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Collection
Study of water repellency and crystal precipitation on multi-scale functionalized filtration membranes

멀티 스케일 기능성 분리막의 초소수성 및 결정 석출에 관한 연구

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Abstract

Study of water repellency and crystal precipitation on multi-scale functionalized filtration membranes

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In this thesis, we consider the water repellency and salt precipitation on multi-scale functionalized filtration membrane. In particular, the fabrication of superhydrophobic filtration membrane with various industrial applications, experimental investigation of salt crystal precipitation that varies on the surface hydrophobicity and water penetration between superhydrophobic cylinders for the optimization of membrane distillation module are composed of this thesis.

We start with the fabrication of superhydrophobic filtration membrane. Using the chemical vapor deposition, nano-textured polymer membrane was fabricated. The static wetting behavior and condensation behavior was investigated. In addition, robustness of superhydrophobicity after condensation and oil wetting was observed.
Subsequently, it is investigated that salt crystal precipitation can be varied with the hydrophobicity of filtration membrane surfaces. On moderately hydrophobic surface and superhydrophobic surface, specific shapes of aggregation of salt crystal are observed due to surface temperature, which were pizza, pot and pebble structure. From the evaporation theory of the sessile drop that is governed by diffusion and scaling, we compare the evaporation of pure water drop and saline water drop. Using mass conservation and water potential in the vicinity of liquid-air interface, we predict the thickness of precipitated salt crystal. The static contact angle, evaporation modes and particle image tracking were used to find the reason of forming of pizza, pot and pebble structure.

Finally, we consider water drop penetration between superhydrophobic cylinders. To enhance the performance of membrane distillation, it is needed to increase the contact area of hollow fiber that is contact with water. However, since the superhydrophobicity of hollow fiber can disturb the penetration of water, we need to fine optimized distance between adjacent fibers. Using dimensionless analysis and scaling, we predict the distance between two superhydrophobic cylinders, at which a water drop starts to penetrate. As an academic interest, we also investigate water drop impact between two superhydrophobic cylinders. The relation of Weber number and drop radius is studied.

Our work provides the fabrication method of superhydrophobic filtration membrane using a plasma, salt precipitation mechanism on hydrophobic surface and theoretical insight for drop penetration.

**Keywords:** Superhydrophobic, Surface tension, Precipitation, Penetration
Filtration membrane

Student Number: 2007-20808
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Chapter 1

Introduction

There have been numerous studies on super-water-repellent (super-hydrophobic) surfaces to date. Although a majority of the research efforts have been directed to the creation of roughness either in microscales\textsuperscript{1-8} or nanoscales\textsuperscript{5-17} to impose superhydrophobicity on flat substrates since the work of Onda et al.,\textsuperscript{18} the early water repellency technology of the mid-20th century mainly concerned the modification of textiles rather than flat surfaces.\textsuperscript{19-21} Textiles either woven or non-woven are still widely used not only as clothes but also as industrial materials including filters, oil absorption fabrics, hygiene items, and geotextiles.\textsuperscript{22} It has been known that simply lowering the surface energy of polymeric fibers, such as PET (polyethyleneterephthalate), cellulose, polyester and nylon, renders the textiles superhydrophobic.\textsuperscript{23-28} As the roughness of the textiles, determined by the diameter of the fibers, is usually of the order of tens or hundreds of micrometers, some efforts have been made to develop smaller scale structures on the fabric surface to further increase hydrophobicity.\textsuperscript{19-21} It was also reported that nanostructured fab-
ric networks exhibit oleophilicity, suggesting an interesting possibility to use the material for oil recovery and oil-water separation.\textsuperscript{29,30} Therefore, the superhydrophobic filtration membrane has various industrial applications such as membrane distillation, fuel cell addition to above mentioned applications. Here, the fast and cheap fabrication method of superhydrophobic filtration membrane will be introduced. As a fundamental study of the interaction of water on the superhydrophobic filtration membrane, we considered the evaporation of sessile water drop since the precipitation resulting from the evaporation of sessile water drop affects the main factor that decrease the performance of the filtration membranes.

The study of free evaporation of droplet has attracted much interest of many scientists and engineers.\textsuperscript{56-71} Including heat transfer applications, the evaporation of sessile droplets on the substrates are associated with drying problems such as ink-jet printing, spraying of pesticides, spotting of DNA microarray, in addition, common every day phenomena, such as the irksome coffee stains left on surfaces.\textsuperscript{61, 67-69, 71,72} The physics of aerosol droplets in ambient, quiescent atmosphere have been relatively well organized due to the spherical symmetry of the aerosol droplet. Otherwise, the involvement of substrates such as hydrophilic
surfaces obviously complicates the evaporation problem. The theoretical models of the evaporation of small sessile droplet on various surfaces have been achieved, such as “D^2” (R^2 ∝ t_f − t) law, LENS model, NE-OS model and so on. In particular, the evaporation of sessile droplet on hydrophilic surface was widely investigated due to numerous industrial applications mentioned above. Moreover, it was revealed that the coffee stain phenomena can be induced by Marangoni flow inside the droplet during evaporation process. However, previous researches for the evaporation of droplet have been focusing on the process of evaporation of DI water, in which the evaporation rate, flux and lifetime of the droplet were main issues. On the other hand, the study of saline drop evaporation has been rarely carried out. In the realm of climatology and meteorology, the study of evaporation of saline droplet has been conducted, but that was limited to the aerosol droplet. The precipitation behavior of dissolving solute might influence various industrial application such as membrane distillation, marine industry and so on. To understand the precipitation of salt crystal on the surfaces with different structures and surface chemistry, we simplified experiment. Therefore, the single saline droplet was used in this experiment. Since the precipitation behavior on hydrophilic surface that is a representative
phenomenon as coffee stain has been widely studied, we carried out the experiment, in which different shapes of the aggregation of salt crystals were investigated on a moderately hydrophobic surface and superhydrophobic surface. Though those surfaces have similar contact angle, significant differences of receding contact angle would lead totally distinguished precipitation behavior, for which evaporation mode difference, precipitation beginning time and contact angle changes along with evaporation time will be taken into account. To demonstrate that the regions where salt precipitation begins are different on moderately hydrophobic and superhydrophobic surface, PIV (Particle image velocimetry) was employed.

In membrane distillation (MD) system, to maximize membrane distillation flux, it is needed that the surface area that is contact with water should be increased. Thus, MD system that uses hollow fiber as membrane is substituting the flat polymer membrane. For integration of hollow fibers, the membrane distillation module can be used. A single hollow fiber is not sufficient for supplying abundant distilled water. Thus, it is needed that a dozens of hollow fibers should be integrated into a membrane distillation module. In addition, from the previous research, it is well known that superhydrophobicity of the distillation membrane can
increase the water flux between permeate and feed water since the superhydrophobicity of the membrane increase the TMP (trans-membrane pressure), defined as $P_{tm} = \left(\frac{P_i + P_o}{2}\right) - P_p$, where the trans-membrane pressure $P_{tm}$, the inlet pressure $P_i$, the outlet pressure $P_o$, the premeate pressure $P_p$. Increasing the number of hollow fibers in a membrane distillation module guarantee increase of contact area where the surface of hollow fiber is contact with water. In contrast, a distance between adjacent hollow fibers should be decreased. This leads water not to penetrate between hollow fibers. As a result, water flux must be decreased. To overcome this trade-off, we consider the optimization of the distance of adjacent superhydrophobic fibers. To simplify the experiment, we use a single water drop. According to the volume, radius of water drop and the diameter of fibers, penetration distance should be varied. Using dimensionless analysis and scaling, we predict penetration distance.
Chapter 2

Extreme water repellency of nanostructured low-surface-energy non-woven fabrics

2.1 Introduction

Superhydrophobicity has been commonly characterized by the high contact angle of a surface with a (usually millimeter-sized) water drop approaching 180° and the low substrate tilt angle for the onset of drop rolling. However, additional measures of the quality of superhydrophobicity have recently attracted attention. Lafuma and Quéré pointed out that a robust superhydrophobic surface should be able to sustain a high contact angle against increased interior pressure of the drop (that may be caused by squeezing the drop between plates or by reducing the drop size). The work by Cheng et al. called attention to the importance of superhydrophobic robustness against vapor condensation by showing that the lotus leaf, a natural superhydrophobic surface, loses its hydrophobicity after water vapor condenses on its surface.

