# Superhydrophobic treatment of polyurethane sponge and its application in oil-water separation

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**Abstract**

*The superhydrophobicity of the polyurethane sponge was realized by attaching the complex of copper and mercaptan on the outer surface of the polyurethane sponge. As a special case，the complex of 1-dodecanthiol and copper chloride was intensively investigated in this study , with emphasis on the influences of concentration, temperature and residence time on the reaction. SEM and EDS were used to analyze the surface structure and elemental composition of the sponge. The superhydrophobicity of the sponge are contributed by the rough treatment on sponge surface. It is found that a large number of long carbon chains appear on the surface reduces the surface energy. The wettability of the surface was determined by a contact angle meter. The material demonstrates great oil-water separation performance and high repeatability in superhydrophobicity during the the separation process of oil and water before first 39 times.*

**Keywords**: *Superhydrophobicity; Polyurethane sponge; Oil/water separation; Wettability*

## 1. Introduction

*With the continuous development of industry and agriculture, the consumption of petroleum and other energy products has been increasing[1].The environmental pollution[2] caused by the leakage of oil products is becoming increasingly serious[3]. The oil spill accidents reported in recent years have resulted in a spate of water pollution[4] .area variety of treatment technologies, including physical, chemical and biological [567]methods have been developed or the treatment of contaminated water. Physical method is simple but has low efficiency. Both chemical and biological methods require addingchemical reagents in polluted water sources, which can pose a high risk of secondary pollution. With the emergence and development of new materials[8], efficient oil-water separation materials[9]have gain increasing attentions in recent years for the treatment of contaminated water[1011],given its unique advantages of high efficiency and no pollution[12].*

*The understanding of the superhydrophobic surface[13] originates from some plants and animals in nature[14].They are waterproof, anti-fouling, reducing resistance and so on[1516]. There are differences in the way superhydrophobic surfaces are constructed, but there are two main steps :(1) Construct a rough surface (2) Modified with low surface energy substances.*

*Polyurethane sponge[17], as the basis of materials[18], shows great advantages in practical application since it has the characteristics of high porosity, low cost and excellent stability[19202122].*

*In this experiment, the compounds of mercaptan and bivalent copper[2324] were prepared and then covered in the surface of PU sponge[25], so that the sponge had the superhydrophobicity. It is also found that superhydrophobic sponge has excellent performance in oil and water separation[26].*

## 2. Experimental

### 2.1 Reagents

*High-density sponge,200-400 μm; Medium-density sponge,330-480 μm; Low-density sponge,700-850 μm, all sponges were bought from Nanjing Yongsheng sponge factory; Sodium hydroxide, AR; Copper chloride, AR; Decyl mercaptan, AR; 1-Dodecanethiol;AR; 1-Octadecanethiol,AR; Sudan Red, AR; Dimethylbenzene, AR; Ethanol, AR; All reagents were bought from Shanghai Taitan Technology.*

### 2.2 Preparation of superhydrophobic sponge

*First, the sponge(2cm×2cm×1cm) was washed with sodium hydroxide solution for 15 min to remove the grease from the sponge, and then deionized water was used for ultrasonic washing for 15 min, drying and waiting. In the ratio of 4:1, the temperature is 30 ℃, the time is 8 min, and the pH is 8, and the reaction of 1-dodecanthiol and copper chloride is precipitated. By dispersing dry solid ultrasound into ethanol, the dispersion of 8 mg $mL^{-1}$ was obtained. The clean PU sponge was added to the dispersion solution, and the ultrasound was used for 15 min, drying and obtaining the product. The treatments were similar to the preparation of the superhydrophobic sponge using decyl mercaptan or 1-octadecanethiol .*

### 2.3 Characterization

*The surface morphology and structure of the samples were analyzed by scanning electron microscopy (S-3400 N, Hitachi, Japan). The composition of the sample was quantified using an energy spectrometer (ESCALAB 250 xi, Thermo Fisher Scientific, USA). The wettability of the sample was analyzed by static contact angle meter (YIKE-360 A, Chengde Yike, China). The droplets were distilled water, and the water volume was 3 μL, the droplets were discontinuous. In order to ensure the reliability of the experiment, five different areas were selected for the surface of the sample.*

