Hot Embossed Micro-Textured Thin Superhydrophobic Teflon FEP Sheets for Low Ice Adhesion

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Abstract

Various efforts have been conducted by researchers to create synthetic superhydrophobic surfaces. However, most of these fabrication procedures are convoluted and not suitable to be applied on surfaces with complex shapes and sizes. We report a simple and low cost fabrication of a thin superhydrophobic sheet (127 μm thick) of low ice adhesion strength by laser micro-texturing an aluminum master substrate followed by hot embossing on a Teflon fluoroethylene propylene (FEP) sheet for a water contact angle and roll-off angle of 160° and 4° , respectively. The micro-textured aluminum master substrate could be used multiple times to emboss the FEP sheet for a reduction in fabrication complexity and cost. The fabrication procedure also ensured that the structure of the sheet remains intact, therefore allowing it to be wrapped and adhered to target surfaces of different shapes. Ice adhesion experiment on the superhydrophobic sheet showed ice detachment strength at approximately 20 kPa on average, which was less than 2% of the ice detachment strength of an aluminum substrate, 33% of the ice detachment strength of a smooth non-textured Teflon FEP sheet and among the lowest superhydrophobic ice adhesion strength reported in literature. Potential applications of the superhydrophobic sheet include evaporator icing control in refrigeration systems and low ice adhesion surfaces for architectural structures.

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1) Introduction

The extreme water-repellency of superhydrophobic surfaces can provide solutions in a variety of applications such as anti-icing for refrigeration systems, architectural and aerospace industries, anti-fouling and corrosion protection in marine applications, self-cleaning for solar cells, etc. Superhydrophobicity, often quantified by a contact angle ($>150^\circ$) and roll-off angle ($<10^\circ$) wettability measurements, is induced by creating micro/nano-textures on an inherently hydrophobic material.[1,2] The combination of low surface energy and asperities lead to a Cassie-Baxter wetting state, whereby air pockets are trapped in between the gaps of the surface roughness and hence resulting in water suspension on the tips of the micro/nano-features.[3] This drastically increases the mobility of a water drop on a surface. In contrast, a Wenzel wetting state is a wetting condition whereby water penetrates into the surface asperities to fill the gaps between the micro- textures.[4] The increased contact area between the water-surface interfaces reduces water drop mobility on the surface which is often associated with a high roll-off angle, and in certain conditions can also cause water drop pinning.

The attractiveness of superhydrophobic surfaces in providing broad application solutions have prompted researchers to create synthetic water-repellent surfaces using a variety of techniques. These include, but are not limited to, surface etching techniques (plasma, laser, chemical)[5-7], lithography (photolithography, electron beam, X-ray)[8,9], electrochemical deposition processes[10,11], electro-spinning techniques[12], etc. Although these techniques do successfully result in superhydrophobicity, they are complex and are often associated with high fabrication cost. In addition, they could be challenging to implement on applications since target

surfaces are often in complex shapes and sizes. For example, the leading edge of an aircraft wing is curved for aerodynamic efficiency. As such, the goal of this work is to create a thin superhydrophobic sheet that is lightweight, flexible with low ice adhesion strength, so that it could be wrapped and adhered to target surfaces of different shapes for ice protection without adding a significant weight.

The creation of a superhydrophobic sheet requires that the sheet material to be of inherent low surface energy. We chose a fluorinated ethylene propylene (FEP) sheet of 0.005 inch / 127 μm (Teflon FEP, DuPont) and imparted micro-textures on the sheet via hot embossing from a micro-textured aluminum master substrate. The selection of the DuPont Teflon FEP sheet is due to its all-round robust characteristics. For example, it is chemically inert and resistant to virtually all chemicals, has high resistance to impact and tearing and also inert to outdoor exposure (no measurable change after 20 years in a test conducted at Florida).[13] More importantly, it has a lower melting temperature than Teflon polytetrafluoroethylene (PTFE) at between 250°C to 280°C. This allows the hot embossing procedure to be conducted at lower temperatures. Texturing of Teflon materials for superhydrophobicity has been conducted by various researchers by a variety of different techniques.[14-18] However, to the author's best knowledge, there have not been any publications which attempted to texture a Teflon sheet as thin as 127 μm while maintaining the structural integrity of the sheet, with high contact angles ($> 150^\circ$). In addition, ice adhesion properties of these sheets have not been reported. A majority of the work has been focused on texturing bulk Teflon material, such as Liang *et al.*[14] who ablated PTFE blocks by femtosecond lasers, Nilsson *et al.*[15] who roughened solid PTFE by sandpaper and Glariset *et al.*[16] who thermally annealed a 4 mm thick PTFE block for the creation of texture.

Juciuset *al.*[17,18] did hot emboss a thin 200 μm PTFE sheet to create superhydrophobicity but was only able to achieve a contact angle of 145° .