In this work, we develop an extreme water repellent surface with a
surface-treatment method to induce nanoscale roughness on non-woven fabric (NWF) of PET and to lower its surface energy using the plasma enhanced chemical vapor deposition (PECVD) technique. (see the schematic in FIG. 2. 1(a)) This technique is advantageous because it can quickly generate superhydrophobic structure on a large surface area without an aid of photolithography and the aspect ratio (AR) of nanostructures can be controlled only by changing the plasma treatment duration. Upon showing the superior water repellency (from the conventional perspective) of thus-prepared NWF by measuring the contact angle and the contact angle hysteresis (CAH) of the surface with a millimeter-sized water drop, we further investigate the robustness of superhydrophobicity of the surface. By observing the condensation of water drops of submicrometers in radius, we assess the hydrophobicity under increased interior pressure of the drop and the ability to prevent water flooding inside the fabric network. We then measure the contact angle of a millimeter-sized water drop on NWF that has gone through vapor condensation to evaluate the ability to sustain water repellency after condensation. Furthermore, we investigate the effects of the AR of nanohairs on NWF upon the ability to sustain water repellency after deposition of low-surface-energy liquids such as hexane, decane,
octane and silicone oil.

FIG. 2. (a) A schematic of nano-texturing and hydrophobic coating on the NWF using PECVD. (b) SEM images of surface morphology of a nanotextured NWF etched by oxygen plasma for 60 min.
2.2 Experimental

2.2.1 Preparation of superhydrophobic NWF surface

We started with a commercially available NWF (LG Chemical) of PET. As shown in FIG. 2. 1(a), we formed nano-hairy structures on each fabric fiber surface by oxygen plasma etching and then coated the surface with a low-energy material using a radio frequency-plasma enhanced chemical vapor deposition (rf-PECVD) technique. In the oxygen plasma etching, the duration was varied from 1 min to 60 min at a bias voltage of -400 V, and the operating pressure and flow rate were kept at 10 mTorr and 20 cm$^3$ min$^{-1}$, respectively. The resulting hydrophilic surface with nanoscale roughness was hydrophobized with a coating of HMDSO (Hexamethyldisiloxane, Sigma Aldrich) having the surface energy of 24.4 mJ m$^{-2}$. The HMDSO precursor gas was decomposed and its hydrophobic functional group was coated at the bias voltage of -400 V, the pressure of 4 mTorr, and the flow rate of 20 cm$^3$ min$^{-1}$ for 30 seconds, resulting in a SiO$_x$-C:H film with 20 nm in thickness as measured by an atomic force microscope (AFM, Park Systems, XE-100). In addition to NWF, the identical surface treatment was carried out on flat PET
surfaces to compare their water repellent characteristics.

2.2.2 SEM image analysis and contact angle measurement

The nanostructures formed on NWF were imaged with a SEM (Scanning electron microscope, FEI, Nova NanoSEM 200). Prior to observation, 10 nm-thick Pt film was coated on the samples. An electron accelerating voltage was 10 kV. Both the top and tilted views of the surfaces were imaged to measure the AR (a ratio of the height to the diameter) of nanohairs on the surface. The contact angle of water on the surfaces was measured using sessile DI (deionized) water droplets of 5 µL in volume with a goniometer (Kruss, DSA 100). In addition to the static contact angle, the critical advancing (receding) contact angle was measured by increasing (decreasing) the drop volume with an aid of a syringe needle immersed in the drop until the contact line starts to move. The difference between the critical advancing and receding contact angles corresponds to the CAH.

2.2.3 Water condensation experiment in ESEM
Heterogeneous nucleation and subsequent condensation process of water droplets on solid surfaces were observed with an ESEM (Environmental scanning electron microscope, FEI XL-30 FEG). As the substrates, we used a superhydrophilic NWF (etched by oxygen plasma for 30 min) and a superhydrophobic NWF (etched by oxygen plasma for 60 min and coated with SiO$_x$-C:H for 30 sec). The substrate temperature was maintained at 275 K by a cold stage module. The initial chamber pressure was below the saturation pressure of water at 275 K (5.2 Torr) and was gradually increased to induce the droplet nucleation on the surfaces. The surface images were taken every 10 sec.

2.2.4 Post-condensation wetting behavior

We measured the contact angle of water droplets on a surface on which vapor condensation had taken place. To this end, we first placed vertically three different kinds of surfaces (pristine NWF, superhydrophobic flat PET, and superhydrophobic NWF) in an acrylic chamber where the surface temperature and the relative humidity of the surrounding air were kept at 2 ºC and 100%, respectively. The surface temperature increased to approximately 10 ºC during experiment. To induce su-
perhydrophobicity, the surfaces were etched with oxygen plasma for 60 min and coated with SiO$_x$-C:H for 30 sec. After going through vapor condensation for 10 min, the surfaces were horizontally placed in an atmospheric environment (temperature 20 °C and humidity ~50%). The water droplets of 5 µl in volume were deposited on the surfaces to measure the contact angles.

2.2.5 Wetting behavior after low-surface-energy liquid deposition

We first wet NWFs (pristine and superhydrophobic) with liquids of low surface energy, such as hexane, decane, octane and silicone oil, whose properties are listed in Table 1. The liquids were dyed with 1 vol% of blue-colored ink to distinguish them from transparent water droplets. When NWFs were pre-wet by volatile hydrocarbons (hexane, decane and octane), the contact angle of water on NWFs was measured within 5 sec after pre-wetting. When silicone oil was used for pre-wetting which took a considerable time to spread out due to its high viscosity, the contact angle of water was measured twice at 1 and 24 hours after pre-wetting. We also measured the contact angle of a water drop of 5 µL in volume on liquid films of the low-surface-energy hexane and silicone oil.
independently.

Table 1. Surface energy and viscosity of the low-surface-energy liquids

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Surface energy (mN m(^{-1}))</th>
<th>Viscosity (cST) at 20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>18.4</td>
<td>0.51</td>
</tr>
<tr>
<td>Octane</td>
<td>21.6</td>
<td>0.805</td>
</tr>
<tr>
<td>Decane</td>
<td>23.8</td>
<td>1.26</td>
</tr>
<tr>
<td>Silicone oil</td>
<td>21.2</td>
<td>1000</td>
</tr>
</tbody>
</table>

2.3 Results and Discussion

2.3.1 Preparation of superhydrophobic NWF surface

As shown in FIG. 2. 1(b), nanohairy structures are formed on the plasma-irradiated regions of randomly distributed NWF. We plot the average AR of at least 20 nanohairs versus the plasma treatment duration in FIG. 2. 2(a). For short durations from 1 to 5 min, AR is close to unity. As the plasma treatment duration exceeds 10 min, AR increases
dramatically from approximately 4 (10 min) to 50 (60 min). The NWF consists of threads of PET whose molecular formula is \((\text{C}_{10}\text{H}_{8}\text{O}_{4})_n\). The oxygen plasma cuts the link of carbon, hydrogen and oxygen quite efficiently thus has a high etching rate. Polymer chains containing oxygen is known to form a nanofibrillar structure by oxygen plasma through dewetting phenomena.\(^{44}\) For longer duration of oxygen plasma treatment, higher AR for nanofibrils or nanohairs can be achieved on the surface of the NWFs. It is noted that the chemical structure of PET in the modified NWF tends to change, so that C-O bonds (methylene carbon atoms singly bonded to oxygen), and O=C-O bonds (easter carbon atoms) are remarkably increased by oxygen plasma treatment due to the incorporation of oxygen into the PET surface.\(^{42}\)
FIG. 2. Measurement results of (a) aspect ratio of nanohairs, (b) contact angle of a water drop and (c) contact angle hysteresis of a water drop on the superhydrophobic NWF and the superhydrophobic flat PET substrate versus oxygen plasma treatment duration. The SiO$_x$-C:H coating duration is uniformly 30 sec. Insets of (c) show a measurement scheme of the advancing and the receding contact angle.
2.3.2 Contact angle of a sessile water drop on dry surfaces