## 3. Results and discussion

### 3.1 The influence of the ratio of mercaptan to copper chloride

*The weight of copper chloride was controlled at 1g, the complexes were prepared, the ratio of 1-dodecanthiol to copper chloride was 1:2、1:1、2:1、3:1、4:1、5:1. Fig.1 shows the variation of weight with proportion. When the ratio of mercaptan to copper chloride was 4:1, the weight of the product was the largest. It was observed that the color of final solution was blue when the ratio was less than 4:1 and the solution is colorless at 4:1. The experiment found that when the ratio was greater than 4:1, a large amount of mercaptan was wrapped by the product, which resulted in* *a decrease in weight. After the complexes were attached to the sponge, the water contact angle on the sponge was determined.Fig.2 shows the relationship between the water contact angle and the ratio. The maximum standard deviation of the contact angles in this investigation is 2.3 and the average standard deviation is 1.8. The results show that the contact angle has weak relation with the ratio. EDS analysis showed that the ratio of mercaptan to copper in the complexes was n:1, and the proportion of each product was distributed.*

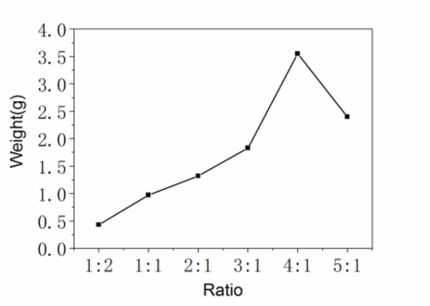


*Fig.1 The influence of the ratio on the weight*

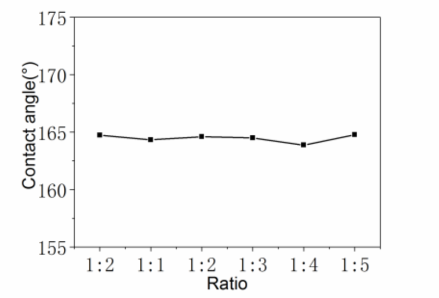


*Fig.2 The influence of the ratio on water contact angle*

**3.2 The influence of temperature on the weight**

*The temperature is an important influence factor in most chemical reactions. In order to determine the optimalconditon, the reaction temperature was controlled to obtain its relationship with the product weight, as shown in Fig.3. The weight of complex increased slowly with the increase of temperature when below 30 ℃, and became stable when above 30 ℃. In general, little influence has been found of temperature in the product weight. , which is caused by a high reaction rate . The optimal reaction temperature is found to be 30 ℃.*

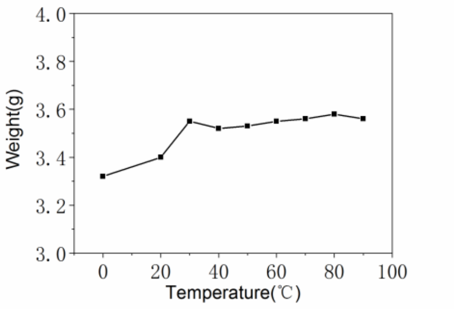

*Fig.3 The influence of temperature on the weight of products.*

### 3.3 The influence of reaction time on the weight

*The reaction time isanother important factor in chemical reactions. In order to explore the influence of reaction time on the product weight, the weight of the product at different times was measured to determine the optimal time. The reaction of complex was enhanced by applying ultrasonic at 50 kHz. According to the Fig.4, the product weight increased with the reaction time at first 7 mins, and reached plateau afterwards. So the optimal reaction time is found to be 8 min.*

