Do We Need Better Materials than Teflon in Marking?

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Abstract

Teflon materials such as PTFE and PFA are generally known to be chemical inert and thermally stable with low surface energy. They have been the favorite materials for a variety of applications, ranging from filler in photoreceptor to additive in toner to release layer in oil less fusing to overcoat in inkjet printhead. In this work, we systematically investigate its wetting and adhesion properties using static and dynamic contact measurement techniques. In addition to model liquids such as water and hexadecane, we also studied the wetting and adhesion performance with ink and toner. Our results indicate PTFE, although, is highly hydrophobic, it is actually oleophilic and sticky towards traditional imaging materials. In most applications in xerography and inkjet printing, being non-stick with low adhesion is paramount. The requirement of a high static contact angle may be secondary. Here we also report the fabrication of a superoleophobic model surface by photolithographic technique and superior anti-offset performance was demonstrated. The need of easy clean, non-stick surfaces for future xerographic and inkjet printers is evident.

Introduction

Digital color printers and presses are complex electromechanical devices that put marks on papers. Traditional approaches to design and optimize these devices have primarily been focused on the electrical and mechanical properties. Print surfaces with custom-made surface properties are critical and are usually the after thoughts. We believe that designer surfaces with controlled wetting or de-wetting properties or adhesion properties would be the performance differentiator for future engines. Features, such as easy-clean, self-clean in certain components, or offset free in fusing would be considered as a breakthrough. To date, Teflon materials have been very popular due to its hydrophobicity, low surface energy, anti-wetting properties as well as chemical inertness and high thermal stability.

Generally water contact angle lower than 90° is defined as hydrophilic and water contact angle higher than 90° is hydrophobic. However, researchers recently realized that apparent contact angles cannot fully describe the interactions between the liquid and solid surfaces. McCarthy and co-workers [1,2] argued that contact angle hysteresis, specifically the difference between the cosines of the advancing and receding angles, and not maximum achievable contact angle should be used to quantify hydrophobicity. The authors also accused some recent published papers only reported single water contact angle which cannot fully describe the surface wetting properties without additional information. Murase and co-workers [3] showed that a high contact angle does not necessarily relate to a low sliding angle. Rios etc. [4] also showed that a fluoropolymer with a water contact angle of 112° possesses a higher sliding angle than poly(dimethylsiloxane) with a contact angle of 103°, even higher sliding angle than PMMA and polycarbonate whose contact angles are at 72.5° and 81.3° respectively.

Giving this background and the important of Teflon in the printing industry, we decide to carry out a system investigation of the surface wetting properties of PTFE towards water, hexadecane, and the Xerox imaging materials, solid ink and toner. Our data reveal that, PTFE is hydrophobic, but oleophilic. PTFE actually exhibits moderate to high adhesion towards water, hexadecane and the Xerox imaging materials. In most applications, having a low adhesion, non-sticking surface is more critical than having a high contact angle. In this work, we further fabricated a superoleophobic model surfaces by photolithography and demonstrate its superior release performance relative to PTFE.

Experimental

Teflon films (PTFE ~ 50 μm) were obtained from Dalau Incorporated (Merrimack, NH, USA) and were cleaned before use. The cleaning procedure included ultrasonic bath treatments with isopropanol and then acetone at room temperature for 5 min followed by drying in an oven for 1 h at 90–100°C. A model superoleophobic surface was created by photolithography by first spin-coating photoresist SPR700 on a Si wafer, followed by exposure of the resist through a mask, and then developed, etched, striped off the remaining resist and piranha clean the surface. The resulting textured surfaces then was modified by tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane (FOTS) via molecular vapor deposition on a MVD100 reactor from Applied Microstructures.

Contact angle and sliding angle measurements were performed on a goniometer model OCA20 from Dataphysics. The drop size of the test liquid was controlled to be ~ 5 μL. The sliding angles were measured using the tilting base unit accessory to the Dataphysics goniometer. After dispensing a 10 μL droplet, the stage was tilted about one degree per second to a maximum of 90°. For imaging material, solid ink and toner spheres of ~1 mm in diameter were used for both contact and sliding angle measurements. The accuracy of contact angles is ±2° and sliding angle measurements is ±1.5°.

Results and Discussion

Does hydrophobic surface mean low adhesion? Is hydrophobic surface also oleophobic?

Figure 1 shows the contact angle measurements for 5 μL DI water and hexadecane drops on a PTFE surface. The data is summarized in Table 1 along with the sliding angle data. Table 1 also includes two Xerox proprietary surfaces with slightly lower water contact angles (113.0° and 101.0°) and significantly lower water sliding angles (5° and 25°).

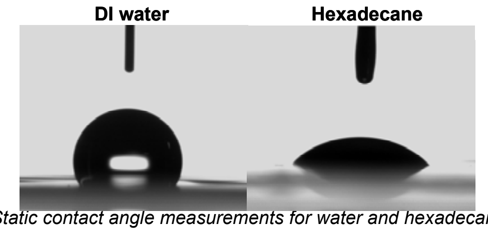

Figure 1. Static contact angle measurements for water and hexadecane PTFE.

