Wettable Slippery Surfaces. Self-cleaning Effect and Mechanism

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ABSTRACT

Self-cleaning surface is usually superhydrophobic and non-wettable, and is characterized by a very large contact angle and a small sliding angle. Wettable surfaces, on the other hand, are characterized by small contact angles (e.g., < 90^{o}). It is very uncommon to have surfaces that are highly wettable and slippery (sliding angles $\leq 10^{o}$) at the same time. In this report, recent work on wettable, slippery surfaces from the author's lab as well as others is reviewed. The fundamental mechanism leading to the slipperiness, despite the small contact angles, is proposed and discussed. The self-cleaning effect exhibited by these uncommon surfaces is reported.

Keywords: self-cleaning, wetting, slippery surfaces, contact angle, sliding angle

1 BACKGROUND

The phenomenon of self-cleaning displayed by the Lotus leaf and many other plant and insect surfaces has attracted tremendous attention recently. Self-cleaning surface is usually superhydrophobic and non-wettable. It is characterized by a very large (static) contact angle ($\boldsymbol{\theta}$ $\geq 150^{o}$), a small sliding angle ($\boldsymbol{\alpha}$ $\sim 10^{o}$) and/or a small contact angle hysteresis.[1] In this work, we report the synthesis and surface properties of surface modified polyurethane coatings that are wettable and slippery at the same time, characterized by small contact angles and small sliding angles. These surfaces also exhibit self-cleaning with hexadecane similar to that displayed by the Lotus leaf. The application of these surfaces in ink printing is discussed. The fundamental mechanism that enables both high wettability and slipperiness is proposed.

2 RESULTS AND DISCUSSION

2.1 Synthesis and Surface Properties of Slippery Polyurethane Coatings

In 2011, we[2] reported the synthesis of surface modified polyurethane coatings by reacting hexamethylene diisocyanate with a hydroxy-terminated polyacrylate in the presence of a surface active cross-linker. Surface cross-linkers studied include SilClean3700, Fluorolink-D and many of their derivatives. SilClean3700 comprises a polyhydroxypolyacrylate backbone with numerous PDMS (polydimethylsiloxane) side chains. Fluorolink-D is a dihydroxy-terminated perfluoropolyether. A general synthetic scheme is given in Figure 1.

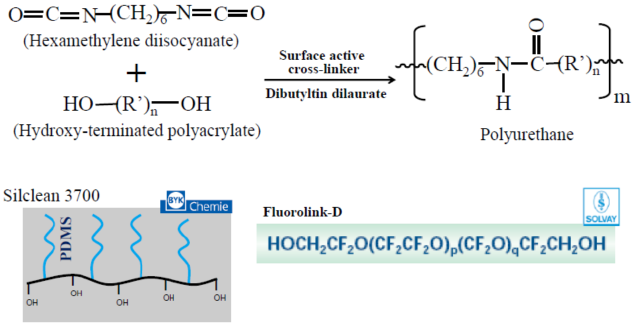
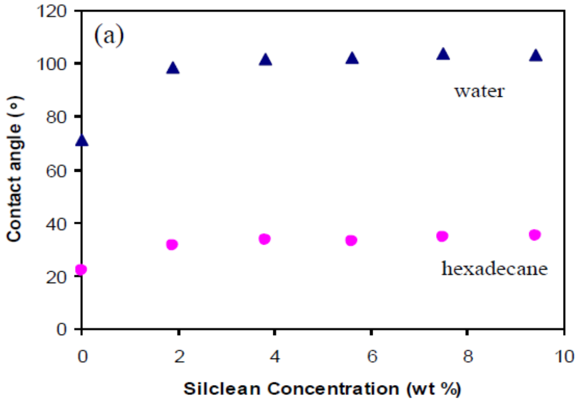


Figure 1. Synthesis of polyurethane coatings in the presence of a surface active cross-linker.

