FABRICATION AND CHARACTERIZATION OF SMOOTH OMNIPHOBIC SURFACES

by

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Abstract

Liquid fouling can reduce the functionality of critical engineering surfaces. Recent studies have shown that minimizing contact angle hysteresis is a promising strategy for achieving omniphobic (all-liquid repellent) properties, thereby inhibiting fouling. Prior omniphobic films can repel a broad range of liquids, but the applicability of these coatings has always been limited to silicon wafers or smooth glass. Here we develop a facile procedure to generate an omniphobic coating on any surface, including metals, paper, ceramics, etc. The coating involves depositing an ultra-smooth, silicon wafer-like silica layer and then treating this layer with a highly reactive chlorosilane, which grafts polydimethylsiloxane chains onto the surface. Negligible contact angle hysteresis ($\leq 1^\circ$) for various liquids, including ultra-low surface tension oils, alcohols, and fluoro-solvents, was achieved on many different substrates regardless of their initial roughness or chemistry. In fact, the contact angle hysteresis was so low we were forced to propose an alternate measurement technique, using tilt angles, that reduced the inherent errors associated with traditional contact angle goniometry. The coating’s durability was characterized and, when it was damaged, could be repeatedly repaired, fully restoring the omniphobic properties to their initial state. Moreover, we introduced another potential application of these surfaces.

Viscosity measurement using a small amount of fluids is crucial since it is one of the most important parameters of a liquid. Recent studies have shown that there is a relation between viscosity and dynamic behavior of droplets on a surface. Our coating showed a promising performance confirming these relationships due to its ultra-low contact angle hysteresis. Hence, we used them to create a surface viscometer which can measure the viscosity of a wide range of liquids using only one droplet.
Lay Summary

In this work a new liquid repellent coating so called omniphobic was designed which can be applied to any substrate including metals, papers, glass, etc. This results in a more environmentally friendly layer compared with many former techniques to develop surfaces with such characteristics. The coating involves a simple and easy two-step coating procedure and can be repeatedly re-applied if damaged. Also, as a new application of these surfaces, a surface viscometer was designed and developed to measure the viscosity of liquids through dynamic properties using only one droplet.
Preface

The research submitted in this thesis was originally conducted by its author and was supervised by Dr. Kevin Golovin at the Okanagan Polymer Engineering Research and Applications (OPERA) Lab in the School of Engineering, The University of British Columbia. Parts of this thesis have been published in different journals and presented in conferences. Publications and contributions of author are as followed:

Journal publications:


**Contribution:** Design and characterization of the coating, experimental tests, writing the manuscript.


**Contribution:** Experimental tests, editing the manuscript.


**Contribution:** Surface characterization, editing the manuscript.

Conference papers and presentations:


**Contribution:** Design and characterization of the coating, experimental tests, presenting the work.

Contribution: Statistical Analysis, editing the manuscript.


Contribution: Experimental tests, editing the manuscript.

Patent:

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<td>CAH</td>
<td>Contact Angle Hysteresis</td>
</tr>
<tr>
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<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>POSS</td>
<td>Polyhedral oligomeric silsesquioxane</td>
</tr>
<tr>
<td>SLIPS</td>
<td>Slippery Liquid-Infused Porous Surfaces</td>
</tr>
<tr>
<td>SOCAL</td>
<td>Slippery Omniphobic Covalently Attached Liquids</td>
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<td>Atomic Force Microscope</td>
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<td>Scanning Electron Microscope</td>
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<td>Isopropyl alcohol</td>
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To my beloved mother who will always be remembered.
Chapter 1: Introduction

Liquid repellency has lately received a lot of interests in research and industry. Firstly, for the purpose of self-cleaning and water repellency, however, these surfaces have also been proved to be useful in other aspects and applications such as anti-icing. Most commonly, liquid-repellent surfaces are used as non-stick cookware using polytetrafluoroethylene (PTFE)\(^1\). However, there are many more applications that increase the interest towards these materials such as microfluidics\(^2,3\), self-cleaning\(^4,5\), anti-fogging/icing/corrosion\(^6–9\), in-line optical characterization in oil pumps\(^10\), etc. Fabrication of liquid repellent materials was inspired by natural hydrophobic surfaces and gained a lot of attention, not only for repelling water, but also to repel other liquids such as oils. Researchers started to develop their knowledge about wettability of materials and categorizing surfaces based on their interaction with droplets of liquids. Many researchers only investigate the static properties of droplets to study the repellency of liquids on a substrate. However, dynamic properties of droplets are one of the most important aspects of liquid repellency that had been ignored by many.

1.1 Background

1.1.1 Young’s contact angle:

When a liquid droplet is placed on a surface it will shape as a sessile drop. A sessile drop is defined as a spherical shape liquid on a surface when its height is less than twice the size of capillary length. The capillary length is related to the surface tension, gravitational constant, and liquid density. The angle that the three-phase contact line of this droplet makes with the surface is called the contact angle (\(\theta\))\(^11\). In 1804-1805, Thomas Young\(^12\) suggested a force balance between the three phases of liquid, solid, and vapor at the contact point of a droplet as, \(F_{SV} = F_{LV} \cos \theta + F_{SL}\).
were $F_{SV}$, $F_{LV}$ and $F_{SL}$ are forces. Generally, it is a relation between surface tension of the liquid, surface energy of solid and interfacial tension between solid and liquid.

$$\cos \theta_Y = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

(1.1)

Here $\gamma_{SV}$, $\gamma_{SL}$ and $\gamma_{LV}$ are surface free energies (Figure 1.1a). Surfaces that make contact angles more than 90° with water are called as hydrophobic and surfaces with less than 90° water contact angles are defined as hydrophilic. If the contact angle is higher than 150°, the surface is superhydrophobic, however the maximum water contact angle on smooth surface is $\theta_Y = 120°$ with a perfluorinated material ($\gamma_{SV} \sim 6$ mN/m). Therefore, further surface treatments (other than surface chemistry) are required to achieve superhydrophobicity which are going to be discussed here. Similar terms are used for oleophobicity, which is for oil repellent surfaces, and omniphobicity, which is for liquid repellency in general. As it is shown in Young’s equation, beside the surface tension of liquid, contact angle is directly related to the surface energy of a solid.

It should be clear that the interfacial tension between solid and liquid is only on the contact line and it does not include the interaction of molecules inside of the droplet bulk in contact with the solid. In a general sense, interfacial tension is the force required to increase the size of interface between two phases. When the interface is liquid/vapor we refer to it as surface tension (N/m) and when it is solid/vapor it refers to surface energy (J/m²). Although surface energy and surface tension are mathematically interchangeable, they are different quantities. Surface energy can be understood from generating additional surface area or more specifically, the energy needed for bringing molecules out from the bulk to the surface. According to Young’s equation, a lower surface energy leads to higher contact angles.
1.1.2 Wenzel contact angle:

Wenzel\textsuperscript{14} investigated the effect of roughness on contact angles (Figure 1.1c). Multiplying the roughness coefficient, which is defined as the ratio of total surface area over the projected surface area, by the cosine of Young’s angle as,

\[ \cos \theta^* = R \cos \theta_Y \]  \hspace{1cm} (1.2)

where \( \theta^* \) is the apparent contact (macroscopic contact angle), and \( R \) is the roughness coefficient. He showed that for contact angles more than 90°, adding roughness would increase the contact angle and for contact angles less than 90°, it will decrease the apparent contact angle. This is because \( R \) is always ≥ 1 which leads to enhancing the basic wetting behavior of the surface. In other words, adding roughness makes hydrophobic surfaces more hydrophobic and hydrophilic surfaces more hydrophilic. However, it only is correct if the liquid completely wets the surface. Non-wetted roughness on the surface lead to a heterogeneous surface.

1.1.3 Composite interfaces:

In Young and Wenzel models, it was assumed that the droplet is completely in contact with the whole area of solid.\textsuperscript{14} However it is possible to trap air pockets in between the liquid and solid interface. These surfaces first were explained by the Cassie-Baxter\textsuperscript{15} model,

\[ \cos \theta^* = R_\varphi \varphi_s \cos \theta_Y + (1 - \varphi_s) \cos 180^\circ \]  \hspace{1cm} (1.3)

where \( \varphi_s \) is the fraction of solid area, and \( R_\varphi \) is the roughness of solid fraction. However, composite interfaces can be expanded to other compositions than air/solid which have their own fractions and Wenzel roughness:\textsuperscript{16}

\[ \cos \theta^* = R_1 \varphi_1 \cos \theta_1^Y + R_2 \varphi_2 \cos \theta_2^Y \]  \hspace{1cm} (1.4)

where \( \varphi_1 \) and \( \varphi_2 \) are the area fractions of two components, and \( R_1 \) and \( R_2 \) are the Wenzel roughness of each fraction.
However, hydrophobicity or omniphobicity of materials does not only depend on apparent contact angles since neither of these equations describe contact angle hysteresis.

Figure 1.1 a) shows the three interfacial surface energies that are affected at the triple contact line. 

b) Illustrates advancing contact angle ($\theta_A$) and receding contact angle ($\theta_R$) for a droplet on an inclined surface with an angle ($\alpha$). c) Illustration of the Wenzel and Cassie-Baxter models. 