FIG. 2. 2(b-c) shows the measurement results of the static contact angle and CAH of sessile water drops on various dry surfaces. The flat surface of PET has a static contact angle of 73°±3°, revealing its slightly hydrophilic nature. The NWF, an entangled structure of PET threads with tens of micrometers in diameter, has an increased contact angle of 100°±5° owing to the microscale roughness. Upon the oxygen plasma etching, the NWF surface becomes superhydrophilic regardless of plasma irradiation duration because it corresponds to the high-surface-energy chemical modification. As the hydrophobic SiO$_x$-C:H film was deposited to reduce the surface energy, the static contact angles on a flat PET surface and an NWF surface not treated by oxygen plasma were measured to be 93°±5° (31°±5°) and 151°±3° (19°±5°), respectively. The high contact angle and a low CAH of the SiO$_x$-C:H film coated NWF (without etching) indicates that merely hydrophobizing microthreads can impose strong water repellency on NWF to an extent.

However, it is seen that the oxygen plasma treatment longer than 10 min, which creates nanohairs of a high AR on the surfaces, further increases the static contact angle and greatly reduces CAH for both flat
PET and NWF. The static contact angle reaches 163°±2° and 160°±2° for flat PET and NWF with 60 min of the oxygen plasma treatment and Si-Ox-C:H coating. The minimum CAH attainable by the oxygen plasma treatment and SiOx-C:H coating is 1° for NWF (30 min plasma treatment) and 2° for flat PET (60 min plasma treatment). These results show that oxygen plasma treatment and SiOx-C:H coating can create super-water-repellent nanohairy structure both on flat PET and NWF surfaces.

2.3.3 Water vapor condensation on NWF

Here we compare the condensation behavior of water on a superhydrophilic NWF (etched by oxygen plasma for 30 min) and a superhydrophobic NWF (etched by oxygen plasma for 60 min and coated with SiOx-C:H for 30 sec) using the images taken by an ESEM. As shown in FIG. 2.3(a), film-wise condensation around the fibers occurs on the superhydrophilic NWF under a super-saturation condition. The growing water film fills the interstitial spaces and eventually leads to flooding. On the other hand, as shown in FIG. 2.3(b), dropwise-condensation occurs on the fibers of the superhydrophobic NWF. Upon nucleation, the water droplets grow and coalesce with neighboring droplets. The rate of
nucleation is significantly lower than that on the superhydrophilic NWF, which can be explained by the following Sigsbee’s equation that gives the rate of heterogeneous nucleation as a function of the contact angle and the surface tension:  

\[ J = J_0 \exp\left[-\frac{\pi \gamma r^*}{2 \cos \theta + \cos^3 \theta}(2 - 3 \cos \theta + \cos^3 \theta)/3kT\right] \]  

(1)

where \( J \) is the nucleation rate, \( J_0 \) a kinetic constant, \( \gamma \) the liquid-vapor surface energy per unit area, \( r^* \) the critical radius, \( \theta \) the equilibrium contact angle, \( k \) the Boltzmann constant and \( T \) the absolute temperature. It states that the nucleation rate sharply decreases with the increase of the contact angle. Owing to the low nucleation rate and the dropwise condensation of water on the superhydrophobic NWF, the interstitial space of the fiber network largely remains dry, implying that it can provide a passage for vapor flow even in wet environment. This aspect of strong water repellency can be beneficial in a variety of applications, including the water management of fuel cell membranes\(^{46,47}\) and the fabrication of functional fabrics\(^{19,21,48,49}\).
FIG 2. 3 ESEM images of condensation behavior of water vapor on the (a) superhydrophilic NWF and (b) superhydrophobic NWF. The pressure value in each panel indicates the vapor pressure in the chamber.

FIG. 2. 4 The images of sessile water drops on (a) pristine NWF, (b) flat superhydrophobic PET, and (c) superhydrophobic NWF. The insets of each FIG. show the water drop deposited on dry surfaces.
(d) The contact angle of water drops on the superhydrophobic NWF and flat superhydrophobic PET substrate before and after condensation of water vapor versus the oxygen plasma treatment duration.

The ability of ESEM to observe microscale water drops enables us to measure the robustness of the superhydrophobic surface against a high liquid pressure. The Young-Laplace equation relates the pressure difference ($\Delta p$) across the gas-liquid interface to the surface tension and the interface curvature:

$$\Delta p = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right)$$  \hspace{1cm} (2)

where $R_1$ and $R_2$ are the principal radii of curvature. For a spherical-cap shaped sessile drop, $R_1 = R_2 = R$, thus we get $\Delta p = 2\gamma / R$. The radii of small droplets formed and observed in the ESEM chamber allow us to measure the contact angle of water on a solid surface under a very high Laplace pressure ($\Delta p$). Although it is not easy to accurately measure the contact angle of droplets on fibers through ESEM images, we
find that even the smallest droplet observable in the setup, having the radius of 2.4 µm, maintained the contact angle higher than 90º. This implies that the superhydrophobic NWF fiber with high AR nanohairs can maintain its hydrophobicity at least up to 62 kPa, which is much higher than the threshold pressure (the pressure over which the contact angle abruptly reduces below 90º because of the transition from the Cassie-Baxter state\textsuperscript{50} to the Wenzel state\textsuperscript{51}) of the superhydrophobic surfaces reported by other researchers.\textsuperscript{8, 37, 52, 53}

### 2.3.4 Post-condensation hydrophobicity

FIG. 2. 4 shows the images of sessile water drops of 5 µL in volume placed on the pristine NWF (see FIG. 2. 4(a)), the superhydrophobic flat PET substrate (4(b)), and the superhydrophobic NWF (4(c)), all of which went through condensation of vapor on the surfaces. Both the superhydrophobic flat PET substrate and the superhydrophobic NWF were etched by oxygen plasma for 60 min and coated with SiO\textsubscript{x}-C:H for 30 sec. In dry states, the surfaces had the contact angle as 105º (FIG. 2. 4(a)), 165º (4(b)) and 162º (4(c)) as shown in the insets. It is seen that on
the pristine NWF and the superhydrophobic flat PET, the post-condensation contact angles of water are greatly reduced as compared with those on dry surfaces: the contact angle on the pristine NWF and the superhydrophobic flat PET was reduced to 64° and 137°, respectively. However, the superhydrophobic NWF maintains a high contact angle (156°) even after condensation.

FIG. 2. 4(d) quantitatively shows the change of the contact angle that is measured before and after vapor condensation for NWF and flat PET substrate depending on the oxygen plasma treatment duration. For pristine materials, both the NWF and the flat PET substrate show significant reduction of the contact angle (by approximately 40°) after vapor condensation. This implies that residual water on the surface after condensation facilitates the spreading of a newly added sessile drop. For the flat PET surfaces etched by oxygen plasma and coated with SiO$_x$-C:H, the contact angle in the dry state is very high (165°) but it decreases by about 37° when the oxygen treatment duration is 10 min. The amount of contact angle reduction decreases to about 26° when the oxygen treatment lasts 30 min or longer. On superhydrophobic NWF, the contact angle is reduced by 15°, 9° and 6° after condensation when the oxygen treatment lasts for 10 min, 30 min and 60 min, respectively. These re-
Results indicate the roles of microscale and nanoscale topographic features in suppressing the reduction of the contact angle after condensation: Microscale fibers of NWF play a dominant role in maintaining superhydrophobicity, and nanohairs (commonly existing on both flat PET substrate and NWF that are etched by oxygen plasma) tend to decrease the contact angle reduction as their AR increases.