Table 1. Summary data of contact angle and sliding angle on various substrates for water and hexadecane

	Contact angle (sliding angle)	
Surface	DI water	Hexadecane
PTFE film	117.7° (~64°)	48.0° (~31°)
Xerox proprietary material 1	113.0° (~5°)	64.0° (~4°)
Xerox proprietary material 2	101.0° (~25°)	33.0° (~1°)

Since sliding angle is a measure for adhesion between the liquid droplet and the surface [4], our result clearly show that high hydrophobicity does not always mean low adhesion.

Hexadecane is the surrogate for oil. The data in Table 1 show that there is no direct correlation between hydrophobicity and oleophobicity. Equally important is the sliding angle data, a high static hexadecane contact angle does not necessarily translate into the lowest adhesion, confirming the observation with water. Work is in progress in our lab trying to understand the fundamental as well as the design for synthesizing surface with high contact angle and low sliding angle.

Microscopy and property of the model fluorinated textured surface

To extend the range of surface design, we have initiated work to explore surface roughness on surface hydrophobicity and oleophobicity [5]. Figure 2 shows a SEM micrograph of a textured surface consisting of ~ 3 μm diameter pillars ~ 7 μm in height with an inter-pillar distance of ~ 6 μm on Si wafer. The surface was chemically modified by a fluorosilane coating (FOTS) using the molecular vapor deposition technique.

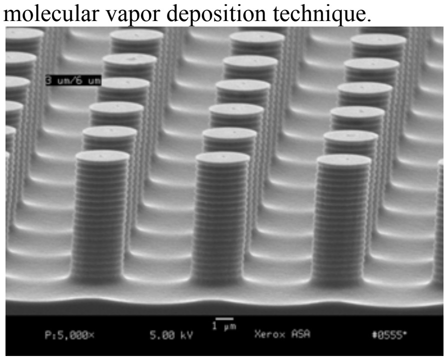

Figure 2. SEM micrograph of the texture on Si wafer created by photolithography

The surface property was studied by contact angle measurements using water and hexadecane (oil) as test liquids. The contact angle data for the textured surface are depicted in Figure 3. Sliding angle data and data from all the controls (smooth and textured surfaces without FOTS modification) are summarized in Table 2.

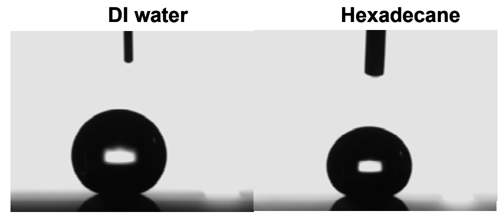

Figure 3. Static contact angle measurements for water and hexadecane on the fluorinated textured surface

Table 2. Contact angle and sliding angle data for smooth and textured surfaces

Si wafer	Coating	Contact angle (sliding angle)	
		Water	Hexadecane
Smooth	None	-	-
Texture	None	<5°	<5°
Smooth	FOTS	107.3° (14°)	73.3° (9°)
Texture	FOTS	156.2° (10°)	157.9°(10°)

Our results indicated that the textured FOTS surface is both water and oil repelling with water and hexadecane contact angles approaching ~ 160°. In addition, the sliding angles are very low, ~ 10°, for oil and water, indicative of achieving both superhydrophobicity and superoleophobicity. By comparing with the contact angle data of the smooth FOTS surface and the textured bare Silicon surface, we conclude that the attainment of superoleophobicity and superhydrophobicity for the textured surface in Figure 2 is the result of both surface texturing and surface fluorination.

The super model surface obviously gives the highest water contact angle and very low sliding angle. Although Teflon has second highest water contact angle in Table 1 and 2, it has the highest sliding angle indicating its strong adhesion with water.

Hexadecane (surrogate for oil) has the second lowest contact angle on PTFE surface in Table 1 and 2. Its sliding angle on PTFE is the highest among all the surfaces studied in this work, suggesting the Teflon is actually oleophilic with strong adhesion towards oil!

Will the superoleophobic model surface perform better than Teflon?

Figure 4 shows the contact angle measurements for solid ink, waxy polyester toner and polyester toner spheres on the superoleophobic model surface, PTFE and transparency (surrogate for paper), respectively. The data are tabulated in Table 3.

