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Particle adsorption in evaporating droplets of polymer latex dispersions on hydrophilic and hydrophobic surfaces

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Abstract Stain patterns formed by drying up of droplets of polymer latex dispersion on hydrophilic and hydrophobic surfaces were examined in light of the mechanism of particle adsorption in evaporating droplets. On hydrophilic surfaces, the volume of droplets decreased with time, keeping the initial outline of contact area, and circular stain patterns were formed after the dry-up of droplets. By the microscopic observation of particles in the droplets, it was found that a large portion of the particles were forced to adsorb on the outline of the contact area where a microscopic thin water layer was formed because of hydrophilicity of the surface. On hydrophobic surfaces, on the other hand, the contact area of

droplets decreased as evaporation proceeded, while no particle was adsorbed on the surface at the early stages. The particles in the droplets started to aggregate when the concentration of particles reached a critical value, and the aggregates adsorbed on the surface forming tiny spots after the dry-up. Time evolutions of contact angle, contact area and volume of the droplets were analyzed in light of differences in the adsorption mechanisms between hydrophilic and hydrophobic surfaces.

Key words Contact angle – hydrophobicity – droplet of latex dispersion – adsorption pattern of particles

Introduction

Recently, pollution-proof materials and surface finishing techniques for keeping the exterior of buildings clean have been in demand to lower the cost of maintenance. There are many studies on the evaluation of exterior materials in relation to adhesability and cleansability of stains [1–4], but few studies were carried out on the mechanisms of pollutant adhesion in spite of their importance in developing new materials and finishing techniques for the exterior of buildings. We are interested in studying a mechanism of the formation of stripe patterns by stains frequently observed on outer walls, especially beneath eaves and windows of modern buildings. It is known that this kind of

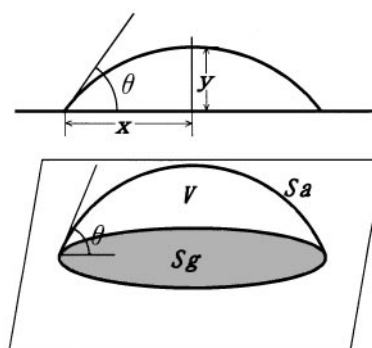
stain pattern is more conspicuous on hydrophobic surfaces, such as fluoro-resin coatings, than hydrophilic surfaces, such as an anodic oxide film of aluminium [5]. We considered that a drying process of rain drops containing pollutant particles might be important for the formation of stripe patterns. Therefore, we examined here the difference in mechanisms of the particle adsorption in droplets on hydrophobic and hydrophilic surfaces using polymer latex dispersions as a model of rain drops. Previously, some studies on the drying behaviors of latex dispersion were done by Nagayama et al. [6, 7]. In our work, the motion of particles in evaporating droplets was observed with an optical microscope, and time evolutions of contact angle, contact area and volume of droplets were analyzed

relating with the mechanism of particle adsorption and the formation of stains.

Experimental

The latex dispersions used were synthesized in our laboratory [8] by copolymerization of styrene and *p*-styrenesulfonate with divinylbenzene as a cross-linking agent at 70 °C for 7 h. The reaction was initiated with potassium persulfate in a water–methanol mixture (5:7) without any emulsifier. The dispersions obtained were dialyzed against distilled and deionized water for a week. Before the use in the measurements, the dispersions were thoroughly purified by ultrafiltration (model 202, Amicon, with a Millipore membrane, pore size 0.22 μm, filter type: GSWP) and mixed-bed ion exchange resin beads (AG501-X8(D), Bio-Rad, CA). The diameter of the latex particle was estimated with a dynamic light scattering apparatus (DLS-7000, Otsuka Electronics, Hirakata, Osaka) as 0.41 μm. The surface charge density was estimated by conductometric titration as 1.1 μC/cm².

