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Study on polyurethane-based porous materials and their adsorption properties

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Abstract:
The flexible superhydrophobic thermoplastic polyurethane(TPU) porous material was prepared by heat-induced phase separation method with two cooling steps. The influence of the preparation process on the microstructure of the material was discussed in depth. The microstructure, hydrophobicity and specific surface area of porous TPU materials were analyzed in detail. The surface wettability, separation selectivity, saturated adsorption capacity and adsorption rate, mechanical properties, environmental adaptability and cyclic properties of porous TPU materials were studied.The results show that the TPU-8% porous monolithic material prepared by heat-induced phase separation method shows good performance when the polymer concentration is 8%, the phase separation temperature is 0 ℃, the phase separation time is 30min, and the mixing solvent ratio is 9:1.
Keywords: *Polymer-based porous materials; Separation of oil and water; Oil recovery*

1 Introduction

In recent years, frequent oil spills and organic chemical spills around the world have caused almost irreversible damage to ecological environment and human health. How to efficiently and environmentally remove and recycle organic pollutants from polluted water bodies has become a key problem that governments all over the world urgently need to solve, and has attracted wide attention from the scientific community.[1-2]Current methods fall into three broad categories: physical methods (e.g. filtration, flotation and absorption), chemical methods (e.g. dispersion, solids and combustion) and biological methods (e.g. bioremediation).[3-7]Polymer-based porous materials show excellent water absorption and separation properties because of high porosity, large specific surface area and three-dimensional connected porous structure. So it shows excellent water absorption and separation performance. However, the high brittleness of the material leads to its poor durability, which makes it far from practical applications.In this case, the aim of this paper is to develop a sustainable, economical and durable oil-water separation material with efficient and rapidly recyclable oil-absorbing properties that can be used to treat contaminated water.

2 The experiment

2.1 Experimental materials and instrument and equipment

1, 4-dioxane and cyclohexane were purchased from Shanghai Zhanyun Chemical Co., Ltd.The polyurethane was purchased from BASF Co., Ltd.、Electronic balance, constant temperature heating magnetic stirrer, vacuum freeze dryer, ultrasonic cleaner, magnetic stirrer, scanning electron microscope, surface contact Angle measuring instrument, Fourier near infrared spectrometer.

2.2 Preparation of porous polyurethane materials

First, dissolve 8g TPU in a mixture (100ml) of 1, 4-dioxane / deionized water (v/v=9/1) under vigorous magnetic stirring at 60 ℃ for 90 min until becoming a homogeneous

solution.After the initial dissolution, the TPU was further dissolved in an ultrasonic cleaner at 80 ℃, so that the TPU was completely dissolved, and the homogeneous solution of 8% TPU was obtained.The mixture was then quickly transferred to a test tube with 20 mm outside diameter, and the test tube was placed in an ice bath (0 ℃)

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for 30 min for preliminary phase separation. Then the tube was moved to the refrigerator (-20 ℃) for 48h to complete the phase separation. Finally, the tube was put into the freeze dryer (-80 ℃) for 72h to prepare porous TPU composite.

The experimental conditions were changed to conduct a comparative experiment:T-1(TPU concentration: 4%, separation temperature: 0 ℃, separation time: 30min, mixing solvent ratio: 9:1),T-2(TPU concentration of 6%, separation temperature of 0 ℃, separation time of 30min, mixing solvent ratio of 9:1),T-3(TPU concentration: 8%, separation temperature: 0 ℃, separation time: 30min, mixing solvent ratio: 9:1),T-4(TPU concentration: 10%, separation temperature: 0 ℃, separation time: 30min, mixing solvent ratio: 9:1).

2.3 Characterization method

Scanning electron microscopy (SEM) was employed to observe the morphology of TPU monoliths, and contact angle (CA) measurements were performed on a Powereach JC2000C instrument at ambient temperature. The size of water droplets was 2μL, and the mode was circle fitting. Fourier infrared spectrometer (FTIR) was used to plot the relevant infrared spectra, and the scanning speed was $1cm^{-1}$, ranging from 650-4000.

2.4 Performance Detection

Take TPU-8% of samples for bending resistance, compression resistance, The physical properties of the samples were tested by weight test, the selective adsorption capacity of the TPU materials for the two typical separation of oil/organic solvent and water mixture was tested, and the stability and environmental adaptability of the samples were tested by the oil-water separation process of the whole TPU-8% material under the strong magnetic stirring simulation of ocean wave motion (-600rpm). Easily remove the oil and organic solvent adsorbed by the sample to test the recycling and recyclability of the sample.

