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Super Toner and Ink Repellent Superoleophobic Surface

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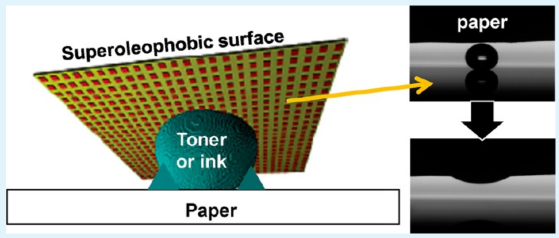
S *Supporting Information*

ABSTRACT: Offset of imaging material from a fuser surface to paper during fusing is highly undesirable in printing. Here the wetting and repellent characteristics of three imaging materials (a solid wax ink, a waxy polyester toner, and a polyester toner) in their molten states have been studied on three model print surfaces: a transparency (surrogate for paper), a PTFE film, and a model superoleophobic surface, with the aim of assessing their performance in fusing. The superoleophobic surface, with water and hexadecane contact angles of ~156° and sliding angles at ~10°, comprises 3 μm diameter pillar arrays on silicon wafer and was fabricated by photolithography followed by surface modification with a fluorosilane. The contact angles of the three imaging materials range from 40 to 79° on the transparency and the sessile drops do not slide even at 90° tilted angle, indicating that they all wet, adhere, and pin on the transparency. Although the contact angles of the three imaging materials are slightly higher (63−85°) on PTFE, the sessile drops do not slide on PTFE either. Because PTFE is widely used as a fuser surface material in combination with different waxy imaging materials commercially, we attribute the successful implementation of PTFE to the use of the wax additive. With the superoleophobic surface, there is a dramatic increase in advancing and static contact angles for all three imaging materials. The advancing and static contact angles are in the 150−168° range for waxy toner, indicative of superhigh repellency. Although the advancing and static contact angles for the polyester toner decrease slightly at 147 and 130°, respectively, the repellency is still very high. More importantly, the sessile drops of all three imaging materials are mobile upon tilting and they all have high receding contact angles. The overall results suggest that the adhesion between the superoleophobic surface and the ink and toner materials are very small relative to those with paper and PTFE. The important of high repellency and low adhesion to offset performance is discussed.

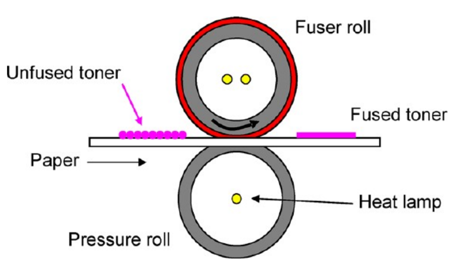


KEYWORDS: *superoleophobicity, repellency, superhydrophocity, wetting, contact angle, sliding angle*

■ INTRODUCTION

Printers are basically electromechanical devices that put marks of imaging materials, such as toner and ink, on paper. Fundamental understanding of wetting and adhesion between imaging materials and print surfaces at different locations of the printer are crucial not only to engine design but also to the development of the printing process. For example, in electrophotography, the electrostatic latent image was first generated on the photoreceptor.[1] The latent image was then developed electrostatically by toner, followed by transfer of the toner image to paper and fusing.[2] Scheme 1 depicts the most common configuration of a fusing subsystem used in the printing industry.[3−] In its simplest configuration, the fusing subsystem consists of a fuser roll and a pressure roll where the unfused toner image is fixed onto the paper at an elevated temperature under pressure as it passes through the fusing zone formed between the two rolls. Depending on the process speed, the toner material and the fuser design, the toner is normally fused at temperature ranging from 130 to 180 °C under a pressure range of 300 to 700 kPa in 10−20 ms in the fusing zone. It is imperative that molten toner is fixed onto the paper rather than adhering to the fuser surface after leaving the fusing zone. Any toner adhered on the fuser surface after fusing will lead to image quality defect known as offset. When offset occurs, additional cleaning will be required before the next fusing cycle.[6] Teflon has been the most popular material for fusing[7,8] because of its high thermal stability, chemical inertness and low surface energy owing to its high hydrophobicity.[9,10] However, as shown in this work, our data as well as those reported by Lee and co-workers[11] show that Teflon is oleophilic with a measured hexadecane contact angle of 48°. To reduce the chance of offset in Teflon fusing systems and enhance paper releasing, researchers often employ release aids,

Scheme 1. Schematic of a fusing Subsystem Showing Fixing of the Toner Image from Left to Right



