Robust thermo-responsive polymer composite membranes with switchable superhydrophilicity and superhydrophobicity for efficient oil-water separation

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Abstract

In this paper, we report for the first time on the fabrication of a robust, thermo-responsive polymer membrane produced by the combination of an elastic polyurethane (TPU) microfiber web and poly (N-isopropylacrylamide) (PNIPAM). PNIPAM hydrogel is evenly coated on the surface of TPU microfibers, thus, the wettability of TPU-PNIPAM membrane are amplified by taking advantage of the hierarchical structure and increased surface roughness. The TPU-PNIPAM membrane possesses switchable superhydrophilicity and superhydrophobicity as the temperature of membrane changes from 25 to 45 °C. The composite membrane is shown successfully able to separate a 1 wt. % oil-in-water emulsion and 1 wt. % water-in-oil emulsion at 25 and 45 °C, respectively, with a high separation efficiency of ≥ 99.26 %. Furthermore the composite membranes show excellent mechanical properties, and they are highly flexible and mechanically tough. The smart composite membranes reported here have shown great potential for further development for practical high-efficiency oil-water separations.
Abstract art

1. Introduction

The ability to separate oil-water mixtures has recently attracted worldwide attention because of increasing amounts of oily wastewater, frequent oil spill accidents and the ongoing development of petroleum industry. In general, immiscible oil-water mixtures are separated using conventional separation techniques, such as gravity separation and oil-absorbing materials. In the case of the separation of oil-water emulsions, the conventional separation processes (air flotation, coagulation and flocculation) are costly, energy intensive and are not effective. Pressure-driven membranes, especially ultrafiltration (UF) membranes, have been successfully used for the separation of oil-water emulsions. However, the size-sieving mechanism of UF membrane limits the practicality of this process, due to the resultant high energy consumption, low flux and rapid decrease in permeability with usage. Recently, a series of superwetting membranes have been produced for efficient oil-water separation, including polymer-coated copper meshes, hydrogel-coated copper meshes, surface-modified copper meshes and polymer networks, all taking advantage of surface chemistry and roughness. It has been shown that a superhydrophilic / superoleophobic membrane is suitable for separating oil-in-water emulsions, while a superhydrophobic / superoleophilic membrane separates water-in-oil emulsions. The oil-water separation process with a superwetting membrane has been proven to be energy-efficient and cost-effective, as the membrane separates the oil-water mixture or oil-water emulsion according to
the different interfacial effects of oil and water on the superwetting surface. For example, the superwetting membrane prepared by Kota et al. allowed for the removal of dispersed-phase droplets that were considerably smaller than the membrane pore size. \(^{12}\) It is important to be able to prepare a responsive membrane with switchable superwettability, not only for controllable oil-water separation, but also for fabricating intelligent materials. Stimuli-responsive surfaces have been used to prepare smart membrane for some years, but to date there have been only a few reports on responsive membranes with switchable underwater superoleophilicity and superoleophobicity, and fewer membranes with switchable superhydrophilicity and superhydrophobicity for oil-water separation. In particular, the membranes with such switchable underwater superoleophilicity and superoleophobicity are pH-sensitive; \(^{19-23}\) whereas the membranes with switchable superhydrophilicity and superhydrophobicity are photo-induced or pH-responsive. For instance, the aligned ZnO nanorod arrays-coated mesh film was fabricated by Tian et al., which was switchable between superhydrophilicity and superhydrophobicity, driven by photo-stimulation. \(^{24}\) The other membranes with switchable superhydrophilicity and superhydrophobicity for oil-water separation are pH-responsive and can be controlled using solutions with different pH values. \(^{25, 26}\)

Although some responsive membranes exhibit stimuli-responsive ability, they are not capable of switching between superwettabilities. For example, a PDMAEMA hydrogel-coated copper mesh has been reported which was both thermo- and pH-responsive; however, it is solely underwater superoleophobic without switchable superwettability. \(^{27}\) A PVCL-co-PSF copolymer membrane shows thermo-responsive, but it is hydrophilic with a contact angle of 49.5 °C at room temperature. \(^{28}\) Table S1 (Supporting Information) shows some attractive superwetting membranes published in recent years. For example, single-walled carbon nanotube network films and ammonia-modified PVDF membrane were found to be able to separate 99 % oil-water emulsion, and a PAA-g-PVDF membrane was able to efficiently
separate a 1 % oil-water emulsion; \(^2,16\) what’s more, a superamphiphilic PVDF membrane could separate oil-in-water and water-in-oil emulsions. \(^29\) However, the responsive membranes with a switchable superwettability were applied to separate \(\geq 10\) % oil-water mixtures, which are not emulsions. Apart from oil-water separation properties, the mechanical properties and durability of membranes are other key factors important for practical application. \(^2\) For instance, polymeric UF membranes are mainly prepared via phase inversion; however, the porous structure formed in the phase inversion process greatly weakens the mechanical properties of the membranes, and thus restricts their applicability. To meet the mechanical requirements for practical ultrafiltration, support materials (glass, metal, polymer, non-woven fabrics) have been applied to improve their mechanical property, although it may decrease the permeation flux. \(^8,10,30,31\)

