Journal Name RSCPublishing

ARTICLE

Three-Dimensional Structured Sponge with High Oil Wettability for Clean-up of Oil Contaminations and Separation of Oil-Water Mixtures

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Gang Wang,[a,b] Zhixiang Zeng,*[a] Xuedong Wu,*[a] Tianhui Ren,[b] Jin Han[a] and Qunji Xue[a]

*E-mail: zzx1572000@aliyun.com

Oil spills not only result in extensive economic losses but also bring marine ecological damages. A series of materials having special wettability are investigated for the separation of oil-water mixtures. But few literatures investigate the adsorption behaviors of sponges to crude oil (high viscosity). In order to solve the restrictions of high viscosity oil absorption, low oil absorption rate and oil-water emulsion separation of the oil absorption materials, a superhydrophobic and superoleophilic polyurethane (PU) sponge was synthetized via environment-friendly surface grafting of polymer molecular brush. This grafted sponge exhibited high oil absorption rate due to the expanding in oil and collapsing in water of the polymer molecular brushes. The grafted PU sponge also possessed high absorption capacity (23 times to self-weight), high oil retention (93%), high mechanical strength and good recyclability (more than 400 times). We anticipate that the grafted sponge will have numerous applications and show outstanding performance on larger scale and quick clean-up of marine spilled oil/organic solvents and separation/ recycling of oil-water mixture/emulsion.

Introduction

Due to the increased marine transportation and oil gas exploitation, frequent oil spills result in extensive economic losses and marine ecological damages.[1-4] In order to clean up the spilled oil, machines of oil collection, oil absorption materials, oil dispersing agents and oleiphilus are often used.[5] Therein, oil absorption materials attract researchers' attentions in respect that they are convenience and low cost. Traditional oil absorption materials include silica, pearl rocks, graphite, straw, polypropylene etc. Now the researches in the field of oil absorption materials focus on how to improve the efficiency, velocity and reusability of the oil absorption materials. And it is also expected to reuse both the oil absorption materials and the spilled oil, for the economic consideration.[6-11] In order to achieve above aims, some studies have been devoted to design materials which could absorb oil rapidly and also desorb oil easily as they encounter external force.[12-16] The self-cleaning foam,[17] recyclable carbon nanotube sponges[18], marshmallow-like macroporous gels[19] and nanoporous polystyrene fiber[20] are investigated. Recently, porous polymers with three-dimensional (3D) networks structure are considered as a new type material for oil contaminations clean-up due to their high surface area, high porosity, gas permeability and low density. With the development of porous polymers, new kinds of porous polymers like nanoporous polydivinylbenzene,[21] conjugated microporous polymers,[22] graphene-based sponges[23, 24] and carbon aerogel[25] have been fabricated and exhibit high efficiency for clean-up of oils and organic solvents on water. However, the high price, severe production conditions or low mechanical strength make them not suitable for large scale oil and organic solvents clean-up and oil-water separation.

Moreover, the pore size[26] of some porous polymers is less than 50 nm or uncontrolled, which restricts them to be used for high viscosity oil spill clean-up.

The flexible PU sponge is a kind of porous polymers with 3D networks. Its good elasticity and low cost let it has huge potential on the oil spill clean-up and oil-water separation. However, the disadvantages of hydrophobility and low oil absorption rate restrict its application. In recently literatures, a series of modified PU sponges having special wettability are investigated for the separation of oil-water mixtures. But in many related previous studies, most of them are focus on the preparation of superhydrophobic surface and the "oil" is replaced by organic solvent.[22, 27] And, few literatures investigate the absorption behaviors of sponges to crude oil. In practice， the viscosity of spill oil is much higher than the organic solvent, which requires the stronger oil absorption ability of the sponge. And the viscosity of oil spill increases with the quick oil spreading, evaporation and emulsification.[28] So the oil absorption rate to high viscosity oil is one of the key factors of oil absorption materials. Unfortunately, there are rare studies in terms of the high viscosity and absorption rate of oil. In this study, the PU sponge with high oil wettability property was synthetized via environment-friendly surface grafting of polymer molecular brush. The absorption behaviors to various organic solvents, crude oil and especially the high viscosity oil were investigated. The grafted PU sponge can not only absorb various organic solvents well, but also absorb high viscosity crude oil efficiently.

Experimental

Materials

PU sponges (88% in porosity and 250-500μm in pore size) were collected from the abandoned packaging material. 1,3-oxazolidine[29] synthesis was referred to previous literature. Oil red O, methylene blue, stearoyl chloride (CP), hexadecane (AR), chloroform (AR), petroleum ether (AR), methanol (AR), ethanol (GR) and 1, 4-dioxane (AR,99%) were purchased from Aladdin Reagent. Crude oil was obtained from Zhenhai Oil Refining and Chemical Company, Sinopec.

