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Breath Figure of Water and Ethanol on Contaminated Solid Surfaces

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We observed the condensation of water and ethanol on a hydrophobic polymer film coated with fluorinated silicone particles and identified five states: the circular droplet, ellipsoidal droplet, network, huge droplet, and film states. The shape of the condensed droplets changed with the particle density and the wettability of the particles by the liquid.

Breath figures are the patterns of water droplets that form when one breathes on a cold surface. The moisture from the breath forms tiny droplets on hydrophobic contaminated areas but forms a uniform film on hydrophilic areas.[1] These figures have been used as a simple tool to detect oil contamination on glass surfaces.[2] Some material scientists have recently prepared well-ordered arrays from breath figure patterns on polymer solution surfaces.[3,4]

The growth pattern of the figures is determined roughly by the wettability of a solid surface by a liquid.[5] When water droplets form on a glass surface, their size is proportional to a power of the time when the contact angle θ of the water on the glass is 90°. However, a uniform layer forms when θ is 0°. Leach et al. observed dropwise condensation of water vapor on a hydrophobic polymer film and a silanized glass slide during natural cooling.[6] The observed drop growth kinetics suggested that the smallest drops grew principally by the diffusion of water adsorbed on the substrate to the drop perimeter, whereas drops larger than about 50 µm in diameter grew primarily by direct deposition from the vapor onto the drop surface. In addition, drop coalescence played a critical role in determining the drop size distribution. Chen et al. were the first to show that the presence of nanoscale topographical features is necessary for a surface to sustain superhydrophobic characteristics during water condensation.[7] Boreyko et al. demonstrated that the release of excess surface energy during coalescence of microdroplets growing on nanostructured superhydrophobic surfaces leads to self-propelled motion of the new droplet.[8]

Here, we focus on the effect of solid particles on condensation phenomena because in everyday life, most hydrophobic surfaces are contaminated with solid particles called dust. The particles can change the condensation phenomena on hydrophobic surfaces because rough structures affect the wetting properties of solid surfaces.[9–11] In this study, we observed condensation of water and ethanol on a hydrophobic polymer film coated with fluorinated silicone particles to investigate the effect of the particle density on the surface and the wettability of solid surfaces by liquids.[12,14,15]

First, we observed water condensation on the polymer surface. As shown in Supporting Information Figure S1,[19] a Petri dish of diameter 10 cm and height 1 cm containing 50 mL of water at 60 °C was placed on the stage of a microscope in a room at 25 °C. The dish was covered with a plate, to the center of which a square polymer film of area 1 cm^2 was attached. When there were no particles on the polymer film, circular water droplets of diameter 10–15 µm were found seconds after observations began (circular droplet state). Their size increased continuously, reaching 50–100 µm at 5 min (Figure 1a). Next, we observed condensation on a polymer film covered with 0.05–10 g m^{-2} of spherical fluorinated silicone particles of diameter 5 µm. Although the particle film appeared homogeneous to our unaided eye, voids and aggregations of solid particles were observed by microscope (Figure S2[19]). The surface coverage of the particles is shown in Figure S3.[19] At a particle density of 0.05 g m^{-2}, ellipsoidal droplets 50–100 µm formed just after observations began and grew to 50–200 µm at 5 min (ellipsoidal droplet state, Figure 1b and Table 1). The solid particles were adsorbed on the air–water interfaces of these ellipsoidal droplets. At a particle density of 0.5 g m^{-2}, we found a network structure that formed by the connection of water droplets (network state, Figure 1c). The structure changed to millimeter-sized droplets in just a few minutes (huge droplet state, Figure 1d and Table 1). These results predict that the particles on the polymer film change the shapes of the water droplets anisotropically and facilitate their growth.

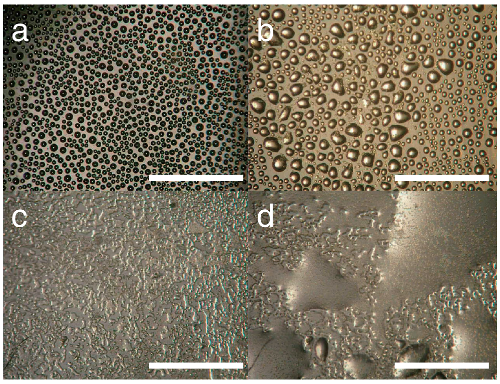

Figure 1. Microscopic images of water droplets on polymer film surfaces in (a) circular droplet state (particle density 0 g m^{-2}, exposure time 10 min), (b) ellipsoidal droplet state (0.05 g m^{-2}, 10 min), (c) network state (0.5 g m^{-2}, 0 min), and (d) huge droplet state (0.5 g m^{-2}, 10 min). Bars: 1 mm.

We also observed the condensation of ethanol on the polymer film. Interestingly, no circular or ellipsoidal water droplets were observed under any conditions. When the particle density was 0–0.5 g m^{-2}, the network state appeared just after observations began, and the condensation changed to millimeter-sized droplets in just a few minutes (Table 1). On the other hand, when the density was 5–10 g m^{-2}, the brightness of the particle film increased 1–2 min after observations began (film state). This change results from penetration of the condensed ethanol into the interspaces between solid particles and the inhibition of light scattering on the particle surfaces. Adsorption of solid particles at the air–ethanol interfaces was not observed.