Ordinary cover glasses for a microscopy were used as base plates on which droplets of the latex dispersion were placed to evaporate. The plates were cleaned by dipping in concentrated sulfuric acid and concentrated nitric acid solutions, and rinsed repeatedly with pure water. The cleaned glass plates were denoted as UM (unmodified) plates. In order to change the hydrophilic surface into an hydrophobic one, two silane coupling agents, methyltrichlorosilane (Shin-etsu, Tokyo) and octadecyltriethoxysilane (Shin-etsu) were coupled to –SiOH groups on the surface of UM glass. The plates were dried in an oven at 100 °C for about 1 h and were immersed in a 5% methanol solution of methyltrichlorosilane or in a 5% hexane solution of octadecyltriethoxysilane for 10 h at 30 °C. The former was rinsed with methanol and pure water, and the latter was rinsed with hexane, methanol and pure water to remove unreacted reagents on the surfaces. The plates were dried for 30 min at 80 °C before use. The modified plates were denoted as MTCS and ODTES plates, respectively. Initial contact angles of droplets of pure water were measured to evaluate surface properties of the plates, and were about 38 and 60° for UM and MTCS plates, respectively. These values were steady and reproducible. The



$$\theta = 2 \tan^{-1} \left(\frac{y}{x} \right)$$

$$S_g = \pi x^2$$

$$V = \frac{\pi x^3 (1 - \cos \theta)^2 (2 + \cos \theta)}{3 \sin^3 \theta}$$

Fig. 1 Measurement and calculation of droplet size

contact angle for ODTES plates, on the other hand, varied from 80 to 100° in our experiment due to uncontrollable factors, but the contact angles measured on each modified plate were equal wherever they were measured. We chose two groups of ODTES plates with the static contact angles of about 80 and 100°, ODTES₈₀ and ODTES₁₀₀, respectively, and used them as the plates with different surface properties. Advancing and receding contact angles were also measured and shown in Table 1.

During drying processes, droplets of pure water and latex dispersion on the plates were observed with a CCD video camera to record time evolutions of size and contact angle of the droplets at an interval of 5 min after the placement of droplets. Recorded images were analyzed using a digital image processing computer (IBAS, Carl Zeiss, Oberkochen, Germany). The motions of latex particles in the droplets were observed with a reversed-type microscope (AXIOMAT, Carl Zeiss) through the base glass plates.

Figure 1 shows drawings and equations for the calculations of contact angle θ , contact area S_g and volume V using the size of droplets (x and y in the drawing). It was assumed here that the concave outline of the droplet was a part of a sphere.

Table 1 Contact angles of unmodified and modified glasses

	UM	MTCS	ODTES ₁₀₀
Static contact angle [°]	38	60	102
Advancing contact angle [°]	42	67	111
Receding contact angle [°]	12	37	89

Results and discussions

Figure 2 shows time evolutions of θ , S_g and V values for droplets of pure water. The values except θ were given as

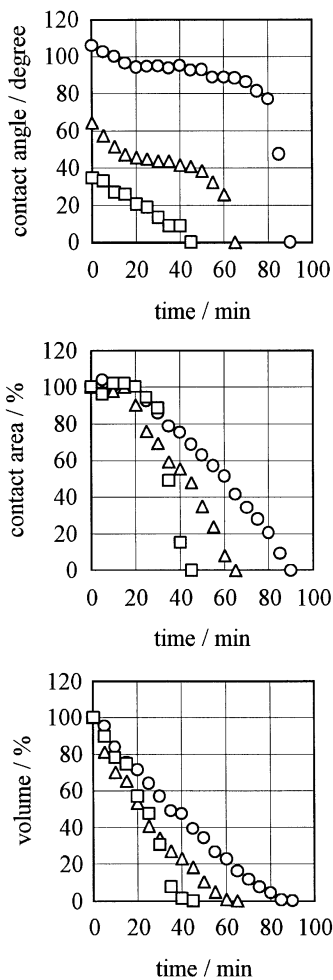


Fig. 2 Time evolutions of θ , Sg and V values of pure water droplets. \square : UM, Δ : MTCS, \circ : ODTES₁₀₀

a percentage of their initial values ($t = 0$). At the beginning of drying (within about 20 min), the Sg value changed little with time and the difference in the time evolution between the modified and unmodified plates was negligible in spite of the difference in their surface properties. In compensation for the unchanging Sg , the θ value decreased with time to fulfill the decrease in the volume of droplets. This tendency indicates that the decrease of V by the evaporation causes the decrease of θ instead of Sg , because the θ value is larger than the receding contact angle θ_r at the beginning. After the θ value reached θ_r , the Sg value started to decrease with time and the decreasing rate of θ reduced to nearly zero on hydrophobic (MTCS and ODTES) plates. In other words, the droplets reduced their volumes while keeping similarity in their shapes.

