Preparation of superhydrophobic and superoleophilic cotton-based material for extremely high flux water-in-oil emulsion separation

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HIGHLIGHTS

- Superhydrophobic cotton-based materials (SCM) were prepared by a simple dipping method.
- The SCM was stable under different chemical and physical tests keeping its superhydrophobicity.
- The compressed SCM showed an outstanding performance for water-in-oil emulsion separation.
- The flux is up to $867,500 \text{ L m}^{-2}\text{h}^{-1} \text{ bar}^{-1}$ and the oil purity of filtrate > 99.97% for emulsion separations.

GRAPHICAL ABSTRACT
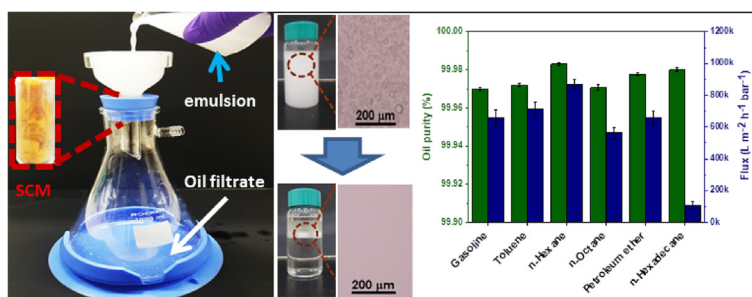
ABSTRACT

Highly stable emulsified water-in-oil mixtures from industrial processes have severe impact on the environment. As their abundance is increasing worldwide, the methods to effectively separate these emulsified water–oil mixtures have attracted significant interest in recent years. Herein, a durable superhydrophobic cotton-based material (SCM) using poly(vinyl phenol), 1,3-phenylene bisoxazoline, and raw cotton was developed. The as-prepared SCM possesses superhydrophobicity (water contact angle > 150°) and superoleophilicity (oil contact angle < 5°). The SCM has excellent repellence not only toward pure water, but also hot water and corrosive aqueous liquids. The superwetting composite also exhibits durable superhydrophobicity after long-term immersion in organic solvents. Moreover, after the compression process, the superwetting material exhibits a remarkable oil–water separation performance. Very high permeation flux values of up to $10,400 \pm 400 \text{ L m}^{-2}\text{h}^{-1}$ and $867,500 \pm 30,300 \text{ L m}^{-2}\text{h}^{-1} \text{ bar}^{-1}$ are observed for the surfactant-stabilized water-in-oil emulsion by employing gravity-driven and external pressure filtration, respectively, with excellent efficiencies (oil purity of $\geq$ 99.97 wt%). The outstanding separation performance for various oils and organic solvents, stability in harsh chemical and physical environments, robustness, and recyclability of the superhydrophobic composite make SCM an excellent candidate for large scale application.

1. Introduction

With increasing demand and consumption of petroleum products, highly stable emulsified water-in-oil waste from industrial processes are increasing, thereby causing adverse impacts on aquatic ecosystems [1,2]. Effective remedies to separate the emulsified water–oil mixtures are urgently needed to address environmental and ecological problems caused by this waste [3]. The traditional solutions for oil/water separations employing either oil depth filters, coalescence, settling tanks, skimmers, centrifuges, flotation technologies, combustion, or magnetic separation are energy-intensive strategies with low-efficiency rates [4] and are effective only for separation of immiscible oil/water mixtures, but are not useful for separating oil/water emulsions. Therefore, the development of highly efficient and economical materials for the separation and assortment of oils from water is required.

Recently, several studies have focused on producing novel superhydrophobic and superoleophilic materials with unique surface properties. Reducing the material surface energy by instituting surface-roughness produces material that is efficient in separating oil–water mixtures, adsorbing oil or organic solvents, and completely repulsing water [5]. Cotton is the most commonly harvested crop with a large productivity and low processing costs. Cotton-based products are often made of multiple fabrics and are generally cheap. Raw cotton is even cheaper as no additional cost for further processing is involved. It is an ideal oil absorbing substrate when modified as a superoleophilic and superhydrophobic material because of its low density, and loose internal structure with high liquid-adsorption capacity [6]. Superhydrophobic and superoleophilic cotton based materials have attracted significant attention because of their abilities to efficiently separate the oil–water mixtures [3,7–11]. Wang and co-worker developed a superhydrophobic and superoleophilic material by remodeling the modified cotton fibers into bendable and squeeze-resistant macroporous cellulose aerogel with high oil retention capability for oil removal from water [2]. Liu et al. prepared a superhydrophobic porous material from cotton for removal of floating oils from water surface via a magnetic-driven method [4]. Wang et al. fabricated a novel cotton fabric composite with pH controlled switchable wettability for the efficient separation of both water-in-oil and oil-in-water emulsions [12]. Pan et al. prepared glass, steel mesh and cotton surfaces with controllable super-wettabilities in applications of smart oil–water separation [13]. Guo et al. developed a robust material for high-flux oil–water separation by coating the polydimethylsiloxane-based copolymers on cotton textiles via a simple sol–gel method [14]. However, most of the few literature reports on modifying raw cotton for oil–water separation used the material as a sorbent or for oil removal from water. Such techniques are time-consuming and tedious, and cannot be used for large scale application as these are difficult to use in the field to separate large amounts of oil from water at one instant of time.

Furthermore, although most of these materials can be applied for the separation of heterogeneous oil–water mixtures, these are not effective in removing water droplets from the water-in-oil emulsions, particularly for surfactant-stabilized emulsions containing droplet sizes of < 20 μm, with the desired separation performance. Therefore, development of efficient, cost-effective, and durable materials is needed for the separations of surfactant-stabilized emulsions with high permeation fluxes retaining their outstanding selectivities.

Herein, a facile dipping method to prepare a superhydrophobic and superoleophilic material using poly(vinyl phenol) (PVPh), 1,3-phenylene bisoxazoline (PBO), and raw cotton is reported. The hydrophobic polymer coatings were anchored onto the skeletal structures of cotton to transform the wettability from superhydrophilic to superhydrophobic. The resulting as-prepared superhydrophobic cotton-based material (SCM) exhibited excellent repulsion of pure water, hot water, and corrosive aqueous liquids. Moreover, the SCM exhibited durable superhydrophobicity after long-term (48 h) immersion in organic solvents. Interestingly, the compressed SCM prepared by self-designing could separate surfactant-stabilized water-in-oil emulsions with fluxes of up to 10,400 L $m^{-2}h^{-1}$ and 867,500 L $m^{-2}h^{-1}$ bar^{-1} by employing gravity or external pressure driven filtration, respectively, with high separation efficiencies (≥ 99.97 wt% in terms of oil purity in the filtrate). The outstanding performance of this material in the separation of water-in-oil emulsions and its facile preparation method indicated its excellent potential applicability in industrial discharge treatment and fuel purification.

2. Experimental section

2.1. Materials

PVPh, MW: 11000 g/mol was purchased from Sigma–Aldrich Corp. (St. Louis, Missouri, USA), and PBO from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Span 80 was obtained from Acros Organics (Geel, Belgium). All chemicals were used as received.

2.2. Preparation of polymer thin films

Polymer stock solutions were prepared by dissolving PVPh and PBO in tetrahydrofuran (THF) in different ratio with a concentration of 50 mg mL^{-1}. Each solution was filtered using a polytetrafluoroethene (PTFE) syringe filter (0.2 μm), after which 1.5 mL of the polymer solution was spin-coated onto a glass slide (1 × 50 × 50 mm) using a photoresist spinner (1500 rpm, 45 s).Thereafter, the spin-coated sample was left to dry for 2 h at 65 °C. The as-prepared polymer film was thermally treated by placing it in an oven at 180 °C for the desired time.