Here, we report for the first time a robust, thermo-responsive poly (N-isopropylacrylamide) (PNIPAM) hydrogel-coated thermoplastic polyurethane (TPU) microfiber membrane for efficient oil-water emulsion separation. The membrane is superhydrophilic at room temperature (25 °C) and becomes superhydrophobic at a temperature over the lower critical solution temperature of PNIPAM (LCST, 32°C). TPU was selected for its high elongation, tensile strength, toughness, wear resistance and good flexibility over a wide temperature range. PNIPAM is a thermally responsive polymer that switches between hydrophilicity and hydrophobicity at temperatures lower and higher than its LCST. The force-spinning method was used to produce a non-woven TPU microfiber mesh or web, and is a fast and productive technique to produce a micro- or nanoscale fiber mats in less than a minute. It works by producing a jet of polymer in solution due to a high-speed, rotating nozzle and produces the fiber mesh without the need for a high-voltage power source and the limitation of solution conductivity, as is required for example, by electrospinning. \(^32-35\)
The TPU-PNIPAM composite membrane has excellent mechanical strength, elasticity and switchable superhydrophilicity and superhydrophobicity, and shows a high efficiency in separating SDS-stabilized oil-in-water and water-in-oil micro-emulsions, but not mixtures, at room temperature and at an elevated temperature, respectively.

2. Materials and Methods

Materials

The following chemicals were used as supplied: thermoplastic polyurethane (TPU, TETON*206) particles were kindly provided by Urethane Compounds Pty. Ltd. Tetrahydrofuran (THF) was purchased from Merck (Kenilworth, NJ, USA). N-isopropylacrylamide (NIPAM), N, N'-methylenebis(acrylamide) (MBA), and ammonium persulfate (APS) were purchased from Sigma-Aldrich (St Louis, MO, USA). Distilled deionized (DDI) water was used in all experiments.

Experimental Procedures

Fabrication of TPU-PNIPAM membrane: Thermoplastic polyurethane particles (12 g) were dissolved in tetrahydrofuran (THF, 88 g) under stirring to obtain a 12 wt. % polymer solution. N-isopropylacrylamide (NIPAM, 2g, monomer), N, N’-methylenebisacrylamide (MBA, 0.04 g, crosslinker) and ammonium persulfate (APS, 0.02 g, initiator) were dissolved in DDI water to form a 16.67 wt. % NIPAM reaction solution. As shown in Figure S1 (Supporting Information), the polymer solution was spun into TPU microfiber mat by a force spinner (Cyclone L-1000M, FibeRio® Technology Corporation, USA), with an operating condition of 5000 rpm and 30 seconds. Five microfiber mats were obtained and stacked up to form a TPU microfiber membrane. The as-prepared TPU microfiber membrane was then cut into a certain shape before wetting with NIPAM reaction solution. Free-radical polymerization of the NIPAM monomer solution was applied to coat the PNIPAM hydrogel on the TPU microfibers’ surface. After 2 hours reaction at 70 °C, TPU-PNIPAM membranes were obtained. The PNIPAM hydrogel loading of TPU-PNIPAM membranes was controlled by...
changing the amount of NIPAM reaction solution added to the TPU microfiber membranes.
The TPU-PNIPAM membranes were washed with 25 °C water and 45 °C water more than 10 times to rinse the excess monomer before use.

*Instruments and Characterization:* Scanning electron microscopy was undertaken with a Nova NanoSEM 450 FESEM, FEI, USA. Optical microscopy images were taken on an Olympus SZX16 Stereo Microscope. The contact angle of the membranes was determined using a contact angle goniometer (Dataphysics OCA15, Dataphysics, Germany). The average value was obtained from more than 5 measurements per sample. The mechanical properties of the membranes were measured using Mini-Instron (Micro Tester 5848, 100 N load cell, Instron Calibration Laboratory, U.K.). The swelling properties of PNIPAM of composite membrane were tested and calculated according to\textsuperscript{36, 37}. The swelling ratio was calculated based on the PNIPAM hydrogel amount of the composite membrane, but not the composite membrane.

*Preparation of oil-water emulsions:* 1 wt. % silicone oil-water emulsion was prepared by mixing silicone oil and water in a ratio of 1:99 w/w with 1 mg/mL sodium dodecyl sulfate (SDS) under strong magnetic stirring and shaken to obtain a milky solution. 99 wt. % silicone oil-water emulsion was prepared by mixing silicone oil and water in a ratio of 99:1 w/w with 1 mg/mL SDS under strong stirring and shaking. Oil-water emulsions with different oils (hexadecane, paraffin, olive oil and fish oil) were prepared in a similar fashion. The SDS-stabilized oil water emulsions were stable more than a month.\textsuperscript{16}

*Oil-water separation Experiment:* The as-prepared membrane was fixed between two glass tubes with an inner diameter of 12.86 mm. At room temperature, the 1 wt. % silicone oil-water emulsion was poured into the upper tube, and the separation was achieved by gravity only. At 45 °C, the swollen membrane was immersed in the 45 °C water to deswell and the excess water on the membrane surface was removed using tissue paper. The 99 wt. % silicone
oil-water emulsion was heated to 45 °C and was poured into the separation setup in an oven set to 45 °C to achieve separation.

