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Visualization Study on Microscale Wetting Dynamics of Water Droplets on Dry and Wet Hydrophilic Membranes

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Abstract – The wetting dynamics of water droplets dispensed on the surface of dry and wet hydrophilic membranes were investigated experimentally from a microscale point of view. By using a high-speed, white-beam x-ray microimaging (WXMI) synchrotron, consecutive images displaying the dynamic motions of the droplets were acquired. Through analyzing the characteristics observed, it was found that the dry hydrophilic membrane showed local hydrophobicity at a certain point during the absorption process with apparent contact angles greater than 90. While on the other hand, the apparent contact angles of a water droplet absorbing into the wet membrane remained less than 90 and showed total hydrophilicity. The observations and interpretation of characteristics that affect the contact, wetting, recoiling, and dynamic behaviors of droplets are significant for controlling liquid droplet impingement in a desired manner.

Key words: White-beam xray microimaging (WXMI), Wetting dynamics, Recoiling

1. Introduction

The spreading and absorption dynamics of liquid droplets dispensed on solid surfaces are of vital importance in various natural phenomena and industrial processes. When discussing the areas of technological applications associated with researches of droplet impacting on solid surfaces, the following are frequently mentioned: spray coating, pesticide control, medical science, inkjet printing, and metal forming [1-3]. In particular, the fundamental knowledge on stable and precise deposition of droplets is exceptionally important in both academic and industrial fields that require printing of very small amount of liquids containing chemical, biological, electronic materials [4-6]. To meet the increasing and diverging requirements for stable and precise deposition of droplets, the fundamental study on visualization of spreading and absorption behaviours of liquid droplets depending on the surface wettability is essential in determining (or designing) the absorbability of solid surfaces to appropriately a liquid droplet [1,7-8].

When a droplet impacts on a hydrophilic or hydrophobic solid substrate, it exhibits various behaviors (e.g., spreading, crown-forming, and recoiling) depending on its physical properties (e.g., surface tension, viscosity, density, and impacting velocity) and the wettability of solid substrates, and consequently reaches various wetting state [7,9]. In other words, the outcomes of the deposition of a liquid droplet are influence by many physical factors, including droplet size, impacting velocity, physical properties of the liquid, and surface wettability [10]. The intriguing features of surface wettability frequently reveal in considering deposition of liquid droplets on textured surfaces [11-12].

When a sessile droplet is gently dispensed on a solid substrate, it has an intrinsic apparent contact angle arised from intermolecular interactions (i.e., interfacial tensions) between the solid-liquid, solid-vapor, and liquid-vapor interfaces [13-16]. In general, the surface wettability is determined to be hydrophilic when the apparent contact angle is less than 90^o, while it is hydrophobic when the apparent contact angle is above 90^o [17-19]. The alteration of apparent contact angles above and below the threshold indicates switching of surface wettability [20]. In general, the wettability switching can be achieved by modification of surface structure and roughness [12]. While many researchers have extensively focused on fundamental properties of hydrophobic and super-hydrophobic surfaces and droplet behaviours on these surfaces [21,22], we here aim to observe interfacial phenomena arising from the interaction between a liquid droplet and a hydrophilic surface, investigating for manifestation

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of local hydrophobicity.

In the present study, we visualize the microscale, interfacial dynamic behaviors of the collision of a water droplet against both dry and wet surfaces of hydrophilic membranes. A highspeed, white-beam x-ray microimaging (WXMI) technology in synchrotron facility is utilized to acquire information on spatial-temporal shape variation of the water droplet on the hydrophilic membrane and analyze its impacting, spreading, and penetration dynamics. This visualization strategy is of superiority due to the inclusion of a high frame rate, short exposure time, miniscule pixel size, large field-of-view, and phase-contrast imaging enhancement. The wettability characteristics at various temporal stages of the absorption process can be experimentally found out from high-speed recorded image sequence of the variation of droplet shape at near contact line area.

2. Experimental Details

2-1. Experimental setup for synchrotron-based microimaging of water droplet-membrane interface

For visualizing the morphology of a water droplet on the surface of hydrophilic membranes, the Pohang Light Source II (PLS-II) 9D beamline was utilized, as shown in Fig. 1. We employed the same experimental setup used in the previous our research [23], which enabled to obtain high-resolution images through a fast shutter and high-speed camera that provided high frame rate and short exposure times.