The current fabrication of the superhydrophobic thin sheet requires 4 steps. The first step is to use laser irradiation on an aluminum substrate to ablate the surface and to create micro-textures. The second step involves embossing the previously ablated micro-textured aluminum surface on a fluorinated ethylene propylene (FEP) thin sheet at high temperatures. The third step is to peel off the textured FEP sheet under low heat from the aluminum textured surface, and finally, the fourth step is to post-treat the textured FEP sheet to smoothen any curved edges and wrinkles. A schematic of these four steps is shown in Figure 1. It should be noted that after the completion of Step 1, the micro-textured aluminum master substrate could be used multiple times for hot embossing and creation of micro-textured FEP thin sheets. This drastically simplifies the fabrication steps and reduces the fabrication cost as well. The ice adhesion properties of this superhydrophobic sheet was then investigated. In addition, the repellency of the sheet from liquids consisting of different surface tensions was studied.

2) Experimental Methods

A. Fabrication of the Superhydrophobic Thin Sheet

A 532 nm wavelength pulsed ytterbium fiber laser (Model YLP-G-10, IPG Photonics) was used to irradiate a square aluminum master of approximately 2.54 cm by 2.54 cm in dimension. This laser system has the capability to generate 10 W of average laser power with a pulse of 1.3 ns and a focused spot size of 25 μm . In order for the entire surface area of the aluminum master to be laser irradiated, a galvanometer (SCANcube 14, SCANLAB) was utilized to deflect the laser beam so that the beam could traverse in longitudinal and lateral directions for

a fast and accurate scanning. The parameters of the pulsed laser processing were optimized so that micro-textures on the aluminum were approximately uniform in height and spacing. These parameters were as follows: a laser pulse energy of 3.9 $\mu\text{J}/\text{pulse}$, a pulse repetition rate of 400 kHz, a scanning speed of 6 cm/sec and a laser deflection lateral length of 14 μm . This lateral length was intentionally chosen to be lower than the spot size of the laser beam so that initial laser irradiation areas would be partially processed again. This was to ensure a uniform micro-texturing of the aluminum master surface without any apparent gaps between textured areas. It should be noted that this laser irradiation technique have been previously used by Bhagat *et al.*[19] and Nayaket *al.*[20,21]to successfullymicro-texture common materials, such as, polycarbonate, silicon, titanium, aluminum, copper and stainless steel.

Step two of the fabrication process involved hot embossing of the previously micro-textured aluminum master on a FEP thin sheet (Teflon FEP Fluorocarbon Film, DuPont) of 127 μm thickness. This virgin FEP sheet is optically transparent and offers a good balance of sheet flexibility and mechanical strength. For example, the sheet could be elongated 300% without break with a folding endurance of 10,000 cycles. These property values show that this product is a good candidate for withstanding the processes of hot embossing and peel-off with minimal effect on the integrity of the sheet. First, an approximately 2.54 cm by 2.54 cm FEP sheet was cut and placed on the micro-textured aluminum sheet and placed on a hot plate. Two kg of weights was used to provide embossing pressure necessary to replicate the micro-textures on the FEP thin sheet. This amount of weight on the samples equate to approximately 30 kPa of embossing pressure.Since the surface of the weight was rough, a polished aluminum substrate was placed underneath the weights to avoid direct contact between the FEP thin sheet and the weights. An additional polytetrafluoroethylene (PTFE) thin sheet (50 μm Teflon PTFE,

McMaster) was sandwiched between the FEP thin sheet and the polished aluminum substrate. This was because the FEP thin sheet would be heated past its melting temperature to potentially cause adherence on the polished aluminum. Since the PTFE has a higher melting temperature ($\sim 320^{\circ}\text{C}$), it will prevent adherence problems while maintaining solid form under embossing temperatures. A schematic of this embossing set-up is shown in Figure 1. The hot embossing process is as follows: First, the hotplate was set at 100°C , after which it was gradually heated at a rate of approximately $6^{\circ}\text{C}/\text{min}$ until the target embossing temperature was reached (310°C). This temperature was maintained for 5 minutes before the hot plate was turned off and allowed to completely cool to room temperature. This process of cooling took approximately 45 minutes. It should be noted that the entire heating and cooling process was conducted with the embossing set-up untouched.

The third step involved the removal of the embossed FEP sheet from the aluminum master by peel-off. Since the sheet and aluminum were cooled to room temperature, the adherence between these two materials was high. Attempts to remove the FEP sheet from the aluminum master by brute force will cause tearing to result in a sheet of no practical use. As such, the FEP sheet and aluminum master was re-heated on the hot plate to 100°C . This allowed the FEP sheet to be slightly expanded and therefore resulting in an easier peel-off. This step is shown in Figure 1. It should be noted that the peel-off step could be performed during the cool-off period of the embossing step if needed, provided that the temperature of peel-off is at approximately 100°C . The peeled-off micro-textured FEP sheet was discovered to be wrinkled with bent edges. Therefore, an extra step (Step 4) of post treatment was conducted by thermal annealing. The micro-textured FEP thin sheet was sandwiched between two PTFE films and placed on a hotplate with 2 kg of weights providing 30 kPa of downward pressure. The inclusion

of the PTFE films in the set-up was to protect the surface of the textured FEP sheet during annealing. A press duration of 5 minutes at 125°C was conducted to allow the combination of slight heat and pressure to straighten and smoothen the micro-textured FEP thin sheet.