2.3. Preparation of superhydrophobic and superoleophilic cotton-based material

SCM was prepared using a facile dipping method. Firstly, a coating solution was prepared by dissolving 0.8 g of PVPh and 0.2 g of PBO into 100 mL of THF. Then, the solution was filtered by using a PTFE syringe filter (0.2 μm). Subsequently, the pristine cotton was immersed into the polymer solution for 10 min, and then squeezed to remove any residual solution. After drying at 65 °C for 1 h, the resulting material was cured at 180 °C for 8 h.

2.4. Preparation of surfactant-stabilized water-in-oil emulsions

As surfactant-stabilized for water-in-oil emulsions, span 80 (0.3 g) was dissolved in oil (petroleum ether, n-hexane, gasoline, n-octane, n-hexadecane, and toluene; 98 mL), and water (2.0 mL) was added, followed by stirring the mixture for 3 h. All prepared emulsions exhibited high stabilities and were stable for more than a week without apparent phase separation.

2.5. Water-in-oil emulsion separation experiment

In the emulsion separation tests, the compressed SCM was fixed in a funnel and a series of surfactant-stabilized water-in-oil emulsions were passed through the compressed SCM employing a gravity-driven process or external pressure of 0.1 bar. In the compression procedure, the SCM was systematically controlled up on compressing into a dense form having a density of 0.15 ± 0.02 g cm^{-3}. The thickness of the compressed SCM layer was about 1.75 cm. The flux was obtained through calculating the permeated time of an emulsion of 25 mL on the unit area.

2.6. Instruments and characterization

The microstructures of pristine cotton and SCM were characterized using scanning electron microscopy (SEM: JEOL JSM-6500, JEOL. Ltd., Tokyo, Japan). Attenuated total reflection Fourier transform infrared

(ATR-FTIR) spectra of the pristine cotton and SCM samples were recorded using a Spectrum Two FTIR spectrometer (PerkinElmer, Inc., Waltham, Massachusetts, USA). The advancing-liquid contact angle on each polymer film was measured through a Magic Droplet-100 contact angle goniometer (Sindatek Instruments Co., Ltd. Taipei, Taiwan) by injecting a 5 μL liquid droplet. The static contact angle and the sliding angle were obtained from the 5 and 10 μL drop, respectively. Water contents in the filtrates of surfactant-stabilized water-in-oil emulsions were determined using a Titrator Compact C10SX (Mettler-Toledo Pac Rim AG, Greifensee, Switzerland) Coulometric Karl Fischer moisture titrator. Optical microscopy images were recorded using a VHX-7000 instrument (Keyence Corp., Osaka, Japan) after placing a drop of the emulsion solution onto a biological counting board. Dynamic light scattering (DLS) measurements were carried out by using an SZ–100 instrument (Horiba, Ltd. Kyoto, Japan).

3. Results and discussions

Previously, by employing a simple thermal treatment process, we found that PVPh had low surface energy and hydrophobicity [15]. Herein, PBO is added in PVPh to enhance the thermal stability and solvent resistance. The development of phenolic resins incorporating phenylene-bisoxazoline via thermal curing was first reported by Culbertson et al. [16]. The phenolic resins cured by phenylene-bisoxazoline had advantages including low cure shrinkage (< 1%), no volatile by-product generation during curing, long-term thermo-oxidative stability, high glass transition temperatures (T_g) and high service temperature [17]. Heat-activation of PBO initiated ring-opening of the oxazoline ring, reaction with the acidic phenolic hydroxyl group of PVPh, and subsequent crosslinking and chain extension of the phenolic resin to form PVPh/PBO cross-linked polymer (PPCP) (Fig. 1).

The surface free energy is one of important characteristics of a solid;

however, it is difficult to measure the solid surface free energy directly, and procedures based on contact angle measurements are typically applied for practical reasons. Advancing-angle data were used to calculate the components of surface free energy because these were less sensitive to surface roughness and heterogeneity [18]. We evaluated the surface free energies of PPCP using the two-liquid geometric method [19] (Supporting information). For film formation, the PVPh/PBO mixtures were spin-coated onto glass slides, and then heated at 180 °C for 8 h to cure the PPCP. Table 1 displays the surface and thermal properties of PPCP thin films with different compositions. The T_g values of PPCP increases as the amount of PBO increases. The water-advancing contact angles increase with increasing PBO until the ratio of PVPh to PBO reaches 1:0.25. The advancing contact angle of diiodomethane (DIM) on the PPCP surface exhibits a similar trend. Further increase in the amount of PBO (sample E) leads to a decrease in hydrophobicity and an increase in the surface free energy. Therefore, the optimum content (sample D) was selected for the following studies.

Typically, the wettability of a material is determined using a combination of its surface topographical microstructural characteristics and chemical compositions. Pristine cotton was dipped into the optimum ratio of PVPh/PBO and then cured to anchor the hydrophobic polymer onto the cotton skeleton (Fig. 2). The as-prepared SCM exhibits superhydrophobicity with a water contact angle (WCA) of 156 ± 2° and superoleophilicity: contact angles were approximately 0° for toluene, n-octane, n-hexane, n-hexadecane, petroleum ether, and gasoline. The water droplets retain almost round shapes on the superhydrophobic surface and roll off with a minimum sliding angle (SA) of 7.5 ± 1°. We also measured the under-oil WCAs of SCM with various oils. Fig. S1a and b revealed that all of the under-oil water contact angles are higher than 150°, indicating the SCM possessed under-oil superhydrophobicity. The effect of PVPh/PBO concentration on the wettability of the SCM was studied by measuring the WCA and SA. As shown
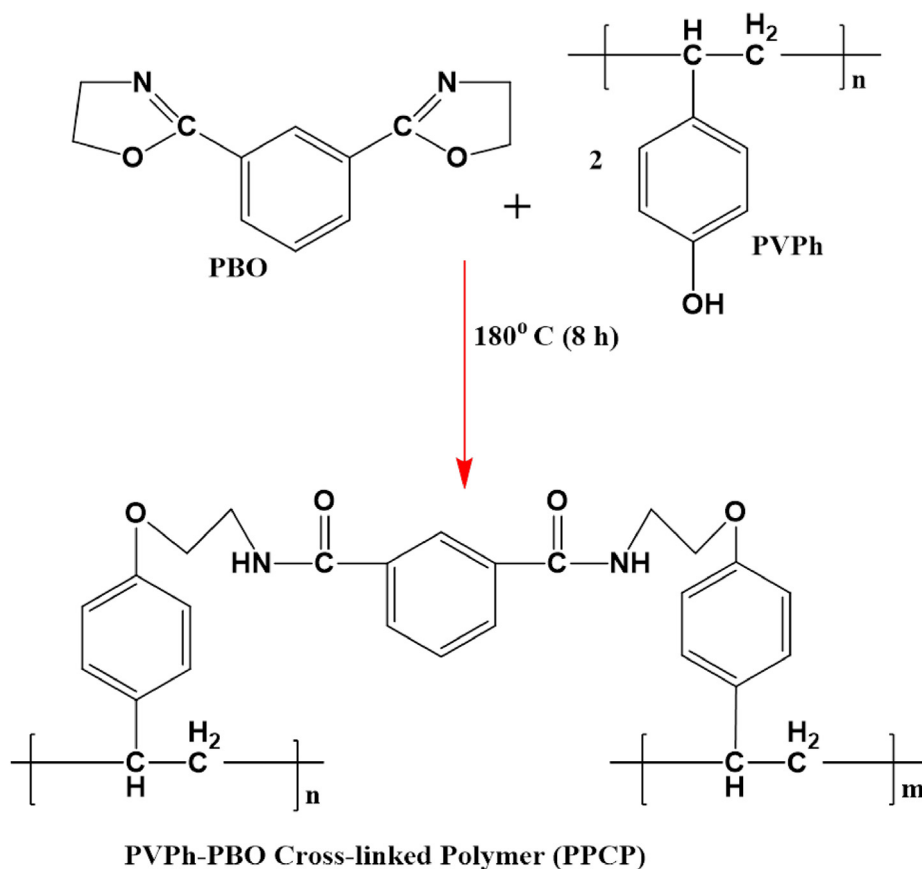

Fig. 1. Illustration of the crosslinking reaction of poly(vinyl phenol) (PVPh) and 1,3-phenylene bisoxazoline (PBO).

