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Superhydro-oleophobic bio-inspired polydimethylsiloxane micropillared surface via FDTS coating/blending approaches

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ABSTRACT

In this work we render superhydro-oleophobic properties to the surface of polydimethylsiloxane (PDMS) elastomer through bio-inspired micropillar surface and chemical modification with a fluorosilane polymer, trichloro(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silane (FDTS). Two different chemical modification approaches were applied on both flat and micropillar PDMS: (1) vapor deposition of FDTS on cured PDMS surface, and (2) blending FDTS with the liquid PDMS precursor before curing. Comparative studies of the water and oil contact angles on the neat and FDTS-modified PDMS (both flat and micropillar) indicated that superhydro-oleophobicity was delivered by a combination of FDTS chemistry and micropillar geometry. FDTS-blended PDMS micropillar displayed better oleophobicity with an oil contact angle of ~141° than FDTS-coated PDMS micropillar (~115°). In contrast to the smooth surface of FDTS-blended PDMS micropillar, rough surface with some structure defects were found on the FDTS-coated micropillar surface caused by the vapor deposition process; the surface defects might be responsible for the observed low oleophobicity of FDTS-coated PDMS micropillar. Superhydrophobicity of FDTS-blended PDMS micropillar in terms of water contact angles was found to be independent of the quantity of FDTS. However, the oleophobicity of FDTS-blended PDMS micropillar was found to be dependent of the quantity of FDTS; with the increased weight concentration of FDTS in PDMS, the oils contact angle first increased and then leveled out at a finite concentration. FTIR and XPS were applied to analyze surface chemistry information suggesting the blended FDTS segregated from bulk PDMS and enriched at the surface to reduce surface tension so as to make surface super-oleophobic.

1. Introduction

Superhydrophobic materials have attracted extensive interests in the past decades [1–4]. By mimicking the micro/nano surface structures from the nature, such as lotus leaf [2,3,5], superhydrophobic materials with micro/nano surface structures (e.g. grooves [5], nanoparticles [4], nanoporous [6], or pillars [2,5]) have been developed as potential self-cleaning [1–10], materials in anti-icing [7–9], erosion prevention [6,9] and friction/drag reduction [10] applications. Nevertheless, materials only with superhydrophobicity are usually not feasible because they can easily be contaminated by organic oily species [11–13] where surface tension is much lower than water. Hence, materials that are both superhydrophobic and oleophobic are in high demand in many applications such as anti-biofouling [11,13–16] for ships, anti-sticking/corrosion [12–17] protective coating, self-cleaning in polluted water [15–18] and microfluidics [11,13,18–21].

To achieve superhydro-oleophobicity, bio-inspired micro/nano patterned structures [11–13,22,23] combined with surface energy reduction treatment [24–26] have been developed. Normally, the trapped air in the gaps of patterned surfaces restrains the spread of a water droplet, causing it to bead up, but the low surface tension of oil (surface tension is around 20–30 mJ/m^2 while surface tension of water is 72.8 mJ/m^2) would wet the patterned surface by breaking the air-pillar barrier and flow into the gaps [27–30]. In order to achieve superhydro-oleophobicity, fluorine compound with a high percentage of $-CF_3$ and $-CF_2$ groups have been applied to reduce the surface tension of the patterned surface [13,16,19,30,31]. The most widely reported technique to fabricate oleophobic materials is to deposit a self-assembled monolayer (SAM) of fluorocarbon onto the patterned surface through vapor deposition [31–36]. For instance, Zhao et al. [31] coated fluorosilane FOTD on silicon micropillars by vapor deposition and obtained a highly oleophobic surface. In the report of Darmanin, fluorinated

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3,4-ethylenedioxypyrrole (EDOP) was electrodeposited on nano particle over-hang structure with hexadecane contact angle of 132° [33].

Polydimethylsiloxane (PDMS) is a soft and hydrophobic material which easily fabricates different structures [33–35]. With these properties PDMS have been widely studied in the research area of self-cleaning [34], microfluidic channel [35], drag reduction [17,36] and many other applications. For instance, Liu et al. [17] utilized the PDMS to duplicate fish scale structure and then was deemed as second template to prepare oleophobic materials by a casting technique. Im et al. [34] achieved oleophobicity by the vapor deposition of tridecafluoro-1,1,2,2-tetra-hydrooctyl trichlorosilane on PDMS inverse trapedoids with methanol contact angle of 135°. However, one main limitation of vapor deposition perfluorocarbon on structure surface to fabricate oleophobic material is that the fluorocarbon tends to form aggregates (normally tens of nano meters thickness) and structural defects such as disordered tail structure or domain boundaries [37–40]. These aggregates and defects often negatively impact the performance of the material [38]. For example, perfluorodecyltrichlorosilane (FDTS) deposited on to the surface can form aggregates such as micelle or lamellar, leading to the degradation of anti-wetting properties and premature delamination of FDTS coating [37].