B. Sample Characterization

Scanning electron microscope (SEM) imaging of the substrates were conducted at the Nanoscale Materials Characterization Facility at the University of Virginia using a Quanta 650 (FEI) microscope under low-vacuum conditions. Low vacuum conditions allowed for the non-destructive imaging of the samples. 3-D surface feature topology and measurements of a surface area of size approximately 350 μm x 250 μm were acquired by a white light interferometer (NewView 7300, Zygo). The substrates were sputter coated with a thin (nm thick) layer of gold and palladium to facilitate the process of the topology imaging. The wettability of the samples were measured using a contact angle goniometer (Model 290, Ramé-Hart). A 10 μL deionized water drop was used for static contact angle (CA) and roll-off angle (ROA) measurements. The measurements were repeated three times on each sample at three different locations and averaged. This was to account for the variance in wettability performance of the surfaces.

C. Ice Adhesion Test

The ice adhesion of the micro-textured superhydrophobic thin sheets was tested using a modified dynamical mechanical analysis (DMA) machine (RSA-III, TA Instruments) located at the Wynne Research Lab at the Virginia Commonwealth University.[22,23] Plastic cylindrical molds cut from the ends of a 1000 μL pipette tip (0.75 cm in diameter) and placed on the superhydrophobic thin sheets which were taped to aluminum substrates for stability. These

molds served as cuvettes to hold 200 μL of deionized water for freezing. Deionized water was used to prevent impurities from affecting the ice adhesion strength.[24]The set-up was then placed in a commercial freezer set at -15°C for 2 hours After freezing, the set-up was removed and placed in the chamber of the DMA machine which was temperature regulated by liquid nitrogen to -10°C . An incubation period of 2 minutes was performed to ensure temperature homogeneity between the air, substrate surface and ice before the ice shearing process commenced. The shearing involved the collision of a probe positioned at 2 mm from the surface and moving at a speed of 0.05 mm/sec with the iced plastic mold. The force that was exerted by the probe to shear the iced cylinder from the surface was recorded by a load cell and determined as the ice release strength. The test was performed for at least 6 times on each substrate and averaged to account for the variance in ice detachment force. This method of evaluating the ice adhesion strength of a surface was previously used by Wang *et al.*[22,23]for measuring ice release strength of polydimethylsiloxane (PDMS) and poly(methyl methacrylate) (PMMA). Further details on the ice adhesion experiment setup could be obtained from Wang et al.[22,23]

3) Results

Figure 2 shows the effect of embossing temperature on the wettability of the thin sheets while fixing the weight and emboss duration parameters. Results showed that at an embossing temperature of 290°C , the wettability of the sheet was high. Even though the contact angles were measured to be very similar to a smooth, un-textured FEP sheet (averaged CA of 113.2° vs 112.3° for smooth surface), the droplet was pinned on the surface. This roll-off angle performance was inferior when compared to a smooth FEP sheet (ROA of 45.3°).Upon increasing the embossing temperature to 300°C , the CA of the thin sheet increased to an averaged value of 145.9° with an

averaged ROA of 52.7° (Figure 2a and b). At a temperature of 310°C , the averaged CA measurement was above 160° with ROA of less than 6° , respectively. At 325°C embossing temperature, it could be observed that no significant improvements in wetting performance could be gained. Averaged CA measurements remained at approximately 160° with averaged ROA of 4° .

Figure 3 shows the visual appearance of an as-received, non-textured FEP thin sheet prior to hot embossing and the FEP thin sheets that were hot embossed at 290°C , 300°C and 310°C . Respective SEM and 3-D surface topology images of hot embossed thin FEP sheets were also shown. Increased presence of texture and surface features could be observed with increasing embossing temperatures. In addition, it could be observed that the thin sheets became gradually opaque with increasing embossing temperatures. SEM images of a superhydrophobic thin sheet embossed at a temperature of 310°C at different magnifications are shown in Figure 4. Surface flakes with sharp edges approximately $20\text{ }\mu\text{m}$ in size could be observed on the surface for images acquired at 400X and 2000X (Figure 4a and b). Higher magnifications at 5000X and 27000X (Figure 4c and d) also revealed the existence of low micron and nano-meter sized flakes and fibers embedded within the micron-sized structures.

