-2}\cdot h^{-1}$ for diiodomethane.

The fluxes in our research were superior to those of other fab-rics with coating [66], but weaker than those of modified fabrics by grafting [35].

Separation efficiency is defined as the volume ratio between the collected oil and the initial oil. The separation efficiency for different oils in this work was all higher than 99.0%, and reached 99.9% for the diiodomethane/water mixture, as shown in Fig. 7(c). Furthermore, SiPuF still retained high separation efficiency up to 96.0% after 50 separation cycles for the diiodo-methane/water mixture, which indicates good recyclability of SiPuF (Fig. 7(d)). The separation efficiency of SiPuF remained almost unchanged after 50 cycles,

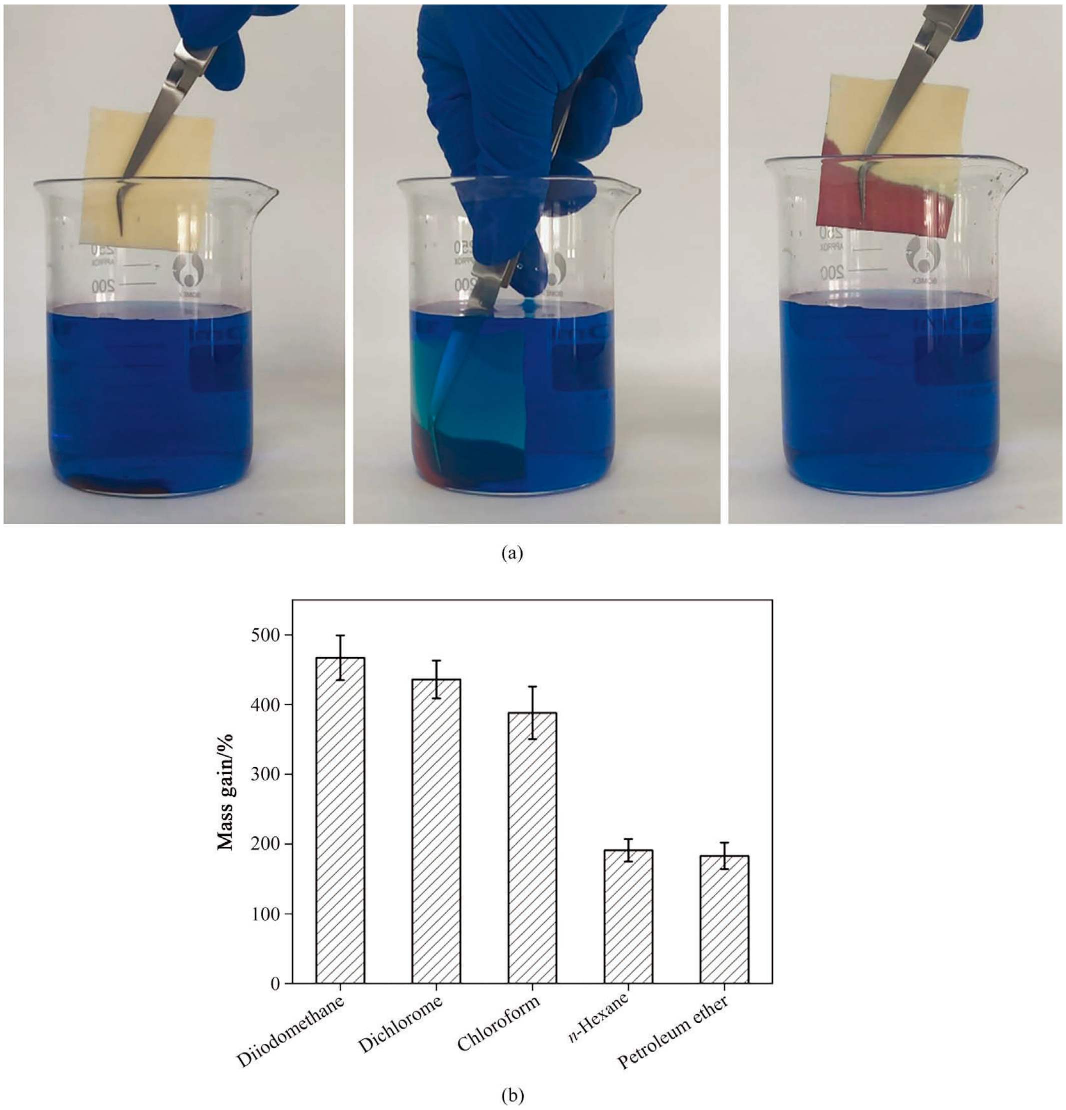


Fig. 6. Adsorption of SiPuF: (a) selective adsorptionfor chloroform from water and (b) adsorption capacities for various oils.

indicating good recyclability. The separation efficiency was similar to the best results reported [3,35].

These results indicate that SiPuF can meet the demands of industrial separation due to its outstanding separation efficiency. Such a fabric has great potential in the water–oil separation application.