The surface properties of these polyurethane coatings were studied by contact angle and sliding angle measurements.[3] Figure 2 plots the contact angle data with water and hexadecane as a function of the concentration of the surface active cross-linkers in the reaction. For both solvents, contact angles increase, indicative of increasing hydrophobicity and oleophobicity, as the concentration of the cross-linker increases. The increase in contact angles parallels to the XPS data, increase of Si for SilClean3700 and increase of F for Fluorolink-D, suggests that the surfaces of these polyurethane coatings are enriched with the surface active functional groups as the films are formed. The contact angle ($\boldsymbol{\theta}$) and sliding angle ($\boldsymbol{\alpha}$) data are summarized in Table 1. To our surprise, hexadecane sliding angles less than 10^{o} are obtained on most coatings indicating that these surfaces are very slippery with hydrocarbon solvents. A snapshot for one of the sliding angle experiments is depicted in Figure 3.



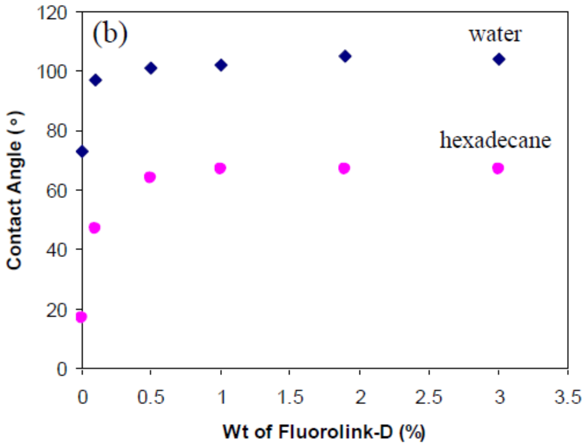


Figure 2. Plots of contact angles versus concentration of the surface active cross-linker: (a) SilClean3700 and (b) Fluorolink-D.

Table 1. Surface properties of polyurethane coatings incorporating various concentrations of surface active cross-linkers

Surface modifier	water		Hexadecane	
	θ $(^{o})$	α $(^{o})$	θ $(^{o})$	α $(^{o})$
0%	71	52	22	a
1.9% SilClean	99	31	31	6
3.8% SilClean	102	29	33	4
5.6% SilClean	102	26	33	2
7.5% SilClean	104	23	35	2
0.5% Fluorolink	101	b	64	14
1% Fluorolink	102	63	67	10
1.9% Fluorolink	105	61	67	9
3% Fluorolink	104	63	67	9

(a) not measurable and (b) not slide at 90^{o}.

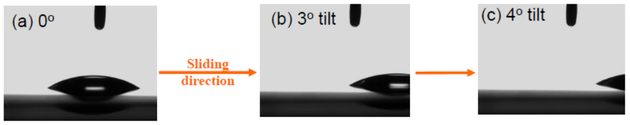


Figure 3. Snapshots of a sliding hexadecane droplet (~10 µL) on a polyurethane coating containing 7.5% of SilClean3700.

2.2 Self-Cleaning and Applications

Contamination of the surface of inkjet printhead (Figure 4a) has shown to be the main cause of machine relability, high operating coat and down time. UV and wax inks are organic materials. The slipperiness observed with hexadecane suggest that UV and wax inks may not stick onto the printhead when these polymers are coated on the printhead surface. Figure 4b shows an offline self-cleaning test involving a PU-SilClean coating on a stainless steel plate (left-hand side, the non-coated right-hand side is the control). The entire plate is showered with paper dust to simulate contamination on the printhead surface. When ink drops are dispensed on the surface, paper dust particles are found cleaning off the surface as the ink slides. No self-cleaning is observed on the uncoated side. The experiment demonstrates that the slippery property has enabled self-cleaning, resulting in a maintenance free, easy-clean printhead design.

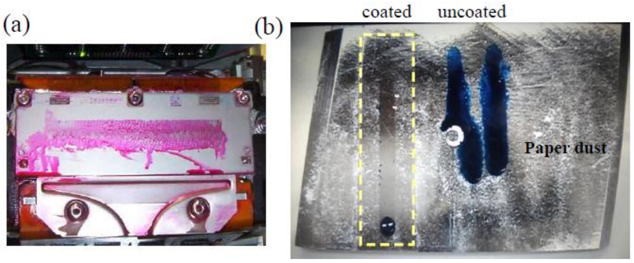


Figure 4. (a) Photograph of a contaminated printhead surface and (b) offline self-cleaning test with a polyurethane-SilClean coating.