3 Results and discussion

3.1 Characterization of the samples

3.1.1 Morphological analysis

The surface shapes and pore SEM maps at different SEM ratios at various TPU concentrations are shown in Figure 1.As shown in Figure 1,we can see from Figure, The T-1 sample did not present clear hole imaging and showed poor connectivity between holes;The T-2 sample showed a larger pore size and presented as filiform;The T-3 sample showed a three-dimensional connected porous pattern with a wide aperture distribution, showing a hemispherical hollow porous structure;The T-4 sample also showed a porous structure with thick connections between the skeletons.Therefore, when the TPU concentration is low (4-6%), the solution system viscosity is low, the phase separation rate is fast, the pore size grows rapidly and the pore size is large, and the irregular porous morphology, and the gap between 8% and 10% is small.

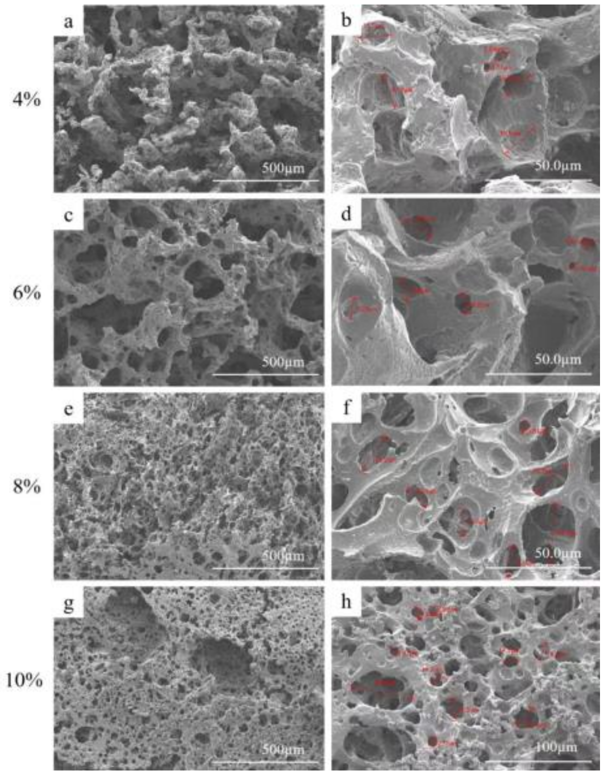

Figure 1 Surface shapes and pores at various TPU concentrations at different multiples of SEM

a:[4%,x100LM] b:[4%,x500LM] c:[6%,x100LM] d:[6%,x500LM] e:[8%,x100LM] f:[8%,x500LM] g:[10%,x100LM] h:[10%,x500LM]

3.1.2 WCA analysis

As shown in Figure 2a, several water droplets (dyed with potassium permanganate) are allowed to remain in astable spherical shape on the cross section of TPU-8% monolith, the water CA (144°) of the monolith reveals highhydrophobicity without any surface treatment. Figure 2b shows the oil wettability of TPU-8% monolith, where a drop of soybean oil (dyed with oil red) is immediately and completely absorbed into the monolith within 1 s once it touches the cross section of the monolith, which suggests that the oil CA is ～0°.

The above phenomena demonstrate the excellent hydrophobicity and superoleophilicity of the porous monolith.

Figure 2c presents the water CA values of the TPU film and porous TPU monoliths with different polymer concentrations.It can be easily observed that all TPU monoliths show hydrophobic property with water CA of ＞120°compared tothe hydrophilic TPU film (water CA of 84°). The maximum CA for TPU-8% monolith is 144°, which is close to superhydrophobicity (150°), reflecting the ultra-highly.drophobicity.

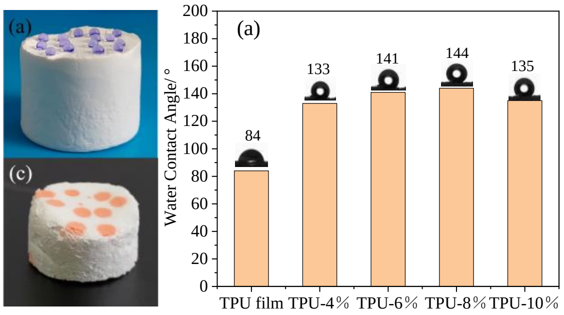

Figure 2 (a) image of water droplets (stained with methyl blue) on the cross section of TPU-8% of the material; (b) droplet angles of TPU and porous TPU, and (c) image of oil (stained with methyl red) on the cross section of TPU-8% of the material

3.1.3 Infrared spectrum analysis

Figure 3 shows the membrane prepared from the TPU-8% of the sample and the raw materials, making the infrared spectrum of the two samples.As shown in Figure 3,1765 – 1729 cm^{-1} as the ether bond, 1718 – 1704 cm-1 as the carboxyl group and 1 690 – 1650 cm^{-1} as the base.The infrared spectrum determined the different functional groups represented by each peak. The peak of this experiment was matched with the raw material and changed, reflecting the stability of the structure of the sample.Among them, 898-1327cm^{-1} is the C-H bending vibration peak, 1243cm^{-1} is the C-O-C vibration, 1505cm^{-1} is the aromatic ring skeleton vibration peak, and 1266cm^{-1} is the C=O expansion vibration.