The oil concentration in collected water and the water concentration in the collected oil after separation were determined using a UV-Vis spectrophotometer (UV mini 1240) by testing the light scattering data. The standard oil-water emulsion and the collected samples were sonicated for 0.5 hour to obtain a homogeneous solution before test. The separation efficiency was calculated by the following equation (1):

\[ S = \left( \frac{C_0 - C_1}{C_0} \right) \times 100\% \]  

where \( C_0 \) (10000 mg/L) is the original oil concentration or water concentration in the feed. \( C_1 \) is the oil or water concentration in permeate after filtration.

3. Results and Discussion

Figure 1 (a) The preparation process of a TPU-PNIPAM composite membrane. The TPU microfiber membrane immersed with NIPAM reaction solution (16.7 wt. %) is polymerized at 70 °C for 2 hours. Photographs of twisting test of (b) TPU microfiber membrane and (c) TPU-PNIPAM membrane with 3.6 wt. % PNIPAM loading (TPU-PNIPAM-3.6). (d) Stress-strain curves of TPU microfiber membrane and swollen TPU-PNIPAM-3.6 membrane.
The TPU microfiber membranes were prepared using force spinning, as shown in Figure S1 (Supporting Information). The PNIPAM-coated TPU microfiber (TPU-PNIPAM) membranes were made using a single step free-radical polymerization (Figure 1a). The schematic diagram of the formation of TPU-PNIPAM composite is shown in Figure S3 (Supporting Information). As shown in Figure 1b-c, the TPU-PNIPAM membrane shows excellent mechanical properties, and can be readily stretched and twisted without failure, and shows significant recovery. The composite membrane has significantly enhanced stretchability, as compared with the TPU membrane. In this study, TPU-PNIPAM membranes with different amounts of PNIPAM (1.4, 3.6, 7.6, 13.4, and 25.3 wt. %) were prepared. As an example of the nomenclature used, a membrane contains 1.4 wt. % PNIPAM hydrogel is denoted as TPU-PNIPAM-1.4.

The TPU microfibers’ diameter is 1-30 µm, and 92 % of them distributes in 1-15 µm (Figure S4, Supporting Information).

Figure 2 SEM images of TPU microfiber membrane and TPU-PNIPAM composite membranes (3.6 and 13.4 wt. %). Membrane surfaces of (a) TPU microfiber membrane (at a magnification of 558×), (b) TPU-PNIPAM-3.6 (811×) and (c) TPU-PNIPAM-13.4 membrane
microfiber surfaces of (d) TPU microfibers (71202×), (e) TPU-PNIPAM-3.6 (67286×) and (f) TPU-PNIPAM-13.4 (35187×); microfiber cross-sections of (g) TPU microfibers (38448×), (h) TPU-PNIPAM-3.6 (43471×) and (i) TPU-PNIPAM-13.4 (2885×).

Figure 2 shows the SEM images of TPU microfiber membrane, TPU-PNIPAM-3.6 and TPU-PNIPAM-13.4 membrane, which were taken after 10 times of cyclic heating. The SEM images of microfiber surface and cross-section (Figure 2d-i) indicate that PNIPAM was evenly coated on the TPU microfibers, and its surface roughness increased with increasing PNIPAM loading. These membranes show similar morphologies before the cyclic heating, as shown in Figure S5 (Supporting Information). In addition, in the TPU microfiber membrane, the microfibers were loosely packed whilst in the TPU-PNIPAM membrane the microfibers were bound by the PNIPAM hydrogel phase. In the latter instance, the pore size of the TPU-PNIPAM membranes was greatly decreased, as shown in Figure 2a-c, and the pore size was found to decrease with increasing PNIPAM loading (Figure S5). The pore size distributions of dry TPU-PNIPAM-3.6 and TPU-PNIPAM-13.4 membrane were 3-27 µm, and 2-15 µm, respectively. Figure S6 (Supporting Information) shows the thickness of the composite membranes and their PNIPAM hydrogel coating thickness. The PNIPAM coating thickness of TPU-PNIPAM with a hydrogel loading of 1.4, 3.6, 7.6, 13.4, and 25.3 wt. % were 106, 160, 227, 3061, and 10124 nm, respectively. With the hydrogel loading increased, the PNIPAM coating thickness increased. The membrane thickness of TPU-PNIPAM with a hydrogel loading of 1.4, 3.6, 7.6, 13.4, and 25.3 wt. % were 1.47, 0.64, 0.63, 0.54, and 1.13 mm, respectively. It decreased with increasing hydrogel loading when the loading amount was lower than 13.4 wt. %. The results of SEM images, PNIPAM coating thickness, and membrane thickness indicated that TPU microfibers were bound by the PNIPAM hydrogel, and increasing space between microfibers was filled by the hydrogel with greater hydrogel loading. However, there was not enough PNIPAM hydrogel in the TPU-PNIPAM-1.4 to bind the TPU microfibers, resulting in a thick membrane and large pores.
The mechanical properties of swollen TPU-PNIPAM membranes increase with increasing hydrogel loading initially, however when the hydrogel loading become greater than 3.6 wt. %, it decreases (Figure 3). The elongation and toughness of the dry composite membranes follow a similar trend, and TPU-PNIPAM-3.6 reaches the maximum as well. However, the tensile strength and Young’s modulus of the dry composite membranes show different trends: TPU-PNIPAM-7.6 exhibits the largest tensile strength, and the Young’s modulus of the composite membranes with the 7.6, 13.4 and 25.3 wt. % hydrogel loading are 10 times higher than those of others. For TPU-PNIPAM-1.4 and TPU-PNIPAM-3.6, the microfibers are coated with the hydrogel uniformly; as the hydrogel loading become greater, the hydrogel coating surface becomes rougher, and thicker hydrogel starts to fill up the space between TPU microfibers (Figure 2i). The dry TPU-PNIPAM-3.6 is flexible and stretchable; whereas the dry TPU-PNIPAM-7.6 becomes hard. Since the dry PNIPAM hydrogel is itself hard and brittle, the dry composite membrane with a hydrogel loading higher than 3.6 wt. % also becomes harder and more brittle with increasing hydrogel loading, resulting in decreased tensile strength and elongation, and high Young’s modulus and low toughness. The swollen TPU-PNIPAM-3.6 membrane is flexible and tough and reaches the optimal values of mechanical properties among the composite membranes. The stress-strain curves of TPU microfiber membrane and swollen TPU-PNIPAM-3.6 membrane (Figure 1d) indicate that the mechanical properties of TPU-PNIPAM-3.6 membrane were significantly enhanced. The elongation, tensile strength, Young’s modulus and toughness of TPU-PNIPAM-3.6 are 2.04 times, 2.88 times, 1.71 times and 5.70 times of those of TPU microfiber membrane alone (uncoated). The elongation and tensile strength of TPU-PNIPAM-3.6 are as high as 288 % and 3.90 MPa, which are much better than those of the other reported oil water separation membranes. For example, the ammonia modified PVDF oil water separation membrane prepared by Zhang et al. exhibited an elongation of 29.2% and a tensile strength of 2.0 MPa, which showed good flexibility and mechanical stability in the oil water separation process.
The toughness of dry TPU microfiber membrane is 1321 kJ/m$^3$; however, the toughness of swollen TPU-PNIPAM-3.6 is 7536 kJ/m$^3$, which is comparable with natural rubber (10000 kJ/m$^3$). The images in Figure 1b-c show the twisting test of TPU microfiber membrane and TPU-PNIPAM-3.6 membrane. Both two membranes had good flexibility that could not only withstand bending, but also complex twisting, while TPU-PNIPAM-3.6 showed greater elasticity and recovery.