1.1.4 Contact angle hysteresis

If a droplet of water that is placed on a substrate starts to evaporate slowly in low humidity, the volume and contact angle of the droplet decreases until it recedes with a constant contact angle which is called receding contact angle ($\theta_R$). If the temperature of the surrendering air cools down below the dew point, the droplet condensates and then volume and contact angle increases until the contact line advances with a constant contact angle which is called advancing contact angle ($\theta_A$). The same contact angles can be achieved by slowly adding or withdrawing water to/from a droplet using a syringe. This could also be achieved by tilting the surface with a specific angle (Figure 1.1b). The difference between advancing contact angle and receding contact angle is called...
contact angle hysteresis ($CAH = \theta_A - \theta_R$). This is one of the most important parameters of liquid repellency. Having high contact angles alone does not lead to hydrophobicity or omniphobicity. Contact angle hysteresis is affected by surface roughness, chemical heterogeneity, surface/fluid interaction, and the surrounding vapor. This term was first investigated by Adam and Jessop\textsuperscript{17} who related it to a friction force per unit length of three-phase contact line. Later, Good\textsuperscript{18} and Bartell\textsuperscript{19} investigated the relation between roughness and contact angle hysteresis. The movement of drops on a surface could occur by different scenarios; i) Sliding, which is due to the molecular exchange between surface and interaction side, ii) rolling, which is the rotation of molecules of drops or iii) a combination of both. Consequently, it takes force to bring molecules out from the bulk to make movement happen. This force is related to contact angle hysteresis. Furmidge\textsuperscript{20} proposed the following equation in 1962,

$$mg \sin \frac{\omega}{w} = \gamma_{LV} (\cos \theta_R - \cos \theta_A)$$  \hspace{1cm} (1.5)

where $\omega$ is the tilting angle at which a sessile drop will spontaneously move, $g$ is the force due to gravity, and $m$ and $w$ are the mass and width (horizontal to the direction of drop movement) of the drop.

In this chapter we will summarize recent studies on fabricating low contact angle hysteresis surfaces. There are numerous methods and techniques for making a surface with such properties. We will first review “super” surfaces with high contact angles. For these surfaces, solid-liquid interaction is minimized which will lead to low contact angle hysteresis. Secondly, the fabrication of lubricated surfaces and their properties are discussed. Although contact angles on these surfaces are significantly lower than super-surfaces, they still possess low contact angle hysteresis with
many liquids. Finally, we will discuss the new, more eco-friendly approaches for reaching a low contact hysteresis.

1.2 Existing techniques

1.2.1 Super liquid repellent surfaces

Superhydrophobicity exists in many natural surfaces like plants\textsuperscript{21} and animal furs\textsuperscript{22}. Lotus leaves are one of the most well-known superhydrophobic surfaces and many studies have been carried out regarding these surfaces. Water contact angles on these leaves are around 160° with contact angle hysteresis of 2°.\textsuperscript{23,24} The hydrophobicity of Lotus leaves comes from the wax attached to its surface.\textsuperscript{25} The contact angle of water on wax is only about 110° but the hierarchical texture of this surface causes the superhydrophobicity\textsuperscript{23,24}. In animals, similar properties of water repellency exist\textsuperscript{26}, such as a water strider’s leg which has been reported by Jiang et al.\textsuperscript{22} The fabrication of superhydrophobic surfaces was inspired by these natural surfaces.

There are two general methods for preparing superhydrophobic surfaces: top-down and bottom up.\textsuperscript{27} The top-down approach is carried out as a removal procedure in a way that it modifies the substrate\textsuperscript{28}. For instance, lithography, micromachining, plasma treatment or etching etc. are some of the methods for fabricating in this way\textsuperscript{29}. In the top-down approach, the creation of air fractions to reach the Cassie-Baxter state is typically only in the microscale and not the nanoscale\textsuperscript{29}. The Bottom-up approach is used to achieve a low air fraction and superhydrophobic surfaces can be fabricated even with hydrophilic materials\textsuperscript{30}. However, superhydrophobic surfaces are only limited to repelling water and will be wet by low surface tension liquids and therefore cannot be used for repelling oils or other low surface tension liquids.

Superomniphobic surfaces make contact angles of more than 150° and low contact angle hysteresis with a broad range of liquids\textsuperscript{31–33}. According to Young’s equation, solid surface energy is
proportional to the cosine of the contact angle, which means that higher surface energy leads to lower contact angle with the liquid. Hence, low surface energy solids are better choices for designing omniphobic surfaces\textsuperscript{34}. Zisman et al\textsuperscript{35} studied the surface energy of different functional groups of substrates and found \(-\text{CH}_2>-\text{CH}_3>-\text{CF}_2>-\text{CF}_2\text{H}>-\text{CF}_3\). Therefore, fluorinated and perfluorinated polymers have been mostly used for fabricating superomniphobic surfaces\textsuperscript{36}. FluoroPOSS has the lowest surface energy among the fluorinated chemicals\textsuperscript{37,38}. However, even with these chemicals, reaching the Cassie-Baxter state for liquids that have \(<90^\circ\) contact angles are not possible with any type of texture\textsuperscript{34}. Consequently, even if they make high contact angles on the surface, some textures can lead to high contact angle hysteresis or zero-degree receding angle. That is where the re-entrant textures play a critical role.

To demonstrate this effect, consider the two different textures in Figure 1.2. In Figure 1.2a the texture is concave down (\(\psi>90^\circ\)) and in Figure 1.2b the texture is convex up (\(\psi<90^\circ\)). A stable Cassie-Baxter state only occurs when \(\theta\geq\psi\)\textsuperscript{37,39–41}. There are hundreds of publications about superhydrophobicity but significantly fewer researchers have reported work demonstrating superomniphobic surfaces. However, the significance of re-entrant textures has been more recognized over time. As mentioned before, reporting just the static contact angle \(>150^\circ\) does not describe the superomniphobicity of that surface. Contact angle hysteresis and roll-off angle are the other important criteria to report about a superomniphobic surface\textsuperscript{34}.

One of the first works on superomniphobicity was reported back in 1997 by Tsujii et al.\textsuperscript{42}. They developed a super repellent surface using perfluorodecyl phosphate or perfluorododecyl on a fractal, oxidized aluminum surface that makes contact angles greater than \(150^\circ\) and low contact angle hysteresis and roll-off angle with some polar oils. Further, perfluorinated silanes have recently been more common for the modification of surfaces due to its commercial availability.
Cao et al.\textsuperscript{43} used electroless etching to fabricate hierarchically porous substrates that finally were silanized by perfluorooctyl trichlorosilane. This surface made a $151^\circ$ contact angle with hexadecane.

![Figure 1.2 Important role of re-entrant texture. (a) A schematic of a concave texture ($\psi>90^\circ$) showing a liquid droplet with $\theta>90^\circ$ in Cassie-Baxter state. (b) A schematic of a convex texture (re-entrant texture, $\psi<90^\circ$) showing a lower surface tension liquid with $\theta<90^\circ$ in Cassie-Baxter state.\textsuperscript{34}](image)

Kota et al.\textsuperscript{32} fabricated hierarchical superomniphobic surfaces with re-entrant textures by the electrospinning of a poly(methyl methacrylate)-fluorodecyl POSS mix on a stainless steel mesh. Low contact angle hysteresis was observed on these surfaces with low surface tension liquids like heptane ($\gamma = 20.1$ mN/m). This low contact angle hysteresis is the result of minimizing the solid-liquid contact area in such a way that $2\mu$l droplets of heptane easily roll-off and bounce on the surface. Golovin et al.\textsuperscript{31} fabricated a transparent coating by spraying polydimethylsiloxane(PDMS)-fluorodecyl POSS particles onto PDMS pillars. A longer duration of spraying led to more repellency of these surfaces towards low surface tension liquids. However, more spraying time decreased the transparency of the surface. These surfaces display very low contact angle hysteresis and can repel high and low surface tension liquids. However, developing durable surfaces with these properties has been challenging\textsuperscript{34}. Moreover, most of these surfaces...
are fabricated with fluorinated compounds which have been recently shown as non-environmentally friendly materials.

1.2.2 Lubricant-infused surfaces

As an alternative for superomniphobic surfaces, fluid-infused porous films were introduced. In this case, they usually use perfluorinated oils since most of other typical lubricants are incapable of repelling oils as they are miscible. A well designed porous or micro/nano-textured surface can adhere the lubricant because of capillarity. Lubricated surfaces exhibit much lower static contact angles, but they have similar low contact angle hysteresis and tilting angle. ‘Slippery liquid-infused porous surfaces’ (SLIPS) was first introduced by Wong et al. Fabricating these liquid-infused porous surfaces was inspired by the Nepenthes pitcher plant. Their paper outlines some key points about how this surface should be designed. The lubricant should wet the substrate and stably adhere to it and the lubricant and the testing liquids must be immiscible. Figure 1.3b illustrates a SLIPS image and the importance of surface chemistry. Lubrication worked better on a perfluorinated epoxy. Figure 1.3a shows a droplet of hexane sliding of the surface with a very low tilting angle which indicates low contact angle hysteresis. The surface also has a healing ability within 1 second since the lubricant can redistribute and repair the surface.

Rykaczewski et al. has studied the condensation of various low surface tension liquids on lubricant impregnated surfaces and compared the results with superomniphobic surfaces with re-entrant textures. Zhang et al. investigated the effect of evaporation of lubricants on wetting properties. They observed an increase in contact angles and sticky behavior on the surface after evaporation by heat.
Figure 1.3 (a) Demonstration of the mobility of a low surface tension liquid (hexane $\gamma=18.6\text{mN/m}$, volume=3.6 ml) (b) A schematic of fabricating a SLIPS.44

Daniel et al.48 has also adjusted the liquid repellency of lubricated surfaces by adjusting the temperature and viscosity of the lubricant. Yao et al.49 fabricated a flexible PDMS-based SLIPS surface. A textured Teflon membrane was deposited on a flexible PDMS substrate and then infused with perfluorinated lubricant. Huang et al.50 used branched poly(ethylene imine) and poly(acrylic acid) as the base substrate for polyelectrolyte layers. Due to the pH differences, pores on the surface formed. A fluorinated silane was used to cover the surface as an intermediate layer before the texture was infused with perfluorinated lubricant. Contact angle hysteresis on these fabricated surfaces was $2^\circ$ with decane.