2-2. Preparation of the test samples used for water absorption on dry and wet hydrophilic membranes

The conventional nonwoven filter paper made from a mixture of cellulose (1.5 g/cm^3) and polyester (1.39 g/cm^3) with a pore size of around 20 μm was used as the hydrophilic membrane. The microscale image on the hydrophilic membrane is illustrated in Fig. 2. On the other hand, for clearer visualization of the dynamic morphology of the water droplets on the fibrous membrane, the imaging contrasts were enhanced by adding an aqueous solution containing iodine (I2, 1% w/v) and potassium iodide (KI, 2% w/v) to the water phase. The water droplet with a volume of 100 μL was gently dropped onto the membrane surface with both dry and wet conditions. Physical properties of the water droplet exhibits following values: viscosity of 0.89 mPa·s, surface tension of water/air of 72.0 mN/m, and density of 997 kg/m.

Fig. 2. The microscale image on the conventional nonwoven filter paper used as the hydrophilic membrane, which is made from a mixture of cellulose (1.5 g/cm^3) and polyester (1.39 g/cm^3) with a pore size of around 20 μm.

3. Results and discussion

3-1. Temporal variation in morphology of droples impacting onto dry and wet hydrophilic membranes

Dynamic behaviours of the water droplet impacting onto dry and wet hydrophilic membranes are observed from the microscopic point of view by utilizing a high-speed, synchrotron WXMI technique. The dynamic morphology of the droplets after impacting on these surfaces over time are shown in Fig. 3. Various dynamic behaviors of the droplet, including spreading, recoiling, and oscillating are observed during entire adsorption process. Here, the initial state (i.e., time of 0 ms) is determined to be when the water droplet in a spherical shape instantly contacts with the membrane surface. Immediately after contacting with the membrane surface, a toroidal shape is initially formed at the base of the spreading droplet, regardless of membrane condition.

On the dry membrane surface, the height of the central cavity of the droplet diminishes rapidly and a hallow concave region appears. Subsequently, the droplet reverses the transformations of its shape, in which the downwards pit disappears, and the central mount reappears. The droplet repeats the movements continuously, oscillates both horizontally and vertically during the absorption process as shown in Fig. 3(a).

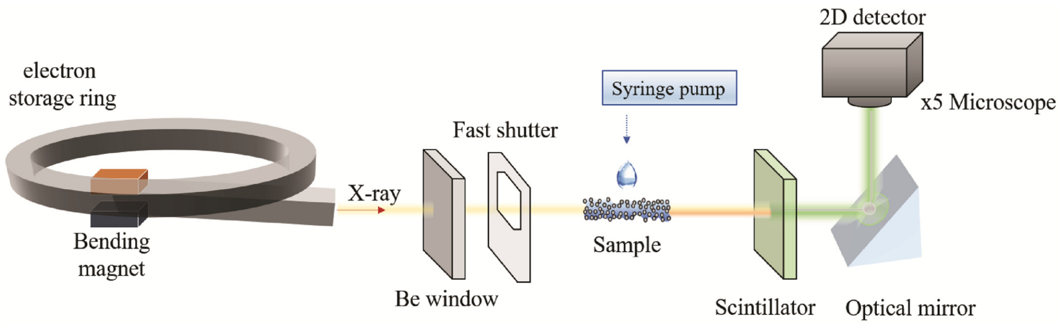

Fig. 1. Schematics of synchrotron white-beam X-ray microimaging (WXMI) for visualizing transient behaviors of the droplets on dry and wet surfaces of hydrophilic membranes.

Fig. 3. Transient deformation of spreading of droplets near the contact line on the (a) dry membrane and (b) wet membrane. The scale bar indicates 500 µm.