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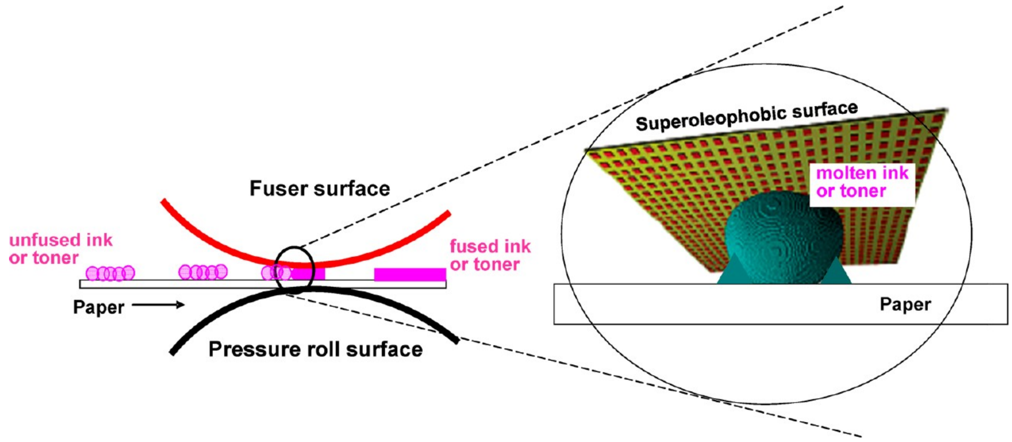
Scheme 2. Schematic of a Concept Fuser Having a Superoleophobic Surface



such as silicone oil[12] and wax.[13] The latter (wax) is usually incorporated into the toner formulation.[14,15] A similar challenge is also encountered during the design of solid wax inkjet printer.[16] Again release oil and low surface energy surface are used.

One of the root causes for offset during fusing is the high adhesion between the imaging material and the fuser surface. Because Teflon is oleophilic, there is a definite attraction between the Teflon surface and the imaging materials. We thus hypothesize that if a superoleophobic surface is used in fusing, it will repel molten toner and ink during fusing and offset should never be observed. A schematic showing the concept fuser is given in Scheme 2.

Recently, we[17] reported the successful fabrication of a model superoleophobic surface which exhibits high repellency toward oil and water. Water and hexadecane contact angles of 156 and 158°, respectively, were obtained along with the low sliding angles (~10°). In this work, we report a study of the wetting and repellent behavior of toner and ink on three model print surfaces: transparency, a Teflon PTFE film, and a superoleophobic surface. Super toner and ink repellency is indeed obtained with the superoleophobic surface. The technology implication is discussed.

Transparency is used as a surrogate for paper in this work. Although the contact angle measurements with water and hexadecane are conducted at room temperature, those with ink and toner have to be performed at an evaluated temperature: 105 °C for ink and 165 °C for the toners, because ink and toner are solid at room temperature. At the high temperatures studied in this work, regular paper degrades and becomes yellow. This results in change of surface properties during the measurement. Transparency is made of PET (polyethylene terephthalate) and is regularly used as a print medium in printers and copiers. Its surface energy is ~41 mN/m by contact angle measurements[18,19] and is in the same range with the reported values of coated print papers, which vary from 30 to 45 mN/m.[19] The surface energies for uncoated print papers are even higher, ranging from 47 to 87 mN/m.[20,21] Transparency, therefore, is a good surrogate for paper because its surface energy is at the low end among all paper types and would not exaggerate the wettability results.

EXPERIMENTAL SECTION

Fabrication of Model Superoleophobic and Superhydrophobic Surfaces. The superoelophobic surface studied in this work, consisting of ~3 μm diameter pillar array (~7 μm in height with a 6 μm center-to-center spacing), was fabricated on 4" test grade silicon wafers (Montco Silicon Technologies, Inc.) by the conventional photolithographic technique followed by surface modification. Specifically, the surface texture was first created by etching the Si-wafer using the Bosch DRIE process. This is followed by chemically modifying the textured surface with a ~1.5 nm thick fluorosilane layer (FOTS), which was obtained by molecular vapor deposition of tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane onto the bare textured surface in a MVD100 reactor from Applied Mircostructures, Inc. The FOTS textured surface was then heat cured in an oven at ~150 °C for ~30 min prior to the contact angle measurement. Details of the etching and stripping steps as well as the chemical modification procedure have been reported earlier.[17]

The superhydrophobic surface was fabricated on Si-wafer using identical photolithographic procedure. The only exception is that the resulting silicon textured surface was coated with a ~100 nm conformal i-CVD PTFE coating instead. The i-CVD PTFE coating was prepared by the initiated chemical vapor deposition technique.[22,23] The surface properties and the microscopy of both the superoleophobic and superhydrophobic surfaces have been given in an earlier report.[17]

Materials and Surfaces. DI Water (18 M·Ω, purified by reverse osmosis process) and hexadecane (certified 99.4% purity, Aldrich) were used as test liquids. In addition to the superoleophobic surface, two more surfaces were studied. Teflon films (PTFE ~50 μm in thickness) were obtained from Dalau Incorporated (Merrimack, NH, USA) and were cleaned with isopropanol before use. Due to the high temperature used in the contact angle measurements (105−165 °C), paper yellowing occurred. Sheet of the HP overhead transparency (for copier use, from Staple) was used as surrogate for paper.