Table 1

Advancing contact angle for water and diiodomethane (DIM), surface free energy, and T_g analysis of PPCP thermoset polymer film through 180 °C thermal treatment procedure for 8 h.

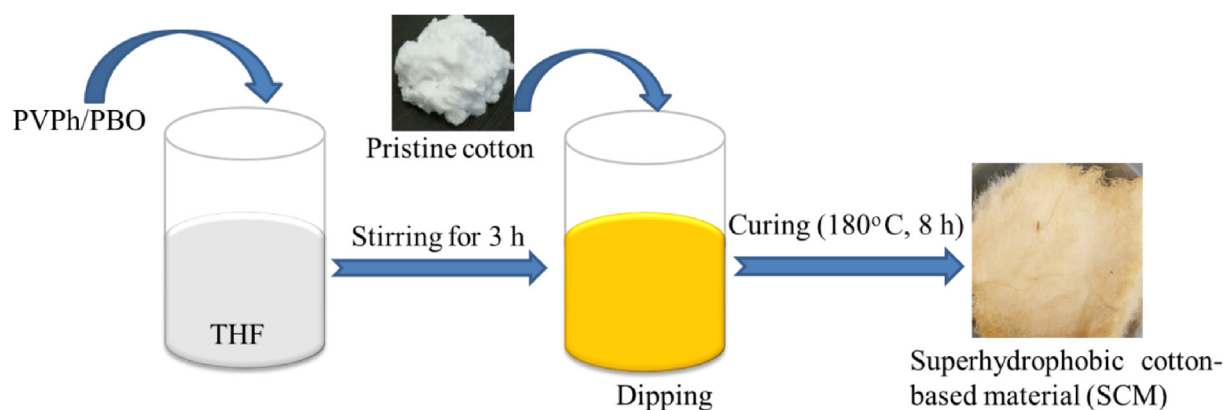| Sample	Polymer		Advancing contact angle (°)		
		T_g(°C)	H_2O	DIM	γ (mJ/m^2)
A	PVPh	175	101 ± 2	79 ± 2	18.4
B	PVPh: PBO = 1: 0.05	190	99 ± 1	76 ± 1	20.0
C	PVPh: PBO = 1: 0.15	198	97 ± 1	76 ± 1	20.3
D	PVPh: PBO = 1: 0.25	203	98 ± 1	77 ± 2	19.7
E	PVPh: PBO = 1: 0.5	228	93 ± 3	76 ± 1	21.2

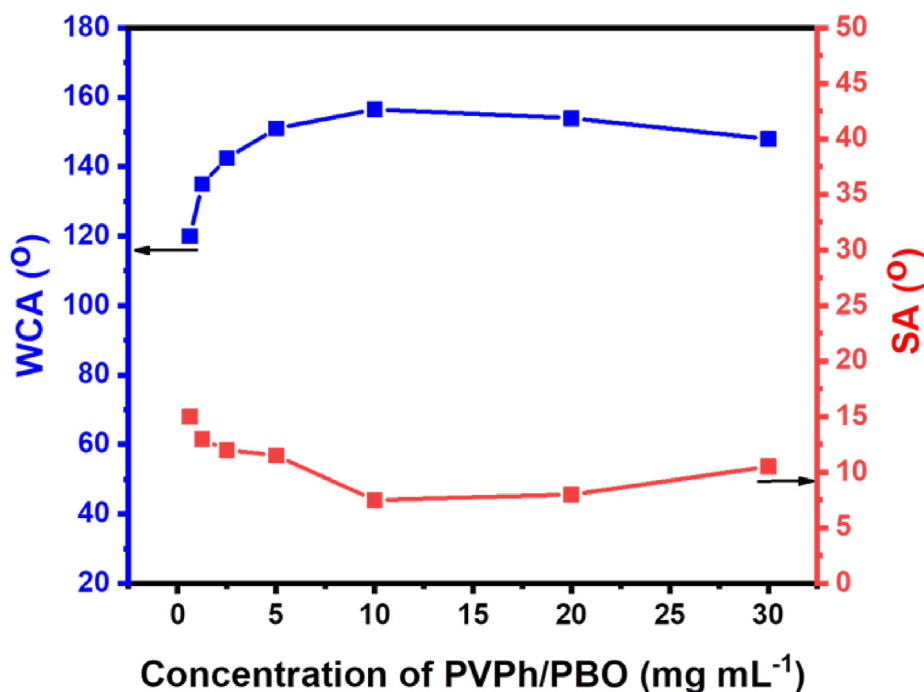**Fig. 2.** Preparation of superhydrophobic cotton-based material (SCM).

Fig. 3. Variation in the wettability of SCM with different concentrations of PVPh/PBO coating.

in Fig. 3, the WCA of SCM increases from 120° to 156° as the concentration of PVPh/PBO increased from 0.625 to 10 mg mL^{-1} and the SA decreased from 15° to 7.5°. Further increase in the PVPh/PBO concentration to 30 mg mL^{-1}, has no significant effect on the WCA and SA values of the composite. Therefore, the optimum concentration (10 mg mL^{-1}) was selected to perform further studies.

The morphologies of the pristine cotton and SCM were examined using scanning electron microscopy (SEM) (Fig. 4a-b), and the results showed that the smooth fibers of pristine cotton were covered with