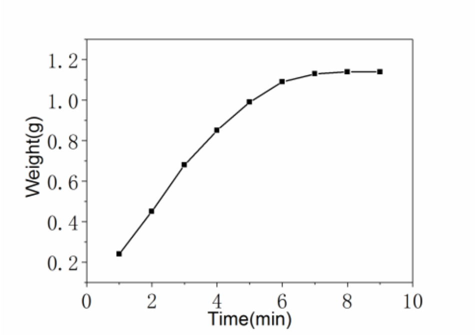


*Fig.4 The influence of reaction time on the weight of the product.*

### 3.4 The influence of pH on the weight

*The pH would affect the ionization of mercapto group in solution and then the forming of complex. The influence of pH on the product weight was explored.Fig.5 shows the relationship between the pH and the product weight . The weight was almost the same as the pH were 2 and 4, then the weight increased sharply with the rise of pH and reached the maximum value at the pH of 8.When the pH of the reaction is less than 8, the degree of -SH ionization in dodecanethiol*[27] *is limited. There are a small ammount of thiols that can be coordinated with copper ions and only little complex forms as the pH of reaction is less than 8.When pH >8, the weight decreased rapidly, which can be explained bythat a large amount of copper precipitated in the form of copper hydroxide.*

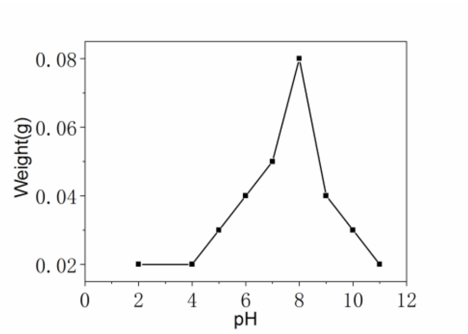


*Fig.5 The influence of the pH on the weight.*

### 3.5 The influence of concentration on wettability

*As shown in Fig.6 A, the pristine sponge is not hydrophobic with the water contact angle of 93 ° ,the hydrophobicity of sponge could be developed by the method indicated in 3.1-3.4 and 2.2. Here, the influence of the concentration of complex in suspension on the wettability was explored. The results are shown in Fig.7,The maximum standard deviation of the contact angles in this investigation is 3.6 and the average standard deviation is 1.9., the water contact angle on the sponge rises slowly from 152°to 164° with the increase of concentration of complex in suspension liquid from 2 mg $mL^{-1}$ to 12 mg $mL^{-1}$.Fig.7 also shows that the contact angle is 147 ° with the concentration of 0.2 mg $mL^{-1}$.The investigation found it was easy for the complex to fall out from the sponge when the concentration was higher than 8 mg $mL^{-1}$. The reason may be the sponge is overloaded for the complex. So the optimal concentration of complex was set at 8 mg $mL^{-1}$.Fig.6 B shows the water contact angle of 166° on the superhydrophobic sponge.*

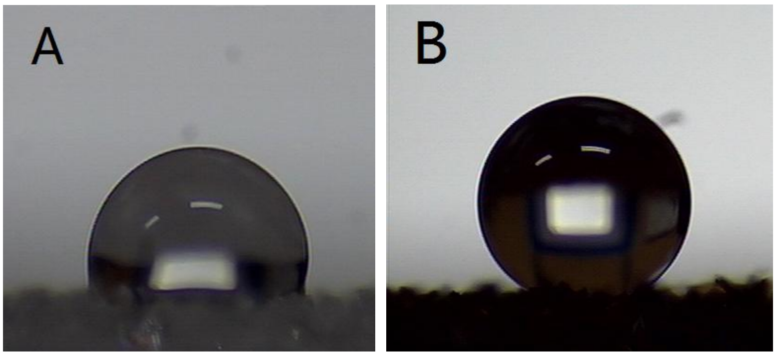


*Fig.6 Static water contact angle on sponge before and after treatment.*

*In order to explore the effect of the pore size on the wettability, three sponges with different pore sizes were investigated. The complex was distributed to those sponges as mentioned in 2.2, and the water contact angle on those sponges attached with complex was measured, the results are also contained in Fig.6,the contact angles differ a little for the medium density sponge and low density sponge, the reason is considered that the size of pore for the medium density sponge and low density sponge is larger than the size of water drop, and the high density sponges with smallest size of pore show the biggest contact angle at different concentration.*