Figure 5 shows the ice adhesion strength of the hot embossed superhydrophobic sheet compared with two control samples: a $500\text{ }\mu\text{m}$ thick, smooth non-textured PDMS elastomer film (Sylgard 184, Dow Corning) and an as-received non-textured Teflon FEP sheet of same thickness as the superhydrophobic sheet. As shown in Figure 5, the ice detachment force of the PDMS film was approximately 90 kPa on average. This value compared favorably with recent measurements by Wang *et al.* using the same ice adhesion test apparatus.[23] Ice adhesion strength of the as-received, non-textured Teflon FEP sheet was measured to be lower than

compared to the PDMS film at approximately 60 kPa on average while the lowest ice adhesion strength was measured to be from the micro-textured, superhydrophobic FEP thin sheet at approximately 20 kPa on average. The deviations in measured ice detachment forces can be attributed to the crystalline nature of ice. Deviations have also been observed in previous ice adhesion experiments as well such as with Wang *et al.*[23] and Meuler *et al.*[25], where errors in ice detachment force ranged from approximately ± 20 kPa to approximately ± 110 kPa. It is also worthwhile to note that the ice adhesion strength of bulk aluminum is over 1000 kPa. This value was not measured in this experiment as the aluminum ice shear strength was out of range for the ice adhesion setup that was used in this study. Rather, this value was obtained from Bharathidasan *et al.*[26]

Figure 6 shows the wettability parameters of averaged CA and averaged receding contact angle (RCA) of the substrates which were tested in the ice adhesion experiment. Results showed no significant correlation between CA and the ice detachment force. Rather, the ice detachment force depended on the RCA of the substrates. In addition, the wetting performance of the superhydrophobic sheet with liquids of different viscosities and surface tensions were studied and compared with those on an as-received, non-textured FEP sheet. The CA and ROA of the FEP sheets with its respective test liquids are shown in Table 1. Results showed that a decrease in surface tension significantly affected the wettability of the superhydrophobic surface. Test liquids of surface tension below 68 mN/m will result in a loss of superhydrophobicity, followed by a complete spreading of the liquid on the surface for test liquids at 20 mN/m or lower. No viscosity effects on wettability was observed.

4) Discussion

The degree of micro-texture embossing on the FEP thin sheet depended on 3 parameters: weight/embossing pressure, duration of emboss and temperature at which the embossing occurred. The concept was to partially soften the FEP so that micro-textures on the aluminum master could be imprinted by pressure on the thin sheet, which upon cooling will set and solidify to result in a superhydrophobic thin sheet. The thin sheets could be embossed at a wide range of parameters but will often carry a cost, e.g. heavier weights for a high embossing pressure to reduce emboss duration but introducing stress on the system or lighter weights to minimize stress but requiring a longer duration of emboss. The weight and duration parameters was intentionally fixed to be 2 kg and 5 minutes, values we believed to be within practical range for large quantity fabrication, and studied the effect of temperature on embossed surface wettability and micro-structure. It should be noted that the described embossing temperatures herein refer to temperature setting of the hot plate. The actual temperature of the FEP sheet during embossing was predicted to be slightly lower (5-10°C) due to heat loss from the hot plate.

The poor ROA performance of a thin sheet embossed at 290°C shown in Figure 2 could be explained by the surface morphology of the thin sheet. As shown in the SEM and surface topology image in Figure 3b, the surface structure was slightly altered by the presence of heat. However, there were barely any noticeable features that were present on the thin sheet. A few holes of approximately 10 μm in diameter or smaller were created but in general, the surface remained “flat” with an averaged surface feature maximum height of less than 5 μm (Figure 3b). This could also be confirmed from the visual appearance of the thin sheet where majority of the surface area were still optically transparent. The presence of these holes created pinning conditions for the water droplet, leading to a poor ROA performance. However, at embossing temperatures at 310°C, the FEP sheet was uniformly embossed with micro-textures (confirmed

by SEM and 3D topology images shown in Figure 3d, as well as the picture of the uniformly opaque sheet). The averaged maximum feature height at this embossing temperature was approximately 20 μm (Figure 2). Further SEM imaging of the superhydrophobic thin sheet embossed at this temperature revealed layers of surface texture at different length scales. (Figure 4) The presence of this hierarchical surface morphology significantly promotes and stabilizes the superhydrophobicity of the sheet.[27]

This improvement in wetting performance at different embossing temperatures was due to the increased roughness stemming from an increased embossed micro-texture height (from less than 5 μm to approximately 12 μm). As shown in Figure 3c, apparent levels of roughness were created on the surface with increased presence of holes. These holes were believed to be embossed by the tips of the textures on the aluminum master. It should be noted however that the wettability of the sheet at this embossing temperature varied significantly. For example, certain spots on the sheet would exhibit superhydrophobic characteristics while at other spots, water drops would be pinned. This variance was also reflected in the error bars of both wettability and averaged feature maximum height measurements as shown in Figure 2. The reason for this large variance was due to the non-uniform levels of embossing on the surface area of the thin sheet. This could be visually observed in Figure 3c whereby certain areas of the thin sheet was more opaque as compared to other areas. The opacity of the thin sheet is directly related to the degree of texture on the surface. The size of the embossed textures (height and width) were significantly larger than the wavelength of visible light (~400 nm to ~700 nm), causing incident light on the micro-textures to scatter and therefore result in opacity.[28] In contrast, optically transparent areas were not fully embossed, therefore allowing more light to transmit through the thin sheet. Hence, opaque areas on the sheet were generally superhydrophobic while optically transparent

areas were not. It should be noted that embossing at even higher temperature of 325°C did not further improve the static and dynamic contact angles of the thin sheet. As such, embossing at such high temperatures should be avoided as it was experimentally observed that the adherence of the FEP sheet on the aluminum master increased with difficulty of peel-off. In addition, severe wrinkles and edge folding would be introduced.