![Graphs showing elongation, tensile strength, Young's modulus, and toughness](image)

**Figure 3** (a) elongation, (b) tensile strength, (c) Young’s modulus, and (d) toughness of TPU microfiber membrane (0 wt. %) and TPU-PNIPAM membranes (1.4, 3.6, 7.6, 13.4, and 25.3 wt. %).

The water contact angle of TPU thin film was 82.0°, after spinning the TPU into microfibers, the water contact angle of TPU microfiber membrane increased to 148.3° (Figure S7, Supporting Information) because of the changing of surface roughness of TPU. Figure 4 shows the wettability of PNIPAM hydrogel and TPU-PNIPAM membranes. As shown in Figure 4a, compared to swollen PNIPAM, the water contact angles of swollen TPU-PNIPAM
membranes were lower at room temperature and increased at 45°C, demonstrating that the
TPU-PNIPAM-3.6 membrane exhibited switchable superwettability. At room temperature,
with increasing hydrogel loading, the contact angles of composite membranes increase;
meanwhile the hydrogel fills the space between TPU microfibers instead of coating on the
surface alone (Figure S8, Supporting Information), and the membrane roughness decreased,
resulting in a similar wettability to PNIPAM hydrogel. At 45 °C, the contact angles of
composite membrane initially increases and then decreases with increasing hydrogel loading,
while TPU-PNIPAM-3.6 reaches the highest value. Generally, the thermo-responsive
property of PNIPAM can be explained by the reversible formation of intermolecular hydrogen
bonding between amide groups of PNIPAM chains and water molecules, and intramolecular
hydrogen bonding between amide groups of PNIPAM chains below and above the LCST. 17,
38, 39 At temperatures below LCST, the stretching PNIPAM chains are wrapped by the water
molecules, showing hydrophilicity; while at temperatures above LCST, the collapsed
PNIPAM chains are wrapped by isopropyl groups, showing hydrophobicity (Figure 4b).
Nevertheless, the synergism of integrating TPU microfibers and PNIPAM amplifies these
properties to superhydrophilicity and superhydrophobicity. Figure 4c-f show that TPU-
PNIPAM-3.6 membrane was superhydrophilic, with a water drop spreading in a timeframe of
less than 0.094 s, and underwater demonstrated oleophobic behaviour (141.3°) at room
temperature; but became superhydrophobic (150.2°) and underwater superoleophilic, with an
oil drop spreading time of 70 s at 45 °C. TPU-PNIPAM-3.6 submerged under water at room
temperature, and floated on the surface of water without a water droplet on the membrane
surface at 45 °C (Figure S9, Supporting Information).
Figure 4 (a) Water contact angles of swollen TPU-PNIPAM membranes (1.4, 3.6, 7.6, 13.4, and 25.3 wt. %) and the swollen PNIPAM hydrogel (100 wt. %) at room temperature (RT) and 45°C. (b) Schematic diagram of switching wettability of TPU-PNIPAM membrane at different temperatures. (c) A water droplet (1µL) spreading on a swollen TPU-PNIPAM-3.6 membrane within 0.094 s at room temperature. (d) Water contact angle (150.2°) of swollen TPU-PNIPAM-3.6 membrane at 45 °C. (e) Underwater oil contact angle (141.3°) of swollen TPU-PNIPAM-3.6 membrane at room temperature. (f) Underwater oil contact angle of swollen TPU-PNIPAM-3.6 membrane at 45°C. Hexadecane was used for testing the underwater oil contact angle.
Figure 5 Swelling properties of the PNIPAM of TPU-PNIPAM-3.6 membrane. (a) Swelling curve of dry TPU-PNIPAM-3.6 membrane. (b) Swelling ratio of TPU-PNIPAM-3.6 membrane at different temperatures. (c) Deswelling curve of TPU-PNIPAM-3.6 membrane tested at 45 °C DDI water. (d) Reswelling curve of TPU-PNIPAM-3.6 membrane tested at 25°C DDI water.