Preparation of the superhydrophobic and superoleophilic PU sponge

Grafting A: A piece of PU sponge (2 * 2 * 2 cm) was ultrasonically cleaned in ethanol and deionized water for 30 min to remove surface stains and oils. After cleaning, the sponge was dried in an oven, and then immersed in a water solution containing 1, 3-oxazolidine (5-10%, v/v) at 100-120ºC for 1 hour. Finally, the sponge was washed in ethanol and dried at 90ºC to remove the unreacted 1, 3-oxazolidine and ethanol.

Grafting B: After the drying, the sponge was immersed in a mixed solution content 150ml 1, 4-Dioxane, 10ml stearoyl chloride and 100mg $NaHCO_3$ at 60ºC for 5 hours. At last, the sponge was washed by deionized water and dried to obtain the superhydrophobic and superoleophilic PU sponge.

Preparation of the oil/water emulsion

The oil/water emulsion makes up of 1 volume of water and 9 volume of crude oil. The crude oil (the crude oil viscosity is 208cp at room temperature) and water are mixing by a stir bar (at 700–1200r.p.m.) for 24 hours to form homogeneous oil/water emulsion.

Oil absorption capacity

A piece of sample was immersed in oil at room temperature. The sample was taken out from the oil after 5 min, stood for 1 minute on the metal net and wiped with filter paper to remove excess oil. The oil absorption capacity k of the sample was determined by weighing the sample before and after oil absorption and calculated according to equation (1):

$$k = \frac{w - w_o}{w_o} \times 100\% \qquad (1)$$

where w is the weight of the saturated PU sponge with oil (g) and w_o is the weight of dry PU sponge (g).

Oil retention

A piece of sample was immersed in oil at room temperature. The sample was taken out from the oil after 5 min, stood for 1 minute on the metal net and wiped with filter paper to remove excess oil. The oil retention r of the sample was determined by weighing the saturated PU sponge before and after be centrifuged of 3000 rotation for 1 minute and calculated according to equation (2):

$$r = \frac{w_c - w_o}{w_s - w_o} \times 100\% \qquad (2)$$

Where w_c, w_o and w_s are the weight of PU sponge after centrifugal (g), the weight of dry PU sponge (g) and the weight of the saturated PU sponge with crude oil (g).

Collection of oils from water surface or bottom

A piece of grafted PU sponge was brought into the oil-polluted region and then removed from the water surface. The absorbed oil was collected through a simple squeezing process by tweezers. After each separation process, the sponge was washed with acetone and dried, and its water contact angle (CA) was measured.

A piece of grafted PU sponge was inserted into the bottom of beaker to contact with the oil (chloroform dyeing by oil red). The sponge was taken out from the water when the oil was completely adsorbed.

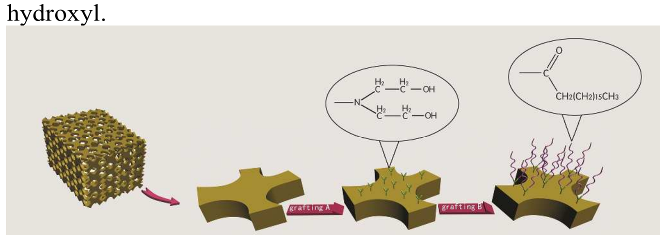
Characterization

Surface morphologies of sponges were examined by a SEM (FEI Quanta 250 FEG, US); Surface contact angle was detected by a contact angle meter (OCA20, Germany). Three measurements were performed per sample and averaged. Water droplets with a volume of 3.0 μL were dropped carefully onto surfaces; Surface composition was examined by a FTIR (NICOLET 6700, Thermo Fisher Scientific, US); Oil viscosity was examined by a viscosimeter (DV-II+PRO, Brookfield, US). The compressive stress and strain were detected by universal material testing machine (Instron 5567, US).

RESULTS AND DISCUSSION

Preparation of the high oil wettability PU sponge

In this study, we prepared a high oil wettability PU sponge via environment-friendly surface grafting of polymer molecular brush. Scheme 1 shows the sketch of the fabrication process (see the experimental section for details) of the modified PU sponge. It involves two grafting reactions: grafting A (Figure 1a) is a ring-opening reaction of 1,3-oxazolidine that mainly occurs in the secondary amine N–H bonds of PU sponge; the grafting B (Figure 1b) is a substitution reaction on the hydrogen atom of hydroxyl.



Scheme 1. Illustration for the fabrication of high oil wettability PU sponge.