In this work, we reported superhydro-oleophobic PDMS micropillar surfaces which were fabricated through trichloro(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silane (FDTS) modification in two approaches. Blending a small amount of FDTS in PDMS precursor making superhydro-oleophobic PDMS micropillars (oil contact angle ~141°) is reported for the first time to the best knowledge of the authors. Oleophobicity of the common approach where FDTS was deposited as coating on PDMS micropillar samples by vapor deposition were fabricated to have an oil contact angle of 115°. The segregation of FDTS from bulk PDMS to the surface showed a smooth surface whereas the coated FDTS on PDMS micropillar induced rough surface and structure defects causing the reduction of oleophobicity. The influence of FDTS on PDMS micropillar superhydro-oleophobicity has been studied and the results showed the superhydro-oelophobicity kept a stable tendency as more FDTS was blended into PDMS.

2. Materials and experiment

2.1. Materials

Trichloro(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silane (FDTS, 97% Sigma–Aldrich Chemicals, USA), and polydimethylsiloxane (PDMS, Sylgard 184 Dow Corning Co., USA,) were used to make the superhydro-olephobic materials. The negative master mold of micropillars was fabricated on silicon wafer using a negative SU-8 photoresist (SU-8-25, MicrochemCo., Newton, MA, USA). Arrays of micropillar (14 mm × 14 mm in size) were prepared with pillars of 15 μm in diameter, 45 μm in height and 32.5 μm of center–center spacing. Diiodomethane (99%, Sigma–Aldrich Chemicals, USA), dimethyl sulfoxide (DMSO, ≥99.8%, Caledon Laboratories LTD.), ethylene glycol (≥99.5%, Sigma–Aldrich Chemicals, USA), formamide (≥99%, Sigma–Aldrich Chemicals, USA), glycerol (≥99%, Sigma–Aldrich Chemicals, USA), *n*-hexadecane (99%, Sigma–Aldrich Chemicals, USA), automatic transmission fluid (ATF, The National Association for Stock Car Auto Racing Inc., USA) and DI water (lab provided) were used as the probing liquids in contact angle measurements and surface tension calculations. The surface tension and the components of the liquids used in this research were listed in supplemental information (Table S1).

Table 1
A list of samples: flat, micropillared, with and without FDTS modification by coating and blending.

	Flat		Micropillar
Sample 1	Neat	Sample 4	Neat
Sample 2	FDTS coated	Sample 5	FDTS coated
Sample 3	FDTS blended	Sample 6	FDTS blended

2.2. Fabrication

Six types of PDMS specimens have been fabricated and listed in Table 1. Sample 1: neat flat PDMS; sample 2: FDTS-coated flat PDMS; sample 3: FDTS-blended flat PDMS; sample 4: PDMS micropillar; sample 5: FDTS-coated PDMS micropillar; sample 6: FDTS-blended PDMS micropillar. In a typical experiment, the PDMS base was mixed with its curing agent with a weight ratio of 10:1. The mixture was poured onto a silicon wafer to make flat samples (about 1.2–1.3 mm thickness and 45 cm^2 in area) and on a silicon negative mold to make micropillared samples. Each sample was fully degassed before they were put into oven to cure at 90 °C for 1 h. Once cured, the micropillared PDMS films were gently peeled from the silicon negative mold. To coat FDTS on PDMS samples, a thin layer of FDTS were deposited onto the surface of PDMS samples by vaporizing 50 μl of FDTS solution per PDMS sample in a sealed container (diameter: 140 mm, height: 20 mm, the density of coated FDTS is 2.14 g/m^2) at 70 °C for 2 h. Note that no plasma treatment of the PDMS was made because of the possible instability and roughening/damage of plasma-treated surface even though it may enhance the surface reactivity with the FDTS. [41–43]. To blend FDTS into PDMS, a certain quantity of FDTS was added into the PDMS solution with varied FDTS/PDMS weight percentage: 0, 0.57%, 1.42%, 2.27%, 3.12% and 3.97%. The mixtures were stirred and fully degassed, and then put into oven to cure at 100 °C for 30 min.

2.3. Characterization

Field emission scanning electron microscopy (FE-SEM, LEO-Ultra, GEMINI, Germany) was used to examine the FDTS-modified PDMS micropillars. Fourier transform infrared spectroscopy (FTIR, Tensor 27, LN-MCT detector, diamond crystal, PIKE Technologies, USA) was used to analyze the $-CF_2$ and $-CF_3$ groups in FDTS-blended PDMS micropillar. The surface roughness of FDTS-coated/blended flat PDMS were measured by an optical profiler (MFP-D WLI 3D surface profilometer, Rtec Instruments Inc., USA) and AFM (Digital Instruments 3100), respectively. X-ray Photoelectron Spectroscopy (XPS, monochromatic Al Ka X-ray source, Thermo Scientific Alpha) was used to analyze the atomic composition at the surface and the cross-section. Water and oil static contact angle measurements were performed by a sessile drop system in ambient environment at room temperature as illustrated in Fig. 1. The liquid was dispensed with a micro size needle (New Era Pump Systems Inc.) through a syringe pump in shape of droplets with volume of 5 μl. Measurements were carried out in ambient environment at room temperature after the droplet settled for 5 s. The contact angle was measured by fitting the profile using a custom-made LabVIEW program.

3. Results and discussion

3.1. FDTS-functionalized PDMS micropillars

Neat and FDTS-modified PDMS micropillars were fabricated using our previously developed mold transfer method [10,44].