1.2.3 Liquid-like brushes

Both superomniphobic and liquid-infused surfaces have textures which in the latter this texture is filled with lubricants. This will make these surfaces more sensitive to damaging. Also, most of the oil repelling surfaces require the use of fluorinated materials. Recent studies have shown that these materials, especially long-chain perfluorinated compounds, cause serious environmental issues since they are difficult to degrade. Moreover, even if they degrade after a long period, their by-products are toxic such as perfluorooctanoic acid and perfluoro(octanesulphonate)51–57. Also, these compounds need the use of toxic and flammable solvents and acids for different techniques of fabrication and reactivation, which can add to the mentioned issues regarding these chemical
compounds. Perfluorinated compounds of 8 carbons or longer (C8) have raised more concern compare to shorter chains of fluorocarbons (C6) since they have been used for food contact uses. Consequently, industry has replaced C8 compounds with C6 which almost has the same hydrophobicity properties without the same toxicity toward human and wildlife. However, C6-based compounds will also degrade to toxic acids similar to C8 compounds. Although by-products of these shorter chain compounds may be less dangerous, they are still toxic. In this section, we review the fabrication methods for making omniphobic surfaces that does not include perfluorinated compounds or fluorine atoms in them. They mostly graft liquid-like polymers onto the surface using reactive silanes which lowers the contact angle hysteresis as if the liquids are moving on another liquid layer which is attached to the substrate by chemical bondings.

There have been some studies regarding water contact angles of organic molecules such as alkylidimethylsilanes (mostly trimethylsilyl), alkyltrichloromethyl silanes etc. on silica or metal oxides and in some cases, they achieve very low contact angle hysteresis. However, they have used numerous and various unoptimized conditions. In 1999, Fadeev et al. used optimized conditions to prepare chemically graft monolayers of alkylidimethylsilanes on silicon wafers. Moreover, they investigated the effect of chain length on contact angles of water, hexadecane and diiodomethane on these surfaces. In their next work, they studied covalently attached monolayers that can be reproducibly prepared through the reaction of alkylmethyldichlorosilanes and alkyltrichlorosilanes with silicon wafers. Their surfaces had 2° contact angle hysteresis with hexadecane. Cheng et al. fabricated an omniphobic surface without using any perfluorinated compounds. They demonstrated a controllable, dynamic de-wetting behavior (low contact angle hysteresis and tilting angle) of both low and high surface tension liquids, by employing PDMS brush films consisting of low molecular weight polymer chains. Vinyl-terminated PDMS was
grafted to the Si-H moieties of a 1,3,5,7-tetramethylecyclotetrasiloxanemonomeric layer on oxidized Si surfaces. Surfaces became omniphobic, with a low contact angle hysteresis value for water ($\theta_A/\theta_R=106^\circ/105^\circ$) and n-hexadecane ($\theta_A/\theta_R=33^\circ/31^\circ$). This resulted from the liquid-like behaviour of PDMS chains at the interface. By applying moderate heat, contact angle hysteresis further decreased.

Urata et al. fabricated hybrid films through a sol-gel method of a mixture of a range of alkyltriethoxysilanes with various carbon atom numbers and TMOS. When the carbon number of alkyl chains was under 10, the hybrids were very smooth and transparent with a very low contact angle hysteresis with different alkane liquids. TMOS molecules played a significant role in both making continues film and the flexibility of alkyl chains that resulted in a smooth, liquid-like film.

Wang et al. described a simple procedure to prepare an omniphobic surface on a silicon wafer. This procedure is based on sulfuric acid catalyzed hydrolysis and step-growth graft polymerization of dimethyldimethylsilane which results in a smooth, slippery, covalently attached liquid (SOCAL) layer. The SOCAL coating shows contact angle hysteresis below 1° towards liquids with a broad range of surface tension. Singh et al. developed a facile process to induce dynamic omniphobicity to various silicon wafers deposited with oxidized metal (Al, Ti, Fe, Ni, and Cu). Smooth polymeric layers with thicknesses of 2-10 nm were grafted to their surfaces by heating trimethylsiloxy-terminated PMHSs. The results were smooth liquid-like layers with both low contact angle hysteresis (< 5°) and tilting angles (< 8°) toward small drops with low and high surface tensions. In general, all these surfaces are very smooth and unlike the superomniphobic and liquid-infused surfaces, they do not have textures. However, applying these coatings are limited to silicon wafers or smooth glass.
1.3 Motivation

As mentioned earlier, smooth fluorine-free omniphobic surfaces have been mostly investigated on silicon wafers and smooth glass. These smooth liquid-like layers can be applied on surfaces with hydroxyl groups using reactive silanes. This will be a disadvantage to the applicability of these coatings on substrates such as metals, polymers, paper, etc. Also, a drastic increase in contact angle hysteresis by surface roughness of substrates is another drawback for smooth liquid-like layers. Hence, we propose a new smooth omniphobic coating method by: i) using environmentally friendly compounds instead of fluorinated materials. ii) minimizing the contact angle hysteresis to near-zero values. iii) enhancing the durability of the coating. iv) applying the omniphobic coating to a wide range of substrates despite their surface chemistry and roughness. And then we study on the potential applications of these coated surfaces. These will lead to a surface with an enhanced liquid repellent coating which can be used in a wide range of applications. Moreover, surface characterization and investigation of contact angles is another goal of the research since it will become apparent that the classical goniometry method has high errors in measurements. If such surfaces with near zero contact angle hysteresis are developed, differentiating the behavior of various liquids on these surfaces only with a goniometer would not be feasible. Moreover, the low contact angle hysteresis of these omniphobic surfaces could be used to investigate the characteristics of sliding droplets. One of these characteristics is liquid viscosity which is usually measured by using large volumes of liquids. Therefore, the dynamic behavior of single droplets on a low contact angle hysteresis surface is studied to measure the viscosity of liquids.

1.4 Objectives and outline

Objective 1: Fabricating a substrate-independent liquid-like omniphobic coating with low contact angle hysteresis.
**Hypothesis:** By applying a silica layer onto different substrates, we can graft liquid-like polymer chains using 1,3-dichlorotetramethyldisiloxane to reach near-zero values for contact angle hysteresis.

**Tasks:**
- Investigating the procedure of synthesizing a smooth, silica layer through a sol-gel method.
- Modifying the silanization methods for coat the silica layer with 1,3-dichlorotetramethyldisiloxane to reach ultra-low contact angle hysteresis.
- Studying the contact angle hysteresis and analyzing it for various liquids on different substrates.
- Surface characterizations and roughness measurements of coated and uncoated substrates.

**Objective 2:** Measuring the viscosity of liquids with only a single droplet.

**Hypothesis:** Low contact angle hysteresis surfaces and the cornering behavior of sliding droplets can be used to measure the viscosity of liquids using a single droplet.

**Tasks:**
- Identifying the characteristics needed to design the surface viscometer.
- Design and fabrication of the surface viscometer.
- Measuring the viscosity of various liquids for accuracy confirmation.
- Recognizing the limitations of the surface viscometer.

In the following chapter, we tackle the fabrication of smooth, liquid-like omniphobic coating and perform surface characterizations as contact angle measurements, contact angle hysteresis analysis, coating procedure, and durability tests. We also discuss the repairability of these coating using the same coating method on damaged substrates. We propose a new method to measure the
contact angle hysteresis which we show is more accurate than the goniometer method and explore the substrate independency of this coating. In the third chapter, we use our coating to create a surface viscometer using the dynamic behaviors of liquid droplets on inclined surfaces. Viscosity ranges, liquid types, and mixtures are investigated on our single-droplet surface viscometer.
Chapter 2: Design and High-Resolution Characterization of Silicon Wafer-like Omniphobic Liquid Layers Applicable to Any Substrate

2.1 Introduction

Recall that surfaces that can repel a broad range of liquids are called omniphobic and have a wide range of applications from microfluidics to solar cell panels.\textsuperscript{71–73} Rather than maximizing the static contact angle, $\theta_s$, that a droplet adopts on a surface, recent studies have focused on minimizing the contact angle hysteresis for omniphobic surface development.\textsuperscript{31,32,34,44,49,69} Currently, there are three promising strategies for minimizing contact angle hysteresis (CAH). Superomniphobic surfaces utilize a composite solid-liquid-vapor interface, enabled by re-entrant texture, and make apparent contact angles $\theta_s \geq 150^\circ$ with various liquids.\textsuperscript{74} Such surfaces can exhibit low CAH due to the small contact area between the liquid and solid, and the disconnected contact line.\textsuperscript{34} However, these surfaces are susceptible to liquid pressure, temperature, and mechanical damage, after which their low CAH disappears once the liquid transitions from the Cassie-Baxter state to wetted, Wenzel state.\textsuperscript{32} Additionally, most superomniphobic surfaces are fabricated with fluorinated compounds which are environmentally hazardous.\textsuperscript{51–53} The fabrication of non-fluorinated superomniphobic surfaces is rare and quite complex.\textsuperscript{37}

To circumvent the pressure instability of superomniphobic surfaces, lubricant-infused surfaces have been developed.\textsuperscript{44,75,76} These surfaces utilize nano-texture infused with a thin layer of liquid lubricant, which provides a smooth, continuous, mobile interface. Lubricated surfaces exhibit low CAH and very low sliding angles with a wide range of liquids, and these properties can be maintained by replacing the oil, once depleted.\textsuperscript{6,44,48,49} Lubrication alters the three-phase contact line, from solid-liquid-vapor to liquid-liquid-vapour, which reduces contact line. The necessary
immiscibility between the lubricant and the liquid to be repelled typically requires the use of fluorinated oils, which again have the problem of toxicity. Mechanical durability of the nanoscale texture remains a challenge, in addition to lubricant loss.