On UM plates, droplets dried in another way. The θ value continuously decreased at the same rate as at the initial stage ($\theta > \theta_r$). The decrease of θ is considered to be

necessary for the UM plates, because the decrease of V could not be accomplished only by the decrease of Sg . The decrease in Sg was slowed down on the hydrophilic surface showing the tendency to enlarge the contact area.

For hydrophobic surfaces, on the other hand, the decrease of θ is not necessary because the surface is slippery enough for water droplets to reduce Sg . At the final stage of drying, a quick decrease in θ was observed on the unmodified plates. It might be said that the drying process of pure water droplets consists of the three stages, which agrees well with the previous work about the contact angle of drying droplets on polymer surfaces at the nearly initial stage [9–11].

Figure 3 shows time evolutions of θ , Sg and V value for the droplets of polymer latex dispersion at different particle concentrations. On UM plates, the θ and V values decreased in the same way as in the case of pure water droplets, whereas the Sg value remained constant until the droplets completely dried up. Similar tendencies were observed on the MTCS plates. On more hydrophobic plates, droplets dried in different ways. On ODTES₈₀ plates, for example, the θ value showed a jump-back during the monotonic decrease and the Sg value fell down quickly in response to the jump-back. The other characteristic points for ODTES₈₀ plates are the particle concentration dependencies of θ and Sg . At higher concentration, the θ value decreased more quickly from the beginning, whereas the Sg value tended to stay unchanged while the θ value decreased quickly when the θ value jumped back. Consequently, the Sg value seemed to decrease stepwise. Considering the dependencies of the time evolutions of θ and Sg on the surface properties and the particle concentration, it was suggested that the unchangingness of Sg observed on UM and MTCS plates and the jump-back in θ on ODTES₈₀ plates might be caused by the interaction of dispersed particles with the plate surfaces. However, on ODTES₁₀₀ plates, time evolutions of θ and Sg were the same as those of pure water droplets, in other words, the dispersed particles had no effect on the time evolutions.

To analyze the relationship between the adsorption behavior and the variation of the time evolutions among the plates with different surface properties, we observed the formation of adsorbates on the plate surfaces. Figure 4 shows pictures of the droplets taken from the position beneath the plate at different stages of drying. On UM plates, particles adsorbed on the contour of contact area at the beginning of drying, and the width of the adsorbed region became wider with time. At the particle concentration examined, most of the particles in the droplets adsorbed on the contour before the complete dry-up of droplets. As a result, almost no particle adsorbed on the central part of contact area and circular adsorbates were formed on the UM glass plates [12].