**FIG. 2.5** Schematic of water repulsion behavior of (a) the superhydrophobic NWF and (b) the flat substrate with high aspect-ratio, hydrophobic nanohairs with small spacings.

FIG. 2.5 schematically illustrates the aforementioned roles of micro- and nano-scale features. In FIG. 2.5(a), water vapor and thus its nucleation sites are distributed over the surfaces of NWF fiber stacks. Hence, it
is less likely that the entire surface is flooded with water due to condensation as also evidenced in the previous section. Moreover, large droplets formed by coalescence of tiny droplets tend to be squeezed out of interstices because they rather stay as spheres (having minimum surface area) on top of NWF than forming large contact area with water-repellent solid surfaces as trapped in interstices. In FIG. 2. 5(b), water droplets nucleated between nanohairs tend to be squeezed out for the same reason as above (to minimize the surface area contacting water-repellent solid surface). The higher the AR of the nanohairs, the more efficient is the separation of water droplets from basal area, which helps to prevent the transition from the Cassie-Baxter state to the Wenzel state.

2.3.5 Hydrophobicity after low-surface-energy liquid deposition

In this section, we investigate how the hydrophobicity of NWF is affected by pre-deposition of low-surface-energy liquids. A major reason that the NWF coated with SiO₅-C:H film has superhydrophobicity is that its surface has a lower surface energy (24.4 mJ m⁻²) than that of water (71.7 mJ m⁻²). However, hydrocarbons such as hexane, decane and octane have lower surface energy than SiO₅-C:H film as listed in Table 1.
Consequently, NWFs with either single (microfiber network only) or dual (nanohairy structure on microfiber network) roughness coated with SiO$_x$-C:H film exhibit superoleophilicity. Drops of all the three kinds of hydrocarbons with 40 µL in volume spread over the superhydrophobic NWF within a few seconds.

We start with hexane-deposited NWFs whose contact angle with water is shown in FIG. 2. 6(a). It is recalled that the measurement of the contact angle of a water drop was performed within 5 sec of the hydrocarbon deposition to reduce the effect of hydrocarbon evaporation. On pristine NWF (no oxygen plasma treatment), the contact angle drops from 151° to 105° due to pre-wetting of hexane. This value is slightly larger than the contact angle of water on hexane film (80°) implying that the hydrocarbon film separates a water droplet from the underlying NWF to an extent. With the increase of oxygen plasma treatment duration corresponding to the increase of the AR for nanohairs on the fibers of NWF, the contact angle of water increases. After deposition of small volumes (10 and 20 µL) of hexane, the contact angle of water is completely recovered to the value of dry NWF when the plasma treatment duration reaches 30 min (for 10 µL) and 60 min (for 20 µL). As the volume of hexane is increased to 40 µL, hydrophobicity of the NWF im-
proves with the increase of the contact angle to about 130°. These results indicate that the superhydrophobic-treated NWF can maintain strong water repellency even after wetting of hexane.

FIG. 2.6 Contact angle of a water drop on superhydrophobic-treated NWF after wetting of (a) hexane, (b) decane and octane, and (c) silicone oil versus oxygen treatment duration. (d) Illustrative comparison of the water drop morphology on pristine NWF and superhydrophobic-treated NWF after low-surface-energy liquid depo-
sition. Water drops in tilted view on (e) the pristine NWF and (f) the superhydrophobic NWF, which are pre-wetted by hexane (dyed in blue).

The above result is attributed to nanohairs on the fibers which facilitate the imbibitions of hexane into fiber network so that only a very thin hydrocarbon film may remain on the fiber surface. See the illustration of FIG. 2. 6(d). Nanohairs taller than the hydrocarbon film thickness are exposed to the atmosphere and thus can support a water droplet, leading to the recovery of strong water repellency. The difference of recovery behavior of hydrophobicity depending on the volume of hexane can be explained along the same line. Since hexane is highly volatile, the smaller the volume is, the thinner the hexane film. Therefore, nanohairs of AR=17 and 49, corresponding to oxygen plasma treatment duration of 30 min and 60 min, respectively, can stick out of the film when hexane volume is 10 µL and 20 µL, respectively. When the nanohair AR is not high enough to be completely exposed to the atmosphere (corresponding to short plasma treatment duration or large hexane volume), the extent of contact angle recovery is limited so that the contact angle reaches about 130º.

It is not clearly known why the partially hexane-wetted nanohairy
structure of NWF exhibits the contact angle of 130° with water although it is reasonably located between the contact angle of the dry superhydrophobic surface and the contact angle of water on hexane film. We see that this value is quite repeatedly obtained when different hydrocarbons, such as octane and decane which are less volatile than hexane, are pre-deposited on the superhydrophobic-treated NWF as shown in FIG. 2. 6(b). Again, pristine NWF exhibits a significant reduction of the contact angle with water after deposition of the hydrocarbons, but superhydrophobic NWFs treated with oxygen plasma and SiO$_x$-C:H coating sustain high contact angle of about 130° despite pre-wetting of the hydrocarbons.

We reproduce the similar tendency with nonvolatile silicone oils whose experimental results are shown in FIG. 2. 6(c). Because of a high viscosity of silicone oil which delays the spreading of oil into a thin film, the contact angle of NWFs with water remains low at about 100° when measured one hour after oil deposition for all the oxygen plasma treatment durations. It is noted that the contact angle of silicone oil film with a water drop is 90°, implying that the thick oil film efficiently blocks the contact of the nanohairy structure with a water droplet. As we allow the silicone oil to spread into a thin film for a day so that nanohairs can contribute to the contact with water, the contact angle of superhydrophobic-
treated NWF with water increases to about 130°, consistent with the foregoing results of the hydrocarbons.

2.4 Conclusions

We have developed a method to induce nanoscale roughness on NWFs of PET using oxygen plasma and lower its surface energy with HMDSO via rf-PECVD technique. Millimeter-sized water drops on the surface were shown to have a contact angle higher than 160° and the CAH less than 10°. In addition to this superhydrophobicity in a conventional measure, it is shown that thus-prepared surface can resist flooding due to high AR nanohairs with vapor condensation experiment in an ESEM chamber. This suggests a way to improve the resistance of functional materials, such as gas diffusion layer (GDL) of fuel cell membranes commonly made of carbon fiber,⁵⁴ to water flooding.

The superhydrophobic NWF is also demonstrated to sustain strong water repellency even after vapor condensation due to high AR nanohairs, which can help water drops to quickly roll off the surfaces. Although the plasma treated NWF is oleophilic, it maintains strong water repellency owing to high AR nanohairs after low-surface-energy liquid
wetting. This implies potential applications of the surface modification technology to the fabrication of effective oil-water separation filters for wastewater cleaning systems, combustion engines and HVAC (heating, ventilation, and air conditioning) apparatus.
Chapter 3

Salt precipitation on moderately hydrophobic and superhydrophobic surface

3.1 Introduction

For decades, the study of free evaporation of droplet has attracted much interest of many scientists and engineers.\textsuperscript{56-67} Including heat transfer applications, the evaporation of sessile droplets on the substrates are associated with drying problems such as ink-jet printing, spraying of pesticides, spotting of DNA microarray, in addition, common every day phenomena, such as the irksome coffee stains left on surfaces.\textsuperscript{61, 67-69, 71, 72} The physics of aerosol droplets in ambient, quiescent atmosphere have been relatively well organized due to the spherical symmetry of the aerosol droplet. Otherwise, the involvement of substrates such as hydrophilic surfaces obviously complicates the evaporation problem. The theoretical models of the evaporation of small sessile droplet on various surfaces have been achieved, such as “D\textsuperscript{2}” (\(R^2 \propto t_f - t\)) law, LENS
model, NEOS model and so on. In particular, the evaporation of sessile droplet on hydrophilic surface was widely investigated due to numerous industrial applications mentioned above. Moreover, it was revealed that the coffee stain phenomena can be induced by Marangoni flow inside the droplet during evaporation process.

