Control of droplet movement on a plate with micro-wrinkle by difference of wettability

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Graphical abstract

The micro-wrinkle was manufactured by the buckling of a thin polymer film (poly(*N*-vinylcarbazole), PVK) on a base polymer (poly(vinyl chloride), PVC). It was observed that there were several degrees of contact angle anisotropy dependent on the direction in vertical and parallel to the wrinkle. When the droplet was set on the wrinkle surface inclined at 45° to the gravitational force, the direction of droplet movement could be changed by $\sim 20^\circ$ from the gravitational direction as shown in the figure below. The deflection angle β can be roughly estimated from a theoretical model with the principle of minimum work of the contact line.

Title Page

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Control of droplet movement on a plate with micro-wrinkle by difference of wettability

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Abstract

In this study, we consider the control of a liquid droplet movement rolling down on an inclined plate with gravitational force using a micro-wrinkle on a wall. The micro-wrinkle was manufactured by the buckling of a thin polymer film (poly(*N*-vinylcarbazole), PVK) on a base polymer (poly(vinyl chloride), PVC). The PVC was stretched once and then PVK (~100-nm thickness) was spin-coated on the surface of the base polymer at ambient temperature. When the strain was released in a thermostatic chamber heated above the glass transition temperature of PVC, a two-dimensional micro-wrinkle having a wavelength of several micrometers was formed on the surface. The advancing and receding contact angles were measured in directions parallel and perpendicular to the wrinkle. It was observed that there were several degrees of contact angle anisotropy. When the droplet was set on the wrinkle surface inclined at 45° to the gravitational force, the direction of droplet movement could be changed by ~20° from the gravitational direction. The deflection angle was estimated from a theoretical model with the principle of minimum work of the contact line.

1. Introduction

In recent times, the controlled movement of small droplets on walls has attracted interest in various devices such as lab-on-chips and microreactors used in the pharmaceutical and chemical engineering fields, to realize rapid heat transfer or to achieve highly efficient interfacial reactions (Abgrall and Gué 2007; Gupta, et al. 2016; Xi, et al. 2017). Thus, many techniques have been proposed to control the droplet movement. For example, some heat sources were embedded in a wall to generate a constant temperature gradient such that the droplet could be driven to the lower temperature side by the Marangoni force (Chen, et al. 2005; Pratap, et al. 2008; Zhao, et al. 2011). Darhuber and Troian (2005) studied the details of droplet dynamics driven by surface tension difference, while Karapetsas, et al. (2017) numerically analyzed the velocity and temperature distributions of a moving droplet. Meanwhile, methods based on wettability changes due to electrowetting on dielectric (EWOD) (Lu, et al. 2007) or due to different chemical species on walls have been frequently reported in literatures. EWOD utilizes the property that wettability is improved by the addition of an electric field; hence, many studies have been conducted on its application to various devices in recent times (Abdelgawad, et al. 2009; Jain, et al. 2017; Nahar, et al. 2016; Suzuki, et al. 2010). Lu, et al. (2007) investigated the motion and splitting of droplets placed in a Hele-Shaw cell using experiments and numerical simulations. Guan et al. (2018) found a dimensionless parameter which determines splitting cessation and producing a satellite drop by numerical simulation. Yamamoto et al. (2018) analyzed one directional simple movement of a droplet in the Hele-Shaw cell numerically and theoretically. Meanwhile, Fobel, et al. (2013) developed an integrated control system for droplet actuation. Furthermore, several researches have demonstrated that other movements, e.g., uphill climbing, jumping, and coalescence of two droplets, can also be achieved by EWOD actuation (Bhaumik et al. 2014; Datta et al. 2015; Datta et al. 2019; Islam and Tong 2018; Lee, et al. 2012).

By setting the chemical property pattern on the wall, a method was proposed to drive the droplet by the gradient of the wettability. Daniel et al. (2001) applied a radially outward gradient of chemical composition that was prepared by diffusion-controlled silanization on silicon surface to remove condensed water droplet. Moumen et al. (2006) measured droplet velocities with different volumes on a surface with linear wettability gradient. Seerha et al. (2017) conducted numerical simulation of a drop climbing along the staircase with chemical wettability gradient.

Other than the use of EWOD or chemical property pattern, some authors have tried to directly move the droplet by applying magnetic fields to the droplets containing magnetized particles (Hutama and Oleschuk 2017; Rigoni et al. 2018; Zhang and Nguyen 2017).

Based on the results above, various devices such as pumps to transport liquid, optical lenses using droplets, separation and aggregation of liquids can be developed. However, in these methods, it is necessary to fabricate fairly complicated devices such as embedding electrodes on walls and to incorporate external energy supply.

In the previous report, the authors attempted to control the moving direction of a droplet sliding down on an inclined wall by simple gravity (Kato et al. 2018). We have used a polymer (PMC) whose wettability can be reversibly changed due to a crosslinking reaction by ultraviolet irradiation, and patterned the regions with different wettability on the wall. The surface tension drag caused by contact angle hysteresis was reduced by adding ultrasonic vibration to the wall. Although the change in the contact angle by ultraviolet irradiation was limited by a few degrees, the droplet movement was efficiently controlled on the surface with saw-tooth pattern of different wettability and was deflected up to 20° from the gravitational direction. The trajectory of the droplet could be theoretically determined by estimating the resultant surface tension force acting on the droplet contact line. Although the movement direction of droplets driven by gravity can be controlled by a simple method which is an advantage, the degradation due to aging was observed because the wettability change was made by chemical reaction.