A promising alternative is to graft liquid-like polymer chains directly onto a surface, creating a smooth, mobile interface that is covalently bonded to the substrate. Such surfaces can repel many liquids with very low CAH. The low CAH results from the polymer chains on the surface remaining in a liquid-like state, which minimizes contact line pinning in a manner similar to lubricant infused surfaces. Fadaav and McCarthy have previously reported very smooth ultralysophobic surfaces that maintains low CAH with water and low surface tension liquids. Wang and McCarthy introduced a facile method to fabricate omniphobic surfaces through acid-catalyzed graft polycondensation of dimethyldimethoxysilane, generating liquid-like polydimethylsiloxane (PDMS) chains. Recently, Singh et al. prepared omniphobic metalized silicon wafer surfaces by thermal treatment of polymethylhydrosiloxane on native oxides deposition layers. Although these surfaces achieved quite low CAH, they have only been applied to silicon wafers and lab-grade glass. Recently, liquid-like layers have been developed exhibiting high adhesion to a wide variety of substrates, but the low CAH was only reported for glass substrates and non-polar liquids. Substrate independent omniphobicity remains elusive. In this work, we develop a facile methodology for imparting negligible CAH to any substrate. The two-step coating involves first depositing a thin, ultra-smooth silica layer that can attach to any substrate, followed by reacting the silica layer with a chlorosilane at ambient temperature and pressure in minutes (Figure 2.1).
Figure 2.1 Schematic of the silica layer and SWOLL coating on glass. The smooth silica layer covers any inherent surface roughness, lowering CAH and tilt angles.

2.2 Materials and methods

2.2.1 Materials:

Toluene, isopropyl alcohol, ethanol, and 12M hydrochloric acid were purchased from VWR. Perfluorodecalin, diiodomethane, n-dodecane, N,N-dimethylformamide, n-hexadecane, and tetraethoxysilane (TEOS) were purchased from Alfa Aesar. 1,3-dichlorotetramethyldisiloxane was purchased from Gelest. Glass slides were bought from VWR. Stainless steel, mirror polished aluminum, and nylon were purchased from McMaster Carr. 6061 aluminum was purchased from Metal Supermarkets. The ceramic (vitreous china) was taken from a toilet cistern cover provided by a local bathroom supply store.

2.2.2 Characterization:

Surface morphology was imaged using a scanning electron microscope (SEM, Tescan Mira 3 XMU, sputtered with Pt to reduce charging). PDMS and silica roughness were measured using a Park NX10 AFM. A silicon probe was used (NSC14/Hard/AI BS) in tapping mode (0.3Hz, 512
pixels) for the PDMS roughness and thickness measurement. A laser interferometer (Olympus LEXT OLS5000) was used to confirm thickness and roughness measurements. Contact angles and tilting angles were measured using a Ramé Hart 260 Contact Angle Goniometer.

2.2.3 Preparation of the silica layer:

A polymeric sol-gel method was carried out for preparing the thin layer of silica on substrates. TEOS was used as a silica alkoxide in an acid-catalyzed reaction. The ratio of TEOS/ethanol/H₂O/HCl was 1/3.8/6.4/0.085. First, ethanol and TEOS were stirred vigorously (600 rpm) at room temperature for 1 minute. Next, water and then HCl were added and the temperature was raised to 60 °C. The solution was stirred at this temperature for 3 hours and then cooled to room temperature. After one day of aging, the solution was found to be ideal for forming the silica layer on the substrates. After around 45 days at room temperature, gelation of the solution occurred. Table 2.1 shows the effect of solution aging on the thickness of silica layer.

A dip coating method was used for applying the silica layer on the substrates. Substrates were first washed with isopropyl alcohol and toluene and then treated with air plasma (Plasma etch PE-25) for one minute at 106 mTorr vacuum pressure. Plasma treated aided in the silica solution perfectly wetting the substrates during dip-coating withdrawal. Substrates were dipped into the silica layer solution at a speed of 600 mm/min using an Ossila automated dip-coater, and then they were withdrawn from the solution at a speed of 20 mm/min. Following dip coating, substrates were cured at 110 °C for 10 minutes in an oven. Multiple layers could be applied onto one another by repeating this procedure in order to increase the silica layer thickness.
Table 2.1 Thickness of the silica layer for various solution aging times, after deposition and curing on bare glass.

<table>
<thead>
<tr>
<th>Aging time [days]</th>
<th>Thickness [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>51 ± 10</td>
</tr>
<tr>
<td>2</td>
<td>79 ± 7</td>
</tr>
<tr>
<td>5</td>
<td>118 ± 5</td>
</tr>
<tr>
<td>8</td>
<td>149 ± 8</td>
</tr>
<tr>
<td>15</td>
<td>289 ± 7</td>
</tr>
<tr>
<td>25</td>
<td>489 ± 11</td>
</tr>
<tr>
<td>30</td>
<td>Gelation</td>
</tr>
</tbody>
</table>

2.2.4 Silanization:

Various approaches (solution and vapor-phase), reaction times, temperatures and concentrations were used to react 1,3-dichlorotetramethyldisiloxane with substrates (Table 2.2).

2.2.5 Vapor-phase:

Substrates were first rinsed with toluene and isopropyl alcohol for 30 seconds and dried with compressed air. Next, substrates were treated with air plasma for one minute at 106 mTorr vacuum pressure. They were then placed in 60 × 15 mm petri dishes with 150 µL of 1,3-dichlorotetramethyldisiloxane held in a small glass container. The petri dish was then closed for 5 minutes. Following exposure, the substrates were removed from the petri dish and were washed...
with toluene and isopropyl alcohol for several minutes before being dried with compressed air.

Figure 2.2 shows the effect of vapor deposition time on contact angle hysteresis for bare glass. After 5 minutes of exposure to 1,3-dichlorotetramethyldisiloxane, advancing and receding contact angles did not change.

![Figure 2.2](image)

**Figure 2.2** Advancing and receding contact angles of glass (no silica layer) exposed to 1,3-dichlorotetramethyldisiloxane in vapor-phase, from 10 seconds to 15 minutes of reaction time.

### 2.2.6 Solution-phase:

A 5 wt% solution of 1,3-dichlorotetramethyldisiloxane in ethanol was prepared and stirred for 2 hours at 60 °C in order for the molecules to hydrolyze, releasing HCl. The hydrolyzed solution was then used for dip coating. First, substrates were rinsed for 30 seconds using toluene and isopropyl alcohol, dried with compressed air, and then treated with air plasma for one minute at 106 mTorr vacuum pressure. Next, substrates were dipped into the solution and withdrawn at a speed of 100 mm/min using an Ossila automated dip-coater. Coated substrates were then dried at
110 °C for 10 minutes in an oven, and then washed with toluene and isopropyl alcohol for several minutes. Treatment of substrates with both approaches (vapor-phase followed by solution-phase or vice versa) was carried out using the same procedures detailed above.

Table 2.2 Advancing and receding contact angles (CA) for various concentrations of 1,3-dichlorotetramethyldisiloxane in solution-phase, and temperatures in vapor-phase coating, on bare glass slides.

<table>
<thead>
<tr>
<th>Coating method</th>
<th>Advancing CA, $\theta_A$ [°]</th>
<th>Receding CA, $\theta_R$ [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution, 2 w%</td>
<td>98</td>
<td>86</td>
</tr>
<tr>
<td>Solution, 5 w%</td>
<td>99</td>
<td>89</td>
</tr>
<tr>
<td>Solution, 7 w%</td>
<td>99</td>
<td>87</td>
</tr>
<tr>
<td>Solution, 10 w%</td>
<td>99</td>
<td>87</td>
</tr>
<tr>
<td>Vapor, 22°C</td>
<td>106</td>
<td>98</td>
</tr>
<tr>
<td>Vapor, 30°C</td>
<td>105</td>
<td>97</td>
</tr>
<tr>
<td>Vapor, 40°C</td>
<td>107</td>
<td>98</td>
</tr>
<tr>
<td>Vapor, 50°C</td>
<td>109</td>
<td>95</td>
</tr>
<tr>
<td>Vapor, 60°C</td>
<td>109</td>
<td>96</td>
</tr>
</tbody>
</table>
2.2.7 **Thickness and roughness measurements:**

A 3D laser scanning microscope (LEXT OLS5000) was used to measure the roughness of the substrates and thickness of the silica layers using a 50X magnification lens. Coated substrates were scanned, and thicknesses were measured by comparing the height difference between coated and uncoated regions of the substrates. Thickness was also measured with AFM by again scanning over regions with and without the silica layer (Figure 2.3). The measured thickness for the same spot on a silica layer deposited from a sol-gel solution aged 15 days was 262 nm using AFM and 279 nm using the laser scanning microscope. We also observed that the increase in thickness due to aging could be slowed down by lowering the temperature of the solution.