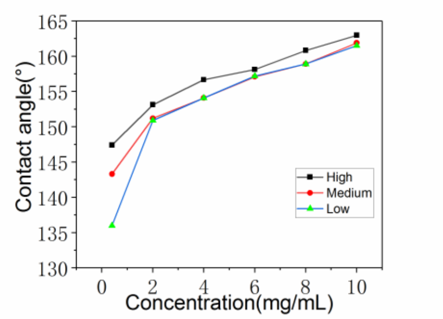

*Fig.7 The influence of concentration on wettability.(High---high density sponge;Medium---medium density sponge;Low---low density sponge)*

## 3.6 The influence of the mercaptans on wettability

*The different lengths of the carbon chains for mercaptans can affect the wettability of the sponge. In this investigation, three mercaptans, decyl mercaptan, 1-dodecanethiol and 1-octadecanethiol were used because they are available in the market. The complexes of those mercaptans with copper chloride were prepared and distributed to the sponges respectively. The water contact angle on those three kinds of sponges were measured and the result is shown in Fig.8.The maximum standard deviation of the water contact angles in this investigation is 1.7 and the average standard deviation is 1.4. According to the Fig.8,with the increase of carbon chain for mercaptans, the contact angle on the sponge rises within for concentration of 2、4、6、8 mg mL$^{-1}$.Since 1-octadecanethiol is more expensive than 1-dodecanethiol and the water contact angle of the sponge attached with complex of 1-dodecanethiol-copper also larger than 150° at the concentrations showing Fig.8. So the 1-dodecanethiol was selected.*

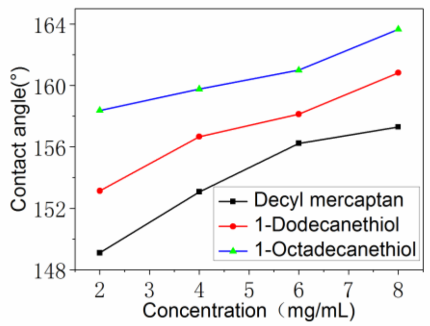


*Fig.8 The effect of the type of mercaptan on the wettability of materials.(Decyl mercaptan---Sponge attached by complex of decyl mercaptan with copper chloride;1-Dodecanethiol---Sponge attached by complex of 1-dodecanethiol with copper chloride;1-Octadecanethiol---Sponge attached by complex of 1-octadecanethiol with copper chloride)*

## 3.7 Surface structure of the sponge

*Fig.9 shows the surface structure of the pristine and superhydrophobic sponge with SEM images. From Fig. 9, the pristine sponge has a smooth surface(Fig.9.A-B), and the surface of superhydrophobic sponge is rough(Fig.9.C-D).The solid particles produced by copper chloride and dodecyl mercaptan are attached to the surfaces of sponges resulting in the sponge's rough surface. It is believed that the roughness of surface is one of key factors for the superhydrophobicity.*