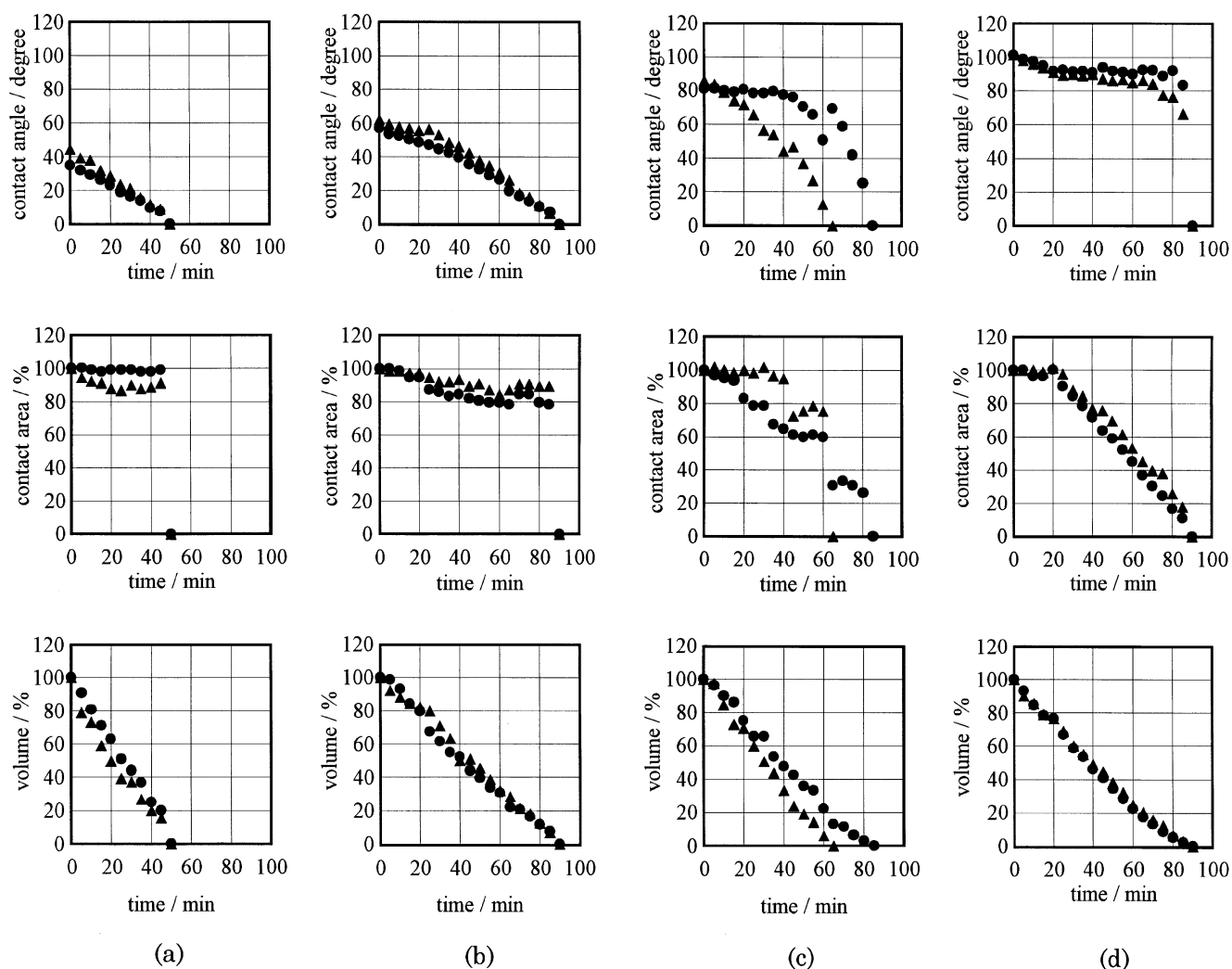


Fig. 3 Time evolutions of θ , S_g and V values of latex dispersion droplets (a) UM (b) MTCS (c) ODTES₈₀ (d) ODTES₁₀₀. ●: latex 0.01 vol%, ▲: latex 0.1 vol%