![Image](image_url)

**Figure 2.3** (a) AFM imaging of the boundary between the silica layer and uncoated glass. (b) 3D scanning laser microscope heightmap of the same boundary between silica/glass.
2.2.8 Damaging procedures:

1) Ultraviolet radiation: SWOLL glass samples were put inside of a UV chamber (8.7 mW cm$^{-2}$) for 4 continuous hours and then removed. 2) Acid: SWOLL glass samples were immersed inside 50 mL of 12M hydrochloric acid in a beaker for one hour. Subsequently, the surfaces were removed from the beaker and washed with copious water and isopropyl alcohol. 3) Droplet impact: 27 µL water droplets were dropped on SWOLL glass from a height of 1 meter. 4) Sonication: SWOLL glass samples were immersed in 100 mL of acetone and were then sonicated for 1 hour using a VWR ultrasonic cleaner. 5) Heat: SWOLL glass samples were heated to 150 °C for one hour in an oven (Across Instrumental, Accutemp-00). 6) Steam: SWOLL glass samples were placed in a closed beaker, saturated with 250 °C steam for 30 minutes. 7) Scratching: SWOLL glass samples were scratched 50 times with random cuts using a razor blade. 8) Abrasion: SWOLL stainless-steel sheets were damaged by 1,000 cycles of Taber abrasion (Shanghai Glomro Industrial Co.) using the CS-10 wheelset, 500 g load, and 60 cycles/min. 9) Heat: SWOLL glass
samples were exposed to 700 °C heat in a furnace (Isotemp Programmable Muffle furnace, Fisher Scientific) for one hour.

2.3 Fabrication

1,3-dichlorotetramethyldisiloxane was used to generate the omniphobic surfaces, as demonstrated previously on glass and silicon wafers. Via a substitution reaction following hydrolysis, this difunctional chlorosilane reacts with surface hydroxyls and self-polymerizes, covalently grafting linear PDMS chains to the substrate. Reaction in solution, vapor, and a mixture of both methods was carried out to graft the PDMS, first using silicon wafers as substrates. The CAH with water was measured to characterize the grafted layer, using the sessile droplet technique. After optimization of both deposition routes (Figure 2.5, Table 2.2), it was found that 1,3-dichlorotetramethyldisiloxane was less reactive in solution which resulted in surfaces with higher CAH. Vapor phase method favors monolayer deposition. However, solution phase following vapor phase deposition resulted in the lowest CAH (Figure 2.5). The subsequent solution deposition homogenized the surface of the vapor-deposited film, reducing the root-mean-squared roughness, $S_q$, from 0.77 nm to 0.24 nm, as measured by AFM (Figure 2.6). This was statistically equivalent to a bare silicon wafer (Figure 2.4). This optimized procedure was then applied on bare glass slides. However, the lowest CAH observed for water was around 7°, due to the inherent surface roughness of the glass. Other substrates (Al, nylon, steel) exhibited even higher CAH, due to roughness and a less reactive surface for grafting the chlorosilane.
To extend omniphobicity to any substrate, we developed a method for forming an ultra-smooth, homogenous thin film of silicon dioxide on a surface through the hydrolysis reaction of tetraethoxysilane (TEOS) in ethanol. When deposited on glass, this silica layer covered the intrinsic roughness and created a smooth surface for further chlorosilane deposition (Figure 2.8). Surface roughness of the silica-treated and untreated glass was measured using a 3D laser scanning microscope. Roughness decreased from $S_q = 19$ nm to $S_q = 4.7$ nm after silica deposition. The thickness of the silica layer was readily controllable by varying the aging of the sol-gel solution at room temperature, from 50 nm (1 day of aging) up to 500 nm (25 days of aging). Silica layer thickness was monitored using laser interferometry and confirmed with AFM (Figure 2.3). By depositing a sufficiently thick layer of silica to cover the intrinsic surface roughness of any surface,
we were able to dramatically decrease the CAH down to $1^\circ$, equivalent to a silicon wafer (Figure 2.5). It was observed that a combination of first vapor deposition then solution-phase silanization provides the lowest CAH on all tested substrates. Figure 2.6 shows that vapor deposition alone possesses higher surface roughness compare to the combination of two silanization methods hence the lower CAH. The roughness of vapor $\rightarrow$ solution procedure is as low as a silicon wafer (Figure 2.4).

![AFM scans of the SWOLL coating deposited on a silicon wafer, and its surface roughness for vapor-phase deposition and vapor-phase deposition followed by solution-phase deposition.](image)

Omniphobicity was characterized using water, diiodomethane, dimethylformamide, hexadecane, ethanol, dodecane, and perfluorodecalin as probe liquids. Figure 2.7 is an illustration of single droplets of these liquids on a SWOLL glass. For all these liquids, our omniphobic silica on glass exhibited $\text{CAH} = 1^\circ \pm 1^\circ$. Table 2.3 shows the advancing and receding contact angles of these liquids on various SWOLL-coated substrates, as measured by a goniometer. Although contact angles on SWOLL surfaces ranged from $105^\circ \pm 2^\circ$ (water) to $24^\circ \pm 2^\circ$ (dodecane), negligible CAH was observed for all probe liquids.
Table 2.3 Advancing / receding contact angles of liquids on SWOLL substrates using a goniometer.

<table>
<thead>
<tr>
<th>Liquids</th>
<th>Surface tension$^a$ [mN/m]</th>
<th>Glass</th>
<th>Mirror polish</th>
<th>Ceramic</th>
<th>Al</th>
<th>Steel</th>
<th>Nylon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>72.8</td>
<td>106/105</td>
<td>105/104</td>
<td>107/105</td>
<td>107/105</td>
<td>107/104</td>
<td>106/103</td>
</tr>
<tr>
<td>Diiodomethane</td>
<td>50.8</td>
<td>74/73</td>
<td>75/73</td>
<td>75/72</td>
<td>75/72</td>
<td>75/72</td>
<td>75/71</td>
</tr>
<tr>
<td>Dimethylformamide</td>
<td>37.1</td>
<td>65/64</td>
<td>64/62</td>
<td>65/63</td>
<td>66/63</td>
<td>65/63</td>
<td>64/62</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>27.5</td>
<td>35/35</td>
<td>36/35</td>
<td>36/35</td>
<td>36/35</td>
<td>38/36</td>
<td>36/34</td>
</tr>
<tr>
<td>Ethanol</td>
<td>22.1</td>
<td>29/29</td>
<td>29/29</td>
<td>28/27</td>
<td>28/27</td>
<td>26/26</td>
<td>27/25</td>
</tr>
<tr>
<td>Dodecane</td>
<td>25.3</td>
<td>25/25</td>
<td>24/24</td>
<td>25/24</td>
<td>27/26</td>
<td>26/26</td>
<td>27/25</td>
</tr>
<tr>
<td>Perfluorodecalin</td>
<td>19.0</td>
<td>35/35</td>
<td>34/33</td>
<td>34/33</td>
<td>34/33</td>
<td>34/33</td>
<td>34/33</td>
</tr>
</tbody>
</table>

$^a$ References$^{86,87}$
Goniometers are only accurate to ± 2° due to errors associated with the light source, the needle altering the meniscus shape, and the speed of advancing and receding, especially for contact angles below 20°.88,89 Accordingly, for low surface tension liquids we observed a contact angle hysteresis around 0° and for perfluorodecalin, even negative CAH was measured in some cases with the goniometer. In many prior works, contact angles with decimals have been repeatedly reported, ignoring goniometer resolution.90–93 To better characterize the omniphobicity and CAH of different liquids on our surfaces, we developed a tilting angle-based method, as described below.
2.4 High resolution CAH analysis

We propose an improved method to measure CAH more accurately using tilting angles on omniphobic surfaces. A simple energy balance relates contact line resistance to the potential energy of a tilted droplet at the onset of sliding,\(^{20,94}\)

\[
\pi \rho g V \sin \omega = 2 \gamma_{LV} D_{TCL} (\cos \theta_R - \cos \theta_A)
\]  

(2.1)

Here \(\omega\) is the tilt angle, \(\gamma_{LV}\) and \(\rho\) are liquid’s surface tension and density, respectively, \(V\) is the droplet volume, and \(D_{TCL}\) is the diameter of triple-phase contact line, calculated using,\(^{94}\)

\[
D_{TCL} \approx 2 \cos(\bar{\theta} - \pi/2) \left( \frac{3V}{\pi(2-3 \cos \bar{\theta} + \cos^3 \bar{\theta})} \right)^{1/3}
\]

(2.2)

where, \(\bar{\theta}\) is the average apparent contact angle. \(D_{TCL}\) can first be calculated from Equation 2.2, considering that \(\bar{\theta} \approx \theta_s\) measured using traditional goniometry (accurate to within \(\pm 2^\circ\)). Low CAH ensures an accurate value for \(D_{TCL}\), as any deviation from an ideally spherical cap is minimal. The highest error calculated for \(D_{TCL}\) was for dodecane (\(\pm 0.205 \text{ mm}\)) and the lowest was for water (\(\pm 0.035 \text{ mm}\)). Equation 2.6 can be rearranged such that plotting \((2\gamma_{LV} D_{TCL})/\pi \rho g \sin \omega\) against droplet volume gives a slope of \((\cos \theta_R - \cos \theta_A)^{-1}\) (Figure 2.9). Unlike contact angles, liquid volume, density, surface tension, and tilt angles can be measured with high accuracy. The value for \(\cos \theta_R - \cos \theta_A\) for each liquid may then be found with high precision using a linear regression.
CAH cannot directly be calculated from the value of \( \cos \theta_R - \cos \theta_A \) as many advancing and receding contact angle combinations result in this value, within experimental error. By additionally stipulating \( \theta_A > \bar{\theta} \pm 2^\circ > \theta_R \), a unique value of CAH may be determined (Figure 2.10 Left). In other words, there are many possibilities for advancing and receding contact angles of liquids, which we are not measuring. However, we can verify using the goniometer that these contact angles cannot possess values more than \( \pm 2^\circ \) different from the liquid’s apparent contact angle. Knowing this fact and each liquid’s apparent contact angle we can iterate through various combinations of \( \theta_A \) and \( \theta_R \) until the term \( (\cos \theta_R - \cos \theta_A)^{-1} \) matches the slope in Figure 2.9, and from these angles calculate CAH. The error in the slope will mean there are more than one combination of \( (\theta_A, \theta_R) \) that gives the correct value, and hence the error in the calculated CAH. Using this methodology, CAH for water \( (1.34^\circ \pm 0.15^\circ) \), diiodomethane \( (2.1^\circ \pm 0.4^\circ) \), dimethylformamide \( (0.92^\circ \pm 0.09^\circ) \), hexadecane \( (0.71^\circ \pm 0.16^\circ) \), and dodecane \( (0.82^\circ \pm 0.19^\circ) \) were measured. The average error in
our CAH measurements using these five liquids was ± 0.2°, an order of magnitude increases in resolution over traditional contact angle goniometry (± 2°). Figure 2.10 compares the goniometer and tilting method measurement of CAH and the variation of their respective errors.