The low ice detachment force of FEP hot embossed film was expected and can be attributed to the higher receding contact angle (RCA) of the Teflon FEP sheet at 97.3° on average as compared to 88° for the PDMS film (Figure 6b). A higher RCA value indicated a surface with greater water drop mobility and had been shown by Meuler *et al.* to affect ice adhesion strength.[29] In contrast, as shown in Figure 6a, the CA of the film was not a reliable indicator of ice adhesion strength. The ice detachment force for the micro-textured Teflon FEP surface was predominantly below 20 kPa, which is among the lowest recorded ice adhesion strength of superhydrophobic surfaces based on recent literature review data of over 20 publications, conducted by Kreder *et al.*[30] A subset of this data (from 10 publications) is shown in Table 2. It should be noted that the surveyed data include measurements from both Cassie and Wenzel ice accretion conditions. In addition, multiple ice adhesion measurements on the same superhydrophobic sheet also revealed that the ice adhesion strength did not significantly degrade even after repeated tests, which showed the robustness of the sheet. According to Dou *et al.*, the adhered ice on this superhydrophobic thin sheet could be detached by wind speeds of 12 m/s.[31] This range of wind speed is classified as Beaufort Number 6 out of 9 on a Beaufort wind scale, where its effects on human body has been described as “difficult to walk steadily” by Penwarden.[32] It should be noted that since the ice adhesion strength of an aluminum surface is generally above 1000 kPa, [33,34] the ice release force of this superhydrophobic thin sheet is

less than 2% of the aluminum. These results showed that the superhydrophobic sheet could be employed in realistic applications. For example, the sheet could be attached to refrigeration components to prevent ice accumulation through water-repellency, and in the event of icing, the adhesion of ice will be low enough to be easily removed from the surface by low external forces. The flexibility of the sheet implies that it could be easily applied to surfaces of complex shapes and sizes by adherence. FEP films have been previously shown to successfully adhere on metal substrates such as aluminum with good bond strength. [35]

The inability of the superhydrophobic thin sheet to repel low surface tensions liquids such as oils was expected. Surfaces that are capable of doing so such as superoleophobic surfaces tend to consist of unique surface morphologies such as re-entrant surface curvatures or micro-hoodoos to provide a third factor in designing low surface tension liquid-repellent surfaces, in addition to surface chemical composition and roughness.[36,37] The micro-textured superhydrophobic sheet did not contain such features and therefore unable to resist penetration of the low surface tension liquid into its asperities. It was interesting to note that although the CA of the test liquids on the as-received, non-textured FEP sheet was lower than the micro-textured sheet, certain liquids (above 47 mN/m) were able to slide off the surface at reasonably low angles. In fact, as surface tension of the test liquids decreased, the slide-off angles on the as-received sheets improved. This was in contrast to the superhydrophobic sheets, whereby roll-off angles degraded quickly to pinning. This could be attributed to the lack of surface roughness on the as-received sheet to hinder fluid mobility on the surface.

An additional test was also performed to quantify the abrasive resistance of the micro-textures. This was accomplished by using a linear abraser (Model 5750, Taber Industries). The linear abraser consisted of an abrasingtip (scotchbrite pad) which was pressed on the micro-

textured FEP sheets and linearly reciprocated to abrade the sheets at a controlled speed (30 cycles/minute) and under the weight of 350 g. This method of testing the abrasive durability of a surface was reported in previous works. [38,39] Results showed that the CA of a micro-textured FEP sheet abraded at 5 cycles degraded from a non-abraded state of above 160° to approximately 145°. The additional abrasion of 5 cycles (for a total of 10 cycles) resulted in a further CA reduction to approximately 130°. These results suggested that the micro-textures of the FEP sheets had been altered by abrasion and therefore affected its wetting state. It could also be plausible that remnants of the abradant was left on the micro-textured sheets, thereby changing its surface energy and wettability. It should be noted that the wettability of a surface after abrasion is dependent on the type of abrasive material that was used. As shown by Steele *et al.*, superhydrophobic surfaces can retain its non-wettability characteristics under certain wear conditions.[40] Further investigation will be required to investigate the effects of different wear mechanisms on the wettability of the micro-textured FEP sheets. Additional future studies should also include chemical characterization of the sheets.