Since oil/water separation is an interfacial issue, designing novel materials with special wettability is an effective strategy. The surface tension of oil and organic liquids is lower than that of water. So a hydrophobic surface is necessary to the oil absorption materials used between oil and water interface. In order to improve the hydrophobility of the PU sponge, in previous studies, chromic acid or sodium hydroxide solution were used to etch the PU sponge so as to increase roughness and generate hydroxyl or carboxyl for grafting with the hydrophobic methyltrichlorosilane or fluoroalkylsilane.[17, 30] However, the strong acid or base would damage the skeleton of PU sponge, and decrease the mechanical property of the base material. Moreover, the chromic acid is toxic to human body. Here, we introduce two hydroxyl groups on one secondary amine N-H bonds of PU surface by the grafting A without toxic or corrosive solution, which can significantly improve the surface reactivity of the PU sponge. By the grafting B, long-chain alkyls are grafted on the hydroxyl of grating A, which can remarkable increase the hydrophobicity and lipophilicity. Figure 1c presents the compared FTIR of blank sponge, sponge after grafting A and sponge after grafting B. It is found that O-H bands absorption peak occurred in 3300-3700cm^{-1} after grafting A. After grafting B, the O-H bands absorption peak almost disappears and the N-H bands absorption peak (3140-3446cm^{-1}) weakens. It indicates that the robust dendrimers polymer brushes were grafted on the surface of the PU sponge.

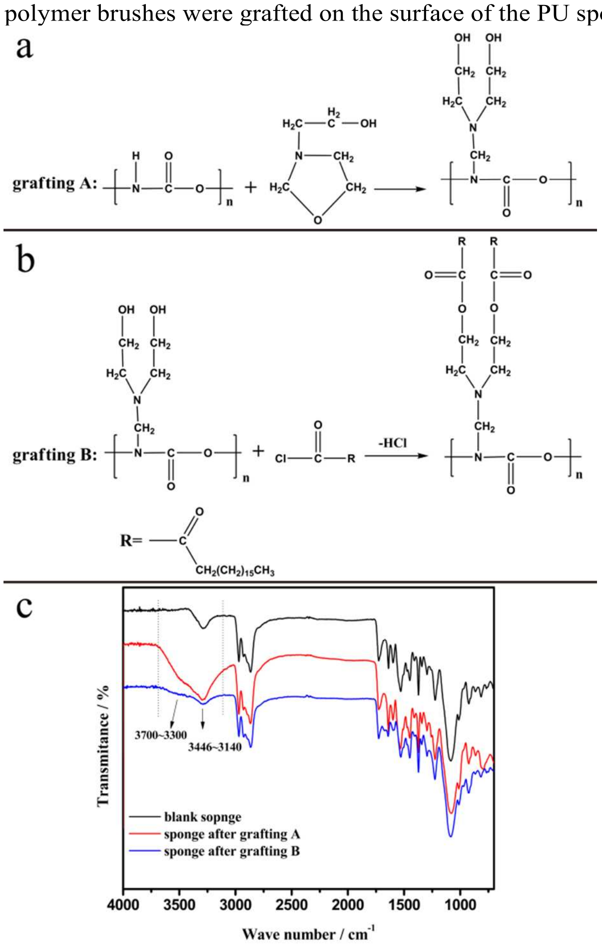


Figure 1. a) Ring-opening reaction of grafting A. b) Esterification reaction of grafting B. c) FTIR spectra of blank sponge, sponge after grafting A and sponge after grafting B.

Water-wetting properties of the grafted PU sponge

The wettability of the blank sponge and grafted sponge to artificial seawater are investigated by analyzing the seawater contact angle (Figures 2a and 2d). For the blank sponge, the seawater contact angle (Figure 2a) is 94º (3μL), showing a slightly hydrophobic character. After the grafting A and B, the seawater contact angle of the resultant sponge is 152º (Figure 2d), exhibiting superhydrophobic[31]. SEM images of PU sponge before and after grafting A and B are shown in Figures 2b, 2c, 2e and 2f. From Figures 2b and 2e, it can be seen that the PU sponge has 3D networks structure and multi-channels. From the high-magnification SEM images (Figures 2c and 2f), there are micro/nanostructures on the skeleton surface. Although there are micro/nanostructures on the surface of the blank PU sponge, it doesn't have a good hydrophobicity. And, the grafted PU sponge is superhydrophobicity. The obviously increased hydrophobicity is attributed to the long chain alkyls with low surface energy on the surface of the PU sponge. In Figure 2g, we can see the seawater droplets (dyeing by methylene blue) stay as spheres on the grafted PU sponge surface. To further test the hydrophobic of the grafted PU sponge, the grafted sponge is placed on the seawater. From Figure 2h, it can be seen the sponge can float on water and never sink in seawater due to their superhydrophobicity and light weight. When it is immersed in seawater by loading an external force, the grafted PU sponge is surrounded by air bubbles (Figure 2i). After releasing the external force, the grafted PU sponge can float immediately on water surface.