However, previous researches for the evaporation of droplet have been focusing on the process of evaporation of DI water, in which the evaporation rate, flux and lifetime of the droplet were main issues. On the other hand, the study of saline drop evaporation has been rarely carried out. In the realm of climatology and meteorology, the study of evaporation of saline droplet has been conducted, but that was limited to the aerosol droplet. The precipitation behavior of dissolving solute might influence various industrial application such as membrane distillation, marine industry and so on. To understand the precipitation of salt crystal on the surfaces with different structures and surface chemistry, we simplified experiment. Therefore, the single saline droplet was used in this experiment. Since the precipitation behavior on hydrophilic surface that is a representative phenomenon as coffee stain has been widely studied, we carried out the experiment, in which different shapes of the aggregation of salt crystals were investigated on a moderately hy-
drophobic surface and superhydrophobic surface. Though those surfaces have similar contact angle, significant differences of receding contact angle would lead totally distinguished precipitation behavior, for which evaporation mode difference, precipitation beginning time and contact angle changes along with evaporation time will be taken into account. To demonstrate that the regions where salt precipitation begins are different on moderately hydrophobic and superhydrophobic surface, PIV (Particle image velocimetry) was employed.

### 3.2 Materials and methods

In this experiment, we used the commercial PP (polypropylene) membrane as a moderately hydrophobic (MH) and PET (polyethylene terephthalate) film as a superhydrophobic (SH) surface that was modified by plasma treatment using CVD (chemical vapor deposition). In order to make superhydrophobic surface on PET film, oxygen plasma was introduced to texture the high-aspect-ratio nano/micro hairy structures, on which the precursor of HMDSO (Hexamethyldisiloxane) that has low surface energy was coated. To observe magnified surface structure, scanning electron microscope (SEM, FEI Nova NanoSEM 200)
was used. Besides the images of bare surfaces of MH and SH substrate was taken by SEM, the surface which was contaminated by the salt crystals after completion of evaporation was taken as well.

FIG. 3.1 The SEM image of (a) MH and (b) SH surface. Left column of images show the surface structure prior to evaporation experiment and right column of images exhibit the surface structure after evaporation finished. The CAs of MH and SH surface (c) at 20 °C and (d) 80 °C.
Measuring the contact angle (CA) of the substrates, a sessile droplet with the volume of 5 µL was placed on the flat surfaces and image of the sessile droplet was taken by the high-speed camera with the lens of 12-fold magnifications with the snap shot mode (Photron, Fastcam SA1.1). From the image, the angle between a tangential line along the liquid-vapor interface and the solid-vapor interface at the three phase contact line was measured. Additionally, the contact angle hysteresis (CAH) was measured, for which the volume of droplets increased to 200 µL and decreased to 5 µL. The advancing contact angle and receding contact angle was measured from the image. We used DI water and saline water with different concentrations in this experiment. The concentrations of saline water varied from 5 % to 20 % with the step of 5%. The mass of droplet with the volume of 5 µL was measured using the electronic scale (Mettler Toledo, XS205DUV). The electronic scale has the resolution with $10^{-5}$ g. The mass of droplet was measured minutely until evaporation finished.

To identify the influence of the surface temperature which is the dominant factor for the evaporation rate, the surface temperature was controlled from the room temperature to 80 °C, on which DI and saline water droplets were place, using a hot plate. Along with the surface
temperature, the humidity is crucial to the evaporation. A dehumidifier was employed to adjust the humidity. Simultaneously, the humidity was measured by a hygrometer.

In this experiment, we are dealing with the evaporation of saline water droplet as well as DI water droplet. On this account, the time that the precipitation begins, including the evaporation completion time, was measured. Actually, the precipitation beginning time might be ambiguous indeed. Thus, it was decided that the time when a first salt crystal was formed should be the precipitation beginning time using a high-speed camera. A droplet with the volume of 5 µL was placed on the surfaces. The evaporation process was taken by high-speed camera until evaporation finished. Meanwhile, the surface temperature that was indicated on display of a hot plate might not exactly match with actual temperature of the surface during evaporation process. Thus, the thermocouple was used for measuring an actual temperature of the surface.

The differences of the precipitation of dissolving solute (salt in this study) were investigated using the PIV method. The fluorescent particles (Duke scientific corp., red fluorescent polymer microsphere) with the diameter of 8 µm were dissolved in the saline water. To visualize the flow pattern in the cross section of the droplet, the laser with the power
of 2 W was generated and then passed through the thin slit. The laser sheet was on the order of 200 µm.

3.3 Results and discussions

3.3.1 The aggregation of salt crystal during evaporation

![Graph showing dependency of the shape of the aggregation of salt crystal on the surface temperature of MH surface.]

**FIG. 3.2** Dependency of the shape of the aggregation of salt crystal on the surface temperature of MH surface.

We observed that the shape of the aggregation of salt crystals varied on the MH and SH surface according to different surface temperatures.
and concentration of salt (FIG. 3. 2). Due to the different surface temperature, on MH surface, a pizza structure that the salt crystals were anchored along with the contact line of the saline droplet (low surface temperature and low concentration) and pot structure consisted of a few layer of salt crystals were evolved (high surface temperature and high concentration) along with the liquid-vapor interface of the droplet. Specifically describing the pizza structure, the salt remains on the bottom of the droplet with thin layer and large amount of salt crystals were aligned at the contact line of the droplet similar with a pizza crust. Meanwhile, the aggregation of salt crystals having the pot shaped structure with open ceiling was observed at high temperature (>40 °C) for relatively high concentration (15~20%) through optical image or SEM images (FIG. 3. 4). On the other hand, on SH surface, pebble-like structure of salt crystals was observed regardless of the surface temperature and concentration of salt.
FIG. 3. 3 Mechanism of developing pizza, pot and pebble structure on hydrophobic surface.

FIG. 3. 4 The hypothesis for precipitation of salt on MH and SH surface. Due to surface temperature and surface chemistry, pot structure (upper-right) and pebble-like structure were formed. The CA of the surfaces lead different
The SEM images of FIG. 3.4 show that the pot structure has a few layer consisted of hexahedral salt crystal. A cross section of pot structure cut by a scalpel was revealed, at which it was confirmed that a number of salt crystal with a hexahedral shape were stacked neatly, forming pot shape.

Above-mentioned ‘pizza shaped’ aggregation of salt crystals at low surface temperature and low concentration of salt is similar to the coffee stain in terms of the structure. The coffee stain has been explained that the coffee particles were aggregated at the contact line induced by Marangoni flow. MH surface used in this experiment, PP membrane, has nano/micro porous structures shown from the FIG. 3.1, and the salt crystals can be stacked among nano/micro pores during evaporation. Thus, the surface that had been below the sessile droplet undergoing evaporation was contaminated with thin layer of salt crystals and a large considerable of salt crystal was stacked at the three phase contact line, for which Marangoni flow induced the salt crystals move outward the edge of droplet.

Meanwhile, at high concentration of salt (15~20%), pot shaped structure was formed at high temperature larger than 40 °C. To give an account of these phenomena, we suggest a simple hypothesis illustrated in
First, the precipitation of salt crystal should begin during the CA of the sessile droplet is still large since the salt crystals formed during the evaporation must be constrained inside the liquid-vapor interface. At low concentration (5~10%), the precipitation must be retarded compared to high concentration (15~20%). Thus, pot structure cannot be observed at low concentration but high concentration except extremely fast evaporation.

Second, the fast evaporation should be allowed during exhibiting high CA. The fast evaporation is corresponding to fast evaporation rate, for which the surface temperature should be high.