Three types of imaging materials were studied. The solid wax ink (yellow) is a Xerox product currently used in the Xerox ColorQube engine.[24] The waxy polyester toner, comprised of an internal wax additive in the formulation, was prepared by the emulsion-aggregated technique,[25,26] These materials were acquired internally. The third imaging material, the polyester toner without wax was a courtesy sample from Dr. K. Moffat of the Xerox Research Centre of Canada. It was made with the same chemistry as the emulsion-aggregated toner, except that wax was not used in the formulation.

Contact Angle Measurements. Contact angle measurements were conducted on an OCA20 goniometer from Dataphysics, which consists of a computer-controlled automatic liquid deposition system and a computer-based image processing system. The measurements with water and hexadecane were carried out at room temperature. In a typical static contact angle measurement, a ~5 μL of the test liquid droplet was gently deposited on the testing surface using a microsyringe and the static contact angle was determined by the computer software (SCA20) and each reported data is an average of >5 independent measurements. Typical contact angle measurement error is ∼2°. Sliding angle measurement was done by tilting the base unit at a rate of 1°/s with a ∼10 μL droplet using titling base unit TBU90E. All measurements were averaged from ∼5 measurements, using a pristine area of the substrate for each measurement. The sliding angle is defined as the angle where the test liquid droplet starts to slide (or move).

As for the solid wax ink and toners, the contact angle and sliding angle were determined inside a heating chamber. The ink material was measured at 105 °C and was in liquid form. The toners were measured at 165 °C and were in a semiliquid state. The size of the ink drop (∼2 μL) was controlled by careful sieving of the ink pallets with a screen. As for the toner, the drop size was controlled via a Teflon mold. Specifically, toner pallets were made by first filling the cavity of the Teflon mold (∼5 μL in volume) with toner particles. The entire mold was then heated and the pallets were formed. After cooling the mold to room temperature, pallets of toner materials were released from the mold for contact angle measurements. The advancing and receding contact angles for the ink and toner droplets were estimated from the tilted drops during the sliding angle experiment. The angle in the leading edge and the trailing edge are measured as advancing and receding contact angle, respectively.[27,28]

Pillar Surface Characterization. The surfaces of the top of the pillars before and after ink slide were studied on a Hitachi S-4800 SEM. The sample was routinely coated with ∼20 nm of gold to eliminate electrostatic charges. The energy dispersive X-ray spectrometry (EDXS) technique was used to examine the elemental content of the surface.

RESULTS AND DISCUSSION

Fabrication and Properties of Superhydrophobic and Superoleophobic Textured Surfaces. Model textured surfaces comprising of ∼3 μm diameter pillar array were fabricated on silicon wafer using the conventional photolithographic technique. The pillars were created by the Bosch etching process which creates a wavy sidewall in the pillar structure from top to bottom. The superoleophobic surface was obtained by coating the resulting textured surface with a fluorosilane, FOTS, synthesized from tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane by the molecular vapor deposition technique. The superhydrophobic surface was obtained by coating the same textured surface with a ∼100 nm i-CVD PTFE conformal layer.[22,23] The SEM micrographs of both surfaces along with their water and hexadecane sessile drop data are summarized in Figure 1. Details regarding the fabrication procedure of these surfaces have been given earlier.[17] The results show that both textured surfaces are superhydrophobic, but only the surface coated with FOTS is superoleophobic. The difference in surface property is primarily due to the different surface coating on the textured surfaces and has been discussed in details in the early report.[17]

Surface Properties of PTFE and Transparency. Figure 2 presents the sessile drop data of water and hexadecane on PTFE and transparency. The PTFE surface is highly hydrophobic with a water contact angle of ∼118° but it is found to be oleophilic with a hexadecane contact angle of 48°. Our data are in agreement with those reported in the literature,[11,29] suggesting that PTFE has a definite affinity with oil and other organic materials. The transparency surface exhibits the lowest contact angles with water and hexadecane indicating that it is hydrophilic as well as oleophilic. The result makes sense because this is the surface where one would need the toner and ink to wet, adhere, and fuse onto it.

Contact Angle Measurements of Toner and Ink on Various Model Print Surfaces. Figure 3 summarizes the sessile drop data for the solid wax ink, the waxy polyester toner

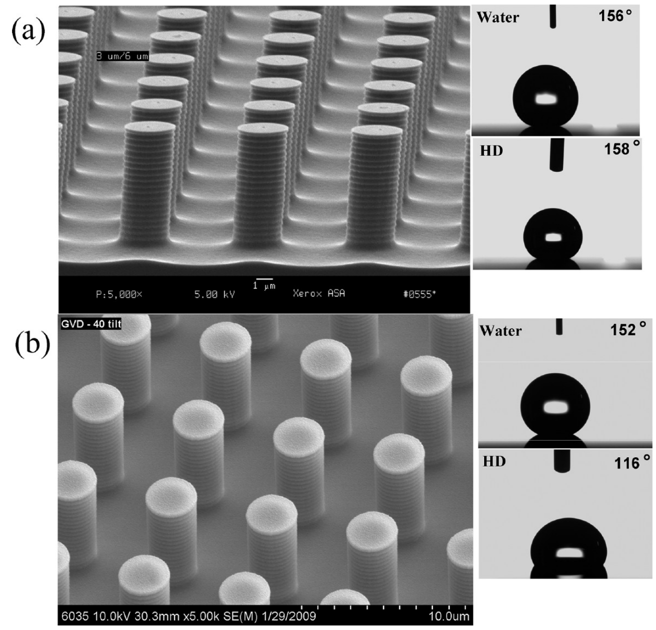


Figure 1. SEM micrographs and water and hexadecane (HD) sessile drop data for textured surfaces coated with (a) fluorosilane FOTS and (b) i-CVD PTFE.