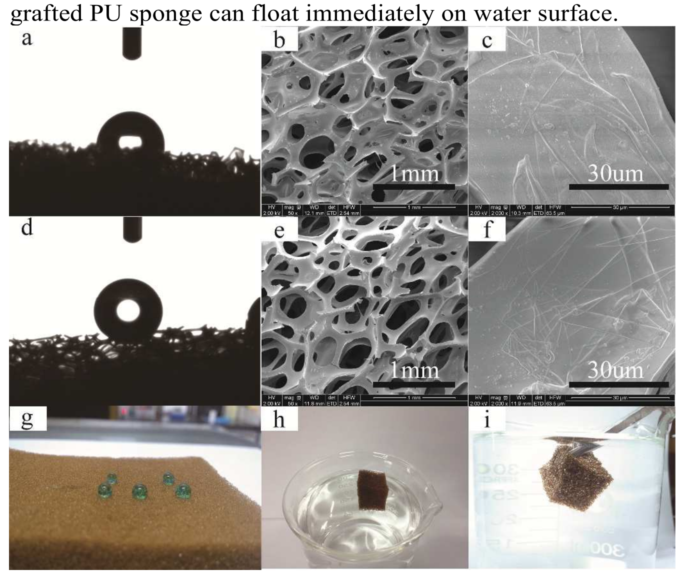


Figure 2. Characterization of PU sponge before (a, b, c) and after (d, e, f, g, h, i) grafting treatment. a) The optical image of seawater contact angle of the blank PU sponge (the seawater contact angle is about 94º). b) Low-magnification SEM image of blank PU sponge. c) High-magnification SEM image of blank PU sponge. d) The optical image of seawater contact angle of the grafted PU sponge (the seawater contact-angle is about 152º). e) Low-magnification SEM image of grafted PU sponge. f) High-magnification SEM image of grafted PU sponge. g) The optical image of seawater droplets on the grafted PU sponge surface. h) Optical image of the grafted PU sponge floated on seawater owing to its hydrophobic and light weight. i) Optical image of the grafted sponge immersed in seawater by an external force, exhibiting a silver mirror-like surface due to the surrounded air bubbles.

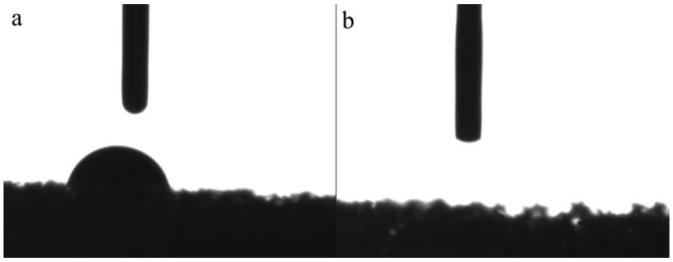


Figure 3. The crude oil contact angle images of PU sponge before (a) and after (b) grafting treatment. a) The oil contact angle of the blank PU sponge is about 81º. b) The oil contact angle of grafted sponge is about "0º".

Oil-wetting properties and oil absorption rate of the grafted PU sponge

The wettability of the PU sponges to oils is investigated via testing the oils contact angle. To the low viscosity oil (hexadecane), both the oil contact angles of the blank and grafted PU sponge are "0º" (the oil could be absorbed into sponge due to theirs lipophilicity and capillary force of the porous). But, to the crude oil (unless otherwise indicated, the crude oil viscosity is 208cp at 25ºC), the crude oil contact angle of the blank PU sponge is about 81º (Figure 3a). And the crude oil contact angle of grafted sponge is about "0º" (Figure 3b). The crude oil spreads on the surface and permeates into the body of grafted sponge, showing the excellent oil-wetting property. To test the crude oil wettability of the blank and grafted PU sponges, both sponges are placed on the surface of the crude oil at the same time (Figure 4, Movie S1 in the Supporting Information). It can be seen that the blank PU sponge floats on the surface of the crude oil in the whole process due to its poor oil wettability. The grafted sponge submerges in crude oil in 70 seconds. The significant difference of the oil absorption rate between blank sponge and grafted sponge also indicates the excellent oil-wetting property of the grafted PU sponge. The hexadecane and crude oil contact angles of the two kind sponges indicate they can be wetted by oil on the thermodynamics. But the difference of the oil absorption rate between the two kind sponges shows the grafted sponge can be easily wetted by high viscosity oil on kinetics. The surface wettability depends on the geometric structure and chemical state of materials.[32] In this study, we think the chemical state of the surface molecules maybe significantly impact on the wettability of the sponge. The superhydrophobicity and superlipophilicity of the grafted sponge are ascribed to the polymer brushes on the surface of grafted PU sponge. The polymer brushes expand in good solvents (Scheme 2a) and collapse in poor solvents and air (Scheme 2b), respectively.[33] The changes of polymer molecule conformations lead to different surface wettability of substrate.[34] To the long chain alkyl, seawater is poor solvent while oil is good solvent. When long chain alkane with low surface energy contact with seawater, it will curl into a ball to form a hydrophobic layer. The hydrophobic layer increases the difficulty of the seawater replacing the air trapped in the surface micro/nanostructures. When long chain alkyl contacts with oil, it will swell and expand to form a transition layer. The transition layer increases the oil spreading rate with replacing the air trapped on the surface of the sponge. With the high wettability, the oil absorption rate will speed up by the capillary forces, based on the Young–Laplace equations.[35]