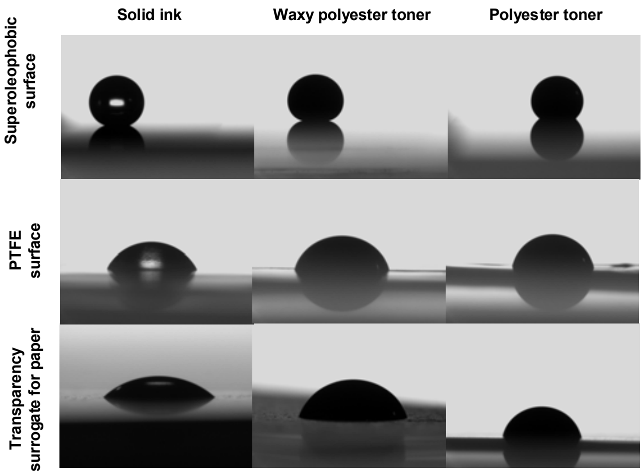

Figure 4. Static contact angle measurements for solid ink, waxy polyester toner and polyester toner

Table 3. Summary of contact angle and sliding angle data for various imaging materials on various surfaces

	Contact angle (sliding angle)		
Surface	Solid ink (105°C)	Waxy polyester toner (165°C)	Polyester toner (165°C)
Superoleophobic (FOTS coating)	154.9° (33°-58°)	159.4° (50°-55°)	129.6° (35°-52°)
Transparency (surrogate for paper)	40.4° (>90°)	65.6° (> 90°)	78.9° (>90°)
Contact angle Δ	~ 114°	~ 94°	~ 51°
PTFE film	63.2° (>90°)	74.6° (>90°)	84.6° (>90°)
Contact angle Δ	~ 23°	~ 9°	~ 6°

To be able to de-wet, the liquid droplet should have a high contact angle on a given surface. Similarly, a small contact angle between a liquid droplet and the surface usually will enable good wetting and spreading. For fusing or transfixing application, in order to achieve no offset on the fuser surface, it is desirable for the molten toner or ink to have a very high contact angle on the fuser surface while wetting the paper at the same time. In the other words, one would like to have a large contact angle on the fuser surface and a small contact angle on paper. The difference in contact angle would become a figure-of-merit in fuser/transfuser design, the large the contact angle Δ, the better the offset performance will be. As shown in Table 3, the contact angle Δ for the superoleophobic surface with the three imaging materials, ranges from 51° to 114°, are significantly larger than those observed on PTFE. The results suggest that, if the superoleophobic surface can be incorporated in the fusing surface, significant improvements in release, offset and paper stripping are anticipated.

Another interesting point is the data between PTFE and the waxy polyester toner. This is the material combination commonly used for oil less fusing. The contact angle Δ for this material combination is 9° and is significantly smaller than the superoleophobic surface–polyester toner combination, which is 51°. The large contact angle Δ for the superoleophobic surface implies that one may be able to practice oil less fusing with wax less polyester toner.

Performance validation

To validate the superior performance of the superoleophobic surface, we manually simulated the interaction between the fuser surface, the molten toner or ink and paper. In the experiment, a molten droplet of ink was created on the two surfaces, PTFE and the superoleophobic model surface, a piece of Xerox plain uncoated paper was then brought in contact with the molten ink drop slowly and carefully while video of the entire event was recorded. Figure 5 depicts the frame-by-frame of the ink offset experiment for the two surfaces. The solid ink drop was found to split between the PTFE surface and paper, implying offset would likely to occur if this is a fusing experiment. In contrast, the ink drop was found behaves very differently. Upon contact, the ink drop just "jumps" onto the paper without leaving any residues behind.

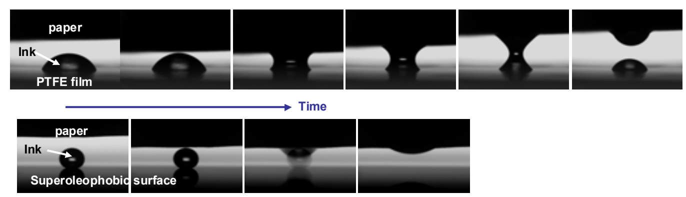

Figure 5. Simulated interactions of the molten ink drop with Xerox plain paper (top) a PTFE film; and (bottom) the model superoleophobic surface

Concluding Remarks

In contrast to common belief, this work demonstrates that Teflon materials, although hydrophobic, it is actually oleophilic and exhibits high adhesion towards water, hexadecane (oil) and imaging materials, such as ink and toner. Yes, we do need better release surface than Teflon. In this work, we have fabricated a model superoleophobic surface that displays extremely high water and oil repellency. The surface exhibits contact angles at ~ 160° and sliding angles ~ 10° with both water and oil. Static and dynamic contact angle measurements of the surface with toner and ink suggest that the surface should performance much better than Teflon if the texture design is incorporated in the surface of an oil less fuser.

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Author Biography

Kock-Yee Law received his BS in chemistry from The Chinese University of Hong Kong (1974) and his PhD in photo-organic chemistry from The University of Western Ontario (1978). He has been at Xerox Webster for over 28 years and he is currently a technical manager in the Xerox Innovation Group responsible for the development and delivery of Nanotechnology for the future.

Hong Zhao received her B.S. in Mechanical Engineering from Petroleum University in China (1996) and her Ph.D. in Mechanical & Aerospace Engineering from Rutgers University in 2007. She has worked in Xerox Research Center at Webster, NY since her graduation. Her primary areas of research are design of superhydrophobic and superoleophobic functional surfaces for different printing engines, especially fusing surfaces.