Third, the empty space at the core of pot structure demonstrates that the precipitation of salt crystal should be constrained at the edge of droplet. That is, the relative concentration difference between the core of droplet and the liquid-vapor interface should exist. This difference leads to local difference of viscosity. Fast evaporation would occur at the edge of droplet, by which the salt precipitation should come first. Consequently, the relative concentration of salt at the edge of droplet should be larger than that at the core of droplet. This allows the ‘neatly aligned’ structure which consists of a number of salt crystals.
As the same manner, to explain the reason why pebble-like structures are evolved, a simple hypothesis will be introduced. The pebble-like structure implies that the aggregation of salt crystals converges at the center of drop-solid contact area of sessile droplet. It is known that strong evaporation occurs near the three phase contact line. On SH surface, from the static CA behavior, it was confirmed that high CA being larger than 160° and short base contact radius were maintained for a long time in the entire lifetime of evaporation. On this account, the wetted perimeter of the sessile droplet on SH surface should be much smaller than that on MH surface. Thus, the precipitation will occur at the center of drop-solid contact area of sessile droplet and the internal flow induced by heating and evaporation will force the salt crystals towards the center of drop-solid contact area of sessile droplet. We verified above-mentioned hypothesis by means of static CA and CAH of the surface, evaporation mode of sessile droplet and PIV method.

3.3.2 Static wetting behavior

The static CAs of the surfaces and those variations along with the evaporation time were measured. In the FIG. 3. 1(a-b), the surface struc-
ture of MH surface used in this experiment shows a number of micro pores and the nano/micro hairy structures with high aspect ratio were fabricated on SH surface. Fabricating these nano/micro structures resembling the hairy structures of water strider leg, superhydrophobicity can be obtained. In FIG. 3. 6(e-g), for MF surface, the CA of the droplet of DI water at room temperature (20 °C) was about 150°, which was similar with the CA of the droplet of 5% and 20% saline. Similarly, the CA of DI water and saline droplet showed analogous trends at 80 °C of surface temperature. In FIG. 3. 6(h-j), the CA of DI water on SH surface was 163° that was same as the CA of 5% and 20% of saline droplet. Even the surface temperature was varied from 20 °C to 80 °C, the CA of DI water and saline droplet on MH and SH surface showed similar values. Thus, it was confirmed that a static wetting behavior of MH and SH surface was independent from the concentration of salt in the range between the room temperature and 80 °C at least. In addition, CAH was measured, which means the difference between advancing and receding contact angle. Especially a receding contact angle of the surface is of greatest significance since the receding contact angle could affect evaporation mode. The CAH (receding contact angle) of MH surface was 110°±15° (less than 30°) while the CAH (receding contact angle) of SH
surface was $5^\circ \pm 2^\circ$ (164$^\circ$). From the static wetting experiment, it was confirmed that MH surface used in this experiment has high CA and low receding CA, which implies contact line pinning can be taken place even though the evaporation is in the very beginning.

FIG. 3.5 (a) The base contact radius remains constant in the CCR mode at 47 $^\circ$C on MH surface (5% saline drop) (b) The mixed mode (constant contact mode and constant area mode) at 52 $^\circ$C on MH surface (5% saline drop) (c) The CCA mode during evaporation on SH surface. (20% saline drop)
3.3.3 Evaporation mode and precipitation of salt crystal

In general, for the entire lifetime of evaporating droplets, constant contact angle (CCA) mode, constant contact radius (CCR) mode and mixed mode (CCA + CCR) can be observed (FIG. 3. 5). Three distinct evaporation modes were observed in the experiment of the evaporation of saline water droplet. For water droplets, it is well known that the CCA mode is observed mainly on SH surface, whereas the CCR mode on hydrophilic surface. A mixed mode, where CA and base contact radius changes simultaneously, can take place towards the end of evaporation. On MH surface used in this experiment, CCR mode and mixed mode were observed. Therefore, we presumed that high CAH induced contact line pinning, subsequent strong evaporation in the vicinity of contact line of saline droplet with high concentration affected the forming of pot structure on MH surface. In case of low concentration, the precipitation must be retarded compared to high concentration and will begin when the CA decrease to receding contact angle with 30° of the surface. Furthermore, the total mass of precipitated salt cannot be sufficient for developing wall of pot structure. On the other hand, SH surface has high receding contact angle with 164° and low CAH with 5°, which
maintains the spherical shape of saline water droplet until the evaporation will be almost finished. Actually, it was confirmed that CCA mode was maintained for entire evaporation process on SH surface regardless of the concentration of salt. From previous research of the evaporation, the precipitation time of saline water droplet can be predicted from the scaling of evaporation time, which is expressed as, \( t \sim m_0^{2/3} - m_L(t)^{2/3} \), where \( m_0 \) is the initial mass of droplet, \( m_L(t) \) is the mass of solvent (water) at time \( t \).\(^{16}\) According to the scaling, we measured the change of mass of drop. FIG. 3. 6(a-b) shows the change of mass of the droplet with respect to the evaporation time at 20 °C. Both on MH and SH surface, the change of mass varies linearly with evaporation time. However, the more the concentration of saline water droplet increase, the more the change of mass is not satisfied with the prediction. Therefore, we didn’t predict the precipitation time using previous theory. The precipitation must occur when the concentration of salt at time \( t \) becomes larger than the concentration corresponding to solubility of salt at certain temperature. This is written as,

\[
m_L(t) \geq \frac{1 - c_s}{c_s} m_s
\]  

(3)
where $c_s$ is the concentration corresponding to solubility, $m_s$, the mass of salt.

The solubility of salt is the function of temperature, but it almost has uniform values in the range of 36~38 (g/100 g) regardless of temperature (20~80 °C). Thus, we measured the mass of saline drop with respect to time ratio, which means time divided by total evaporation time. Since the total evaporation time must be changed with the surface temperature and humidity, we substituted real evaporation time with time ratio to compare the evaporation behavior independent on humidity and surface temperature.

From equation (1), the concentration of saline drop occurring precipitation was 27%, which enabled us to predict precise precipitation time ratio (dashed line in FIG. 3. 6(c-d)).

The results of the variation of CA and the radius of the solid-liquid interface of the droplet, so-called base contact radius, until evaporation finished are shown in FIG. 3. 6(e-j). From the FIG. 3. 6(e-g), on MH surface, CCR modes were dominant at the beginning of evaporation process for DI water, 5% and 20% saline water drop. The change of CA and base contact line for DI water shows general behavior where CCR mode occurs at the beginning of evaporation and CCA mode follows
next to CCR mode. For 5% saline drop, the precipitation was occurred at about 0.7 of time ratio. The CA of saline drop was about 90°, but the CA continued to decrease. This means the precipitation of salt crystals occurred at contact line and this was not sufficient for constraining liquid-vapor interface. Especially, for 20% saline water drop, the result shows that the base contact line maintained constant with 0.7 mm during whole evaporation process since the precipitation of salt crystal occurred at early time with 0.15 of time ratio, by which receding contact line was constrained. Simultaneously, since the CA was 140° when precipitation began, thus the pot structure could be evolved. On SH surface, for DI water, the CA shows about 160° until 0.7 of time ratio, subsequently the CA decreases gently to 140° at 0.9 of time ratio. For saline water droplets with 5% (20%) concentration, the precipitation began after 0.6 (0.1) of time ratio. Even though precipitation occurred, it was confirmed that the CA was maintained.
FIG. 3. (a-b) The graph of mass vs. time on MH surface and SH surface, respectively: \( t \approx m_0^{2/3} - m_2^{2/3} \). (c-d) The concentration of saline drop along with the time ratio. The CA and base contact radius of (e-g) DI water, 5% and 20% saline water on MH surface, respectively. (h-j) shows the CA and base contact radius of DI water, 5% and 20% saline water on SH surface at 60 °C.
FIG. 3. 7 The sequential images of forming of the pizza (22 °C), the pot (80 °C) and the pebble-like structure (60 °C), respectively.

FIG. 3. 8 Schematic of the mechanism forming the pizza structure.
FIG. 3. 9 Schematic of the mechanism forming the pot structure.

FIG. 3. 10 Schematic of the mechanism forming the pebble structure.