PPCP after coating process. The high magnification image of SCM in Fig. 4b exhibits that the PPCP-coated cotton possesses micro-/nano-hierarchical structures that induce superhydrophobicity. Fig. 4c-d show the chemical compositions of pristine cotton and SCM as determined by energy dispersive X-ray spectroscopy (EDS). As shown in Fig. 4c, the major elements present in the pristine cotton are carbon and oxygen, which are consistent with the chemical structure of cotton. In contrast to the spectrum of the original cotton, a peak assigned to the nitrogen of PPCP, is observed in the spectrum of SCM (Fig. 4d). Attenuated total
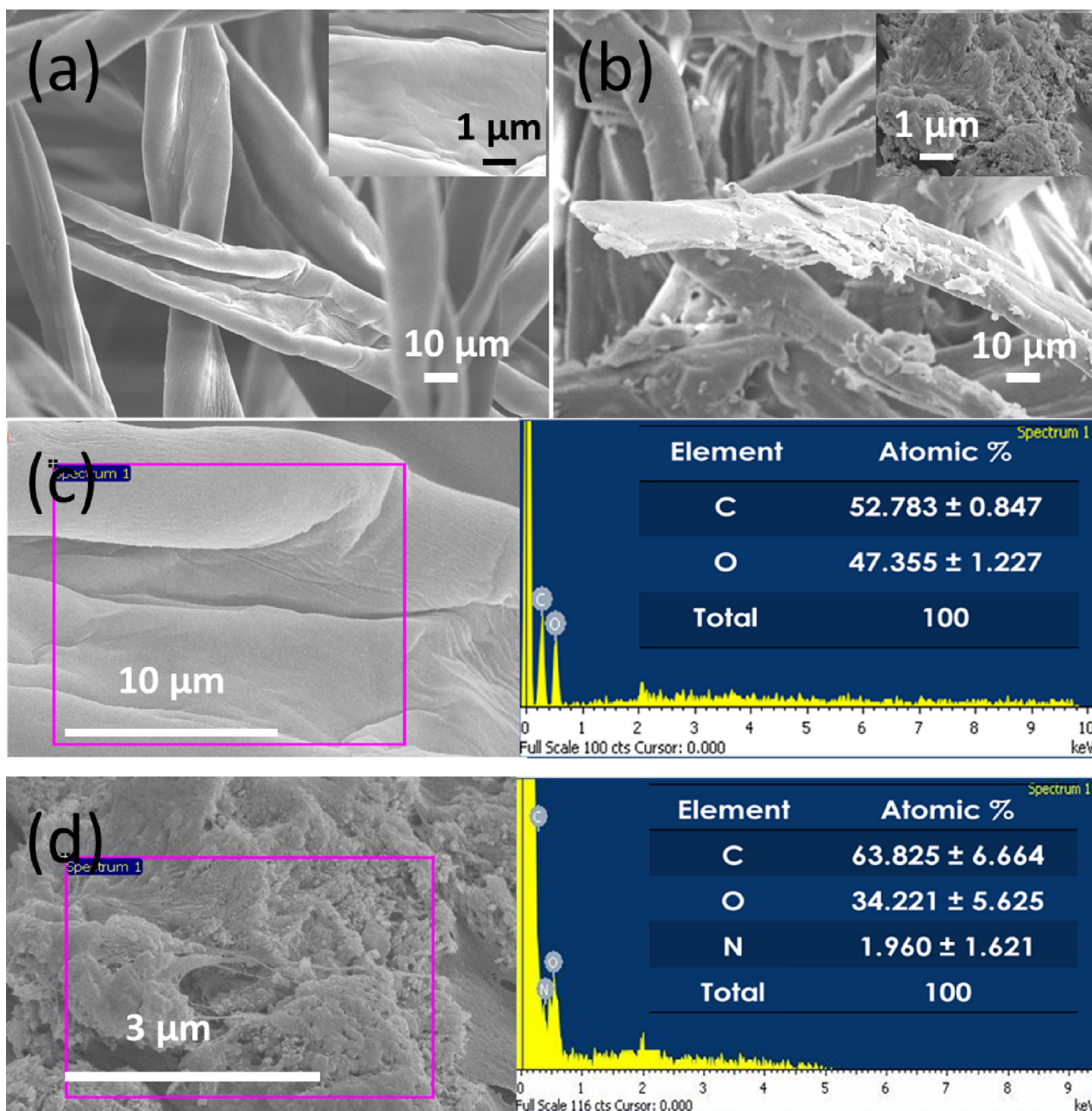
Fig. 4. SEM image of (a) pristine cotton and (b) SCM. SEM and EDS data of (c) pristine cotton and (d) SCM.

reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) was also employed to determine chemical compositions (functional groups) of the pristine cotton and SCM (Fig. 5). The data of pristine cotton show typical characteristic peaks of cellulose at approximately 3336–3294 cm^{-1} (−OH stretching vibration), 2900 cm^{-1} (−CH asymmetric stretching vibration), 1361 cm^{-1} (C−H bending vibration), and 1204–1030 cm^{-1} (C−O stretching vibrations). A peak at approximately 1641 cm^{-1} is attributed to the adsorbed water molecules [20]. New high-intensity peaks are observed at 1611 cm^{-1} (C═C stretching vibrations), 1510 cm^{-1} (ortho/para-disubstituted benzene in addition to the complete aromatic skeletal vibrations including −C═C−C aromatic ring-stretching vibrations), and 827 cm^{-1} (para-disubstituted benzene, ═C−H and −C−H bending vibrations), which corresponds to the benzene rings of PPCP, in the spectrum of SCM. Additionally, a weak intensity peak at approximately 3023 cm^{-1} corresponded to an aromatic C═C−H stretching vibration. The above data confirm that the cotton was modified with PPCP.

Typically, superhydrophobic materials lose their super-hydrophobicities under harsh environments, such as those containing corrosive aqueous liquids and organic solvents. The SCM exhibited excellent repellence toward acidic (pH = 1) and saline (1.0 M NaCl) solutions and hot water (90 °C) (Fig. 6a). The droplets of these solutions had spherical shapes on the SCM (contact angles of all solutions were > 150°) and rolled off easily. Moreover, the SCM was very stable against long-term (48 h) immersion in organic solvents (Fig. 6b). Samples were retrieved every 8 h and dried before performing WCA measurements and the long-term immersion in organic solvents did not result any significant change in the superhydrophobicity of the SCM. However, our SCM was unstable under long term immersion in alkaline aqueous solutions. Fig. 6b shows that after immersion in alkaline aqueous solution (pH = 10) for 16 h the WCA decreased with increasing immersion time (from 150° after 16 h to 130° after 48 h). The stability of the SCM was also investigated through continuous and vigorous rinsing treatments with different organic solvents. After
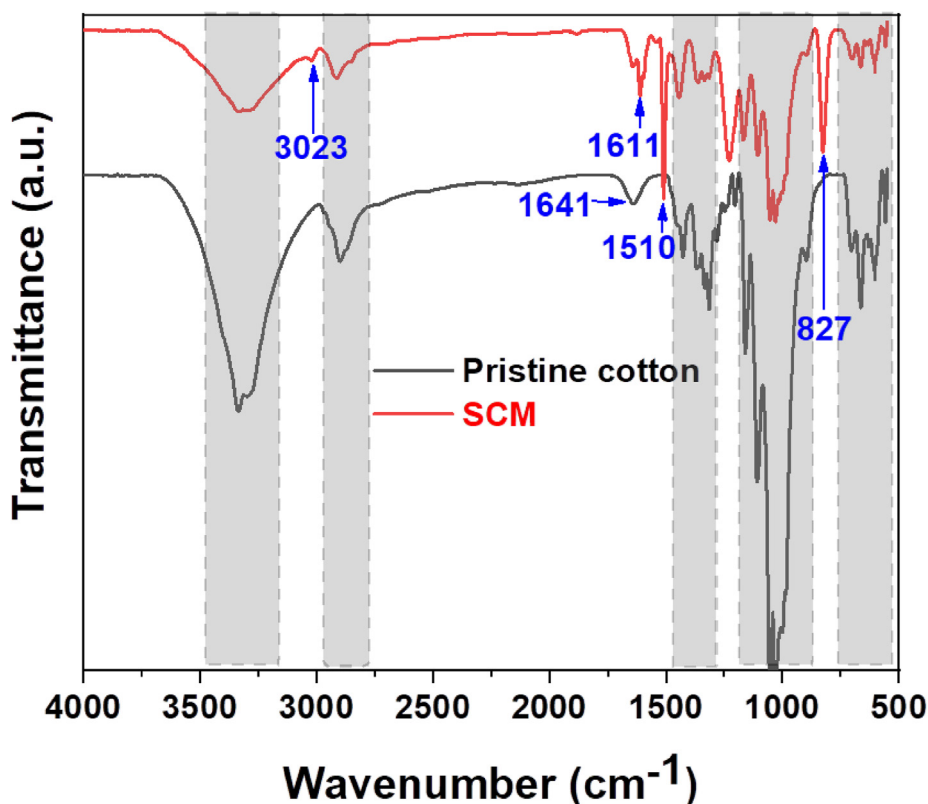
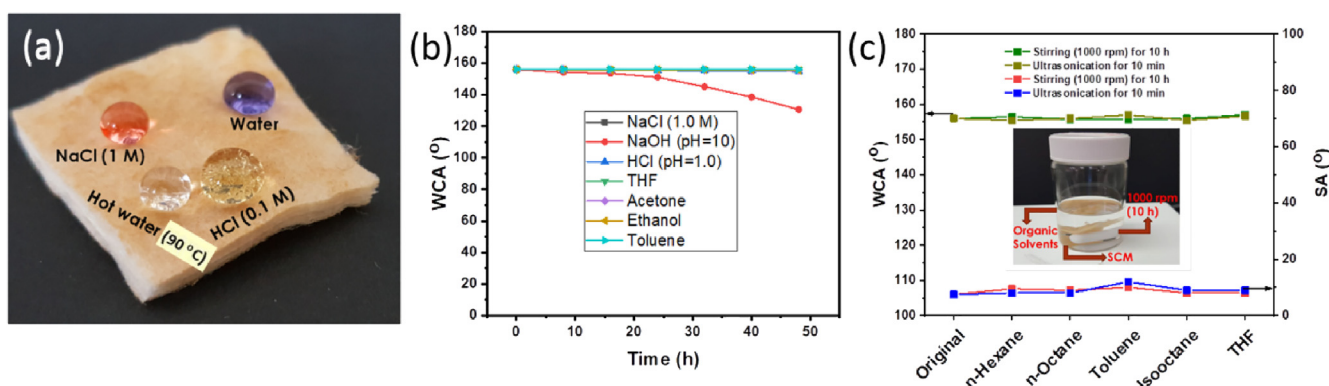**Fig. 5.** ATR-FTIR spectra of pristine cotton and SCM.