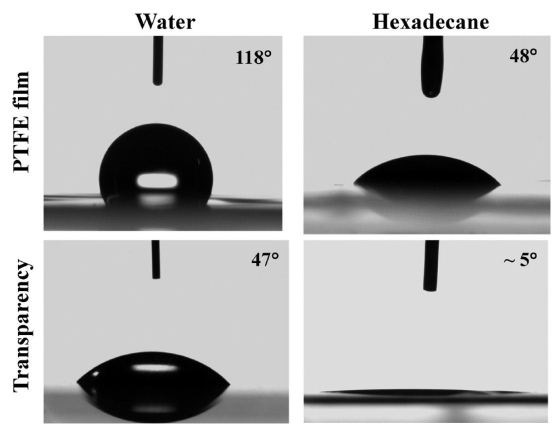


Figure 2. Contact angle data for water and hexadecane on PTFE and transparency.

and the polyester toner on the superoleophobic surface (Figure 1a), PTFE and transparency. Table 1 summarizes the contact angle, sliding angle, advancing contact angle and receding contact angle data for all three imaging materials on the three print surfaces. All the measurements were carried out at an elevated temperature: 105 °C for solid wax ink and 165 °C for the toners. Results show that droplets of the molten solid wax ink and the waxy and non waxy polyester toners display contact angles range from 40 to 79° on the transparency. The droplets of these materials do not slide even at 90° tilted angle. As a result, their advancing and receding contact angles could not be determined. The data clearly indicate that these imaging materials wet and pin on the transparency. The physical behavior is what one would expect from a printing medium.

The contact angles for the three imaging materials range from 63 to 85° on PTFE. Although they are consistently higher than those on transparency, the strong tendency for the molten imaging materials to wet the PTFE surface is still evident. All three imaging materials are shown to pin on the PTFE surface

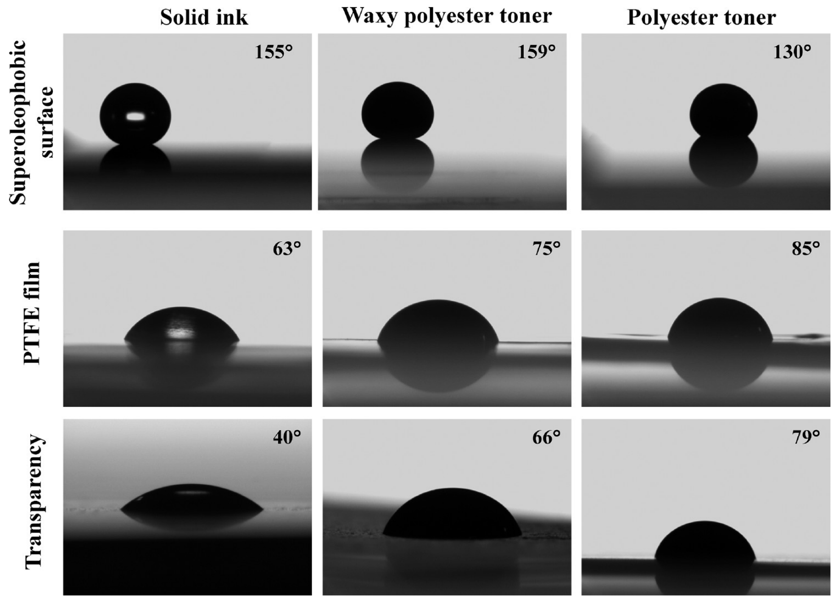


Figure 3. Contact angle data for solid ink, waxy polyester toner, and polyester toner on a model superoleophobic surface, PTFE, and transparency.

Table 1. Contact Angle Data of Ink and Toners on Various Print Surfaces

print surface	solid wax ink (105 °C) (deg)				waxy polyester toner (165 °C) (deg)				polyester toner (165 °C) (deg)			
	θ^a	α^b	$\theta_A{}^c$	$\theta_R{}^d$	θ^a	α^b	$\theta_A{}^c$	$\theta_R{}^d$	θ^a	α^b	$\theta_A{}^c$	$\theta_R{}^d$
transparency	40	[e]	[f]	[f]	66	[e]	[f]	[f]	79	[e]	[f]	[f]
PTFE film	63	[e]	[f]	[f]	75	[e]	[f]	[f]	85	[e]	[f]	[f]
superoleophobic surface	155	34−43	∼160	∼116	159	50−55	∼168	∼100	130	35−52	∼147	∼103