FIG. 3. 11 Mass transfer of sessile drop evaporation
For the pizza structure to be formed, the wedge shape assumption was used. If we assumed that the final shape of salt aggregation of pizza structure is similar with the wedge shape, the thickness of salt layer can be expressed as follow.

\[
\delta = \sqrt{\frac{cm_l}{\pi R \tan \theta_c \rho_s (1-c)}}
\]  

where \( \delta \), the thickness of salt layer, \( R \), the base radius of sessile drop, \( \theta_c \), the contact angle when the precipitation occurs, \( \rho_s \), the density of salt, \( m_l \), the mass of sessile drop. The thickness of salt layer of the pizza structure using equation (4) was listed in Table 2.

For the pot structure to be formed, only a few layers of salt crystals should be remained along the liquid-vapor interface. Using the water potential theory that was illustrated in FIG. 3. 11 and the mass conservation, the thickness of salt layer was calculated.

\[
\psi \sim \psi_\pi = -RTc
\]

where \( \psi \), the total water potential, \( \psi_\pi \), the concentration potential, \( R \),
the ideal gas constant, $T$, the temperature, $c$, the concentration.

Table. 2 The comparison of the thickness of salt layer of the pizza structure.

<table>
<thead>
<tr>
<th>Concentration (%)</th>
<th>Thickness in the experiment (mm)</th>
<th>Thickness from prediction (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>260</td>
<td>190</td>
</tr>
<tr>
<td>10</td>
<td>300</td>
<td>280</td>
</tr>
<tr>
<td>15</td>
<td>300</td>
<td>350</td>
</tr>
</tbody>
</table>

If we assumed that the water flux due to potential difference is same with the evaporation flux, equation (5) can be scaled as $\delta(t) \sim A \Delta \psi / J(t)$, where $\delta(t)$, the thickness of salt layer, $A$, the area of salt layer, $J(t)$, the evaporation flux. The average of $J(t)$ which was measured was almost constant with the value of $9.2 \times 10^{-7}$ (g/s) and the standard deviation of $J(t)$ was $5.1 \times 10^{-7}$ (g/s). Therefore, the thickness of salt layer will not be changed. This means that we can calculate the thickness of salt layer using the mass conservation. From the mass conservation,
\[ \delta^3 - 3R_s \delta^2 + 3R_s \delta - \frac{3\sin^3 \theta}{\pi \rho_s (1-c)(1-\cos \theta)^2 (2+\cos \theta)} m_i = 0 \quad (6) \]

where \( R_s \), the radius of sessile drop. The thickness of salt layer that was measured by SEM was almost 100 µm. Compared with the estimation using equation (6) with the value of 160 µm, this model matched with the experimental result.

From the hypothesis, we assumed different viscosity between near the contact line and the center of contact area of the saline drop due to fast evaporation. It is practically difficult to confirm the viscosity difference in small saline drop experimentally, thus we suggested PIV method as an alternative. As shown in FIG. 3.12, it was confirmed that the precipitation of salt crystal converged in the vicinity of the three phase contact line (center of contact area of the droplet) on MH surface (SH surface) for the sessile droplets with 20% concentration of salt. Subsequently, we magnified the three phase contact line of the saline sessile droplet on MH surface. From FIG. 3.12, it is shown that a number of salt crystals are suspended along the liquid-vapor interface. The behavior of salt crystal appears to be solid, on which the salt crystals move very slowly. However, it must be not solid, but quite slow and viscous.
FIG. 3. 12 The PIV image of sessile droplets on MH and SH surface. (upper, from left to right) multiple exposure of inner flow inside the sessile droplet, the magnified image of salt precipitation of sessile droplet which was placed on SH surface in the vicinity of contact line. The salt precipitation occurred at the center of sessile droplet (0 sec, relative time). After 100 sec, a number of salt crystals were gathered towards the center of droplet. (lower) Multiple exposures were stacked to indicate the motion of the PIV particles inside sessile saline droplet (20% concentration) on MH surface. At zero sec (relative time), salt crystals appeared to be suppressed along the liquid-vapor interface showing viscous behavior. The scale bar is 1 mm.

Simultaneously, obvious movement of PIV particles was captured out of the confocal range. This implied that internal flow exists inside the sessile droplet even after precipitation began. Therefore, it was confirmed that the viscosity difference along circumferential direction was taken place due to fast time ratio. On the other hand, on SH surface,
magnified image shows that fast movement of PIV particles was visualized at the liquid-vapor interface. It was confirmed that the aggregation of salt crystals occur at the center of the sessile droplet and receding dynamic contact line moves towards the center of the sessile droplet due to water repellency as evaporation proceed, subsequently salt crystals confined by liquid-vapor interface were gathered together. The pebble-like structure can be formed through this process.

3.4 Conclusions

We have experimentally investigated that the shape of aggregation of salt crystal are divided into three distinct shapes due to time ratio as well as surface chemistry. The MH and SH surface were used in this study, on which a pizza structure, pot structure and pebble-like structure were formed at varying surface temperatures. For various concentration of salt from 5 to 20% and various surface temperatures from room temperature (20 °C) to 80 °C, on SH surface, the shape of aggregation of salt crystals was shown pebble-like structure. A high receding CA larger than 160° and low CAH smaller than 5° led to allow the precipitation of salt crystal to the center of saline droplet. Additionally, the recirculation
towards the center of contact base area of droplet and floating salt crystal due to superhydrophobicity were responsible for the formation of pebble-like structure. On MH surface, strong evaporation at the contact line of droplet formed high viscous region along the liquid-vapor interface near the contact line comparing to the center of droplet. At low surface temperature, late precipitation led to small CA of the saline water drop due to evaporation. Subsequently, most of salt crystal was anchored at contact line and the amount of salt was not sufficient to be suspended along the liquid-vapor interface. Thus, a pizza structure was formed. On the other hand, at high temperature, the precipitation occurred while the CA showed still large (≥90°). In addition, salt crystals were suspended along with the liquid-vapor interface of the droplet since the viscosity near the contact line was larger than that of the center of contact area of the drop due to fast evaporation.
Chapter 4

Drop penetration between superhydrophobic cylinders

4.1 Introduction

In membrane distillation (MD) system, to maximize membrane distillation flux, it is needed that the surface area that is contact with water should be increased. Thus, MD system that uses hollow fiber as membrane is substituting the flat polymer membrane. For integration of hollow fibers, the membrane distillation module can be used. A single hollow fiber is not sufficient for supplying abundant distilled water. Thus, it is needed that a dozens of hollow fibers should be integrated into a membrane distillation module. In addition, from the previous research, it is well known that superhydrophobicity of the distillation membrane can increase the water flux between permeate and feed water since the superhydrophobicity of the membrane increase the TMP (trans-membrane pressure), defined as \( P_{\text{tm}} = \left( \frac{P_i + P_o}{2} \right) - P_p \), where the trans-membrane pressure \( P_{\text{tm}} \), the inlet pressure \( P_i \), the outlet pressure \( P_o \), the premeate
Increasing the number of hollow fibers in a membrane distillation module guarantees an increase of contact area where the surface of hollow fiber is in contact with water. In contrast, a distance between adjacent hollow fibers should be decreased. This leads water not to penetrate between hollow fibers. As a result, water flux must be decreased. To overcome this trade-off, we consider the optimization of the distance of adjacent superhydrophobic fibers. To simplify the experiment, we use a single water drop. According to the volume, radius of water drop and the diameter of fibers, penetration distance should be varied. Using dimensionless analysis and scaling, we predict penetration distance.

FIG. 4.1 Membrane distillation module.
4.2 Experimental

4.2.1 Drop penetration between superhydrophobic cylinders.

We conducted the experiment, in which at first, water drop placed on two superhydrophobic cylinders that were contact closely. Subsequently, the distance between two superhydrophobic cylinders was increased. The distance between cylinders was controlled by micrometer. When the water drop started to penetrate, the distance was measured. The water drop images were recorded by high-speed camera. The contact angle of superhydrophobic cylinder is 160°. The diameter of superhydrophobic cylinder is 2 mm.