Fig. 6. (a) Photograph of the water droplets on SCM. (b) Variation in the water contact angle (WCA) on SCM with an increase in the immersion time in different aqueous solutions and organic solvents. (c) Effect of organic solvents on the wettability of SCM by stirring at 1000 rpm for 10 h and ultrasonicating for 10 min.

vigorous rinsing for 10 h with THF, toluene, isooctane, n-octane and n-hexane, the WCA of SCM was still ≥150° (Fig. 6c). Furthermore, the SCM retained its superhydrophobicity even after ultrasonic treatment tested for 10 min in organic solvents. The results confirmed the high stability of SCM.

To further confirm the stability of the superhydrophobicity of SCM, we conducted the beating test to determine the binding force of the PPCP with the cotton. The beating object (600 g) was repeatedly dropped from a height of 30 cm (Fig. 7a). After beating with 600 g object for 100 times, the WCA was still > 150° and SA was < 15°, indicating that SCM retained its superhydrophobicity (Fig. 7b). The effect of the beating test was further investigated by ATR-FTIR. Fig. 7c shows that the spectra of SCM before and after 100 cycles of beating test are similar, confirming the excellent stability of SCM.

Emulsified oil–water mixtures in wastewater are also a serious environmental concern that affects various industrial processes. As it is well-known, it is more challenging to treat surfactant-stabilized

emulsions than simple oil–water mixtures due to the micro-scale dimension and good stability of emulsions. Therefore, innovative materials that can efficiently separate emulsions with high performance are highly desirable. Remarkably, the SCM described in this study can be used for the effective separation of surfactant-stabilized water-in-oil emulsions by applying a simple compression process. Fig. 8a and b show the optical microscopy images of original and compressed SCM, respectively. The surface morphology of the compressed SCM (Fig. 8b) was much more compact than the non-compressed sample (Fig. 8a).

Fig. 9a shows a simple set-up that exhibits the separation of the surfactant-stabilized water-in-oil emulsion via a gravity-driven process through the compressed SCM. The surfactant-stabilized water-in-oil emulsion and the filtrates obtained with both the gravity-driven process and external pressure application were examined by optical microscopy (Fig. 9b and c, respectively). Water droplets with micro-scale diameters are observed in the opaque emulsion, while the droplets disappear after separation, yielding similar transparent filtrates in both cases (gravity-
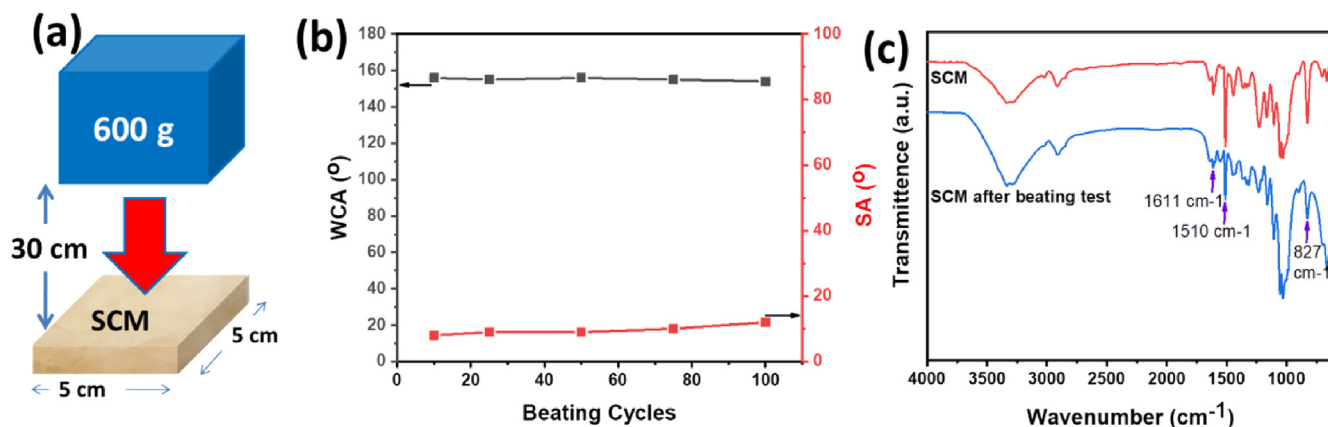
Fig. 7. (a) Schematic of the set-up for testing the long-term resistance of SCM against object impact. (b) Effect of beating cycles on the wettability of SCM. (c) ATR-FTIR data of SCM before and after beating for 100 cycles.
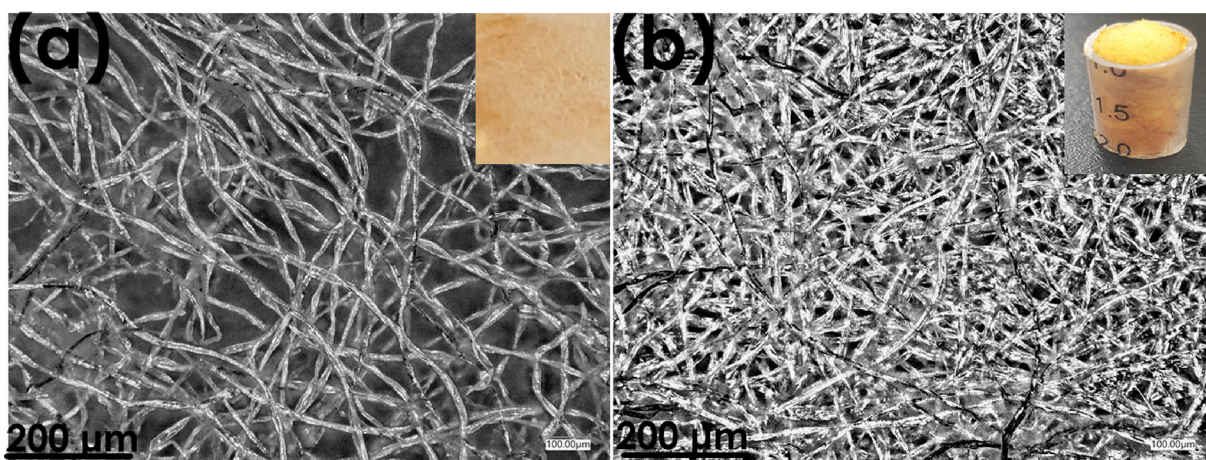

Fig. 8. Optical images of the (a) original cotton and (b) compressed SCM.