[a]Static contact angle. [b]Sliding angle. [c]Advancing contact angle, measured from the sessile drop in the sliding angle experiment. [d]Receding contact angle, measured from the sessile drop in the sliding angle experiment. [e]Sessile drops do not slide at 90° tilted angle. [f]Not determined.

as their liquid droplets are shown to stick on the surface without sliding at 90° titled angle. In any event, based on their consistently higher static contact angles, one may still conclude that these imaging materials would prefer to wet the transparency rather than the PTFE surface. As for fusing application, being slightly higher in contact angle is still insufficient. Any material transfer from paper to the fuser surface during fusing, no matter how small the quantity is, still leads to offset. Offset is an unacceptable image quality defect.[6]

Extremely high advancing and static contact angles, indicative of high repellency, are observed on the superoleophobic surface. The advancing/static contact angles for the solid wax ink and the waxy polyester toner are 160°/155° and 168°/159°, respectively. The advancing/static contact angles decrease to 147°/130° for the nonwaxy polyester toner. Since both solid wax ink and the waxy polyester toner consist of hydrocarbon wax as the release additive in the formulation,[13] the higher advancing/static contact angles observed for the wax ink and waxy toner is a reflection of their higher repellency due to the incompatibility between hydrocarbon and fluorocarbon materials. As the waxy toner and solid wax ink become molten, the wax, which is the low surface energy component material in the formulation, migrates to the outer surface of the molten droplets, resulting in the higher advancing/static contact angles. The slight decrease in repellency for the polyester toner can simply be attributed to the absence of the wax in the formulation.

The sliding angles of all three imaging materials range from 34 to 55° on the superoleophobic surface. The sliding angle values and the variation are relatively large as compared to those measured with water and hexadecane (∼10 ± 3°). In Supporting Information, we present a study of the effect of drop size on the contact angle and sliding angle of the solid wax ink on the FOTS modified silicon wafer (Figure S1). The results clearly show that while drop size has very little effect on the static contact angle, there is a large effect on the sliding angle. The sliding angle on FOTS silicon wafer decreases from not slide at 90° to ∼20° as the drop size increases from ∼4 to 20 μL. Similar magnitude of decrease in sliding angle as a function of drop size was also observed by others.[30,31] Our overall results suggest that the large variability for the sliding angle can be attributed to the difficulty in controlling the size of the toner and ink droplet to a tight size distribution. In any event, the most important message here is that droplets of all imaging materials are mobile. They are not being pinned on the superoleophobic surface as compared to those on PTFE and transparency.

From the sliding droplets of these imaging materials, their receding contact angles were found to range from 100° to 116°. The work of adhesion (W_A) for a liquid droplet on a surface is given by $W_A = \gamma(1 + \cos\theta_R)$, where γ is the surface tension of the liquid−vapor phase.[29,32] The large receding contact angles indicate that there is a significant decrease in ink/toner surface adhesion on the superoleophobic surface as compared to the surfaces of PTFE and transparency. Although the W_A values of PTFE and transparency could not be determined accurately, as seen estimations in the Supporting Information (part 2), they are relatively large as compared to the superoleophobic surface.

Repellency and Adhesion of Imaging Materials on Different Surfaces. In an ideal fusing process, one would like

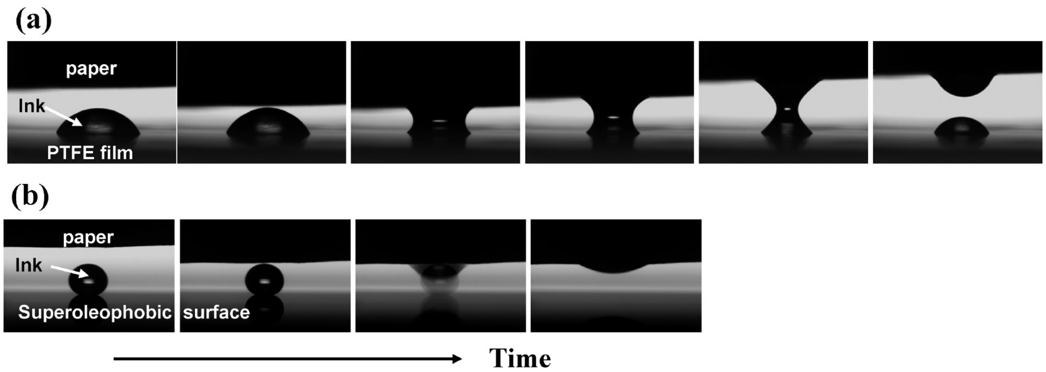


Figure 4. Snapshot of photographs emulating interactions between paper and the molten solid ink drop on (a) a PTFE surface and (b) a superoleophobic surface.