4) Conclusions

A Teflon FEP sheet of 127 μm thickness was successfully micro-textured for the creation of a low ice adhesion, superhydrophobic thin sheet. Results showed that by fixing the embossing weight/pressure and duration to 2 kg/ 30 kPa and 5 minutes, respectively, a temperature setting of 310°C was sufficient to partially soften the FEP sheet for the imprint of micro-textures of approximately 20 μm in height on the surface. The resulting embossed sheet was superhydrophobic with a water CA of above 160° and a ROA of less than 6° with a hierarchical surface feature morphology. Ice adhesion experiment showed a low ice detachment strength at

less than 20 kPa on average, which was less than 2% of the ice detachment strength of an aluminum substrate, 33% of the ice detachment strength of a smooth, non-textured FEP sheet and among the lowest superhydrophobic ice adhesion strength reported in literature. Wettability studies of the superhydrophobic sheet with liquid of various surface tension however showed a loss of superhydrophobicity with liquids of surface tension below 68 mN/m.

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References

- [1] M. Ma, R.M. Hill, Superhydrophobic surfaces, *Curr. Opin. Colloid Interface Sci.* 11 (2006) 193-202.
- [2] X. Feng, L. Jiang, Design and creation of superwetting/antiwetting surfaces, *Adv. Mater.* 18 (2006) 3063-3078.
- [3] A. Cassie, S. Baxter, Wettability of porous surfaces, *Trans. Faraday Soc.* 40 (1944) 546-551.
- [4] R.N. Wenzel, Resistance of solid surfaces to wetting by water, *Ind. Eng. Chem.* 28 (1936) 988-994.
- [5] A. Tserepi, M. Vlachopoulou, E. Gogolides, Nanotexturing of poly (dimethylsiloxane) in plasmas for creating robust super-hydrophobic surfaces, *Nanotechnology.* 17 (2006) 3977.
- [6] B. Cortese, S. D'Amone, M. Manca, I. Viola, R. Cingolani, G. Gigli, Superhydrophobicity due to the hierarchical scale roughness of PDMS surfaces, *Langmuir.* 24 (2008) 2712-2718.
- [7] Z. Guo, J. Fang, L. Wang, W. Liu, Fabrication of superhydrophobic copper by wet chemical reaction, *Thin Solid Films.* 515 (2007) 7190-7194.

- [8] M. Wang, N. Raghunathan, B. Ziaie, A nonlithographic top-down electrochemical approach for creating hierarchical (micro-nano) superhydrophobic silicon surfaces, *Langmuir*. 23 (2007) 2300-2303.
- [9] E. Martines, K. Seunarine, H. Morgan, N. Gadegaard, C.D. Wilkinson, M.O. Riehle, Superhydrophobicity and superhydrophilicity of regular nanopatterns, *Nano Lett.* 5 (2005) 2097-2103.
- [10] M. Qu, G. Zhao, Q. Wang, X. Cao, J. Zhang, Fabrication of superhydrophobic surfaces by a Pt nanowire array on Ti/Si substrates, *Nanotechnology*. 19 (2008) 055707.
- [11] J. Xi, L. Feng, L. Jiang, A general approach for fabrication of superhydrophobic and superamphiphobic surfaces, *Appl. Phys. Lett.* 92 (2008) 053102.
- [12] M. Ma, M. Gupta, Z. Li, L. Zhai, K.K. Gleason, R.E. Cohen, M.F. Rubner, G.C. Rutledge, Decorated electrospun fibers exhibiting superhydrophobicity, *Adv. Mater.* 19 (2007) 255-259.
- [13] DuPont FEP Fluorocarbon Film Properties Bulletin, 2016.
- [14] F. Liang, J. Lehr, L. Danielczak, R. Leask, A. Kietzig, Robust non-wetting PTFE surfaces by femtosecond laser machining, *Int. J. Mol. Sci.* 15 (2014) 13681-13696.
- [15] M.A. Nilsson, R.J. Daniello, J.P. Rothstein, A novel and inexpensive technique for creating superhydrophobic surfaces using Teflon and sandpaper, *J. Phys. D.* 43 (2010) 045301.
- [16] P. Glaris, J. Coulon, M. Dorget, F. Poncin-Epaillard, Thermal annealing as a new simple method for PTFE texturing, *Polymer*. 54 (2013) 5858-5864.