Apart from the wettability, the degree of swelling also plays an important role in the potential use of the hydrogel. It has been recognized that PNIPAM hydrogels would possess low reswelling and deswelling rates at temperatures below or over its LCST, which is responsible for the formation of a dense, hydrophobic layer at the surface of the hydrogels due to the occurrence of volume-phase transition (VPT) that retards the collective diffusion of water molecules in the swelled and/or deswelled hydrogels. 36, 37, 40, 41 Figure 5 shows the swelling property of the PNIPAM phase of the TPU-PNIPAM-3.6 membrane. It took 400 minutes for dry TPU-PNIPAM-3.6 membrane to achieve a swelling equilibrium in DDI water (Figure 5a). Even though the swelling ratio of the PNIPAM was 5.36 g/g, the appearance of the membrane changed little because of the small amount of hydrogel loading. The LCST of
TPU-PNIPAM-3.6 membrane is the same as PNIPAM hydrogel, some 32-33 °C (Figure 5b). Importantly, the deswelling and reswelling equilibrium of TPU-PNIPAM-3.6 membrane could be achieved in less than 3 minutes by immersing it into 45 °C and 25 °C DDI water, respectively, as shown in Figure 5c-d. The rapid deswelling and reswelling properties could be contributed to the morphology of hydrogel nanoparticles on the microfibers surface and the consequent large surface area. The excellent mechanical properties, suitable pore sizes, switchable superhydrophilicity and superhydrophobicity, rapid deswelling and reswelling property make clear the appropriate application of these TPU-PNIPAM membranes for separating oil-in-water emulsion and water-in-oil emulsion at room temperature (25 °C) and 45 °C, respectively.

To study the oil-water separation ability of TPU-PNIPAM membranes, oil intrusion pressure and water intrusion pressure, the relevant water flux and oil flux were all tested, and the results shown in Figure 6a-b. The intrusion pressure indicates the maximum height of oil / water that the TPU-PNIPAM membrane can support at room temperature / 45 °C, which is calculated by the following equation (2):

\[ P = \rho gh_{\text{max}} \]  

where \( \rho \) is the density of the oil / water, \( g \) is gravitational acceleration, and \( h_{\text{max}} \) is the maximum height of oil / water the membranes can support. The fluxes were calculated by measuring the volume of liquid permeated through the membranes over a period of time due to gravity only. Both intrusion pressure and flux were tested more than 5 times to obtain the average value. At room temperature, TPU-PNIPAM membranes are hydrophilic, the oil intrusion pressures of TPU-PNIPAM-1.4, TPU-PNIPAM-3.6, TPU-PNIPAM-7.6, and TPU-PNIPAM-13.4 membrane are 0.35, 1.37, 1.53, and 3.26 kPa, respectively, and the relevant water fluxes are 3288, 3646, 1657, and 41 LMH. With increasing hydrogel loading, the pore size of the composite membranes becomes smaller, which is responsible for the increasing oil intrusion pressure and decreasing water flux. At 45 °C, the TPU-PNIPAM membranes are
hydrophobic, the water intrusion pressure firstly increased and then decreased, while the oil flux decreased with increasing hydrogel loading of the composite membranes. Only TPU-PNIPAM-3.6 exhibited proper water intrusion pressure at 45 °C (0.89 kPa), which was slightly higher than that of TPU microfiber membrane alone (0.80 kPa). TPU-PNIPAM-1.4 showed low water intrusion pressure, because the microfibers were loosely piled up with huge gaps among the membrane (Figure S8a, Supporting Information), on the other hand, coating with PNIPAM decreased the water contact angle of TPU microfiber membrane from 148.3 ° to 105 °. Coating with PNIPAM hydrogel provides the TPU microfibers with switchable hydrophilicity and hydrophobicity, but only TPU-PNIPAM-3.6 possesses switchable superhydrophilicity and superhydrophobicity (Figure 4a). Increasing hydrogel loading led to decreased pore size and surface roughness, thereby decreasing contact angle and water intrusion pressure. The oil fluxes of TPU microfiber membrane and TPU-PNIPAM-3.6 membrane were 4659 and 503 LMH, respectively. The loosened structure of TPU microfiber membrane reduced the water intrusion pressure but enhanced the oil flux. Combining the results of room temperature oil intrusion pressures and 45 °C water intrusion pressures of the membranes, TPU-PNIPAM-3.6 is the membrane that can best be applied to controllable separation of oil-in-water emulsion and water-in-oil emulsion at different temperatures, which is consistent with the contact angle data in Figure 4. The illustration of controllable separation of oil-water mixture with TPU-PNIPAM-3.6 membrane is shown in Figure S10 (Supporting Information). Water selectively permeated through the membrane and oil (hexadecane, red) was retained above the membrane at room temperature. Likewise oil permeated through the membrane, but the permeation of oil was blocked when the membrane surface was covered by water at 45 °C, thus both oil and water were retained. Figure S11 (Supporting Information) shows the variation of flux during 24 hours separation of SDS-stabilized hexadecane-water emulsions. The diameter distribution of oil drops in 1 wt. % hexadecane-water emulsion is 2-15 µm, and that of water drops in 99 wt. % hexadecane-water emulsion is 3-30 µm (Figure
For separating 1 wt. % hexadecane-water emulsion at room temperature, the initial flux was 3700 LMH. It dropped to about 2400 LMH after 1 hour and was remained in the following 23 hours. The flux of separating 99 wt. % hexadecane-water emulsion at 45 °C showed a similar trend. After 2 hours, the flux dropped from 670 to 480 LMH, and it remained in the following 22 hours. No external force was employed during the separation process.