4.2.2 Drop impact between superhydrophobic cylinders.

Drop impact experiment was conducted. Controlling the height of water drop, $We \ (\sim \rho RU^2/\gamma)$ can be controlled. The diameter of water drop was less than capillary length, $l_c = \sqrt{\gamma/\rho_w g}$, where $\gamma$ is the surface tension of water, $\rho_w$ is the density of water, $g$ is the gravitation-
al acceleration. Therefore, the gravity can be neglected.

When the water drop of radius $R$ and density $\rho_w$ impacts between two superhydrophobic cylinders, three different regime which are the perfect penetration, break up of water drop and bouncing (stationary) of drop are observed. From the high-speed sequential images, we can measure the impact velocity of water drop.

4.3 Results and discussions

4.3.1 Drop penetration between superhydrophobic cylinders.

FIG. 4.2 and 4.3 show the penetration of water drop between two hydrophobic cylinders with the contact angle of 100° and 160°, respectively. If the distance between two cylinders, the water cannot penetrate, but flood. Thus, from the force balance in FIG. 4.4, balancing the Laplace pressure, defined as $\Delta p = \gamma \left(1/R_1 - 1/R_2\right)$, with the hydrostatic pressure ($\sim \rho g R$) gives the scale of force balance. While penetration of water drop between superhydrophobic cylinders, the deformation of water drop should be followed. Thus, the advancing (receding) radius of curvature of water drop is $2/w \left(1/R\right)$. 
\[ \Delta p = \gamma \left( \frac{2}{w} - \frac{1}{R} \right) - \rho g R \]  

(7)

This equation leads next equation that is expressed with \( Bo \).

\[ \left( \frac{2R}{w} \right) - 1 \sim Bo \]  

(8)

FIG. 4. 2 Sequential image of drop penetration between hydrophilic cylinders.
FIG. 4. 3 Sequential image of drop penetration between superhydrophobic cylinders.
Plotting the dimensionless length, $(2R/w) - 1$, and $Bo$, it is confirmed that the dimensionless length is proportional to the Bond number with the slope of 0.5.
FIG. 4. 5 Dependence of $(2R/w)−1$ on the Bond number for water drop penetration.

4.3.2 Drop impact between superhydrophobic cylinders.

Mentioned above, from the FIG. 4. 6, three different regime of water impact behavior were observed, which were perfect penetration of water drop, break up and bouncing of water drop. Using the dimensionless analysis, we can assume the distance between superhydrophobic cylinders is the function of various parameters.
FIG. 4. 6 Drop impact between two superhydrophobic cylinders. (a) perfect penetration, (b) break up and (c) stationary water drop.
\[ w = fn(d, \rho, \mu, \gamma, U, a) \]  

(9)

where \( w \), the distance between two superhydrophobic cylinders, \( d \), the diameter of water drop, \( \rho \), the density of water, \( \mu \), the viscosity of water, \( \gamma \), the surface tension of water, \( U \), the velocity of water drop at the moment of impact, \( a \), the diameter of cylinder. This can simplify the dynamics of impact of water drop, leading to the following relationship:

\[ \left( \frac{w}{d} \right) \sim fn \left( \frac{pdU}{\mu}, \frac{pdU^2}{\gamma}, \frac{a}{d} \right) \]  

(10)

where \( \rho dU / \mu \), the Reynolds number, \( \rho dU^2 / \gamma \), the Weber number.

Understanding the water drop impact, the pressure due to impact will be same as following:

\[ \Delta p \sim \frac{1}{2} \rho U^2 \]  

(11)

For the penetration downward force should be larger than the capillary force exerted to the water drop.
\[ \Delta p \geq \frac{-2\gamma \cos\theta}{w} \]  

(12)

where \( \theta \), the contact angle of water drop. The contact angle of superhydrophobic cylinder that is used in this experiment is 160°. Thus, equation (8) and (9) can be substituted with equation (10).

\[
\left( \frac{w}{d} \right) \left( \frac{\rho d U^2}{\gamma} \right) \geq -4 \cos \theta 
\]

(13)

\[
\left( \frac{w}{d} \right) We \geq 3.76
\]

(14)
FIG. 4. 7 Regime map for drop penetration, break up and stationary motion of drop impact.
Chapter 5

Concluding remarks

5.1 Conclusions

In this thesis, we have studied the fabrication of superhydrophobic filtration membrane, the precipitation of salt crystal on hydrophobic surface and the drop penetration and impact on superhydrophobic surface.

In Chapter 2, the fabrication of superhydrophobic surface was introduced, in which non-woven fabric made of PET was textured and the nano-textured surface was coated by low-surface energy chemical through CVD. The fabricated water repellent surface showed the robust superhydrophobicity, for which it was confirmed that the superhydrophobic surface exhibit a high contact angle with water even after the condensation of water and oil-wetting. The fabrication through plasma treatment can develop superhydrophobic surface with fast and cheap process.

In Chapter 3, the precipitation of salt crystal on moderately hydrophobic and superhydrophobic surface was studied. On moderately hy-
drophobic surface, the pizza and pot structure can be formed. Due to the combination of low receding contact angle, low concentration of salt and slow evaporation, the aggregation of salt crystal can be constraint near the contact line. Using the mass conservation and water potential theory, we predicted the thickness of salt crystal and compared with the experimental data. On superhydrophobic surface, pebble structure can be formed due to high receding contact angle and dominant constant contact angle mode. The particle tracking method was used for visualization the process of forming the different structure on the surface.

In Chapter 4, the penetration of water drop between superhydrophobic cylinders under the static and dynamic condition. The penetration of water drop was scaled with dimensionless number, $Bo$ and $We$. We compared the scaling and the experimental data. From the scaling, we predicted the distance between superhydrophobic cylinders, which the water drop can be penetrated inside.

Our work thus provides the fast and cheap fabrication method for superhydrophobic filtration membrane with various industrial applications and physical understanding of the salt precipitation on hydrophobic surface and the water penetration between superhydrophobic cylinders.
References


국문 초록

본 연구에서는 기능성 분리막의 초소수성 확보를 위한 플라즈마공법을 제시하고, 이렇게 제작된 초소수성 기능성 분리막에서의 유체거동 특성과 결정 석출의 차이, 담수화 모듈 제작을 위한 3차원 초소수성 구조에서의 액적 침투 등을 다루었다.

초소수성 기능성 분리막 제작을 위하여 CVD (Chemical vapor deposition)를 이용한 플라즈마 처리 방법을 제시하였다. 플라즈마를 이용한 초소수성 표면 제작 방법은 기존의 리소그래피 방법의 한계인 평면제작을 3차원 표면 제작으로 확장시켰으며 공정비용 및 공정시간을 단축할 수 있다는 장점과 더불어 다양한 폴리머에 적용가능하다는 장점을 가진다.

막종류 및 역삼투에 사용되는 분리막에서 흔히 발생하는 결정석출에 의한 막기능 저하에 대해 알아보기 위하여 접촉각이 높은 소수성 분리막과 접촉각이 매우 낮은 초소수성분리막에서의 소금 결정석출의 차이를 분석하였다. 분리막의 소수성 정도와 증발률에 따라 서로 다른 구조를 가지는 결정석출결과를 확인하였으며, 질량보존 및 water potential 모델을 이용하여 결정층의 두께를 예측하였다. 파티클 이미지추적을 통해 결정석출시
특이점을 가시화하였다.

마지막으로 초소수성 실린더 사이로의 액적 침투 현상에 대해 연구하였다. 초소수성 실린더 사이로의 정적 액적 침투와 웨버수가 큰 경우의 동적 침투 현상을 구분하고, 스케일링을 통해 액적의 크기와 침투가 발생하는 실린더 사이의 거리의 관계를 파악하였다.


주요어: 초소수성, 표면장력, 결정 석출, 액적 침투, 고분자
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