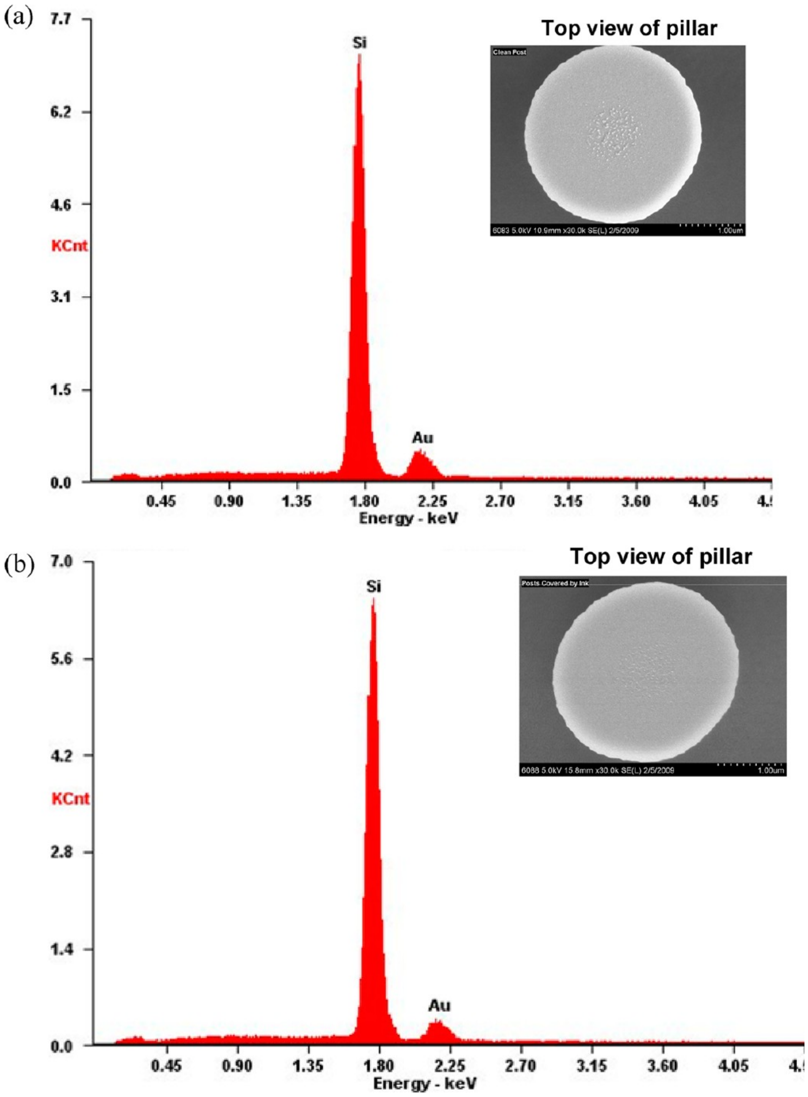


Figure 5. EDXS analysis and SEM micrograph of the pillar (top surface) in the superoleophobic surface (a) before and (b) after ink slide.

to have the imaging material wets and adheres to the paper while showing high repellency from the fuser surface. In practice, the molten material would likely be in contact with both paper and the fuser surface in the fusing zone. As the fused image leaves the fusing zone, having a high ink/toner−fuser surface repellency and low adhesion would be essential to a successful fusing without offset.

The contact angle data in Table 1 suggest that all the toner and ink investigated in this work wet and adhere to the paper well because of their low contact angles and their pinning on the transparency. As with the PTFE surface, the data in Table 1 show that the imaging materials do exhibit higher contact angles on PTFE than those on transparency. However, appreciative adhesion to the PTFE surface still exists because