The limitation of this method is that it only measures the CAH considering the advancing and receding angles as a range of values. Hence, the true values for these angles are unknown in this measurement. Table 2.4 shows the step by step measurement of errors and finding the slope of Figure 2.9 for water.

Figure 2.10 (Left) The unique value of CAH for each liquid was found using the slope from Figure 2.9 by additionally stipulating $\theta_A > \bar{\theta} \pm 2^\circ > \theta_R$. (Right) Variation in measured CAH between the goniometer and tilting method and their respective errors.

2.4.1 Statistical analysis:

Error propagation for independent variables was investigated for the term $y = (2\gamma DTCL)(\pi \rho g \sin \omega)^{-1}$, the y-axis for Figure 2.9, to find the error of each data point for the different liquids as,
\[ \sigma_y = \sqrt{\left(\frac{\partial y}{\partial D_{TCL}}\right)_\omega \sigma_{D_{TCL}}^2 + \left(\frac{\partial y}{\partial \omega}\right)_{D_{TCL}}^2 \sigma_{\omega}^2} \] (2.3)

where \( \sigma_i \) represents the standard error of each variable \( i \). Recall \( D_{TCL} \) is the diameter of the contact line, \( \omega \) is the tilt angle, \( V \) is the droplet volume, and \( \bar{\theta} \) is the average contact angle, for which we assume \( \bar{\theta} \approx \theta_s \) for omniphobic surfaces. Error in the calculated contact line length (Equation 2.4) was similarly found using,

\[ \sigma_{D_{TCL}} = \sqrt{\left(\frac{\partial D_{TCL}}{\partial \bar{\theta}}\right)_V \sigma_{\bar{\theta}}^2 + \left(\frac{\partial D_{TCL}}{\partial V}\right)_{\bar{\theta}}^2 \sigma_{V}^2} \] (2.4)

For determining the CAH of each liquid on the coated substrates, the term \((\cos \theta_R - \cos \theta_A)^{-1}\) was found by calculating the slope, \( m \), of \((2D_{TCL})[\pi \rho g \sin \omega]^{-1}\) versus \( V \) using a linear regression,

\[ m = \frac{1}{\Delta} \left( \sum \frac{1}{\sigma_i^2} \sum x_i y_i - \sum \frac{x_i}{\sigma_i^2} \sum y_i \right) \] (2.5)

with,

\[ \Delta = \sum \frac{1}{\sigma_i^2} \sum x_i^2 - \left( \sum \frac{x_i}{\sigma_i^2} \right)^2 \] (2.6)

Here the total error associated with each data point \((x_i, y_i)\) in Figure 2.9 is \( \sigma_i \).

The uncertainty of the slope, \( \sigma_m \), was then calculated using,

\[ \sigma_m = \frac{1}{\Delta} \sum \frac{1}{\sigma_i^2} \] (2.7)
Table 2.4 shows the calculated errors during the CAH measurement for water.

<table>
<thead>
<tr>
<th>Volume (µL)</th>
<th>(\sigma_{\theta})</th>
<th>(\sigma_{DTCL})</th>
<th>(\sigma_y)</th>
<th>m</th>
<th>(\sigma_m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>0.035001</td>
<td>2.997085</td>
<td>44.1847</td>
<td>2.2716</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>0.041121</td>
<td>10.02005</td>
<td>(\cos\theta_R - \cos\theta_A) (\sigma_{\cos\theta_R - \cos\theta_A})</td>
<td>0.0226</td>
</tr>
<tr>
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<td>2</td>
<td>0.044049</td>
<td>6.458615</td>
<td></td>
<td></td>
</tr>
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<td>36.21902</td>
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<tr>
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<td>69.18715</td>
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</tr>
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<td>2</td>
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<td>2</td>
<td>0.070022</td>
<td>134.1247</td>
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</tr>
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</table>

2.5 Substrate independency and repairability

Armed with our ability at accurately measure CAH, we then applied the omniphobic silica coating to a number of different substrates. Metals, polymers, paper, and ceramics were coated to illustrate efficacy on substrates with varying roughness and chemistry (Table 2.3, Figure 2.11). Using hexadecane as a probe liquid, all CAH values measured on these surfaces with the goniometer were CAH = 1° ± 1° (Table 2.3). In contrast, our tilting method revealed the surface-to-surface variations (Figure 2.12). Curves in Figure 2.8 were found using Equation 2.6 for different values of hexadecane CAH, assuming \(\theta_s = 35° ± 2°\). Predicted tilt angles using the measured CAH closely
matched experimental values. 5 µL hexadecane droplets slid off coated glass at $\omega = 1^\circ$ and off coated ceramic (vitreous china, from a toilet bowl) at $\omega = 2.5^\circ$.

![Image](image_url)

**Figure 2.11** 10 µL hexadecane droplets on different SWOLL substrates. All exhibited CAH < 2°.

![Graph](graph_url)

**Figure 2.12** Experimental tilt angles versus hexadecane droplet volume on four substrates. Equation 1 is also plotted for three different values of CAH. Error bars account for droplet diameter uncertainty.

The slightly larger CAH values for ceramic and Al substrates resulted from the roughness of underlying substrates which were not completely covered by the chosen thickness of our silica
layer. Such rough surfaces can still be rendered omniphobic, either by using a more aged sol-gel solution, or by initially infilling the roughness of the substrate with curable polymers such as polyurethanes. As a demonstration, aluminum substrates were scratched with sandpaper, resulting in $S_q = 10 \pm 1 \mu m$. Coating this rough aluminum with our omniphobic silica resulted in a water CAH = $20^\circ \pm 4^\circ$. By pre-coating the rough aluminum with polyurethane, surface roughness decreased to $S_q = 400 \pm 10 \text{ nm}$. Water CAH on the pre-coated rough aluminum was $2.6^\circ \pm 0.8^\circ$ (Figure 2.13). Intentionally scratched patterns could also be covered and rendered omniphobic without altering the pattern appearance (Figure 2.14). However, there are still some limitations of the applicability of our coating for a few substrates. Teflon is one of the substrates that silica layer cannot be coated onto using the dip coating method because of its liquid repellency. Also, very rough substrates should be coated with a base layer (such as the polyurethane in Figure 2.13) in order to apply the SWOLL coating on top. Moreover, the SWOLL coating contains a rigid silica layer which would be problematic for coating flexible materials.

![Image](image1.png)

**Figure 2.13** A 5 µL droplet of hexadecane sliding on scratched SWOLL aluminum with an initial roughness of $S_q = 10 \pm 1 \mu m$. The initially rough Al was first pre-coated with polyurethane.
A 30 µL droplet of hexadecane easily sliding off a mirror polished aluminum substrate scratched with a pattern and then coated. The tilt angle was $\omega = 10^\circ$.

The coating was resistant against numerous exposures that could potentially damage other omniphobic surfaces. Elevated temperature, acid and base submersion, ultraviolet exposure, high speed droplet impact, and sonication in acetone all did not significantly affect the CAH of the coating (Figure 2.15). In contrast, exposure to steam, heating to 700 °C, large cycles of abrasion, and severe scratching all raised the water CAH significantly (Figure 2.16 Left). However, because the coating could be applied to any substrate it was possible to re-coat a damaged surface. The original, ultra-low CAH was regained by re-application using the same procedure on top of the damaged substrates (Figure 2.16 Left). By repeatedly damaging our coating using steam, we found that the omniphobicity could be restored at least ten times on the same damaged surface (Figure 2.16 Right).
Figure 2.15 CAH of SWOLL glass exposed to UV radiation (8.7 mW cm$^{-2}$) for 4 hours, immersed in hydrochloric acid for one hour, impacted by water droplets (4.4 m/s impact speed), sonicated in acetone for 1 hour, and heated at 150 °C for one hour. The inset shows sequential frames of the high-speed droplet impact.

Figure 2.16 (Left) CAH of coated glass after four damaging exposures. Surfaces were damaged by 250 °C steam for 30 minutes, 50 razor blade scratches, 1,000 cycles of Taber abrasion, and exposure to 700 °C for one hour. Blue bars show CAH after repairing the surface by re-applying the SWOLL coating. (Right) CAH of SWOLL glass after ten repeated steam exposures at 250 °C for 30 minutes, followed by repairing the surface by re-application.
Chapter 3: Surface Viscometer

3.1 Introduction

The viscosity measurement of liquids using a small liquid volume is both extremely challenging but also crucial since it is one of the most important properties of a liquid. Several types of viscometers are widely used in laboratories and in industry, such as rotational viscometers, capillary viscometers, falling ball viscometers, etc. However, these conventional viscometers typically utilize large volumes of liquid, require frequent cleaning, and involve time-consuming procedures. Here we introduce a new viscometer which can measure the viscosity of common liquids with only one droplet in a simple procedure. Firstly, we introduce a brief background on liquid droplet dynamics on an inclined surface.