driven and external pressure application). This indicates the elimination of water from the surfactant-stabilized water-in-oil emulsion. We also detected the particle size of water in the surfactant-stabilized water-in-toluene emulsions and the corresponding collected filtrates by using dynamic light scattering (DLS). As the DLS results indicate that the droplet size changed from 1123 ± 86 nm (Fig. S2a) to 6.8 ± 0.3 nm (Fig. S2b) in case of gravity-driven separation process and to 181 ± 12 nm (Fig. S2c) using external pressure of 0.1 bar. This result indicated that the compressed SCM can effectively separate the surfactant-stabilized water-in-oil emulsions with outstanding performance. For the water-in-oil emulsions including n-hexane, gasoline, petroleum ether, toluene, n-octane, and n-hexadecane, the fluxes are surprisingly high, i.e., 10,400 ± 400, 10,300 ± 300, 10,160 ± 360, 9640 ± 250, 8950 ± 340, and 3910 ± 30 L m^{-2}h^{-1}, respectively, using only gravity-driven process (Fig. 9d). Similar to the results obtained when the emulsions are separated under gravity-driven conditions, no oil droplets are observed in the filtrate when using external pressure of 0.1 bar, confirming that the compressed SCM is effective for the separation of the water-in-oil emulsion by the application of external pressure. The fluxes of all surfactant-stabilized water-in-oil emulsions upon the application of external pressure are 867,500 ± 30,300, 711,600 ± 45,300, 657,900 ± 45,650, 651,600 ± 54,000, 563,900 ± 34,000, and 108,000 ± 23,000 L m^{-2}h^{-1} bar^{-1} for n-hexane, toluene, petroleum ether, gasoline, n-octane, and n-hexadecane, respectively (Fig. 9e). As shown in Fig. 9d and e, the oil purities of all separated emulsions are > 99.97 wt%, with few up to 99.99 wt%, indicating significantly high separation efficiencies. The purities of the original oils used in the

experiments were also tested (Table S2); the purities of the filtrates nearly matched those of the pure reagents.

Some researchers have successfully separated water-in-oil emulsions using superwetting materials with high fluxes (Table 2). Wang and co-workers prepared superwetting porous materials for the ultrafast separation of water-in-oil emulsions with the application of external pressure [21]. Yue et al. developed a laminated superwetting composite of aerogel/membrane with large pore sizes for effective separation of the surfactant-stabilized water-in-oil emulsions [22]. Chu et al. used silicone nanofilament to decorate the surface of porous glass filter plate to prepare superhydrophobic and superoleophilic material that could be used for the separation of water-in-oil emulsions with ultrahigh permeation fluxes and excellent efficiencies using both gravity-driven and external pressure-based systems [23]. Hu et al. constructed an ultrathin bilayer membrane with asymmetric wettability for pressure-responsive oil–water emulsion separation [24]. Gu and co-workers synthesized superhydrophobic polymer/CNT hybrid membranes for highly effective separation of numerous surfactant-stabilized water-in-oil emulsions. Recently, Han et al. reported novel metal-based polybenzoxazine micro/nano spheres for highly efficient separation of water-in-oil emulsions with ultrahigh fluxes [25]. Compared to various other types of superwetting materials, the SCM described herein exhibits ultrahigh fluxes and excellent efficiencies in the separation of surfactant-settled water-in-oil emulsions (Table 2). The method described herein is simple and can employ compounds that do not contain fluorine. Fig. S4 reveals the procedure of the compressed SCM for water-in-oil emulsion separation. When we poured the surfactant-stabilized water-in-oil emulsion into the compressed SCM surface, the
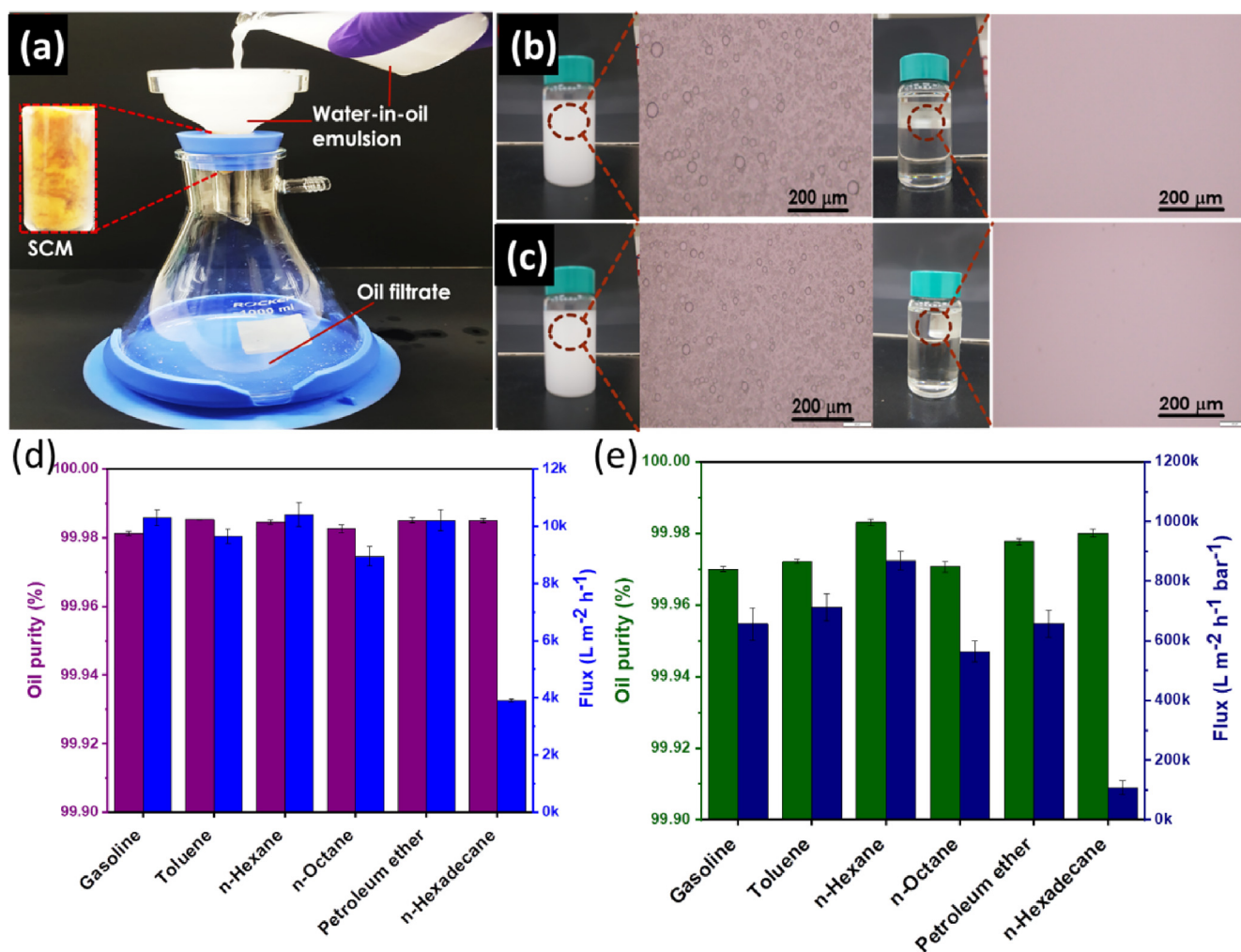
Fig. 9. (a) Set-up for water-in-oil emulsion separation. Optical microscopy images of water-in-oil emulsions (left) and the corresponding filtrates (right) obtained by (b) gravity-driven process and (c) after applying external pressure. Separation performance of SCM with surfactant-stabilized water-in-oil emulsions with (d) gravity-driven process and (e) external pressure application.