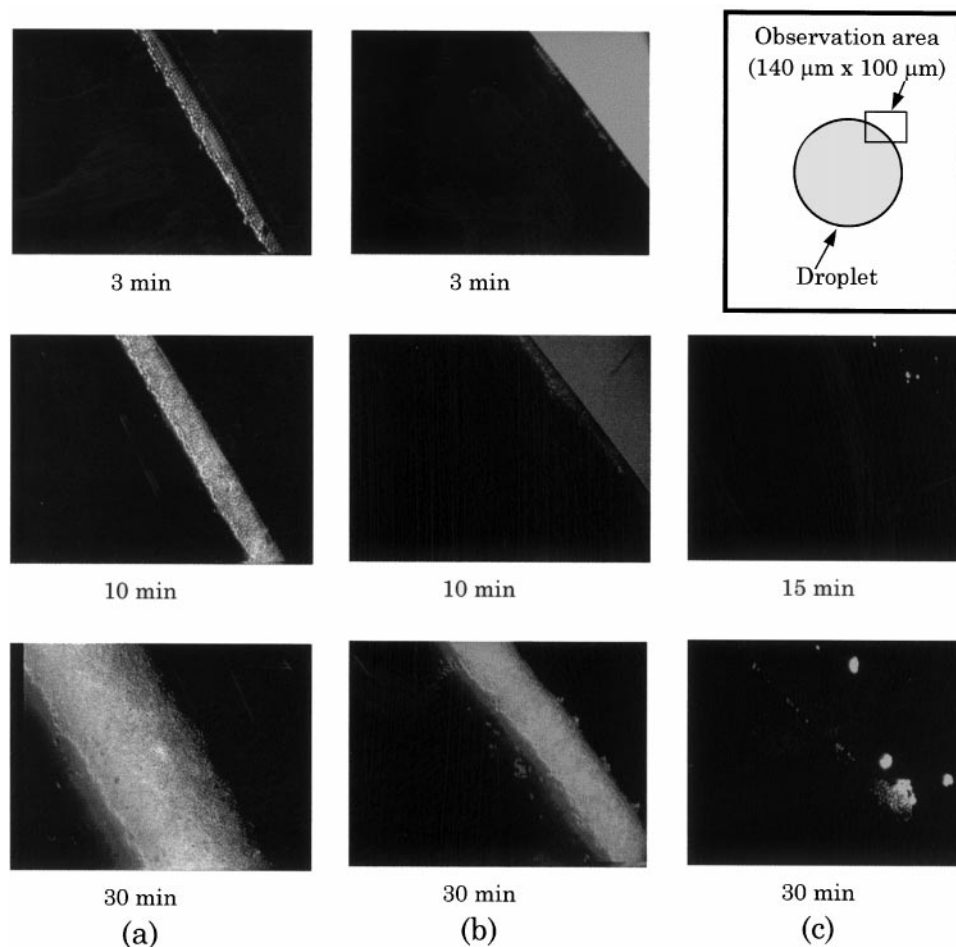
At the initial stage of drying on MTCS and ODTES_{80/100} plates, on the contrary, such adsorption behaviors were not observed. About 30 min after the onset of drying, observable amount of particles adsorbed along the contour of droplets on the MTCS plate. However, any kind of circular adsorbates were not observed on the ODTES_{80/100} plates. Though a small number of aggregates adsorbed along the contour, tiny spots of adsorbates instead of the circular one were formed after the dry-up.

To understand the difference in the final shape of adsorbates, we observed the particles adsorbing on the contour with an optical microscope. On the UM plates, thin layers of particle aggregates of about 20 μm in thickness and 10 μm in width were formed around the droplets. (inset of Fig. 5a). A quick dry-up occurred on the upperside

of the layer and the dried region spread toward the inside of droplets. Due to the quick dry-up, particles in the layer were forced to attach and adsorb on the plate forming latex film adhered to the surface. Inside the droplets, particles were transferred from the interior to the contour by convection and piled up at the contour. The particles in the pile aggregated and adsorbed on the plate surface due to the pressure produced by the convection and the quick dry-up that spread from outside (Fig. 5a).

In the case of ODTES_{80/100} plates, such a layer could not be observed. Consequently, no adsorption of particles was observed on the contour at the early stages of drying. As drying proceeded, the particles in the droplets were condensed and formed aggregates which were moved by convection, and sedimented near the contour. A small

Fig. 4 Ridge formations at the contour of droplets
latex: 0.1 vol% volume: 10 μl
(a) UM (b) MTCS (c) ODTES₈₀



portion of the aggregates adsorbed on the surface, and the rest were swept and gathered at the center of the contact area with the reduction of droplet volume (Fig. 5b). Finally, tiny spots of adsorbates were formed after the dry-up of droplets. At the higher particle concentration, such aggregates were formed at earlier stages of drying, so the Sg value tended to stay constant from the beginning. The particle concentration dependence of the time evolutions of θ and Sg can be explained by the difference in the onset of the aggregation. On the most hydrophobic plates (ODTES₁₀₀), neither particles nor aggregates adsorbed on the contour and the same kind of adsorbates as on the ODTES₈₀ plates were formed. On MTCS plates, on the contrary, a portion of particles in the droplets adsorbed on the contour as observed on the UM plates and the rest of the particles aggregated as the drying proceeded. The aggregates got adsorbed on the contact area after the dry-up. The adsorption behavior on the MTCS plates went intermediate between UM and ODTES₈₀ plates, which can be rationalized by the hydrophobicity of the MTCS plate in between those of the two plates.