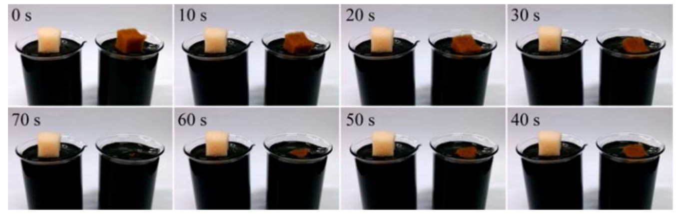
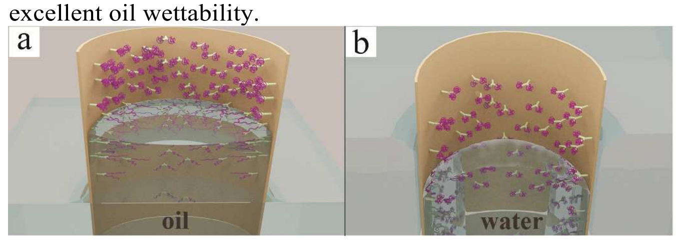


Figure 4. Photographs showing the immersion process of crude oil of blank (left) and grafted sponge (right). The blank sponge floats on the surface of the oil with poor oil wettability and the grafted sponge completely submerged in oil in 70 seconds with excellent oil wettability.



Scheme 2. Illustration for planar polymer brushes: a) A homogeneous smooth layer of stretched chains in good solvent. b) A layer of collapsed chains in poor solvent.

When oil leaking accident happens, the quick spreading, evaporation and emulsification processes lead to an increase in oil viscosity and a decrease in oil liquidity. So the velocity of oil absorption and absorption ability of high viscosity oil are particularly important for the oil absorption materials. In Figure 5a, it can be seen that the immersion time increases along with the increase crude oil viscosity. Even for the crude oil with a high viscosity of 1082cp, the grafted sponge is completely immersed in 166s. And the immersion time of blank sponge is more than 1 hour. In Figure 5b, it is shown that the grafted sponge can absorb about 23 times crude oil (the crude oil viscosity is 208cp at 25ºC) of its own weight at saturated state. In contrast, the crude oil capacity of blank sponge still keeps very low with the increase of time. Except for crude oil, the grafted sponge also exhibits a good adsorption of wide range of organic solvents (Figure 5c) such as chloroform, methanol, toluene, n-hexane, petroleum ether, etc. In table 1, the viscosity of organic solvents is much lower than that of crude oil and peanut oil. So the oil capacity and immersion time of the grafted sponge are similar to that of the blank sponge to organic solvents. However, to the much higher viscosity oil of crude oil and peanut oil, there are significant differences between the grafted and blank sponge on oil capacity and immersion time due to the poor oil wettability of blank sponge.

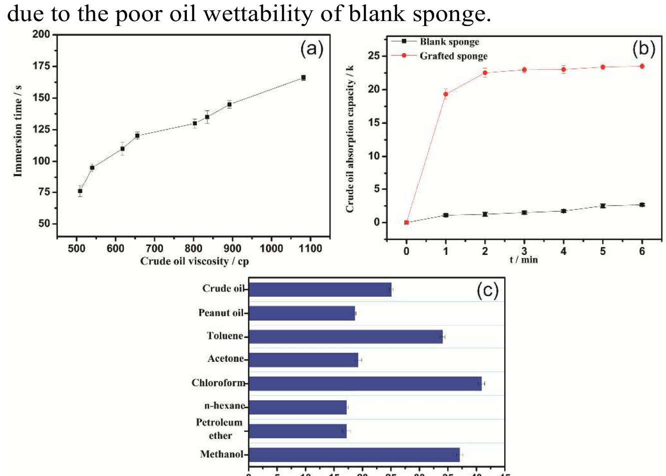


Figure 5. a) The variation of immersion time of the grafted sponge in different viscosity of crude oils. b) The crude oil absorption capacities of blank (black line) and grafted (red line) sponges under different time. c) Absorption capacities of the grafted sponge for oils and organic solvents.