2.3 Mechanism for Simultaneous High Wettability and Super Slipperiness

The interaction between a liquid droplet and the solid surface is expected to be very strong when the liquid is highly wettable. High liquid wettability also means small θ value. Intuitively, the mobility of the liquid droplet is expected to be low too. It is thus very uncommon to have surfaces that are highly wettable and very slippery ($\alpha \leq 10^{o}$) at the same time. Literature studies however reveal that this phenomenon is not new. For instances, Langmuir and Blodgett[4] observed a completed roll-off of a white mineral oil droplet on a trimolecular stearate Langmuir-Blodgett (LB) film on glass, which exhibited a contact angle of ~55^{o}. They described the unexpected observation as “de-wetting”, attributable to both the tight packing of the C18 hydrocarbon chain in the LB film as well as the non-interacting nature of the CH_3 end group. In 1996, Schmidt et al.[5] reported the synthesis of a new family of non-sticking, wettable polymers by cross-linking reactive perfluoroalkyl polymeric surfactants with poly(2-isopropenyl-2-oxazoline) at different reactant ratios under various reacting and curing conditions. Static, advancing (θ_A), receding (θ_R) and sliding angles with water and hexadecane were reported. With hexadecane, four of the polymer coatings exhibit contact angles range between 58^{o} to 67^{o} with sliding angles less than 15^{o}. In addition to the Law group at Xerox,[6-9] surfaces with small hexadecane contact angles and small sliding angles ($\theta << 90^{o}$ and $\alpha \leq 10^{o}$) have been reported by several research groups recently: the McCarthy group at University of Massachusetts,[9,10] the Hozumi group at AIST Japan,[11-14] and the Liu group at Queen’s.[15] All of these films (surfaces) are flat and smooth. The common features among these surfaces are that they are all hydrophobic with water $\theta > 90^{o}$, but that the water droplets are found to be moderately mobile to sticky on these surafces. With hexadecane, θ become smaller due to the low surface tension. θ ranges between 30^{o} to $<70^{o}$. Most interestingly, hexadecane droplets are found to be very slippery on these surfaces. Sliding angles less than 10^{o} are obtained in most cases.

Figure 5 shows a schematic of a sliding droplet on an inclined surface. The driving force (F) for the droplet to slide is equal to mg.sin$\boldsymbol{\alpha}$, where $\boldsymbol{\alpha}$ is the inclination angle, m is the mass of the liquid droplet and g is gravitational constant. The frictional force (*f*) that keeps the drop from sliding is given by:[17-19]

$$f = \gamma_{LV}.\ R.k.(\cos\boldsymbol{\theta_R} - \cos\boldsymbol{\theta_A}) \qquad (1)$$

where γ_{LV} is the surface tension of the liquid, R is the length scale for the contour of the drop and k is an adjustable parameter based on experimental data.

At the moment of drop sliding, F = f and $\boldsymbol{\alpha}$ becomes the sliding angle. The relationship between $\boldsymbol{\alpha}$ and ($\cos\boldsymbol{\theta_R} - \cos\boldsymbol{\theta_A}$) becomes:

$$\sin\boldsymbol{\alpha} = C.\ \gamma_{LV}.(\cos\boldsymbol{\theta_R} - \cos\boldsymbol{\theta_A}) \qquad (2)$$

where C is a constant that includes the gravitational acceleration, density of the liquid, the geometric parameters of the drop.

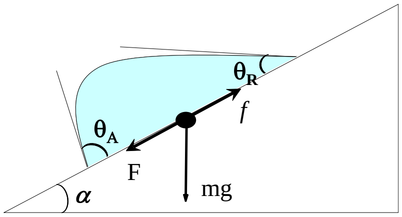


Figure 5. Schematic showing different forces acting on a liquid droplet on an inclined surface.