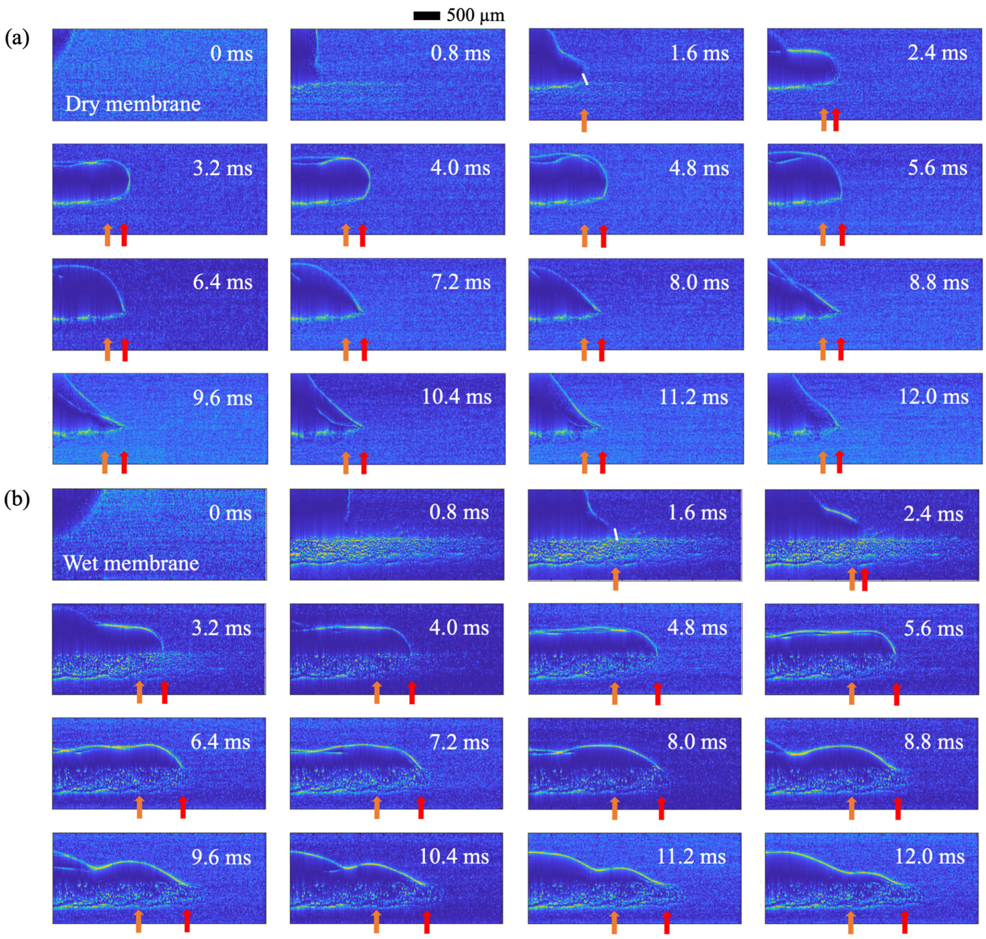

Fig. 4. Subtraction images of the transient deformation of spreading of droplets near the contact line on the (a) dry membrane and (b) wet membrane. The orange and red arrows indicate the starting point and moving distance of the contact line, respectively. The scale bar indicates 500 µm.

On the other hand, the central mount of the water droplet on the wet membrane retains its shape and does not form any hallow pits. Instead, the central mount of the droplet slowly oscillates vertically while naturally decreasing its height. The droplet on the wet membrane reaches the equilibrium state much earlier compared with the case of the dry membrane, as shown in Fig. 3(b).

To clearly identify the interfaces of the spreading dynamics of the droplets, subtraction analysis is carried out as shown in Fig. 4. The yellow and green colors indicate weaker absorption intensity, depending on material density; dense components absorb X-rays and thus exhibit highlevel attenuation, whereas less dense materials facilitate X-ray transmittance. As shown in Fig. 3, when the density difference between the two media is small, it is difficult to distinguish between the two materials. This method of subtraction emphasizes the edges, providing a clear interface.

Based on the consecutive images of the spreading droplets illustrated in Figs. 3 and 4, temporal variations of apparent contact ane and spreading velocity for the contact line are quantitatively analyzed (Fig. 5). As shown above, the water droplet on the dry membrane initially oscillates, and then settle at the stable equilibrium state. Accordingly, the initial fluctuations and subsequent damping of apparent contact angle and spreading velocity are exhibited. That is, the spreading behavior of the water droplet on the dry membrane corresponds to an underdamped response. On the contrary, the water droplet on the wet membrane initially spreads to the maximum spreading diameter with maintaining an acute dynamic contact angle. Subsequently, its contact line is almost pinned at the equilibrium state. That is, the spreading behavior of the water droplet on the wet membrane corresponds to an overdamped response.