Table 1. Comparisons of different oils on oil viscosity (20ºC), oil capacity and immersion time of grafted sponge and blank sponge

		Crude oil	Peanut oil	Toluene	Acetone	Chloroform	n-hexane	Petroleum ether	Methanol
Viscosity (cp)		377.00	96.00	0.58	0.33	0.56	0.64	0.23	0.51
Oil capacity (g/g)	Grafted sponge	25.06	18.65	34.04	19.23	40.91	17.23	17.18	37.08
	Blank sponge	3.74	6.83	32.51	18.95	40.15	17.31	16.88	36.85
Immersion time (s)	Grafted sponge	45.7	32.9	1.4	1.7	1.8	1.2	1.4	2.2
	Blank sponge	>>3600	>>3600	2.5	3.0	3.6	1.9	3.0	4.1

Oil retention rate of the grafted sponge

When the sponge is saturated in the process of oil clean-up, we need to recycle the saturated sponge. So the sponge needs to have a certain oil retention property to avoid desorption of oil caused by oil own gravity or other external force before the recovery of oil. The oil retention property of sponge is not only determined by the porous of sponge and oil surface tension but also the adhesive force between oil and sponge surface. To test the oil retention rate of the sponge, we make the blank and grafted sponge saturated with crude oil before the test and centrifuged of 3000 rotation for 1 minute. By calculating, the oil retention (the crude oil viscosity is 803cp at 25ºC) of grafted sponge (93.7%) is higher than that of the blank sponge (85.3%) which will effectively avoid the secondary pollution in the process of saturated sponge recycling. From Figure 6a, we can see the oil retention rate increases with the crude oil viscosity due to the decrease crude oil fluidity. To the same oil viscosity, oil retention rate of the grafted sponge is higher than that of blank sponge which indicates the adhesive force between the grafted molecules and oil molecules. The mechanical properties and reusability of the grafted sponge are tested by squeeze of a clip. After 400 times squeeze, the sponge still has good hydrophobicity (Figure 6b), owing to the robust grafted hydrophobicity molecular. And the oil retention keeps above 90%, as shown in Figure 6b. The mechanical properties of the grafted sponge were evaluated by cyclic stress–strain measurements (Figure 6c). The cyclic stress–strain curves show that the grafted sponge is able to be compressed to large strains (80%) at a relatively low stress (5 to 12 kPa), owing to the high porosity and elasticity of the sponge. In Figure 6c, there is about 10% compressive strain of the grafted sponge recovered slowly after 100 times compression without plastic deformation after release of the pressure, which indicates its good mechanical strength and reusability.

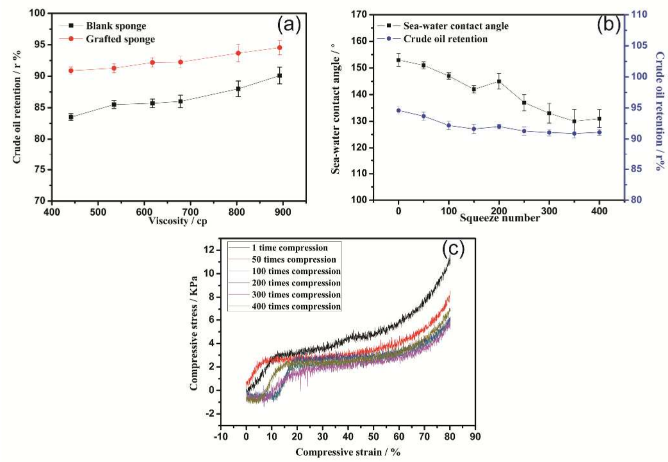


Figure 6. a) Oil retention of variation crude oil viscosity of blank and grafted sponge. b) Variation of seawater contact angles and crude oil retentions of the grafted sponges in repeated absorption/collection processes. c) Stress–strain curves of the grafted sponges in the process of mechanical compression.

Oil/water separation

Oil/water separation has great significance to water environmental and many studies work on the oil/water separation.[36,37] The above excellent performances imply that the grafted sponge can be suitably used to absorb oil and organic solvents when they are leaked on the seawater. In Figure 7a, when a piece of grafted sponge was brought into contact with oil on water surface, it rapidly and completely absorbed the oil (Movie S2 in the Supporting Information). Subsequently, when the sponge was picked up, clean water remained. After the absorption, a simple squeeze could achieve the oil recycle.

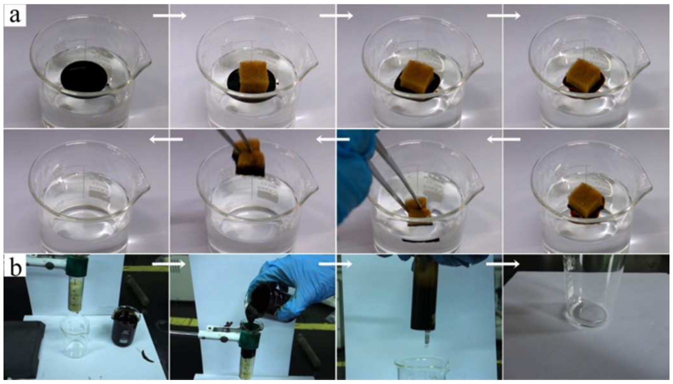


Figure 7. a) Sorption process of crude oil by the grafted sponge. b) Separation process of water-in-oil emulsion.

