Self-Replenishable Anti-Waxing Organogel Materials**
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SI guide

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1. General Materials

PDMS oligomer & curing agent kit (Sylgard 184) and primer coating (1200 OS) is purchased from Dow Corning. Benzene-modified PDMS gel (with the concentration of benzene monomer at 0%, 5%, 10%) is kindly provided by Prof. Zhijie Zhang’s group from Institute of Chemistry, Chinese Academy of Sciences (ICCAS). The crude oil sample is by the courtesy of Prof. Jinben Wang from ICCAS. Steel, glass, PE and PVC plates are purchased from Huawei Company. Paraffin wax (m.p. ~50°C) is purchased from Sinopharm Chemical Reagent Co., Ltd. N-decane (C10), n-tetradecane (C14), n-heptadecane (C17), n-eicosane (C20), n-tetracosane (C24) are purchased from Sigma-Aldrich.

2. Scanning electron microscope characterization of paraffin wax

Paraffin wax (with melting point being ~ 50°C) was melted at 80°C. About 20 μL of paraffin wax was deposited on OG or PDMS sample surfaces, which had been kept at room temperature. Then the solidified paraffin wax deposits were carefully peeled off and fixed on SEM sample stage. Since the sample preparation for scanning electron microscope generally require high temperature which would cause melting of the paraffin wax deposit, environmental scanning electron microscope (Quanta FEG230, FEI, USA) was utilized for the characterization. All wax samples were characterized at 0°C and under 400 Pa.

3. Wax adhesion test

To test the adhesion of paraffin wax to solid surfaces, we devised a set of measuring apparatus which comprises a platform with a sample socket (where the
samples can be horizontally fixed) and a dynamometer with cylindrical steel probe (7 mm in diameter) fixed on a 2D translational stage.

Before the tube test, 1-cm-high wax liquid was allowed to solidify and form wax plugs inside steel, PE and OG tubes (10 mm in inner diameter). The tubes were then fixed horizontally on the platform. The probe and the tube are coaxial. During the test, the probe approaches to the tube in the velocity of 0.5 mm/s. The probe entered into the tube and make contact with the wax. Then a growing pressure was applied onto the wax plug until it was separated from the tube inner surface. The computer will record the force data as the time. The shear stress was calculated by the maximum force divided by wax/tube contact area (~ 3.14 cm²).

For the adhesion vs. time test, disposable colorimetric cuvette was utilized. Typically, a colorimetric cuvette (1 × 1 × 1 cm³) with no bottom was placed on a sample surface at room temperature. Paraffin wax (at 80°C) with a volume of 1 mL was filled in the cuvette. After wax solidification, control the probe to approach the cuvette in speed of 0.5 mm/s. Computer recorded the maximum force for the probe to remove the cuvette. The resulting shear stress was calculated by the maximum force divided by wax/sample contact area (~ 1 cm²).

4. Wax sliding angle measurements

The sliding angle of solidified paraffin wax on the OG surfaces (swollen by gasoline, diesel, crude oil, and n-decane) was characterized by the OCA20 contact angle measuring system (Dataphysics, Germany). In a typical process, paraffin wax (m.p.
~50°C) was heated up to 80°C, after which a pre-heated micro-syringe was used to deposit a 3-μL drop of wax on the OG surface. The wax drop and the OG substrate were then kept horizontal at room temperature until the shrinking of wax drop due to solidification was clearly observed. Increasing the tilting angle of the platform at an increment of 1° to determine the sliding angle of wax on OG surface. The CCD camera is fixed to the platform so that the displacement of wax can be accurately captured from the image. Due to gasoline evaporation in air, sliding angle of wax on OG swollen by gasoline is slightly higher than those on other samples.

5. **AFM force curve on the OG surface**

As shown in Figure S4, the red and blue curves represent a loop motion of AFM needle tip dipping in, touching and drawing out of the sample surface. A typical loop of AFM force curve obtained from common solid surfaces is shown in Figure S4-A, the red curve and blue curve have similar shapes and no obvious hysteresis was observed. Consequently, the solid surface was nearly dry in this situation (the AFM test chamber was pre-dried by inert gas to eliminate the influence of humid air). The sudden jump in the curves occurred because of electrostatic attraction or other weak interactions between tip and the sample surface.[1] However in Figure S4-B, the drawing-out (blue) curve is clearly asymmetric with the dip-in (red) curve, showing a “hysteresis” as disconnecting the surface and resuming its initial position in the mid-air later. Earlier studies showed that this disconnection hysteresis reflects the interaction of a hard, solid probe tip leaving the surface of a liquid behavior.[2] In this case, probe tip gradually rises above the liquid horizon and a capillary bridge is formed, which
poses attraction to that tip. This capillary attraction becomes weaker and weaker as the
cantilever ascends, until the bridge finally breaks. Consequently, by the existence of
hysteresis in the drawing-out curve, it is deduced that the tip was leaving a liquid surface.
Therefore, the hysteresis in the blue curve shown in Figure S4-B proves that the OG
surface was covered by a thin liquid layer.