3.1.1 Cornering effect

Droplets sliding on an inclined surface can exhibit complex behaviors. Droplets with high static contact angles (>150°) possess roughly spherical shapes hence they roll down the inclined surface rather than slide down it. However, droplets sliding off an inclined surface with lower contact angles can lead to contact-line singularities, coalescence, and break up at high velocities. Podgorski et al. explained the various shapes that a droplet can adopt on an inclined surface. Moreover, they showed that the transition between the droplet shapes only depends on physical properties.

The main properties used to identify the dynamics of wetting are the droplet velocity, $U$, and dynamic contact angle, $\theta_D$, which can be referred to as either advancing or receding contact angles. In our case, which can be called forced wetting, the contact line is moved by higher external forces (tilting angle higher than the minimum to start the droplet sliding from the substrate). Hence, a
relationship between these two parameters is required to explain the behavior of droplets under certain conditions.

![Figure 3.1 a) rounded droplets at low velocities. b) droplet corners as the velocity increases. c) pearling droplets start point.](image)

At low velocities the droplet shape is regular and spherical (Figure 3.1a). By increasing the velocity, the end tail of the sliding droplet starts to deform and a singularity develops at the tip with a certain angle ($\beta$)(Figure 3.1b). With further increasing the velocity, the angle ($\beta$) decreases up to 60° then it jumps to 0° where it eventually leaves small droplets at the trailing end.\textsuperscript{101} This unstable tail may be explained by a Rayleigh-like instability.\textsuperscript{103} By associating the shape of the droplet in a three dimensional flow field, an overall force balance equating the capillary number ($Ca = \eta U / \gamma_{LV}$, where $\eta$ is dynamic viscosity, $U$ is the droplet velocity, $\gamma_{LV}$ is surface tension of the liquid) and Bond number (Bo) to the dynamic contact angles ($\theta_D$) has been proposed for the cornered droplet regime.\textsuperscript{101} In general, the relation between $Ca$ and $\theta_D$ have complicated integral functions as was shown by Cox.\textsuperscript{104} However, these integrals may be simplified for liquids with contact angles less than $3\pi/4$ with less than 3% error,\textsuperscript{101}

$$\theta_D^3 = \theta_s^3 + 9 \left( \ln \frac{Y}{Y_w} \right) \eta U \ n$$

\textsuperscript{(3.1)}
where $\theta_s$ is the static contact angle, $U$ is the droplet velocity, $Y$ is the macroscopic length scale where the contact angle is measured, $Y_w$ is the microscopic length scale, and $n$ is the external normal to the contact line (Figure 3.2). Podgorski et al.\textsuperscript{101} assumed that keeping $U\cdot n = Ca \sin \Phi$ in a way that $\theta_D \approx 0^\circ$, in the cornered regime we have,

$$\frac{\eta U}{\gamma_{LV}} \sin \Phi = A\theta_R^3$$  \hspace{1cm} (3.2)

where $\Phi$ is the angle between the contact line and the direction of motion at the trailing edge in the cornered drop regime (Figure 3.2), and $A = (9\ln[Y/Y_w])^{-1}$. Values for these properties on some substrates are listed in Table 3.1. Therefore, with a very accurate $\theta_R$, we can measure the velocity and $\Phi$, and calculate the viscosity from known surface tension and $A$.

**Table 3.1 characteristics of liquid-substrate interface.**\textsuperscript{101}

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Substrate</th>
<th>$\eta$ (cP)</th>
<th>$\gamma_{LV}$ (mN/m)</th>
<th>$\theta_R$ [$^\circ$]</th>
<th>$Y_w$ (nm)</th>
<th>$A$ (comp.)</th>
<th>$A$ (exp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>47V2</td>
<td>FC725</td>
<td>2.33</td>
<td>18.7</td>
<td>35 ± 2</td>
<td>10</td>
<td>$9.7 \times 10^{-3}$</td>
<td>$1.1 \times 10^{-2}$</td>
</tr>
<tr>
<td>47V10</td>
<td>FC725</td>
<td>9.15</td>
<td>20.5</td>
<td>42 ± 2</td>
<td>20</td>
<td>$1.0 \times 10^{-2}$</td>
<td>$1.1 \times 10^{-2}$</td>
</tr>
<tr>
<td>47V50</td>
<td>FC725</td>
<td>50.2</td>
<td>20.7</td>
<td>43 ± 2</td>
<td>60</td>
<td>$1.1 \times 10^{-2}$</td>
<td>$1.2 \times 10^{-2}$</td>
</tr>
<tr>
<td>water</td>
<td>polyacrylate</td>
<td>0.891</td>
<td>72.0</td>
<td>30 ± 2</td>
<td>1</td>
<td>$8.0 \times 10^{-3}$</td>
<td>$4.4 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
3.2 Materials and methods

3.2.1 Materials:
Toluene, acetone, isopropyl alcohol, ethylene glycol, and ethanol, were purchased from VWR. Perfluorodecalin, n-dodecane, n-decane, n-tetradecane, and n-hexadecane, were purchased from Alfa Aesar. Glass slides were bought from VWR, Castor oil was purchased from Now Solutions, and Olive oil from ITALIAPASTA.

3.2.2 Characterization:
Contact angles were measured using a Ramé Hart 260 Contact Angle Goniometer. Surface tensions were measured through the pendant droplet method using the goniometer.

3.2.3 Statistical analysis:
Error propagation for independent variables was investigated for Equation 3.2 to find the error of each data point for the different liquids as,

$$\sigma_\eta = \sqrt{\left(\frac{\partial \eta}{\partial \theta_R}\right)_\phi U^2 \sigma^2_{\theta_R} + \left(\frac{\partial \eta}{\partial U}\right)_{\theta_R, \phi} \sigma^2_U + \left(\frac{\partial \eta}{\partial \phi}\right)_{U, \theta_R} \sigma^2_{\phi}} \quad (3.3)$$
where $\sigma_i$ represents the standard error of each variable $i$. Recall $\eta$ is dynamic viscosity, $U$ is the droplet velocity, $\Phi$ is the angle between the contact line and the direction of motion at the trailing edge in the cornered drop regime, and $\theta_R$ is the receding contact angle.

### 3.3 Design

The proposed viscosity measurement highly depends on the droplet’s shape and contact angle, since all the properties are considered when the droplet adopts its cornered shape. Consequently, contact angle hysteresis is a critical factor here. High contact angle hysteresis result in a change in shape as an activation barrier to move the droplet from a ground state to a transitional state. Also, high contact angle hysteresis means that values for advancing and receding might vary during the movement of the droplet on the surface. Hence, many shape changes might occur on a surface with high CAH. Accordingly, a surface with minimum contact angle hysteresis for every possible liquid is desirable. For these reasons we used SWOLL substrates.

We used SWOLL glass slides as our low contact angle hysteresis, omniphobic surface to act as the tilting substrate for our test liquids. Although they cannot repel every single liquid, they are a valid candidate for viscometers since they have repellency behaviours toward a wide range of liquids. The SWOLL glass was attached to a tilting stage (Figure 3.3) with controllable tilting angles using a digital inclinometer. The tilting stage was equipped with a ruler which can be seen through the SWOLL glass due to its transparency and can be used to measure droplet speed. Next, small volumes of different liquids were placed on the tilted SWOLL glass until the droplet reached its desired cornered shape. Finally, the velocity of droplets was captured by recording the droplet movement on camera. This simple design viscometer was used for further investigations of liquid viscosities.
3.4 Viscosity measurement

We used Equation 3.2 to calculate the viscosity of tested liquids by knowing the droplet velocity, surface tension, and receding contact angle of each liquid. These values can be easily measured using simple laboratory facilities. However, values for \( Y \) and \( Y_w \) would be still unknown for liquids on our SWOLL surfaces. In other studies, they referred to \( Y \) (macroscopic) as the capillary length \( \lambda_c = \sqrt{\frac{\gamma L V}{\rho g}} \), where \( \lambda_c \) is the capillary length, \( \rho \) is the density, and \( g \) is the gravity, which can be easily calculated,\(^{106}\) and \( Y_w \) (microscopic) as the slip length.\(^{102}\) We predicted the slip length for various liquids on liquid-like coated surfaces by experimental tests using liquids with known viscosities. Various common liquids were placed on the surface viscometer and their slip length was measured through Equation 3.2. As shown in Table 3.1, and in Cox’s analysis, these macro/microscopic lengths are usually set as \( Y = 10 \mu m \), which is the approximate macroscopic distance where the contact angle can be measured, and \( Y_w = 1 \text{ nm} \), which is on the order of the molecular size. Consequently, \( \ln(Y/Y_w) \) is on the order of 10.\(^{101,102,104}\) However, these prior values were for the liquids which completely wet the substrate. Larger values have been reported for non-
wetting surfaces which are more applicable for our surfaces. The estimated value for \( \ln(Y/Y_w) \) on our surfaces is 19 ± 1 and the slip length was calculated around 0.021 ± 0.006 nm (Table 3.2). Accordingly, we used the average of these parameters in our viscosity calculation of other fluids.