When the oil spill accident happened, the oil will float on the sea water and they are in a state of macroscopic phase separation. Under the action of external force of wind and tides, oil will interact with water and form two kinds of emulsion: water-in-oil and oil-in-water. The diameter of dispersed phase in the emulsion is less than 20μm.[38] Moreover, the stability of the water-in-oil emulsion is higher than that of oil-in-water, which increases the difficulty of the separation of oil/water.[39] Due to its high oil wettability and oil retention rate, we use the grafted sponge to realize demulsification of water-in-oil emulsion. From figure 7b (Movie S3 in the Supporting Information), it is found that when the water-in-oil emulsion flows in the body of the sponge, the oil absorbed on the surface of the sponge and the water will separate from the oil realized demulsification. To accelerate the high viscosity emulsion' moving and the extrusion of the water, external force is loaded. Due to the strong adsorption capacity of the sponge, there is no oil flowing out. And the extrusion of the water is clean and transparent.

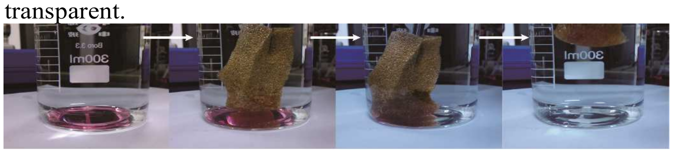


Figure 8. Sorption process of oil under water by the grafted sponge.

In addition, if an oil droplet is placed on a solid surface in water, the contact angle of an oil droplet in water, θ_{OW}, is given by Young's equation:

$$\cos\theta_{OW} = \frac{\gamma_{OA}\cos\theta_O - \gamma_{WA}\cos\theta_W}{\gamma_{OW}} \quad (3)$$

Where θ_O and θ_W are the contact angles of oil-air and water-air interfaces, respectively. Where γ_{OA}, γ_{WA}, and γ_{OW} are the surface tensions of the oil-air, water-air, and oil-water interfaces, respectively. [40] As predicted by equation 3, the superhydrophobicity ($\cos\theta_O > 0$) and superlipophilicity ($\cos\theta_W < 0$) PU sponge is oleophilic ($\cos\theta_{OW} > 0$) in the water. So the grafted PU sponged can clean up oil under water. From Figure 8, we can see the chloroform (dyed by oil red O) is completely absorbed by the grafted sponge.

Conclusions

In conclusion, a superhydrophobicity/superoleophilicity PU sponge is fabricated by environmentally friendly surface grafting polymer molecular brushes. It exhibits high absorption capacity (23 times to self-weight), high oil retention (93%), high mechanical strength and good recyclability (more than 400 times). And it can be used for the larger scale and quick cleanup of marine spilled oil/organic solvents and separation/recycling of oil-water mixture/emulsion. The method in this study not only provides way to the functionalization of polyurethane but also makes its industrialized possibility.

Acknowledgements

Projects 51105356 and 51335010 supported by National Nature Science Foundation of China. This material is also based upon work funded by National Basic Research Program of China (No. 2014CB6433), Zhejiang Provincial Innovation Team (Grant No. 2011R50006) and Ningbo Municipal Innovation Team (Grant No. 2011B31023).

Notes and references

[a] Key Laboratory of Marine New Materials and Related Technology, Zhejiang Key Laboratory of Marine Materials and Protection Technology, Ningbo Institute of Material Technology & Engineering, Chinese Academy of Sciences, Ningbo, 315201, P. R. China.

[b] School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai, 200240, P. R. China..

† Electronic Supplementary Information (ESI) available: Movie S1, S2, S3, S4 of oil absorption rate comparison, surface oil absorption, oil-water separation, under water oil absorption, respectively. See DOI: 10.1039/b000000x/