Table 2
Comparison of Different Special Wettable Materials for Separation of Surfactant-Stabilized Water-in-Oil Emulsions.*

S.N.	Material	Gravity-driven		External Pressure Applied		Reference
		Flux ($Lm^{-2}h^{-1}$)	Oil Purity (wt%)	Flux ($Lm^{-2}h^{-1} bar^{-1}$)	Oil Purity (wt%)	
1	Hydrophobic-polymer-coated melamine sponge	–	–	155,000	99.98	[21]
2	Acrylonitrile-butadiene-styrene copolymer coated on filter paper	–	–	13,000	99.90	[26]
3	superhydrophobic 3D melamine sponge	–	–	32,500	99.97	[27]
4	Metal coordinated PBZ	2100	> 99	37,526	> 99	[25]
5	Superhydrophobic copper foam	6560	99.89	–	–	[28]
6	SiO_2-nanoparticles-treated PVDF membrane	–	–	16,400	99.95	[29]
7	PFDTS/CNT hybrid membrane	–	–	41,880	99.89	[30]
8	SWCNT network films	–	–	16,810	99.95	[31]
9	SWCNT-based bilayer membrane	–	–	48,300	99.95	[24]
10	silicone-nanofilament-coated porous glass substrates	6200	99.99	120,000	99.98	[23]
11	Cellulose Aerogel/membrane composite	12,890	99.5	–	–	[22]
12	Ffluoroalkyl silane and Al_2O_3 nanoparticles modified raw cotton	–	–	11,540	99.74	[32]
13	Castor oil-based Nano-composites-coated cotton fabric	2225	99.99	–	–	[33]
14	Fluorosurfactant and TiO2 nanoparticles-coated cotton fabric	600	98.5	–	–	[34]
15	PVPh/PBO coated raw cotton	10,400	99.98	867,516	99.97	This Work

* -Not Reported.

stability of emulsion could be seriously disrupted because of the superhydrophobic and superoleophilic properties of SCM, and then the demulsification appearance would occur instantly. The oils were quickly sucked up and penetrated through the compressed SCM,

making the emulsion droplets to demulsify. As the demulsification effect continued on the separation process, various water droplets conjoined gradually with each other and composed larger droplets, therefore being effectively rejected in the tortuous channels of the
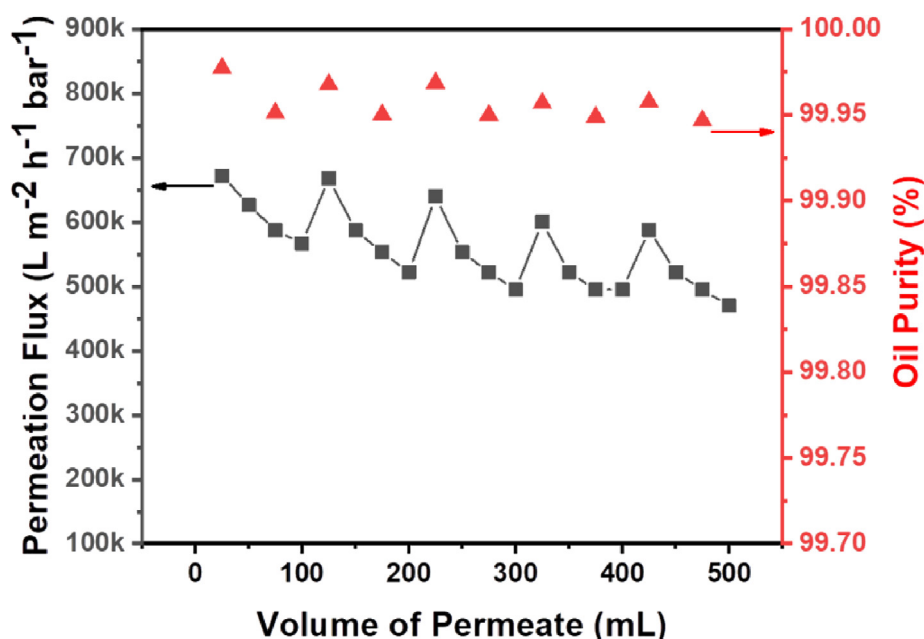
Fig. 10. Real-time monitoring of the separation flux and oil purity during the cycles of the surfactant-stabilized water-in-toluene emulsion separation test using SCM.

compressed SCM. In addition, we found that oils could be transported very quickly along the fibrous structure of SCM (Fig. S5). Above phenomena induced to the outstanding performance and extremely high flux for surfactant-stabilized water-in-oil emulsions separations of the compressed SCM. The densities of compressed SCM influence the flux and separation performance of water-in-oil emulsions separation. The flux of the emulsion separation could be effectively and easily controlled by directly adjusting the density of the compressed SCM layer. Moreover, the separation performance for emulsions is also affected. Fig. S3 reveals the changes of filtrate flux and separation performance with increasing the density of compressed SCM layer from 0.085 to 0.225 g/cm^3. It can be clearly observed that the filtrate flux of the water-in-oil emulsion quickly decreases with the increase of compressed SCM layer thickness, but, at the same time, the separation performance of the emulsion improves.

Antifouling properties of filtration materials are also important for the separation performance of oil-water mixtures. The antifouling property of the SCM was investigated by performing filtration/wash cycles with water-in-toluene emulsion (Fig. 10). In each cycle, 100 mL of surfactant-stabilized emulsion was filtered through the compressed SCM followed by washing the SCM with acetone. A decrease influx was observed throughout the filtration of the 100 mL. However, after washing with acetone, the flux recovers to 83% during four cycles. The oil purity in every cycle is > 99.95 wt%; thus, the separation performance is not significantly affected during four cycles. The results confirm the excellent antifouling properties of the SCM during long-term usage in the treatment of water-in-oil emulsions.

4. Conclusions

The separation of emulsified oil–water mixtures is typically challenging, and this is a commonly encountered issue in petroleum industries. In this study, a simple method for the preparation of durable superwetting composite using PVPh, PBO, and raw cotton is developed. The as-prepared superwetting composite possesses superhydrophobicity (WCA > 150°) and superoleophilicity (oil contact angle < 5°), exhibiting excellent oil–water separation performance. Very high permeation fluxes of up to 10,400 ± 400 L m^{-2}h^{-1} and 867,500 ± 30,300 L m^{-2}h^{-1} bar^{-1} was obtained for surfactant-stabilized water-in-oil emulsion employing gravity-driven and external

pressure filtration, respectively, with excellent efficiencies (oil purity of ≥99.97 wt%). The outstanding separation performance for various oils and organic solvents, stability in harsh chemical and physical environments, robustness, and recyclability of the superhydrophobic composite make it an excellent candidate for large scale application.

Declaration of Competing Interest

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

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2020.126289.

References

[1] Y. Bu, J. Huang, S. Zhang, Y. Wang, S. Gu, G. Cao, H. Yang, D. Ye, Y. Zhou, W. Xu, Robust superhydrophobic surface by nature-inspired polyphenol chemistry for effective oil-water separation, Appl. Surf. Sci. 440 (2018) 535–546.
[2] J. Wang, S. Liu, Remodeling of raw cotton fiber into flexible, squeezing-resistant macroporous cellulose aerogel with high oil retention capability for oil-water separation, Sep. Purif. Technol. 221 (2019) 303–310.
[3] J. Yang, Y. Pu, H. He, R. Cao, D. Miao, X. Ning, Superhydrophobic cotton nonwoven fabrics through atmospheric plasma treatment for applications in self-cleaning and oil–water separation, Cellulose 26 (12) (2019) 7507–7522.
[4] L. Liu, Y. Pan, B. Bhushan, X. Zhao, Mechanochemical robust, magnetic-driven, superhydrophobic 3D porous materials for contaminated oil recovery, J. Colloid. Interf. Sci. 538 (2019) 25–33.
[5] J.H. Lee, D.H. Kim, Y.D. Kim, High-performance, recyclable and superhydrophobic oil absorbents consisting of cotton with a polydimethylsiloxane shell, J. Ind. Eng. Chem. 35 (2016) 140–145.
[6] N. Lv, X. Wang, S. Peng, L. Luo, R. Zhou, Superhydrophobic/superoleophilic cotton-oil absorbent: preparation and its application in oil-water separation, RSC Adv. 8 (53) (2018) 30257–30264.
[7] B. Doshi, M. Sillanpää, S. Kalliola, A review of bio-based materials for oil spill

treatment, Water Res. 135 (2018) 262–277.