According to the microscopic observation, it was confirmed that the unchangingness in Sg of the droplets evaporating on UM and MTCS plates was caused by the adsorption of particles on the contour which was induced by the quick dry-up of layer of aggregates and a convection in the droplets. The jump-back in the θ value on ODTES₈₀ plates might be related with the adsorbed aggregates which could be taken off from the plate surface by the sweep of air-droplet interface.

Time evolutions of θ , Sg and V values were examined also on cover glasses coated with various resins used for the exterior of buildings. Hydrophilic fluoro-resin (HF), urethane resin (U) and fluoro-resin (F) were used to coat the surface of cover glasses and their contact angles were about 45°, 78° and 92°, respectively. As was expected, the drying processes of pure water droplets on the coated plates were in accordance with the chemically modified plates with corresponding contact angles. However, a slight difference between the chemically modified and the resin-coated plates was observed in the case of droplets of latex dispersion. While the drying behavior of the droplet

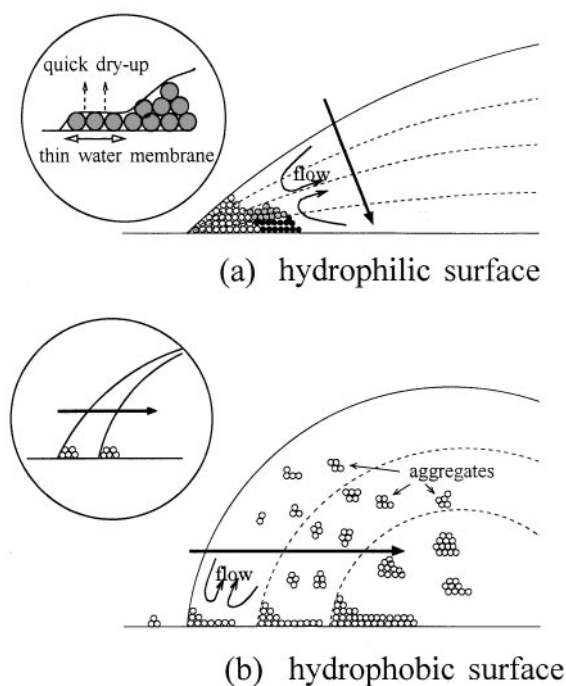


Fig. 5 Scheme for dynamic motion of dispersed particles in the drying droplet

on the HF plates was the same as on the UM plate, the drying on the U plates was like that on the MTCS plates and, on the F plates, it was similar to that on the ODTES₈₀ plates. In both cases, the drying on the resin-coated plates corresponded to that on the plates with lower contact angles. This tendency indicates that the

formation of a layer of aggregates might be easier on the resin-coated plates than on the chemically modified plates. It was suggested that the drying of dispersion droplets was influenced not only by the contact angle but by the other surface properties such as surface roughness of the plate examined.

Conclusion

On hydrophilic glass plates, the reduction of contact area of droplets of polymer latex dispersion was hindered by the rigorous particle adsorption induced by the quick dry-up of the layer of aggregates formed around the droplets and the particle condensation caused by a convection in the droplets. The dried layer (film) adhered firmly to the plate surface and let the condensed particles adsorb on the surface and pile up as a ridge at the contour. Consequently, circular adsorbates were formed after the dry-up. On hydrophobic plates, on the other hand, the reduction of contact area was obstructed because the contour was hooked by the aggregates adsorbed on the plate surface. However, "the hooks" were removed when the force to take off the aggregates increased with the progress of evaporation and overcame the adhering force of the aggregates. The aggregates gathered at the center of the contact area with the decrease in droplet volume, and the spots of adsorbates were formed after the dry-up. It might be concluded that the formation of the microscopic layer of aggregated particles around the droplets is the key to determine the shape of adsorbates.

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