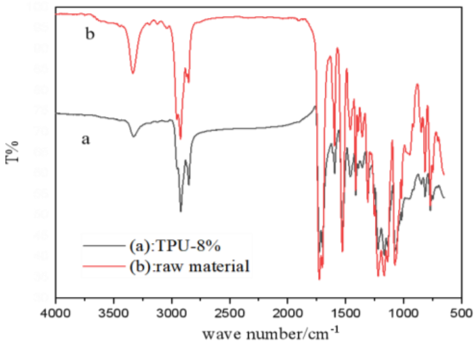

Figure 3 Sample infrared spectrum diagram: (a): TPU-8% solid; (b): raw material

3.2 Performance analysis

3.2.1 Analysis of the physical properties

Figure 4(a) presents after multiple manual bending, the sample can always quickly recover to its original state, reflecting the good bending resistance of the sample.Figure 4(b) presents a 400 g weight was placed for the compression test, and the sample showed good compression resistance.Figure 4(c) presents places the sample on the blade, and the blade is less variable and can be placed upright on the blade, indicating that the sample is relatively light.as illustrated in following figure.[11]

Figure 4 Photo of the TPU-8% material block showing (a) sample bending resistance test, (b) sample compression test, (c) light performance test

Figure 5 presents the curve of absorption capacity (Qt) for vegetable oil as a function of absorption time (t) to evaluate the absorption kinetics of TPU-8% monolith, where vegetable oil was chosen as a representative because of its difficult absorption induced by high viscosity. During testing procedure, the absorption equilibrium state of TPU-8% monolith is quickly reached within 20s, meaning a very rapid oil absorption rate. The absorption rate constant (k) can be obtained from the slope of linear regression plot of ln (Qs − Qt) [8]versus t. The highly consistent fitting result (R2 = 0.979) exhibited in the inset of Figure 3c reveals that the sorption kinetics of the monolith conforms to pseudo-first-order kinetics model with a k value of 6.96 The fast absorption rate of TPU-8% monolith is mainly attributed to its hierarchical interconnected macroporous structure and superoleophilicity.

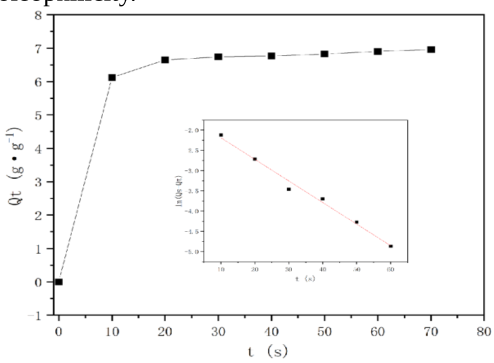

Figure 5 The picture shows the relationship of absorption capacity on adsorption time and the pseudo-first-order kinetic model of vegetable oil absorption by TPU-8% monomer (inset)

As shown in Figure 5, the absorption dynamics of TPU-8% material was evaluated by the function curve of the absorption capacity and absorption time of vegetable oil, among which vegetable oil was selected as a representative due to the difficulty in absorption caused by its high viscosity.During the test process, the TPU-8% material reached an adsorption equilibrium state between 20s and 30s, which means that the oil absorption rate is very fast, with an absorption rate constant of 6.96.The highly consistent fit shown in Figure results in R2=0.979.The rapid absorption rate of the TPU-8% material column is mainly attributed to its macroporous structure and superlipophilicity.[10]

3.2.2 Analysis of saturated adsorption performance

Figure 6 shows the bar graph of the saturated adsorption of TPU-8% monomer. The saturated absorption capacities (Qs) of TPU-8% monolith for different types of oils (vegetable oil, pump oil) and organic solvents (cyclohexane, ethanol, dichloromethane, tetrachloromethane) are shown in Figure 6. All Qs values are in the range of 6.64−35.87 g g−1[12],which are closely related to the viscosity and density of the absorbed oil and organic solvents.[9]

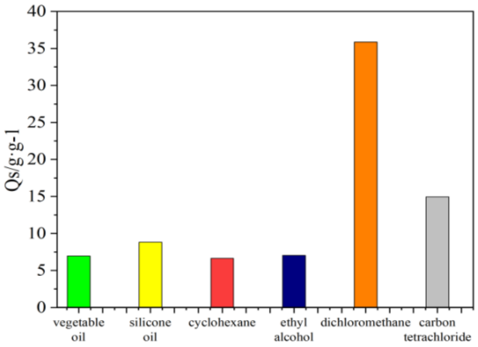

Figure 6 Bar chart of saturated adsorption amount of monomer to oil and organic solvent of TPU-8%

3.2.3 Analysis of stability energy and environmental adaptability energy

Figure 7 shows the oil-water separation process of the TPU-8% material under strong magnetic stirring simulating wave motion (-600rpm).Vegetable oil, suspended in a turbulent oil-water mixture, can be fully absorbed by the porous body within a few seconds, indicating good mechanical stability and environmental adaptability.