**Figure 6** (a) Oil intrusion pressure and water flux of TPU-PNIPAM membranes (1.4, 3.6, 7.6, 13.4, and 25.3 wt. %) at room temperature. (b) Water intrusion pressure and oil flux of TPU microfiber membrane and TPU-PNIPAM membranes at 45 °C. Hexadecane was used as the test oil. (c) Separation efficiency of TPU-PNIPAM-3.6 membrane for reversibly oil-water separation at room temperature and 45 °C. The inset shows the 1 wt. % SDS-stabilized silicone oil-water emulsion and the collected water before and after separation at room temperature (left), and the 99 wt. % SDS-stabilized silicone oil-water emulsion and the collected oil before and after separation at 45 °C (right). (d) Separation efficiencies of TPU-PNIPAM-3.6 membrane for separating different 1 wt. % oil-water emulsions at room temperature.
Silicone oil, with a density approaching that of water, was used to prepare the emulsion with water for testing the oil-water emulsion separation capability of TPU-PNIPAM-3.6 membrane. 1 wt. % silicone oil-water emulsion contains 1 wt. % silicone oil, 99 wt. % DDI water and 1 mg/mL sodium dodecyl sulfate (SDS), it is oil-in-water emulsion. Similarly, 99 wt. % silicone oil-water emulsion contains 99 wt. % silicone oil, 1 wt. % DDI water and 1 mg/mL SDS, and thus is a water-in-oil emulsion. The silicone oil-water emulsions were much more stable than the hexadecane-water emulsions. The diameter of silicone oil drops in water is 2-25 µm, and that of water drops in silicone oil is 5-30 µm (Figure S12, Supporting Information). The TPU-PNIPAM-3.6 membrane was able to demonstrate excellent ability to separate oil-water emulsions. At room temperature, 1 wt. % silicone oil-water emulsion was separated, and the separation efficiency was higher than 99.26 %; at 45 °C, 99 wt. % silicone oil-water emulsion was separated, and the separation efficiency was 99.85 %. TPU-PNIPAM-3.6 showed switchable superhydrophilicity and superhydrophobicity, it separated oil-in-water and water-in-oil emulsions at temperatures below and above LCST respectively. However, the TPU microfiber membrane showed hydrophobicity, it separated a water-in-oil emulsion only. The TPU microfiber membrane was applied to separate 99 wt. % silicone oil-water emulsion, and the separation efficiency was 99.78 %. For separating water-in-oil emulsion, even though TPU-PNIPAM-3.6 was swollen in 45 °C water, it showed similar separation efficiency with the dry TPU microfiber membrane. The separation efficiencies of TPU-PNIPAM-3.6 membrane for reversely separating 1 wt. % and 99 wt. % silicone oil-water emulsions at room temperature and 45 °C individually are shown in Figure 6c. It was found that the separation efficiencies were stable both at room temperature and 45 °C, demonstrating that the TPU-PNIPAM-3.6 membrane is stable and shows excellent separation ability under switching temperatures. The inset of Figure 6c shows photographs of oil-water emulsions and the collected liquids, before and after separation, which also indicates that the TPU-PNIPAM-3.6 membrane separated emulsions successfully. Other than for silicone oil-water emulsions, the
TPU-PNIPAM-3.6 membrane was able to separate other oil-water emulsions with high separation efficiency (Figure 6d). The optical microscopy images of emulsions before and after filtration are shown in Figure S13 and Figure S14 (Supporting Information).