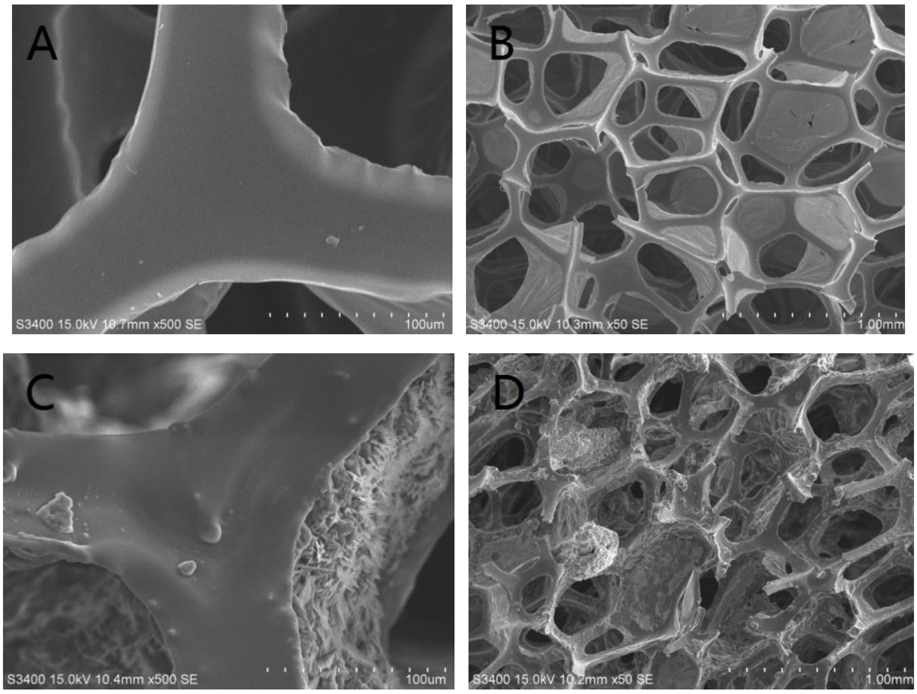


*Fig.9 SEM analysis of sponge surface.(A and B are SEM images of the pristine sponge;C and D are SEM images of superhydrophobic sponge)*

### 3.8 EDS for the surface of sponge

*To verify the complex of mercaptan and copper chloride were attached to the surface of the superhydrophobic sponge, EDS was used to identify the presence of sulfur and copper on the sponge. The result was shown in Table.1.From the Table.1, sulfur and copper are found in the superhydrophobic sponge and their content in weight reach 8.16％and 8.24％.It demonstrates that the complex was attached to the surface of the sponge.*

*Table.1 EDS for the surface of pristine sponge and superhydrophobic sponge*

| Elements | Pristine sponge(Wt％) | Superhydrophobic sponge(Wt％) |
|---|---|---|
| C | 61.42 | 71.04 |
| N | 9.00 | 02.83 |
| O | 28.63 | 08.90 |
| Cu | 0 | 08.24 |
| S | 0 | 08.16 |

### 3.9 The application of the hydrophobic sponge

*The superhydrophobic sponge has a potential application in the separation of oil and water. Firstly, the superhydrophobic sponge is compared with the pristine one. Dimethylbenzene, 1, 2-dichloroethane, isocinol and hexane were used as oil phases respectively, and Deionized water as another phase. To mark the oil phase, a little Sudan red is dissolved in it. 20 mL water and 20 mL organic solvent with sudan red were added into a 50 mL beaker, then the superhydrophobic sponge(2cm×2cm×1cm) was fully compacted put at the surface of oil and water. The sponge was taken out from the beaker after the sponge fully absorbed the mixture. In the next step, the liquid in the sponge was squeezed out completely into the measuring cylinder. the oil and water were observed in the measuring cylinder. The result, as shown in Fig.10, indicates that the pristine sponge shows no obvious selectivity in the separation of oil and water while the superhydrophobic sponge only absorb the oil for the four organic solvents in the investigation.*

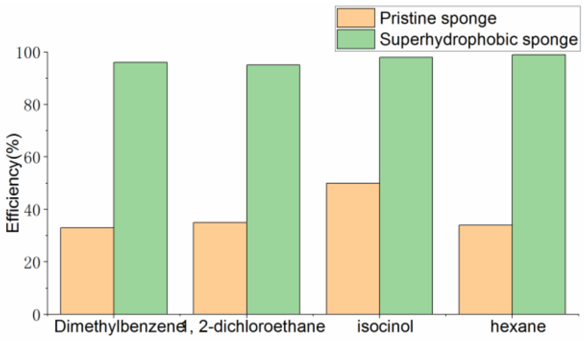


*Fig.10 The efficiency of pristine and superhydrophobic sponge to absorb the oil phase.*