6. Preparation of the OG as a coating material

According to standard procedure, the glass and steel substrates were cleaned with
ample water and acetone successively and dried by compressed nitrogen. Apply primer
coating (1200 OS, Dow Corning) on half of the materials surface (as shown in Figure
S6) and the substrates were dried in ambient condition for at least 15 min. The
admixture of PDMS oligomer and curing agent prepared according to Experimental
Section was brushed onto the substrates. Bubbles were eliminated by vacuum pumping
and the resulting substrates were cured in an oven at 80°C for 1 h. In order to
demonstrate the anti-waxing performance of the OG coating on conventional solid
surfaces, only half of the substrates had been applied with primer coating, which made
it easy to cut and peel off the cured PDMS gel on the area without primer coating.
Whereas on the area with primer coating, PDMS gel has been firmly attached. The
resulting substrates were immersed in diesel oil for 24 h, forming the OG-coated
substrates shown in Figure S6.
7. Supporting Figures (Figures S1–S13)

**Figure S1**, A), swelling ratio of PDMS in weight percent increases with the carbon number of the oil used to swell the gel materials. The shear stress of crude oil on OG surface in static (B) and flow (C) situations with OG swollen by oil of different carbon numbers. The result indicates that increasing swelling ratio of PDMS using lighter oil results in lower adhesion to crude oil.

**Figure S2**, A), swelling ratio of PDMS in weight percent decreases with the crosslinking density. The shear stress of crude oil on OG surface in static (B) and flow (C) situations with different PDMS crosslinking density. This result indicates that increasing swelling ratio of PDMS via lowering the crosslinking density results in lower adhesion to crude oil.

**Figure S3**, A), swelling ratio of PDMS in weight percent increases with the benzene monomer concentration in the PDMS network. The shear stress of crude oil on OG surface in static (B) and flow (C) situations. Contrary to the cases in Figure S1 and S2, although the addition of benzene
side groups also increased the swelling ratio of PDMS, this treatment leads to an inferior anti-waxing performance, which suggests that the oil content that benzene side groups had introduced into the PDMS network was mainly benzene-rich heavy oil such as asphaltenes from the crude oil. Such oil component is in solid state at lowered temperatures and cannot benefit the reduction of crude oil adhesion on the OG surface.

**Figure S4,** Gas chromatography–mass spectrometry (GC-MS) analysis on the oil consistent inside the organogel network, which has been immersed in crude oil for different time lengths. Results in this diagram show that the ratio of absorbed paraffin wax decreases with the increase of the molar mass and this trend remained as the time elapsed.
Figure S5, Polarized optical microscope images showing the wax crystallization in the crosslinked silicone network as the decrease of temperature. Only trace amount of wax crystal can be spotted when the temperature is at 0°C and below, which indicates that there had entered very small amount of paraffin wax with relatively large molar mass inside the organogel.

Figure S6, atomic force microscopic force curve recording one cycle of probe tip touching and leaving the (A) PDMS and (B) OG (diesel-swollen) surface. On PDMS surface, the force curves are symmetric, which is the typical situation for a dry and elastic solid surface. Whereas asymmetric curves in the OG case suggest that the OG surface is covered by a thin liquid layer.
Figure S7, a demonstration of paraffin wax solidified and (A) slid off from OG surface, (B) stuck to PDMS surface. The result indicates that the adhesion of solidified paraffin wax on OG is so low that it can even be slid off the OG surface by an action of its gravity.

Figure S8, SEM morphology of paraffin wax solidified on organogel surface for 6 min (A) and 60 min (B), respectively. The similar structure and dimension from the above two situations to the one appear in Figure 2A indicate that the micro-scale structure of paraffin wax crystal at the wax/organogel surface was resulted from a fully developed wax crystallization process instead of intermediated states.
Figure S9, Shear stress of paraffin wax on organogel surface as a function of the cooling rate. After an initial increase of shear stress (from ~ 0.25 kPa to ~ 1 kPa), the adhesion strength was stabilized at around 1 kPa upon any slower cooling rate, indicating that the cooling rate has a limited influence within a limited time scale (1 h) on the adhesion strength of paraffin wax on organogel surface.

Figure S10, Wax adhesion strength measured on different sample surfaces. The paraffin wax was kept in liquid state at 40°C for 24 h, followed by the exact experiment protocol shown in Fig. 3C in the main text.
Figure S11, Shear stress of paraffin wax in contact with organogel surface at different time lengths before cooled down. The adhesion is steady around 0.5 kPa at different contact time, indicating that the contacting time of paraffin wax before solidification does not have significant influence to the resulting adhesion strength on the organogel surface.

Figure S12, A), coating strategy of OG materials on conventional solid surfaces. B) and C), comparison of wax adhesion on surfaces without(left) and with(right) OG coating ((B), for glass surface and (C), for steel surface ). Result indicates that the OG materials can be applied to different surfaces as coatings.
8. Supporting Movies

Movie 1 and 2, the video clips corresponding to Figure 1-D. In Movie 1, paraffin wax was deposited on OG surface and slid along the tilted surface. In Movie 2, paraffin wax was deposited on PVC surface, which stuck firmly on the surface. The videos are played three times as fast as the real one.

Movie 3 and 4, the video clips corresponding to Figure S6-A and S6-B, respectively. In Movie 3, paraffin wax was deposited on OG surface which was slid off the surface as the time elapsed. In Movie 4, paraffin wax was deposited on PDMS surface, which stuck firmly on the surface. The videos are played five times as fast as the real one.

Movie 5 and 6, the video clips corresponding to Figure S7-B and S7-C, respectively. In Movie 5, solidified paraffin wax slid along the OG-coated glass surface while stuck on the bare glass surface. In Movie 6, solidified paraffin wax slid along the OG-coated steel surface while stuck on the bare steel surface. The videos are played five times as fast as the real one.

9. Supporting References

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