To sum up, the TPU microfiber-PNIPAM hydrogel composite membrane (e.g., TPU-PNIPAM-3.63) exhibit excellent oil-water emulsion separation performance: (1) it separates water-in-oil and oil-in-water emulsions effectively and efficiently under switching temperatures, with an separation efficiency of ≥ 99.26 %, while the TPU microfiber membrane without hydrogel coating separates water-in-oil emulsion only; (2) the swollen TPU-PNIPAM-3.6 (45 °C) shows similar separation efficiency with the dry TPU microfiber membrane; and (3) other oil-water emulsions can be separated by TPU-PNIPAM as well, and excellent separation efficiency was achieved.

In conclusion, a robust thermo-responsive polymer membrane with switchable superhydrophilicity and superhydrophobicity was successfully fabricated by combining a thermoplastic polyurethane (TPU) microfibers and poly (N-isopropylacrylamide) (PNIPAM) nanoparticles. Among the polymer composite membranes prepared, the TPU-PNIPAM-3.6 material performed best, exhibiting excellent mechanical properties with an elongation of 288 % and a toughness of 7536 kJ/m³, comparable with natural rubber (10000 kJ/ m³). The water contact angles of TPU-PNIPAM-3.6 membrane switched between 0° (room temperature) and 150.2 ° (45 °C), and the PNIPAM hydrogel of the composite membrane reached deswelling and reswelling equilibrium in 3 minutes. Driven by gravity only, the TPU-PNIPAM-3.6 membrane could separate 1 wt. % silicone oil-water emulsion at room temperature with a separation efficiency of ≥ 99.26 %, and separate 99 wt. % silicone oil-water emulsions at 45 °C with a separation efficiency of ≥ 99.85 %. Our membrane is thus a good candidate for not only oil-water emulsion separation, but also for fabricating smart materials for rapidly responsive drug delivery systems and sensors. In addition, other...
polymeric micro- or nanofibers membranes could be used as the substrates for fabricating superwetting materials, which broadens the methods of preparation of such materials.

Acknowledgements

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Supporting Information

Additional experimental description, diameter distribution of TPU microfiber (Figure S4), pore size distribution of TPU-PNIPAM (Figure S5), membrane thickness and coating thickness results (Figure S6), water contact angle of TPU and TPU-PNIPAM (Figure S7-S8), separation flux (Figure S11), optical microscopy images of oil/water droplet (Figure S12-S14).

This information is available free of charge via the Internet at http://pubs.acs.org.

References


(41) Stenzel, M. H.; Davis, T. P., Star polymer synthesis using trithiocarbonate functional
Supporting Information

Robust thermo-responsive polymer composite membrane with switchable superhydrophilicity and superhydrophobicity for efficient oil-water separation

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Figure S14 Optical microscopy images SDS-stabilized 99 wt. % oil-water emulsions before and after filtration. (Page S12)
Table S1 Superwetting membranes and relevant properties for oil-water separation published in recent years.