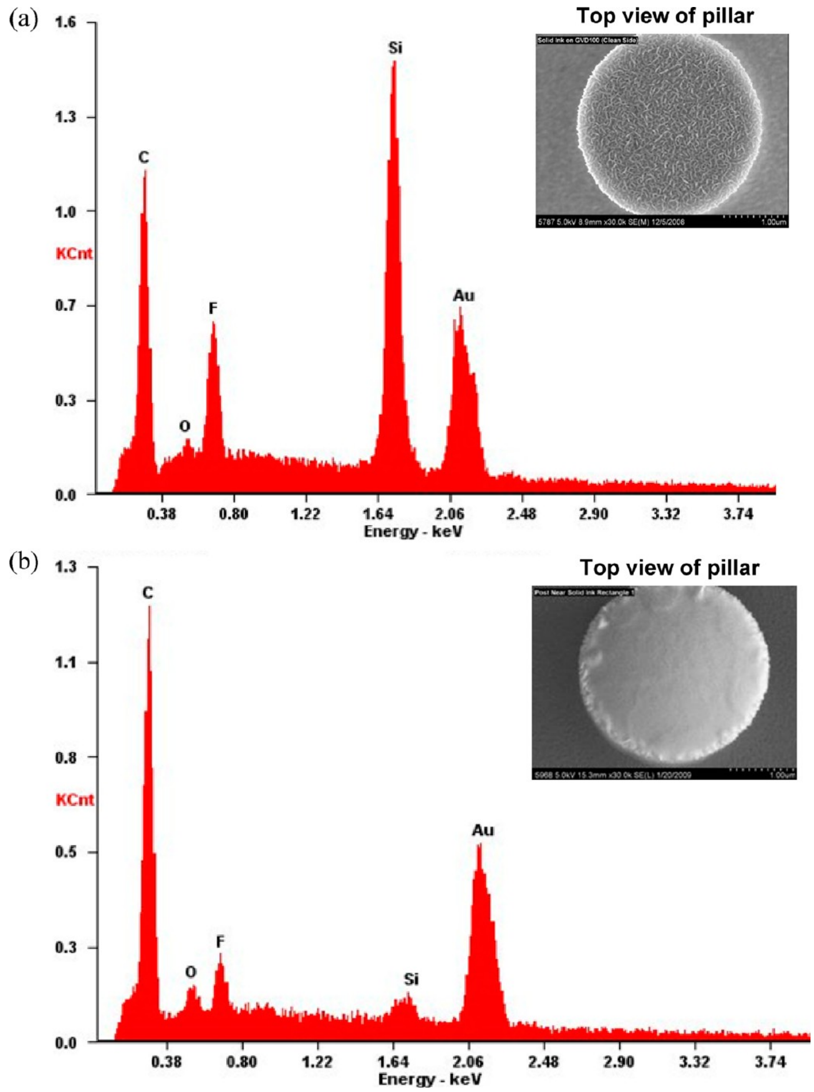


Figure 6. EDXS analysis and SEM micrograph of the pillar (top surface) in the superhydrophobic surface (a) before and (b) after ink slide.

their static contact angles are still below 90°. Sliding angle experiments indicate that droplets of these materials pin on the PTFE film too. Although this may be a surprise to some because PTFE is generally regarded as a low surface energy material, we as well as others consistently show that PTFE is oleophilic and it interacts strongly with oil and organic materials despite its so-called low surface energy.[11,29,33]

The superoleophobic surface is shown to exhibit superhigh repellency against the solid wax ink and the waxy polyester toner as indicated by their large advancing and static contact angles (>150°). These materials are mobile on the superoleophobic surface too, as revealed by their relatively low sliding angles. More importantly, the work of adhesions for the solid wax ink and the waxy polyester toner as estimated from their receding angles are between 16 and 28 mN/m. They are significantly lower than the W_A of PTFE which is >58 mN/m (see Table S1 in Supporting Information). The superhigh repellency coupled with the relatively low surface adhesion suggest that the superoleophobic surface will offer a significant advantage in eliminating offset in fusing as compared to PTFE.

As for the polyester toner without wax, although there is a slight decrease in repellency according to the advancing and static contact angles, the molten toner drop is still mobile. The work of adhesion value between the superoleophobic surface and the polyester toner is estimated to be 27 mN/m, identical to that of the waxy polyester toner. This result suggests that the offset performance of the toner containing no wax with the superoleophobic surface may be comparable to that of the waxy polyester toner. This may represent a cost saving opportunity in toner manufacturing.

Validation of the Superoleophobic Advantage. To validate the conclusion about the superiority of the superoleophobic surface in fusing, we manually emulate the interaction between the imaging material with paper and the fuser surface. Two fuser surfaces, PTFE and the superoleophobic surface, were studied. Solid wax ink was chosen because the experiment can be conducted at a lower temperature, 105 °C instead of 165 °C for the toner. Basically, a drop of solid wax ink was first placed on the experimental fuser surface which was kept at 105 °C. A piece of Xerox 4024 paper was then manually lowered slowly toward the drop. Once the paper touched the ink drop, the paper was retracted and the entire action was captured in videos, which are provided as Supporting Information in this paper. Images a and b in Figure 4 depict the snapshots showing the interaction between the paper and the molten ink drop on PTFE and the superoleophobic surface, respectively. On the PTFE surface, the ink drop splits after retract. In practice, this implies the occurrence of offset in fusing. On the other hand, the ink drop on the superoleophobic surface just jumps onto the paper upon contact, clearly showing the high repellency between the ink drop and the superoleophobic surface. No ink residue was left on the superoleophobic surface.

Comparison between Superhydrophobic and Superoleophobic Surfaces. One of the key hypotheses in this work is that superoleophobicity is needed for offset free fusing in printing because superhydrophobic surface may not be imaging material phobic enough.[33] To validate this point, we compare the offset performance of the solid wax ink on a superhydrophobic surface (Figure 1b) with that on the superoleophobic surface (Figure 1a). The two surfaces have the same surface texture and the only difference is that they have a different conformal coating after surface texturing. The solid ink contact angle for the solid wax ink on the superhydrophobic surface is ~156° and the sliding angle varies between 60° to not slide at 90° from several different measurements. As noted earlier, the variability in the sliding angle is due to experimental difficulty in controlling the precise drop size. In any event, the result suggests that the sessile drop is marginally mobile on the superhydrophobic surface. The real differentiation between these two surfaces comes from analysis of the surfaces of the pillar top before and after ink sliding. Panels a and b in Figure 5 show the EDXS (elemental) analysis and the SEM micrographs of the top of the pillar in the superoleophobic surface before and after the slide of the ink droplet, respectively. Within experimental uncertainty, we detect no change in surface morphology and elemental content on the top of the pillar. Very different results were obtained for the superhydrophobic surface. Panels a and b in Figure 6 show the EDXS (elemental) analysis and the SEM micrographs of the top of the pillar in the superhydrophobic surface before and after the slide of the ink droplet, respectively. Before the ink drop slides, the roughness feature from the i-CVD PTFE coating is visible (inset of Figure 6a). After the ink slide, the surface becomes smooth (inset of Figure 6b). Elemental analysis from EDXS indicates that surface become richer in carbon and less in fluorine and silicon. The overall results lead us to conclude that the top of the pillar is coated with the solid wax ink as the ink drop slides off the pillar surface. In other words, offset of solid ink onto the superhydrophobic surface has just occurred. The superiority of the superoleophobic surface on offset performance is demonstrated.