- [17] D. Jucius, V. Grigaliūnas, M. Mikolajūnas, A. Guobienė, V. Kopustinskas, A. Gudonytė, P. Narmontas, Hot embossing of PTFE: Towards superhydrophobic surfaces, *Appl. Surf. Sci.* 257 (2011) 2353-2360.
- [18] D. Jucius, A. Guobienė, V. Grigaliūnas, Surface texturing of polytetrafluoroethylene by hot embossing, *Appl. Surf. Sci.* 256 (2010) 2164-2169.
- [19] S.D. Bhagat, M.C. Gupta, Superhydrophobic microtextured polycarbonate surfaces, *Surf. Coat. Technol.* 270 (2015) 117-122.
- [20] B.K. Nayak, M.C. Gupta, Self-organized micro/nano structures in metal surfaces by ultrafast laser irradiation, *Opt. Laser. Eng.* 48 (2010) 940-949.
- [21] B.K. Nayak, P.O. Caffrey, C.R. Speck, M.C. Gupta, Superhydrophobic surfaces by replication of micro/nano-structures fabricated by ultrafast-laser-microtexturing, *Appl. Surf. Sci.* 266 (2013) 27-32.
- [22] C. Wang, W. Zhang, A. Siva, D. Tiew, K.J. Wynne, Laboratory test for ice adhesion strength using commercial instrumentation, *Langmuir*. 30 (2014) 540-547.
- [23] C. Wang, T. Fuller, W. Zhang, K.J. Wynne, Thickness dependence of ice removal stress for a polydimethylsiloxane nanocomposite: sylgard 184, *Langmuir*. 30 (2014) 12819-12826.
- [24] S. Alansatan, M. Papadakis, SAE Technical Paper. 1999-01-1584 (1999).

- [25] A.J. Meuler, J.D. Smith, K.K. Varanasi, J.M. Mabry, G.H. McKinley, R.E. Cohen, Relationships between water wettability and ice adhesion, *ACS Appl. Mater. Inter.* 2 (2010) 3100-3110.
- [26] T. Bharathidasan, S.V. Kumar, M. Bobji, R. Chakradhar, B.J. Basu, Effect of wettability and surface roughness on ice-adhesion strength of hydrophilic, hydrophobic and superhydrophobic surfaces, *Appl. Surf. Sci.* 314 (2014) 241-250.
- [27] N. Michael, B. Bhushan, Hierarchical roughness makes superhydrophobic states stable, *Microelectron. Eng.* 84 (2007) 382-386.
- [28] H.K. Raut, V.A. Ganesh, A.S. Nair, S. Ramakrishna, Anti-reflective coatings: A critical, in-depth review, *Energy Environ. Sci.* 4 (2011) 3779-3804.
- [29] A.J. Meuler, J.D. Smith, K.K. Varanasi, J.M. Mabry, G.H. McKinley, R.E. Cohen, Relationships between water wettability and ice adhesion, *ACS Appl. Mater. Interfaces.* 2 (2010) 3100-3110.
- [30] M.J. Kreder, J. Alvarenga, P. Kim, J. Aizenberg, Design of anti-icing surfaces: smooth, textured or slippery? *Nat. Rev. Mater.* 1 (2016) 15003.
- [31] R. Dou, J. Chen, Y. Zhang, X. Wang, D. Cui, Y. Song, L. Jiang, J. Wang, Anti-icing coating with an aqueous lubricating layer, *ACS Appl. Mater. Inter.* 6 (2014) 6998-7003.
- [32] A.D. Penwarden, Acceptable wind speeds in towns, *Build. Sci.* 8 (1973) 259-267.

- [33] L. Zhu, J. Xue, Y. Wang, Q. Chen, J. Ding, Q. Wang, Ice-phobic coatings based on silicon-oil-infused polydimethylsiloxane, *ACS Appl. Mater. Inter.* 5 (2013) 4053-4062.
- [34] P. Kim, T. Wong, J. Alvarenga, M.J. Kreder, W.E. Adorno-Martinez, J. Aizenberg, Liquid-infused nanostructured surfaces with extreme anti-ice and anti-frost performance, *ACS Nano.* 6 (2012) 6569-6577.
- [35] S. Ebnesajjad, C. Ebnesajjad, *Surface Treatment of Materials for Adhesive Bonding*, William Andrew, 2013.
- [36] A. Tuteja, W. Choi, M. Ma, J.M. Mabry, S.A. Mazzella, G.C. Rutledge, G.H. McKinley, R.E. Cohen, Designing superoleophobic surfaces, *Science.* 318 (2007) 1618-1622.
- [37] A. Tuteja, W. Choi, J.M. Mabry, G.H. McKinley, R.E. Cohen, Robust omniphobic surfaces, *Proc. Natl. Acad. Sci.* 105 (2008) 18200-18205.
- [38] A. Steele, B.K. Nayak, A. Davis, M.C. Gupta, E. Loth, Linear abrasion of a titanium superhydrophobic surface prepared by ultrafast laser microtexturing, *J. Micromech. Microeng.* 23 (2013) 115012.
- [39] Y.H. Yeong, A. Davis, A. Steele, E. Loth, I.S. Bayer, Spray deposition effects on superhydrophobicity and durability of nano-coatings, *Surface Innovations.* 2 (2014) 70.
- [40] A. Steele, A. Davis, J. Kim, E. Loth, I.S. Bayer, Wear Independent Similarity, *ACS Appl. Mater. Interfaces.* 7 (2015) 12695-12701.