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Table 1. State of the condensed water on polymer film surfaces; C: circular droplet state, E: ellipsoidal droplet state, N: network state, H: huge droplet state, and F: film state

Liquid	Particle density /g m^{-2}	Time/min		
		0	5	10
Water	0	C	C	C
	0.05	E	E	E
	0.5	N	H	H
	5.0	—	H	H
	10	—	H	H
Ethanol	0	N	H	H
	0.05	N	H	H
	0.5	N	H	H
	5.0	—	F	F
	10	—	F	F

The solid particles on the film surface changed the shapes of the water droplets from circular to ellipsoidal. This deformation is caused by the pinning effect, which involves a discontinuous change in the contact angle on nonuniform surfaces because of the energy barrier at the edges. That is, at the edges, the spreading of a liquid is inhibited, and the contact angle changes from θ_{eq} to $\theta_{\mathrm{eq}} + \alpha$, where θ_{eq} is the contact angle of the liquid droplet on a flat substrate, and α is the angle at the edge.[16,17] On the polymer film, the existence probability of solid particles, which have strong hydrophobicity,[12] was not homogeneous owing to the voids and aggregations of solid particles. This heterogeneity can induce spatial anisotropy in the event probability and the intensity of pinning phenomena at the three-phase contact line. That is, water spreads toward the region with low particle density. Moreover, the solid particles facilitated the growth of water droplets and induced the formation of huge droplets. We consider that small liquid droplets of water or ethanol can move through the interspaces between solid particles because of the capillary force.

We observed some interesting phenomena during condensation. Solid adsorption appeared only on water surfaces. Solid particles are generally adsorbed at liquid surfaces when they have a suitable affinity for both fluids. Levine et al. showed that the adsorption energy F, which is the energy change with adsorption from a fluid phase at an interface, is derived as[13,18]

$$F = \pi R^2 \gamma (1 - \cos\theta)^2 \qquad (1)$$

where R is the radius of a solid particle, γ is the surface tension of the liquid, and θ is the contact angle of the solid particle at the three-phase contact line. The particles were not adsorbed at the ethanol surfaces because the γ value of ethanol is lower than that of water. In contrast, penetration of the condensed liquid was observed only during ethanol condensation. The wettability of the fluorinated silicone particles by water is too low to contain enough water in the interspaces between the particles. The present results contribute to our understanding of condensation phenomena.

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12 Materials: Hydrophobic polymer film (cling film) was obtained from Japanese Consumers' Cooperative Union. The main component was polymethylpentene. The contact angles of water and ethanol on the film were 97 and 29°, respectively. The arithmetic average roughness R_{a}, which was evaluated by atomic force microscopy, was about 20 nm. We used the commercially available silicone resin powder Tospearl 145A (Momentive Co., Ltd.; specific gravity, 1.00 g cm^{-3}; spherical, average diameter 4.5 µm, standard deviation 1.2 µm), which was treated with a fluorinated agent, diethanolamine salt of perfluoroalkyl phosphate in Daito Kasei Co. Wettability of the powder was evaluated from the sinking time into water and ethanol t.[13] Fifty milligrams of powder was placed carefully and evenly on the surface of 20 cm^3 of the liquids contained in a tube of diameter 32 mm. The time taken for all of the powder to disappear from the liquid surface was measured: $t > 48$ h (water), $= 20$ s (ethanol). These results predict that the powder has strong hydrophobicity and affinity to ethanol.

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14 Preparation: The fluorinated silicone particles were dispersed in a ternary mixture consisting of water, ethanol, and propanol (1:1:1, wt/wt/wt) with a vortex mixer (Vortex-genie 2; Scientific Industries Inc.) in a screw-cap test tube to obtain 0.001–2 wt% dispersions. The dispersions (0.05 g) were casted on the polymer film with a perforated sample holder and dried to form 0.05, 0.5, 5, and 10 g m^{-2} particle films. The sample holder had a square hole 1 cm on a side as shown in Figure S1a in Supporting Information.[19]

15 Observation: Figure S1b in Supporting Information[19] shows an observation system for condensation phenomena. A Petri dish of diameter 100 mm and height 10 mm containing 50 mL of water at 60 °C or ethanol at 45 °C was placed on the stage of an Olympus BHT optical microscope in a room at 25 °C. The dish was covered with a poly(ethylene terephthalate) plate (P-8010, Kyoei Plastic Co., Ltd.) of area 12 cm^2, and a polymer film of area 1 cm^2 was attached to the center of this plate. The space between the Petri dish and the plate was sealed with a paste consisting of butyl rubber and inorganic filler (tape-shaped caulk 23119, Konishi Co., Ltd.) to prevent dissipation of water vapor. The condition of the film surface was observed from above the Petri dish by the microscope. A thermocouple was placed in the water to detect its temperature.

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