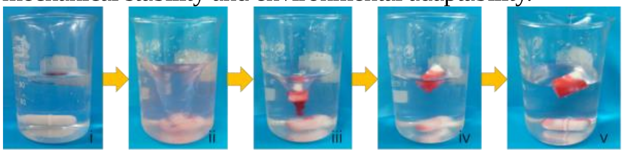

Figure 7 (i-v): The picture shows the separation of pump oil (oil red staining) from water (TPU-8% monomer) under strong magnetic stirring

3.2.4 Analysis of cycle performance and recyclable performance

Figure 8 shows the process of pumping the oil out of the water through the three absorption and extrusion cycles.As shown in Figure. 8, a typical absorption and extrusion process from oil floats or organic solvents in water, in which the floating pump oil can be removed through three cycles of absorption and extrusion processes.

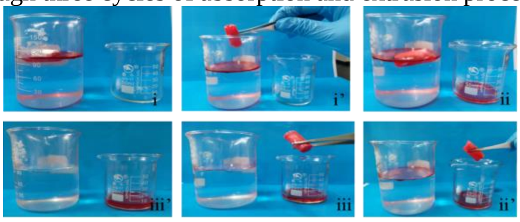

Figure 8 (i - i ’; ii - ii ’;iii-iii’):The picture shows the process of pumping oil out from the water through three absorption and extrusion cycles

Figure 9 shows the line diagram of the saturated adsorption of TPU-8% monomer to vegetable oil by absorption extrusion.As shown in Figure 9, for reused TPU materials of vegetable oils, stable Qs values were shown when tested for 20 cycles, but it is noteworthy that the tested Qs were significantly reduced in the second cycle, because the high viscosity of the oil was difficult to be completely removed by the manual extrusion process.Materials reused in subsequent cycles maintained stable Qs values even by centrifugation and evaporation methods.

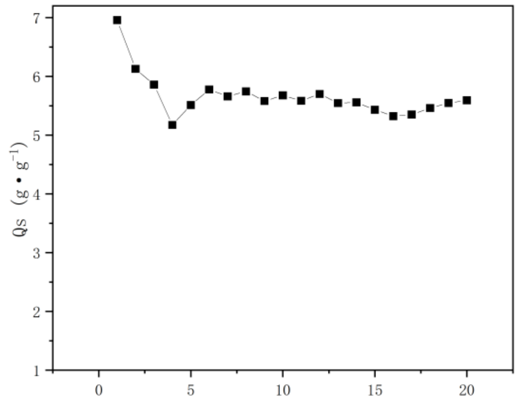

Figure 9 [Line plot of TPU-8% monomer to vegetable oil by absorption and extrusion method]

4 Conclusion

(1) When the polymer concentration was 8%, the phase separation temperature was 0℃, the phase separation time was 30min, and the mixing solvent ratio was 9:1, the TPU-8% porous monolithic material prepared by the heat-induced phase separation method showed good performance.

(2) It can be seen that the overall material at TPU-8% shows good reversible compressibility and fatigue resistance characteristics, showing excellent super elasticity. The environmental adaptability test shows that TPU-8% porous monolithic material has good environmental adaptability in different solvents.

(3) The oil or organic solvent adsorbed by T-3(8%) porous material can be removed by adsorption/extrusion, and the sample can be reused many times, up to 20 or more times, showing better recycling performance and durability.

(4) Three-dimensional TPU-8% material with non-stratified porous structure was successfully prepared by a simple heat-induced phase separation method through two cooling steps.Can effectively absorb various oils and organic solvents from water and greasy. The prepared materials have many excellent properties, such as high saturation absorption capacity, fast absorption rate, excellent mechanical stability and recycling performance.The maximum saturation adsorption capacity of dichloromethane was 35.87 times its own weight, and the TPU-8% material remained intact, returning to its original shape even after the compression release cycle.Therefore, porous TPU materials will be a

promising eco-friendly adsorption material for large-scale removal and collection of petroleum/organic solvent contaminants in water.

Acknowledgements

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