- [41] S. Kulinich, M. Farzaneh, How wetting hysteresis influences ice adhesion strength on superhydrophobic surfaces, *Langmuir*. 25 (2009) 8854-8856.
- [42] S. Farhadi, M. Farzaneh, S. Kulinich, Anti-icing performance of superhydrophobic surfaces, *Appl. Surf. Sci.* 257 (2011) 6264-6269.
- [43] L. Ge, G. Ding, H. Wang, J. Yao, P. Cheng, Y. Wang, Anti-icing property of superhydrophobic octadecyltrichlorosilane film and its ice adhesion strength, *J. Nanomater.* 2013 (2013) 3.
- [44] G. Momen, R. Jafari, M. Farzaneh, Ice repellency behaviour of superhydrophobic surfaces: Effects of atmospheric icing conditions and surface roughness, *Appl. Surf. Sci.* (2015).
- [45] M. Susoff, K. Siegmann, C. Pfaffenroth, M. Hirayama, Evaluation of icephobic coatings—Screening of different coatings and influence of roughness, *Appl. Surf. Sci.* 282 (2013) 870-879.
- [46] M. Zou, S. Beckford, R. Wei, C. Ellis, G. Hatton, M. Miller, Effects of surface roughness and energy on ice adhesion strength, *Appl. Surf. Sci.* 257 (2011) 3786-3792.
- [47] A. Davis, Y.H. Yeong, A. Steele, I.S. Bayer, E. Loth, Superhydrophobic Nanocomposite Surface Topography and Ice Adhesion, *ACS Appl. Mater. Inter.* 6(12) (2014) 9272.
- [48] Q. Fu, X. Wu, D. Kumar, J.W. Ho, P.D. Kanhere, N. Srikanth, E. Liu, P. Wilson, Z. Chen, Development of sol–gel icephobic coatings: effect of surface roughness and surface energy, *ACS Appl. Mater. Inter.* 6 (2014) 20685-20692.

[49] Y. He, C. Jiang, X. Cao, J. Chen, W. Tian, W. Yuan, Reducing ice adhesion by hierarchical micro-nano-pillars, Appl. Surf. Sci. 305 (2014) 589-595.

Figures

Figure 1 Schematic showing the four steps required to fabricate a FEP micro-textured superhydrophobic thin sheet.

Figure 2 Effect of embossing temperature on FEP surface wettability and averaged feature maximum height of the micro-textures. The embossing weight/pressure and duration were fixed at 2 kg/30 kPa and 5 minutes, respectively.

Figure 3 Visual appearance of (a) an as-received, non-textured FEP thin sheet and the embossed FEP sheet with corresponding SEM surface morphology images and 3-D surface topology scans at different embossing temperatures (b) 290°C (c) 300°C and (d) 310°C. The embossing weight/pressure and duration were fixed at 2 kg/30 kPa and 5 minutes, respectively.

Figure 4 SEM images of a superhydrophobic thin FEP sheet embossed at a temperature of 310°C with 2 kg weight and 5 minute emboss duration at different magnifications (a) 400 X (b) 2000X (c) 5000X (d) 27000X

Figure 5 Ice adhesion strength of the textured superhydrophobic FEP sheet compared to non-textured FEP sheet and non-textured PDMS elastomer film. It should be noted that the ice adhesion strength of aluminum is over 1000 kPa. [26]

Figure 6 Wettability effects (a) contact angle and (b) receding contact angle, on ice detachment force of test substrates. The test substrates are non-textured PDMS elastomer, non-textured Teflon FEP sheet and textured Teflon FEP sheet.

Table 1 Wetting performance of the micro-textured, superhydrophobic and plain (non-textured), as-received Teflon FEP sheet with liquids of different viscosities and surface tension.

	Viscosity (cP)	Surface Tension (mN/m)	Averaged Contact Angle (°)		Averaged Roll Off Angle (°)	
	Plain & Textured FEP	Plain & Textured FEP	Plain FEP	Textured FEP	Plain FEP	Textured FEP
Water	1.3	71.9	112	159	45	2.5
Water+50% Glycerol	6	68.6	101	154	31	11
Ethylene Glycol	16.9	47.7	91	116	19	Pinned
Silicone Oil	100	20.9	32	Spread	Spread	Spread
Fluorinert FC-40	2.2	16	Spread	Spread	Spread	Spread

Table 2 Reported ice adhesion strength values of superhydrophobic coatings by various researchers. Note that the values reported herein include Cassie and Wenzel icing conditions. [26,41-49]

Authors	Year of Publication	Ice Adhesion Strength (kPa)
Kulinich <i>et al.</i>	2009	~65
Farhadi <i>et al.</i>	2011	~55-100
Zou <i>et al.</i>	2011	~230
Ge <i>et al.</i>	2013	~40
Sussoff <i>et al.</i>	2013	~78
Davis <i>et al.</i>	2014	~680
Fu <i>et al.</i>	2014	~75
Yang <i>et al.</i>	2014	~400
Bharathidasan <i>et al.</i>	2014	~270
Momen <i>et al.</i>	2015	~65