[8] A. Bazargan, J. Tan, C.W. Hui, G. McKay, Utilization of rice husks for the production of oil sorbent materials, Cellulose 21 (3) (2014) 1679–1688.

[9] C. Jiang, W. Liu, M. Yang, C. Liu, S. He, Y. Xie, Z. Wang, Robust multifunctional superhydrophobic fabric with UV induced reversible wettability, photocatalytic self-cleaning property, and oil-water separation via thiol-ene click chemistry, Appl. Surf. Sci. 463 (2019) 34–44.

[10] Y. Zhang, Y. Zhang, Q. Cao, C. Wang, C. Yang, Y. Li, J. Zhou, Novel porous oil-water separation material with super-hydrophobicity and super-oleophilicity prepared from beeswax, lignin, and cotton, Sci. Total. Environ. 706 (2020) 135807.

[11] J. Ren, F. Tao, L. Liu, X. Wang, Y. Cui, A novel TiO2@stearic acid/chitosan coating with reversible wettability for controllable oil-water and emulsions separation, Carbohydr. Polym. 232 (2020) 115807.

[12] Q. Wang, J. Wu, G. Meng, Y. Wang, Z. Liu, X. Guo, Preparation of novel cotton fabric composites with pH controlled switchable wettability for efficient water-in-oil and oil-in-water emulsions separation, Appl. Phys. A-Mater 124 (6) (2018) 422.

[13] Y. Pan, L. Liu, Z. Zhang, S. Huang, Z. Hao, X. Zhao, Surfaces with controllable super-wettability and applications for smart oil-water separation, Chem. Eng. J. 378 (2019) 122178.

[14] H. Guo, J. Yang, T. Xu, W. Zhao, J. Zhang, Y. Zhu, C. Wen, Q. Li, X. Sui, L. Zhang, A robust cotton textile-based material for high-flux oil–water separation, ACS Appl. Mater. Interfaces 11 (14) (2019) 13704–13713.

[15] H.-C. Lin, C.-F. Wang, S.-W. Kuo, P.-H. Tung, C.-F. Huang, C.-H. Lin, F.-C. Chang, Effect of intermolecular hydrogen bonding on low-surface-energy material of poly (vinylphenol), J. Phys. Chem. B 111 (13) (2007) 3404–3410.

[16] H. Ishida, T. Agag, Handbook of Benzoxazine Resins, second ed., Elsevier, Oxford, 2011.

[17] C.P.R. Nair, Advances in addition-cure phenolic resins, Prog. Polym. Sci. 29 (5) (2004) 401–498.

[18] S.-W. Kuo, Y.-C. Wu, C.-F. Wang, K.-U. Jeong, Preparing low-surface-energy polymer materials by minimizing intermolecular hydrogen-bonding interactions, J. Phys. Chem. C 113 (48) (2009) 20666–20673.

[19] S.W. Fowkes, Adhesion and adsorption of polymers, polymer science and technology, first ed., Plenum Press, New York, 1980.

[20] C. Chung, M. Lee, E.K. Choe, Characterization of cotton fabric scouring by FT-IR ATR spectroscopy, Carbohydr. Polym. 58 (4) (2004) 417–420.

[21] C.-F. Wang, L.-T. Chen, Preparation of superwetting porous materials for ultrafast separation of water-in-oil emulsions, Langmuir 33 (8) (2017) 1969–1973.

[22] X. Yue, W. Li, Z. Li, F. Qiu, J. Pan, T. Zhang, Laminated superwetting aerogel/membrane composite with large pore sizes for efficient separation of surfactant-stabilized water-in-oil emulsions, Chem. Eng. Sci. 215 (2020) 115450.

[23] Z. Chu, S.J.A.M. Seeger, Multifunctional hybrid porous micro-/nanocomposite materials, Adv. Mater. 27 (47) (2015) 7775–7781.

[24] L. Hu, S. Gao, Y. Zhu, F. Zhang, L. Jiang, J. Jin, An ultrathin bilayer membrane with asymmetric wettability for pressure responsive oil-water emulsion separation, J. Mater. Chem. A 3 (46) (2015) 23477–23482.

[25] X. Han, J. Hu, K. Chen, P. Wang, G. Zhang, J. Gu, C. Ding, X. Zheng, F. Cao, Self-assembly and epitaxial growth of multifunctional micro-nano-spheres for effective separation of water-in-oil emulsions with ultra-high flux, Chem. Eng. J. 352 (2018) 530–538.

[26] W. Deng, M. Long, Q. Zhou, N. Wen, W. Deng, One-step preparation of super-hydrophobic acrylonitrile-butadiene-styrene copolymer coating for ultrafast separation of water-in-oil emulsions, J Colloid Interf. Sci. 511 (2018) 21–26.

[27] J. Yang, H. Wang, Z. Tao, X. Liu, Z. Wang, R. Yue, Z. Cui, 3D superhydrophobic sponge with a novel compression strategy for effective water-in-oil emulsion separation and its separation mechanism, Chem. Eng. J. 359 (2019) 149–158.

[28] Z. Wang, C. Xiao, Z. Wu, Y. Wang, X. Du, W. Kong, D. Pan, G. Guan, X. Hao, A novel 3D porous modified material with cage-like structure: fabrication and its demulsification effect for efficient oil-water separation, J. Mater. Chem. A 5 (12) (2017) 5895–5904.

[29] C. Wei, F. Dai, L. Lin, Z. An, Y. He, X. Chen, L. Chen, Y. Zhao, Simplified and robust adhesive-free superhydrophobic SiO2-decorated PVDF membranes for efficient oil-water separation, J. Membr. Sci. 555 (2018) 220–228.

[30] J. Gu, P. Xiao, Y. Huang, J. Zhang, T. Chen, Controlled functionalization of carbon nanotubes as superhydrophobic material for adjustable oil-water separation, J. Mater. Chem. A 3 (8) (2015) 4124–4128.

[31] Z. Shi, W. Zhang, F. Zhang, X. Liu, D. Wang, J. Jin, L. Jiang, Ultrafast separation of emulsified oil-water mixtures by ultrathin free-standing single-walled carbon nanotube network films, Adv. Mater. 25 (17) (2013) 2422–2427.

[32] F. Li, Z. Wang, Y. Pan, X.J.P. Zhao, A facile and effective method to fabricate superhydrophobic/superoeophilic surface for the separation of both water/oil mixtures and water-in-oil emulsions, Polymers 9 (11) (2017) 563.

[33] Q. Shang, C. Liu, J. Chen, X. Yang, Y. Hu, L. Hu, Y. Zhou, X. Ren, Sustainable and robust superhydrophobic cotton fabrics coated with castor oil-based nanocomposites for effective oil–water separation, ACS Sustain. Chem. Eng. 8 (19) (2020) 7423–7435.

[34] F. Li, W. Kong, X. Zhao, Y. Pan, Multifunctional tio2-based superoleophobic/superhydrophilic coating for oil–water separation and oil purification, ACS Appl. Mater. Interfaces 12 (15) (2020) 18074–18083.