1 P. W. Sammarco, S. R. Kolian, R. A. F. Warby, J. L. Bouldin, W. A. Subra, S. A. Porter, Mar. Pollut. Bull. 2013, 73, 129.
2 C. Spier, W. T. Stringfellow, T. C. Hazen, M. Conrad, Environ. Pollut. 2013, 173, 224.
3 S. H. Newman, D. W. Anderson, M. H. Ziccardi, J. G. Trupkiewicz, F. S. Tseng, M. M. Christopher, J. G. Zinkl, Environ. Pollut. 2000, 107, 295.
4 L. M. Romero, M. Wikelski, Spill Sci. Technol. Bull. 2002, 7, 309.
5 A. Bayat, S. F. Aghamiri, A. Moheb, G. R. Vakili-Nezhaad, Chem. Eng. Technol. 2005, 28, 1525.
6 H. M. Choi, R. M. Cloud, Environ. Sci. Technol. 1992, 26, 772.
7 S. Cunneff, D. Devitis, J. Nash, Spill Sci. Technol. Bull. 2000, 6, 353.
8 P. S. Daling, I. Singsaas, M. Reed, O. Hansen, Spill Sci. Technol. Bull. 2002, 7, 201.
9 R. D. Delaune, C. W. Lindau, A. Jugsujinda, Spill Sci. Technol. Bull. 1999, 5, 357.
10 R. G. M. Hanna, Spill Sci. Technol. Bull. 1995, 2, 171.
11 J. V. Mullin, M. A. Champ, Spill Sci. Technol. Bull. 2003, 8, 323.
12 H.-M. Choi, J. P. Moreau, Microsc. Res. Tech. 1993, 25, 447.
13 T.-T. Lim, X. Huang, Chemosphere 2007, 66, 955.
14 T.-T. Lim, X. Huang, Ind. Crops Prod. 2007, 26, 125.
15 M. Toyoda, M. Inagaki, Carbon 2000, 38, 199.
16 B. Wu, M. H. Zhou, Waste Management 2009, 29, 355.
17 X. Zhang, Z. Li, K. Liu, L. Jiang, Adv. Funct. Mater. 2013, 23, 2881.
18 X. Gui, H. Li, K. Wang, J. Wei, Y. Jia, Z. Li, L. Fan, A. Cao, H. Zhu, D. Wu, Acta Mater. 2011, 59, 4798.
19 G. Hayase, K. Kanamori, M. Fukuchi, H. Kaji, K. Nakanishi, Angew. Chem. Int. Ed. 2013, 52, 1986.
20 J. Lin, Y. Shang, B. Ding, J. Yang, J. Yu, S. S. Al-Deyab, Mar. Pollut. Bull. 2012, 64, 347.
21 Y. Zhang, S. Wei, F. Liu, Y. Du, S. Liu, Y. Ji, T. Yokoi, T. Tatsumi, F.-S. Xiao, Nano Today 2009, 4, 135.
22 A. Li, H.-X. Sun, D.-Z. Tan, W.-J. Fan, S.-H. Wen, X.-J. Qing, G.-X. Li, S.-Y. Li, W.-Q. Deng, Energy Environ. Sci. 2011, 4, 2062.

23 D. D. Nguyen, N.-H. Tai, S.-B. Lee, W.-S. Kuo, Energy Environ. Sci. 2012, 5, 7908.
24 C. Wu, X. Huang, X. Wu, R. Qian, P. Jiang, Adv. Mater. 2013, 25, 5658.
25 H. Bi, Z. Yin, X. Cao, X. Xie, C. Tan, X. Huang, B. Chen, F. Chen, Q. Yang, X. Bu, X. Lu, L. Sun, H. Zhang, Adv. Mater. 2013, 25, 5916.
26 M. Inagaki, New Carbon Materials 2009, 24, 193.
27 P. Calcagnile, D. Fragouli, I. S. Bayer, G. C. Anyfantis, L. Martiradonna, P. D. Cozzoli, R. Cingolani, A. Athanassiou, ACS Nano 2012, 6, 5413.
28 P. F. Kingston, Spill Sci. Technol. Bull. 2002, 7, 53.
29 I. Rotaru, M. Ionescu, D. Donescu, M. Vuluga, Mater. Plast. 2008, 45, 23.
30 Q. Zhu, Y. Chu, Z. Wang, N. Chen, L. Lin, F. Liu, Q. Pan, J. Mater. Chem. A 2013, 1, 5386.
31 C. Su, Appl. Surf. Sci. 2009, 256, 1413.
32 F. Zhang, W. B. Zhang, Z. Shi, D. Wang, J. Jin, L. Jiang, Adv. Mater. 2013, 25, 4192.
33 Z. Xue, S. Wang, L. Lin, L. Chen, M. Liu, L. Feng, L. Jiang, Adv. Mater. 2011, 23, 4270.
34 X. Liu, Q. Ye, X. Song, Y. Zhu, X. Cao, Y. Liang, F. Zhou, Soft Matter 2011, 7, 515.
35 N. Tas, N. Brunets, J. Honschoten, J. Haneveld, H. Jansen, in Transport and Reactivity of Solutions in Confined Hydrosystems, (Eds: L. Mercury, N. Tas, M. Zilberbrand), Springer Netherlands, 2014, 29.
36 L. Feng, Z. Zhang, Z. Mai, Y. Ma, B. Liu, L. Jiang, D. Zhu, Angew. Chem. Int. Ed. 2004, 43, 2012.
37 S. Minko, J. Macromol. Sci., Polym. Rev. 2006, 46, 397.
38 A. K. Kota, G. Kwon, W. Choi, J. M. Mabry, A. Tuteja, Nat Commun 2012, 3, 1025.
39 M. Fingas, Spill Sci. Technol. Bull. 1995, 2, 55.
40 Y. C. Jung, B. Bhushan, Langmuir 2009, 25, 14165.