*For some reasons, the wettability of the superhydrophobic sponge will decrease after repeated use. To learn how many times the sponge can be used, the relationship between the contact angle and the number of separation times of oil and water for sponge was studied. Using dimethylbenzene as the oil phase. The process[28] of the study was carried out as show in Fig.11,(A)Add 50 mL water to a clean beaker;(B) Add 1 mL dimethylbenzene in the beaker, containing a little sudan red;(C)Put a piece of superhydrophobic sponge(2cm×2cm×1cm) in the beaker to absorb the oil phase.(D)Took the sponge absorbed the oil out the beaker, the water in the beaker was clear without the oil phase;(E)The sponge squeezed out the oil with tweezers and used to absorb the dimethylbenzene again, as described in step C, then repeat D and E；When the number of repetition for the absorption reached 1、2、4、7.......as shown in Fig.12.In this investigation, the maximum standard deviation and the average standard deviation of the water contact angles on the sponge are 3.3 and 2.0 separately. The sponge was dried in the oven at 80 ℃ until it evaporated fully, then measured the contact angle to identify its wettability. The result was illustrated in Fig.12,from the Fig.12, the water contact angle decreases from 166° to 153° in the* *first 11 times and goes down slowly to 150° at the 39 th times, while the repeatability in previous studies was only about 10 times*[29,30]*. It is believed that the the superhydrophobic sponge can be used for at least 10 times in practice.*

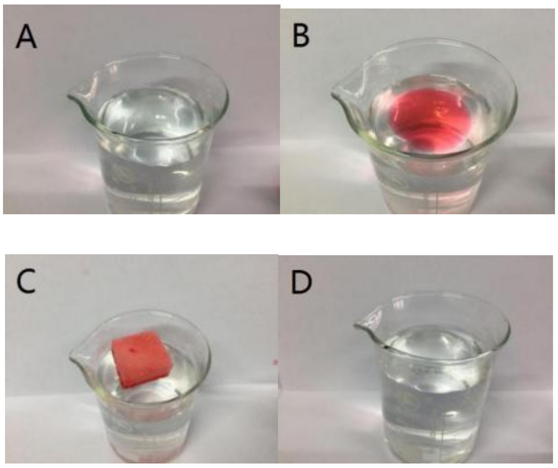


*Fig.11 The process of oil and water separation .*

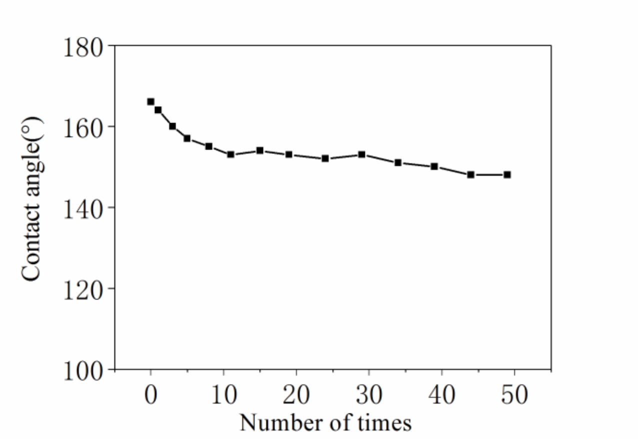


*Fig.12 Relation between the number of separation and wettability.*

## 4. Conclusion

*In this paper, a novel superhydrophobic sponge made of complex of 1-dodecanthiol and copper chloride was developed for separation of oil and water. The surface structure and elements of the sponge were identified by SEM and EDS, showing the complex was attached to the sponge surface and increased the surface roughness. The water contact angle on the sponge was measured to characterize its wettability. It was found that the superhydrophobic sponge was developed successfully as indicated by a large water contact angle ,which is larger than 150°. The superhydrophobic sponge was studied in application of separation of oil and water. The results show that the developed superhydrophobic sponge only adsorbs the oil phase and demonstrated excellent selectivity for separation of oil and water. The sponge can be used repeatedly up to 39 times. The superhydrophobic sponge developed in the paper have unique advantages, which provides new insights in oil-water separation.*

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