<table>
<thead>
<tr>
<th>Year</th>
<th>Materials</th>
<th>Pore Size</th>
<th>Wettability</th>
<th>Oil-water mixture concentration</th>
<th>Separation efficiency/ % or residual oil/ ppm</th>
<th>Remarks (flux, intrusion pressure (IP) or mechanical properties)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2011</td>
<td>Hydrogel-coated mesh</td>
<td>50 µm</td>
<td>Superhydrophilic</td>
<td>30 v/v % hexane water mixture</td>
<td>99.8%</td>
<td>2.0 kPa (IP)</td>
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<tr>
<td>2012</td>
<td>Aligned ZnO nanorod array-coated mesh</td>
<td>25-270 µm</td>
<td>Photo-responsive, superhydrophilic and superhydrophobic</td>
<td>30 v/v % oil-water mixture</td>
<td>&gt;95%</td>
<td>--</td>
<td>2</td>
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<tr>
<td>2012</td>
<td>Fluorodecyl POSS+X-PEGDA coated mesh/ fabric</td>
<td>30.5-138 µm</td>
<td>Superhydrophilic and superoleophobic</td>
<td>10 v/v % water-in-hexadecane emulsion</td>
<td>&gt;99%</td>
<td>--</td>
<td>3</td>
</tr>
<tr>
<td>2012</td>
<td>P2VP-b-PDMS-grafted textile</td>
<td>--</td>
<td>pH responsive, underwater superoleophobicity and superoleophobicity</td>
<td>Superoleophilic</td>
<td>--</td>
<td>--</td>
<td>4</td>
</tr>
<tr>
<td>2013</td>
<td>Single-walled carbon nanotube network films</td>
<td>10-200 nm</td>
<td>Superhydrophobic</td>
<td>99.13 v/v % toluene-water emulsion</td>
<td>Oil purity 99.97%</td>
<td>3100 lm·h⁻¹·bar⁻¹</td>
<td>5</td>
</tr>
<tr>
<td>2013</td>
<td>Ammonia modified PVDF membrane</td>
<td>--</td>
<td>Superhydrophobic</td>
<td>99.01 v/v % isoctane-water</td>
<td>Oil purity 99.98%</td>
<td>900 LMH, tensile strength 2.0 MPa, elongation 29.2 %</td>
<td>6</td>
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<tr>
<td>2013</td>
<td>Zeolite-coated mesh</td>
<td>5-42 µm</td>
<td>Underwater superoleophobic</td>
<td>50 v/v % diesel-water mixture</td>
<td>2.5 ppm</td>
<td>25 Lm·s⁻¹, 729 Pa (IP)</td>
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<tr>
<td>2013</td>
<td>Cu(OH)₂ nanowire-haired membrane</td>
<td>1-75 µm</td>
<td>Superhydrophilic</td>
<td>10 v/v % hexane-water emulsion</td>
<td>25 ppm</td>
<td>150000 LMH</td>
<td>8</td>
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<tr>
<td>2013</td>
<td>Chromic acid-treated PU foam with FAS modification</td>
<td>Hundred s micron</td>
<td>Superhydrophobic</td>
<td>Crude oil-water mixture</td>
<td>98 %</td>
<td>--</td>
<td>9</td>
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<tr>
<td>2014</td>
<td>PVDF membrane</td>
<td>--</td>
<td>Superamphilic</td>
<td>3.2 % and 99.13 % toluene-water emulsion</td>
<td>--</td>
<td>Water flux 9860 LMH, Oil flux 1820 LMH with 0.09 MPa 679 Pa (IP)</td>
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<tr>
<td>2014</td>
<td>Dual-scaled porous nitrocellulose membranes</td>
<td>450 nm</td>
<td>Underwater superoleophobic</td>
<td>46.7 v/v % gasoline-water mixture</td>
<td>99.92 %</td>
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<td>11</td>
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<tr>
<td>2014</td>
<td>PDMAEMA hydrogel coated mesh</td>
<td>40 µm</td>
<td>Thermo- &amp; pH-responsive, underwater superoleophobic</td>
<td>30 v/v % gasoline-water mixture</td>
<td>99.97 %</td>
<td>Water and oil permeate through the mesh orderly</td>
<td>12</td>
</tr>
<tr>
<td>2014</td>
<td>PAA-g-PVDF membrane</td>
<td>--</td>
<td>Superhydrophilic</td>
<td>1 % hexadecane-water emulsion</td>
<td>40 ppm</td>
<td>130 LMH</td>
<td>13</td>
</tr>
<tr>
<td>2015</td>
<td>PNIPAM-coated TPU microfiber membrane</td>
<td>3-27 µm</td>
<td>Thermo-responsive, switchable superhydrophilicity and superhydrophobicity</td>
<td>99.45 % (55 ppm) at RT, 99.95 % (4.8 ppm) at 45 °C</td>
<td>99.45 %</td>
<td>7536 kJ/m², elongation 288 %, RT: 3646 LMH (water flux), 1.37kPa(IP); 45 °C: 503 LMH (oil flux), 0.89 kPa (IP)</td>
<td>This paper</td>
</tr>
</tbody>
</table>
Figure S1 The preparation process of TPU microfiber mat by a force spinner.

Figure S2 Contact angle-time curves of TPU film with DDl water and NIPAM solution (16.67 wt. %) as testing medium.
Figure S3 Schematic diagram of formation of TPU-PNIPAM composite. (a) Free radical polymerization of PNIPAM hydrogel, (b) chemical structure of TPU, (c) polymerization of PNIPAM hydrogel on the TPU microfiber’s surface. The hydrogen bonds are formed between urethane groups and acrylamide groups combined two polymers.

Figure S4 (a) SEM image and (b) diameter distribution of TPU microfiber membrane. The diameter distribution was measured using Nano Measurer 1.2.
Figure S5 (a) SEM image and (b) pore size distribution of composite membrane with 3.6 wt. % PNIPAM (TPU-PNIPAM-3.6), and (c) SEM image and (d) pore size distribution of TPU-PNIPAM-13.4 membrane.

Figure S6 Membrane thickness and PNIPAM coating thickness of composite membranes (1.4, 3.6, 7.6, 13.4, and 25.3 wt. %).
Figure S7 Water contact angle images of (a) TPU film and (b) TPU microfiber membrane. The water contact angle of TPU film was 82.0 °, and that of TPU microfiber membrane was 148.3 °.

Figure S8 SEM images of composite membranes and the relevant water contact angle. (a) TPU-PNIPAM-1.4, (b) TPU-PNIPAM-3.6, (c) TPU-PNIPAM-7.6, (d) TPU-PNIPAM-13.4, (e) TPU-PNIPAM-25.3. (f) Water contact angle of composite membranes and PNIPAM hydrogel at room temperature and 45 °C.
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Figure S10 Controllable oil-water separation using TPU-PNIPAM-3.6 membrane at (a) room temperature and (b) 45 °C respectively (hexadecane: red, water: transparent). Oil-water separation at 45 °C was conducted in a 45 °C oven.
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Figure S13 Optical microscopy images SDS-stabilized 1 wt. % oil-water emulsions before (a1-e1) and after (a2-e2) filtration. (a) 1 wt. % silicone oil-water emulsion, (b) 1 wt. % hexadecane-water emulsion, (c) 1 wt. % paraffin-water emulsion, (d) 1 wt. % olive oil-water emulsion, (e) 1 wt. % fish oil-water emulsion.
Figure S14 Optical microscopy images SDS-stabilized 99 wt. % oil-water emulsions before (a1-b1) and after (a2-b2) filtration. (a) 99 wt. % hexadecane-water emulsion, (b) 99 wt. % silicone oil-water emulsion

References