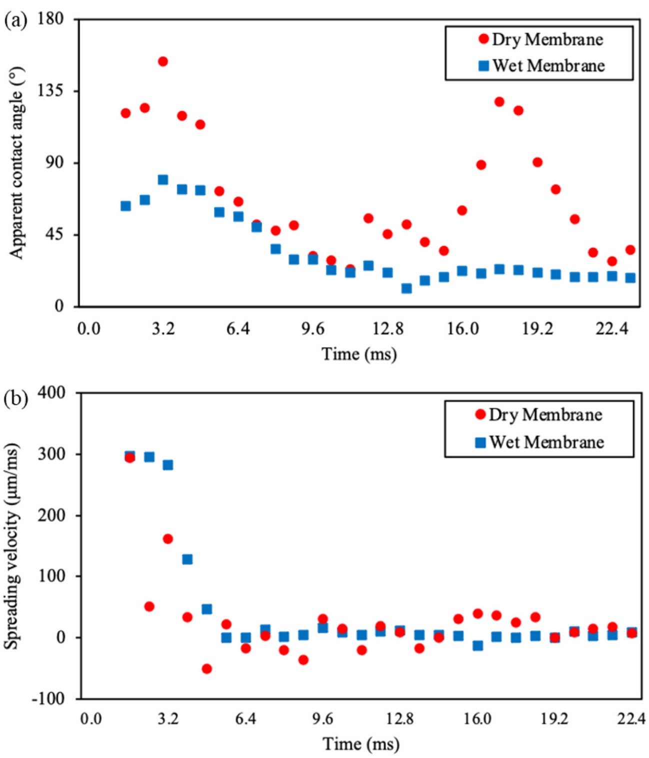

Fig. 5. Dependencies of temporal variations for (a) apparent contact angle and (b) spreading velocity on membrane condition.

The difference in the temporal variation of dynamic contact angle of water droplets on the dry and wet surfaces can originate from surface roughness and resultant spreading velocity. The resistance of a water droplet from penetrating the surface of a dry membrane is due to the low interfacial energy caused by the air pockets present between the droplet and the surface [24]. The Cassie-Baxter equation suggests that as the roughness increases, the thickness of the interfacial air film proportionally increases [1,7,25-26]. When the droplet was dispensed on the dry surface, hollow craters of entrapped air were formed between the two surfaces [27]. The development of this air film decreased the interfacial energy and made the surface of the solid substrate non-wetting, leading to the enhancement of hydrophobicity. [28] For this reason, it was found to retain local hydrophobicity for a period of time during the absorption process of the droplet on the dry membrane. Without the presence of spaces of entrapped air between the water droplet and the membrane, the introduction of deduced surface roughness amplifies the wetting property of the original surface to be more hydrophilic [29-30]. As a result, the dynamic contact angle of the droplet on the wet membrane retain acute angle until it reaches the equilibrium.

On the other hand, the absorption time for dry and wet membrane surfaces are measured to be 180 ms and 108 ms, respectively. The different spreading patterns depending on the membrane condition is found to affect the absorption time.

4. Conclusions

In the present study, dynamic behavior of the water droplet impacting on the dry/wet membrane is directly visualized by employing a high-speed, synchrotron X-ray white-beam microimaging (XWMI). With our synchrotron-based X-ray microimaging techniques, capture of the whole droplet motion (large FOV of 4.4 × 4.4 mm) was enabled. The dynamic characteristics of a spreading water droplet dispensed on membrane surfaces with different conditions (i.e., dry and wet conditions) was analyzed with measuring temporal variations of apparent contact angles and spreading velocity and adsorption time. The spreading behaviors of the droplets on dry and wet membranes are found to exhibit an underdamped and overdamped responses, respectively. In addition, the different spreading patterns depending on the membrane condition is found to affect the absorption time. The present study will provide in-depth understanding of the early interfacial dynamics on porous media and will guide you in developing technical strategies for improving the control of wettability on the surface of hydrophilic membranes.

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