### Table 3.2 main characteristic of liquids on SWOLL surfaces.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>( \eta ) (mPas)</th>
<th>( \gamma_{LV} ) (mN/m)</th>
<th>( \theta_R ) [°]</th>
<th>( Y_w ) (nm)</th>
<th>( \ln(Y/Y_w) )</th>
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</thead>
<tbody>
<tr>
<td>dodecane</td>
<td>1.494</td>
<td>25.3</td>
<td>26 ± 2</td>
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<td>tetradecane</td>
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<td>31 ± 2</td>
<td>0.027</td>
<td>18.06</td>
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<tr>
<td>hexadecane</td>
<td>3.447</td>
<td>27.47</td>
<td>35 ± 2</td>
<td>0.015</td>
<td>18.67</td>
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<td>acetone</td>
<td>0.322</td>
<td>25.2</td>
<td>30 ± 2</td>
<td>0.026</td>
<td>20.36</td>
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<td>IPA</td>
<td>2.25</td>
<td>21.7</td>
<td>19 ± 2</td>
<td>0.0145</td>
<td>18.45</td>
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</table>

At a certain tilting angle, various liquid volumes should be used to reach the desirable cornered shape of the droplet. It was observed that for more viscous liquids a larger volume of droplet was needed rather than liquids with lower viscosities (Figure 3.4). Surface tension is also another factor that should be considered in this matter.
Figure 3.4 droplets of isopropyl alcohol (6 µL), hexadecane (8 µL), and castor oil (15 µL) respectively from left to right, running down the surface viscometer.

The surface tension of liquid PDMS is 19 mN/m.\(^6\) Consequently, liquids with surface tensions lower than 19 mN/m should not be repelled by this layer, hence it was not possible to measure the viscosity of these liquids with this surface viscometer. Moreover, liquids with contact angles higher than 90° (such as water) were found to be another limitation to this viscometer. The high contact angle of water makes it extremely difficult to shape a singularity at the tail of the droplet since SWOLL surfaces exhibit very low contact angle hysteresis. The cornered shape of a water droplet was not achieved even at 90° tilting degrees with large volumes of droplets. Thus, our single-droplet surface viscometer was limited to liquids with surface tensions higher than 19 mN/m, and non-aqueous fluids.

Considering these limitations and analysis, we measured the viscosity of some common liquids to verify the accuracy of our surface viscometer. Viscosities measured for these liquids at 22 °C (ambient temperature) were as followed: perfluorodecalin 5.2 ± 0.6 mPas, hexadecane 3.5 ± 0.65 mPas, tetradecane 2.3 ± 0.5, dodecane 1.5 ± 0.35, decane 0.9 ± 0.28, toluene 0.6 ± 0.15, IPA 2.3 ±
0.8, ethanol 1.4 ± 0.3, acetone 0.4 ± 0.07. Figure 3.5 shows the comparison between these measured viscosities with their literature reference values.

**Figure 3.5** comparison of experimental values for viscosities with actual viscosities at 22 °C.\textsuperscript{108,109}

The results were promising especially for less volatile liquids where evaporation causes an additional frictional term. The highest relative errors were to be found in acetone and ethanol which are more volatile, which could potentially be the reason for the increased error. Moreover, liquids with higher viscosities were also tested to study the range of viscosity our viscometer was capable of measuring.
Table 3.3 experimental values for viscosities of viscous liquids.

<table>
<thead>
<tr>
<th>Liquids</th>
<th>$\gamma_{LV}$ (mN/m)</th>
<th>$\theta_R$ [°]</th>
<th>$\eta_{exp.}$ (mPas)</th>
<th>$\eta_{ref.}$ (mPas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene glycol</td>
<td>47.7</td>
<td>79 ± 2</td>
<td>25 ± 4</td>
<td>20</td>
</tr>
<tr>
<td>Olive oil</td>
<td>33</td>
<td>52 ± 2</td>
<td>113 ± 10</td>
<td>60-80</td>
</tr>
<tr>
<td>Castor oil</td>
<td>39</td>
<td>59 ± 2</td>
<td>793 ± 80</td>
<td>650-800</td>
</tr>
</tbody>
</table>

Errors were much higher for liquids and oils with high viscosities (e.g. ethylene glycol showed 25% relative error). However, our single-droplet surface viscometer still gave a reasonable approximation for the viscous oils, knowing the fact that their viscosities vary base on their types, amount of fatty acids, and compositions.\textsuperscript{110}

Another factor which makes this viscometer more favorable is temperature control. This can be easily varied using our surface viscometer by simply changing the tilting stage to a hot plate. Hexadecane was chosen to further investigate the change of viscosity by temperature because of its measurement accuracy in ambient temperature and its high boiling point. The results followed the trend of actual viscosity until around 70 °C and after this temperature a plateau was measured viscosity (Figure 3.6). This is because the surface viscosity measurement is highly dependant on contact angles, and it was observed that contact angles of hexadecane did not change dramatically after that temperature. This could also be related to the change of the surface energy of the SWOLL coating with increasing the temperature.
Figure 3.6 effect of temperature in surface viscometer measurement. Hexadecane viscosities in different temperatures.¹⁰⁹

Furthermore, the viscosities of binary mixtures of liquids were measured to demonstrate the utility of the surface viscometer. Different compositions of ethylene glycol and acetone solutions were prepared. The surface tension and contact angles on SWOLL glass of these binary mixtures were measured using a goniometer. The experimental values for all the mixtures with different compositions are listed in Table 3.4. The viscosities for these mixtures were not as accurate as the prior viscosity measurements. The high viscosity of ethylene glycol and volatility of acetone could have a part in observing up to 75% relative error in these measurements.
Table 3.4 experimental values for viscosities of ethylene glycol + acetone binary mixture.

<table>
<thead>
<tr>
<th>Ethylene glycol mole fractions</th>
<th>$\gamma_{LV}$ (mN/m)</th>
<th>$\theta_R$ [°]</th>
<th>$\eta_{exp.}$ (mPas)</th>
<th>$\eta_{ref.}$ (mPas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
<td>25.2</td>
<td>79 ± 2</td>
<td>0.4 ± 0.07</td>
<td>0.322</td>
</tr>
<tr>
<td>0.2517</td>
<td>30</td>
<td>39 ± 2</td>
<td>1.14 ± 0.1</td>
<td>0.65</td>
</tr>
<tr>
<td>0.5257</td>
<td>35</td>
<td>49 ± 2</td>
<td>3.41 ± 0.3</td>
<td>1.91</td>
</tr>
<tr>
<td>0.7734</td>
<td>40</td>
<td>64 ± 2</td>
<td>9.81 ± 0.9</td>
<td>6.12</td>
</tr>
<tr>
<td>1.0000</td>
<td>47.7</td>
<td>79 ± 2</td>
<td>25 ± 4</td>
<td>20</td>
</tr>
</tbody>
</table>

References\textsuperscript{86,113}

All things considered, this viscometer is limited to non-aqueous liquids. The viscometer did not show too accurate results for high viscosity liquids and mixtures. The other limitation is the availability of a goniometer in order to measure the receding contact angle and surface tension for the testing liquids. The setup itself is not capable of measuring the other parameters.
Chapter 4: Conclusion

Studies about liquid repellency have dramatically increased in the past a few years. Different approaches and techniques for creating a surface with low contact angle hysteresis were reviewed, including fabricating smooth, homogeneous surfaces, superomniphobic surfaces, and nano-textured surfaces porous surfaces filled with lubricant. These surfaces have a broad range of applications such as microfluidics, self-cleaning, anti-icing, biofouling, liquid separation, anti-fogging, etc. Based on the significant progress of liquid repellency and the huge number of investigations studying these materials, it is expected to see an improvement of these materials in the following years and the fabrication of a new generation of liquid repellent surfaces. Mostly, new techniques will be investigating more environmentally friendly approaches that do not require perfluorinated compounds and hazardous chemicals. Also, it is desirable for smooth omniphobic surfaces to have the ability of coating any substrate rather than just silicon wafers or smooth glass.

4.1 Summary

In summary, a two-layer procedure was developed to treat any substrate with a nonfluorinated, omniphobic coating that could repel a wide range of liquids with extremely low CAH. A thin silica layer that covered substrate roughness and further treatment with 1,3-dichlorotetramethyldisiloxane, first in vapor and then in solution, resulted in surfaces with extreme omniphobicity. The two-layer coating can be applied to any substrate regardless of surface chemistry or roughness. Moreover, the coating was resistant to many harsh exposures such as UV irradiation, high temperatures, acids, and extreme liquid pressure. When the coating was intentionally damaged, it was repeatedly repairable. In addition to the coating, we proposed a tilting-based technique for more accurately measuring CAH on omniphobic surfaces, which
exhibited an order of magnitude improvement in resolution over traditional contact angle goniometry.

Furthermore, a surface viscometer was developed to measure the viscosity of a wide range of liquids by one droplet. This viscometer is limited to liquids with surface tensions higher than 19 mN/m (PDMS surface tension which is the liquid-like layer on our surface), and liquids with contact angles lower than 90°. Our surface viscometer showed promising results in measuring commonly used liquids such as hexadecane, tetradecane, dodecane, decane, toluene, acetone, ethanol, and isopropyl alcohol. The accuracy of the surface viscometer was lower for some high viscosity liquids and mixtures.

4.2 Future works

- Further investigation is needed on the silica layer of our SWOLL surface. Also, transparency and flexibility should be studied on this layer.
- The thickness and liquid-like behavior of PDMS brushes should be further investigated.
- Contact angle hysteresis still exists on our surfaces. More modification is needed to minimize the contact angle hysteresis to near zero values.
- Repelling some liquids such as blood is still a challenge with liquid like layers which could be further investigated.
- High resolution CAH measurement does not provide us exact values for advancing and receding. There should be a study in order to calculate these angles without using a goniometer.
- Different types of liquids, resins, mixtures, and temperatures of liquids should be tested on the surface viscometer in order to fill the gaps of unknown liquids toward the potential utility of our viscometer.
• Aqueous liquids should be further studied in order to develop a possible solution for this limitation.
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