■ SUMMARY AND REMARKS

We have studied the interactions of toner and ink on three different model print surfaces using contact angle measurement techniques. Our results show that toner and ink generally wet, adhere and pin on paper well. Teflon PTFE is one of the most common low surface energy materials used in the printing industry. Contact angle data however suggest that toner and ink also wet, adhere and pin on PTFE too, although it is not as strong as on paper. Despite this shortfall, PTFE is still widely used because of its chemical inertness and high thermal stability. The common approach to circumvent offset is to use release agents. For example, one can apply a small amount of silicone oil on the fuser surface to aid the release. Alternatively, one can place a small amount of wax in the toner formulation. When the toner melts, wax being the low surface component will migrate to the outer surface to facilitate fusing. Advancing and static contact angle data suggest that waxy toner and ink will repel from the superoleophobic surface. In addition, the adhesion between the ink and waxy toner on the superoleophobic is very low as compared with those on PTFE and paper. The overall surface data suggests that superoleophobic surface may offer offset free fusing in the future. Because the superoleophobic surface also repels the non waxy polyester toner and the surface adhesion is very low too, the result suggests that one may be able to achieve offset free fusing with the nonwaxy polyester toner. This may represent an opportunity to reduce material cost.

This work also demonstrates that superhydrophobic surface is inferior to superoleophobic surface because it still exhibits higher adhesion toward waxy ink and toners. The high adhesion results in offset, an unacceptable image quality defect.

Finally, it is important to note that fusing is normally carried out at an evaluated temperature with pressure ranging from 300 to 700 kPa.[3−5] A valid question arises: can the surface remain superoleophobic and perform under high pressure? If it does not, what is the consequence? Recently, we[34] completed an investigation of the effect of surface texturing on the superoleophobicity of the pillar array FOTS surfaces. Preliminary results showed that both hexadecane advancing and static contact angles, which are ~160° and 155°, respectively, are insensitive to pillar diameter (1 to 10 μm), height (>1 μm) and spacing. The results suggest that there exist a wide design window in designing surfaces with super oil repellency. On the other hand, the receding contact angle is shown to vary with the solid area fraction, the larger the solid area fraction the lower the receding contact angle and the higher the surface adhesion. We have also modeled the robustness of the superoleophobicity against mechanical abrasion and pressure induced wetting transition (from Cassie−Baxter to Wenzel state) using mechanical model modeling and Surface Evolver simulation, respectively. Results indicate that the wetting transition (breakthrough) pressure increases as the solid area fraction increases.[34] As seen in results in Figures S2 in the Supporting Information, the breakthrough pressure is also sensitive to the flat surface contact angle and the diameter of the pillar for a given solid area fraction. From these results, we project that superoleophobic surface that can withstand 40 kPa is possible with the design parameters at hand (1 μm diameter pillar with a pitch of ~1.5 μm). Although it is theoretical possible to increase the breakthrough pressure further, the prospect does look bleak since fusing runs at a much higher pressure. On the other hand, recent investigations by Bahadur and Garimella[35] as well as Dash and co-workers[36] suggested that the Cassie−Baxter to Wenzel transition can be prevented with a noncommunicating texture or a hybrid design. It seems that further modification of the pillar array design to enhance its resistance against pressure is possible.

Another interesting twist is that the fusing process is dynamic. Specifically, as the unfused material enters the fusing zone, heat is first provided to melt the toner or ink and the molten material is fused onto the paper under pressure. The entire event is completed in 10−20 ms. Because the polymers used in the toner and ink formulations are usually very high in molecular weight, molten toner and ink are therefore highly viscous. We suspect that even if the fusing pressure exceeds that of the breakthrough pressure, the molten material may not have enough time to wet the texture surface before leaving the fusing zone. The dynamic of the pressure-induced wetting transition and the multicomponent interaction in the fusing process is a challenging research topic and remains to be investigated.

■ ASSOCIATED CONTENT

Supporting Information

(1) Study of the effect of drop size of the molten wax ink on contact angle and sliding angle on the FOTS modified silicon surface, (2) work-of-adhesion (WA) data of the solid wax ink on different surfaces, (3) Surface Evolver simulation of the wetting breakthrough pressure versus different surface texturing parameters, and (4) video files showing the interactions between the molten ink drop and paper with the Teflon surface and the superoleophobic surface. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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