4. Conclusions

In summary, we have demonstrated a method of alkaline hydrolysis and silicon polyurethane coating to modify a polyester fabric into a robust hydrophobic fabric. This method provided appropriate surface roughness and lowered surface energy, resulting in excellent hydrophobic performance of the modified fabric. The surface modification process did not significantly weaken the mechanical properties of the polyester fabric. And it was found that the modified fabric exhibited remarkable resistance against mechanical abrasion, water washing, and chemical corrosion. SiPuF also showed excellent oil/water separation performance and recyclability in the cleaning process of oil from water. Therefore, this kind of environmentally friendly, robust hydrophobic filtration material that can be easily prepared has great potential in the application of oil/water separation.

Data Availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing finan-cial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cjche.2022.05.003.

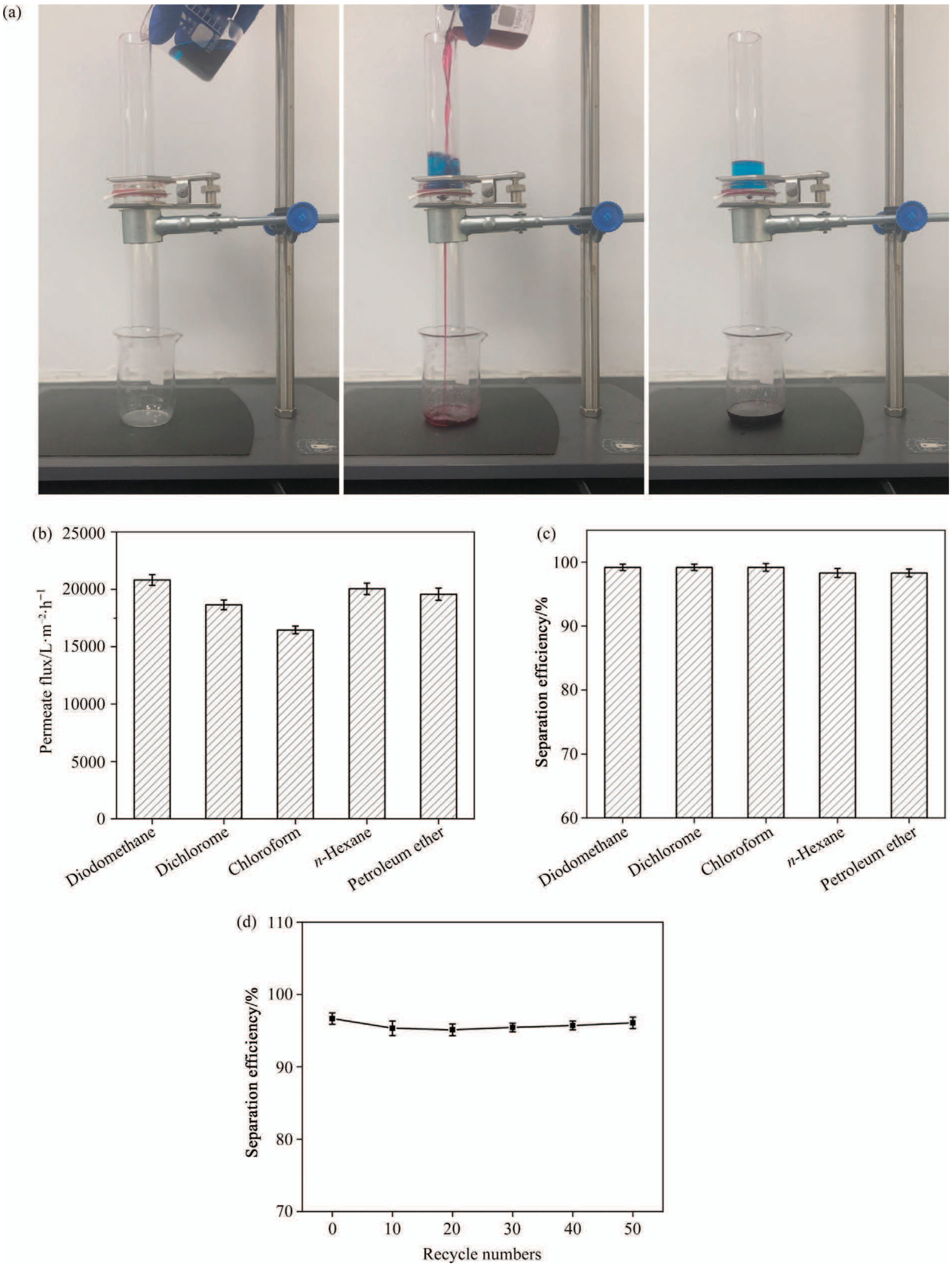

Fig. 7. Separation of oil/water mixtures by SiPuF, which was used as the selective filter membrane: (a) separation process for the chloroform/water mixture, (b) permeate fluxes for various oil/water mixtures, (c) separation efficiency for various oil/water mixtures, (d) separation efficiency for the diiodomethane/water mixture after 50 recycle times.

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