It is clear from Eq(2) that the fundamental driver for having a very small sliding angle (super slipperiness) is when $\boldsymbol{\theta_A} \approx \boldsymbol{\theta_R}$. For a wettable surface, this outcome can be rationalized by a simple thermodynamic consideration. For instance, although the energy requires to de-pin a liquid droplet on a highly wettable surface is very high due to the strong liquid-solid interaction and small $\boldsymbol{\theta_R}$, it can be compensated well as a result of the favorable wetting interaction (small $\boldsymbol{\theta_A}$) along with the potential energy gained through gravity.

One of the remaining questions is why does the water droplet is stickier on the same surface despite having a larger $\boldsymbol{\theta}$? In other words, with water, $\boldsymbol{\theta_A}$ is large than $\boldsymbol{\theta_R}$, whereas $\boldsymbol{\theta_A}$ and $\boldsymbol{\theta_R}$ are comparable with hexadecane. This observation can be attributed to the rate of molecular relaxation between liquid molecules and the polymer chains at the interface. For example, during water receding, the contact line always recedes from the wetted area, where liquid molecules and polymer chains are relaxed and in equilibrium. Liquid molecules and solid surface may not have time or chance to equilibrate as the contact line advances to an non-wetted area during advancing. This results in $\boldsymbol{\theta_A} > \boldsymbol{\theta_R}$. With hexadecane and the slippery surfaces discussed herein, solvent molecules and functional groups at the interface are more compatible. This couples with the fact that the functional groups involved are relatively flexible, implying that some relaxation may occur during liquid advancing. This results in comparable $\boldsymbol{\theta_A}$ and $\boldsymbol{\theta_R}$ and slippery surfaces.

Evidence to support the proposed mechanism comes from data reported by Hozumi et al. in 2012 on a series of PDMS grafted brush surfaces on Si-wafer.[12] The molecular weight of the PDMS brush varies from 2000 to 120,000. The surface properties were studied by advancing and receding contact angle measurements. Plots of ($\boldsymbol{\theta_A}$ - $\boldsymbol{\theta_R}$) as a function of MW of the PDMS brushes with water, n-decane, n-dodecane and n-hexadecane are reproduced in Figure 6.

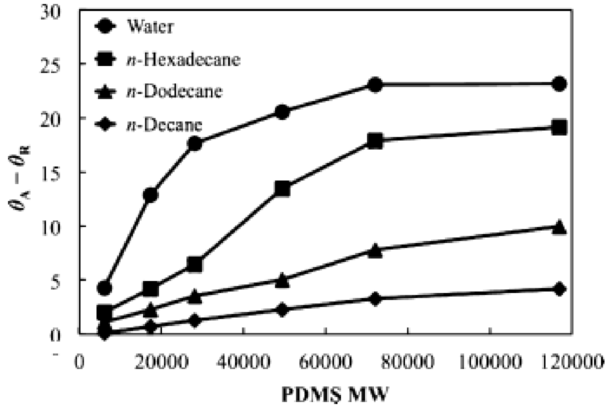


Figure 6. Change of ($\boldsymbol{\theta_A}$ - $\boldsymbol{\theta_R}$) for grafted PDMS surfaces with varying molecular weight.

Consistent with earlier discussion, ($\boldsymbol{\theta_A}$ - $\boldsymbol{\theta_R}$) for water is consistently larger than those with hydrocarbon solvents, attributable to the relative incompatibility between water and the PDMS brush. The significance of the results lies in the PDMS MW effect on the polymer brush and the hydrocarbon chain length effect observed for the wetting liquid. According to the proposed mechanism, a rapid molecular relaxation between liquid molecules and polymer chains at the liquid-solid interface during liquid advancing would lead to $\boldsymbol{\theta_R} \approx \boldsymbol{\theta_A}$. The data in Figure 6 show clearly that ($\boldsymbol{\theta_A}$ - $\boldsymbol{\theta_R}$) decreases as the MW of PDMS brush decreases and as the chain length of the wetting hydrocarbon liquid decreases, fully supporting the molecular relaxation mechanism.

3 SUMMARY

This work shows that the mechanism for super slipperiness on wettable surfaces is a result of their similarity in advancing and receding contact angles. Evidence is provided that fast molecular relaxation of groups at the liquid-solid interface during liquid advancing results in a similar liquid-solid interface between advancing and receding, and $\boldsymbol{\theta_A} \approx \boldsymbol{\theta_R}$.

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