In recent years, a ‘micro-wrinkle’ having regular sinusoidal roughness of μm order on a solid surface has attracted interest in various engineering fields such as in lighting equipment or in the improvement of adhesion performance, in achieve elastic electronic devices, and so on (Khang, et al. 2006, Ohozon, et al. 2013, Park, et al. 2007). On the other hand, Chung, et al. (2007) fabricated a micro-wrinkled surface with a wavelength of $\sim 10 \mu\text{m}$ based on the buckling of thin film on the base matrix under mechanical strain. The surface showed wetting anisotropy, i.e., the contact angle when the contact line moves in the direction perpendicular to the wrinkle is $\sim 20^\circ$ larger than the contact angle in the parallel direction. Parihar et al. (2018) investigated the influence of electrowetting on the anisotropic wettability induced by the micro-wrinkle. Various fabrication techniques of the micro-wrinkled surface have been reviewed by Rodriguez-Hernandez (2015)

In this study, we focus on the anisotropy of wettability caused by a micro-wrinkled surface formed spontaneously under heating, to control the moving direction of the droplet sliding on the inclined surface. The micro-wrinkles are fabricated using thin film buckling phenomenon when the strain of the base material is released. We measure the wetting anisotropy on the micro-wrinkled surfaces manufactured under several amounts of strains, and discuss the possibility of controlling the movement direction of the droplet sliding on the solid surface by gravity. The drag against the droplet sliding is measured when it moves in perpendicular and parallel directions to the wrinkle. The deflection angle of the droplet movement from the gravitational direction is then measured for various experimental conditions. In addition, a theoretical model is proposed to predict the deflection angle and the droplet movement, using the principle of minimum work. The physical background for the deflection is discussed from the comparison of the theoretical model with the experimental results.

2. Experimental method

2.1 Manufacture of micro-wrinkle

The micro-wrinkles were manufactured using buckling phenomenon of thin films coated on the surface

Fig. 1 Roughness curve of micro-wrinkled surface (35% pre-strain).

Fig. 2 Photomicrograph of micro-wrinkled surface (35% pre-strain).

of the base material. Poly (vinyl chloride) (PVC), which transitions into a rubbery state at 80°C, was used as a base material. However, several reports have used metals as solid materials for producing micro-wrinkles. In this study, we used a polymer with small aging of the surface wettability in comparison with metals. Poly (*N*-vinylcarbazole) (PVK) was used as the polymer for the surface thin layer since it has a higher rubbery state transition temperature (190°C) than PVC (80°C). Stretching strain from 16.7%-to 35% was applied to a PVC sample with a 20×1 mm² cross-section in an environmental chamber at a constant temperature of 90°C, using a universal testing machine. The sample was then cooled to an ambient temperature (20°C), and 200 μL of 1.2 wt% dichloroethane solution of PVK was dropped on ~18 cm² area of the PVC surface. The PVK thin film was spin-coated by rotating it at 250 rpm for 10 s and at 2500 rpm for 90 s, using a spin coater (Mikasa MS-B100). Thus, a test plate with a PVK thin film of ~100 nm was formed. The test plate was inserted into the environmental chamber at 90°C to release only the strain of the PVC base material. The micro-wrinkle was then produced from the thin film buckling. Figure 1 shows an example of the measured surface roughness using a shape analysis laser microscope (Keyence VK-X1000). Figure 2 shows an example of a microphotograph of the surface. The 35 % pre-strain shown in the captions indicates the value of pre-strain given to the PVC in the manufacture of micro-wrinkle. Sinusoidal wrinkles were formed on the surface as shown in Figs. 1 and 2, although some inhomogeneities exist. The average roughness was determined from the roughness curve in Fig. 1, and the wavelength λ of the wrinkle was determined from the FFT analysis results.

Table 1 Wavelength, roughness, and contact angles of micro-wrinkled surface.

Specimen	Pre-strain	λ (μm)	Ra (μm)	θ_{PA} ($^\circ$)	θ_{VA} ($^\circ$)	θ_{PR} ($^\circ$)	θ_{VR} ($^\circ$)
S17	16.7%	8.7	0.25	87.7	91.6	68.7	66.9
S19	18.5%	9.4	0.37	87.5	92.3	68.1	67.2
S31	30.8%	9.7	0.56	86.9	96.9	64.2	64.3
S35	35%	12.4	1.08	87.1	100.3	64.2	64.3

Furthermore, the advancing and receding contact angles parallel and perpendicular to the wrinkle (θ_{PA} , θ_{PR}) and (θ_{VA} , θ_{VR}), were measured for distilled water (20°C, density $\rho = 998 \text{ kg/m}^3$, surface tension $\sigma = 72.8 \text{ mN/m}$) under four kinds of specimen plates with pre-strains from 16.7% to 35%. The subscripts P and V represent the parallel and vertical directions to the wrinkle, respectively; while A and R indicate the advancing and receding contact angles, respectively. The measurement method of the contact angle is briefly described: The distilled water droplets were set on the test plate and the liquid was injected (for the measurement of advancing contact angle) or extracted (for the measurement of receding contact angle) with a micro-syringe. To avoid the effect of dynamic wetting, the contact line velocity was set at 0.01 mm/s or less, and the image near the droplet contact line was taken with a still camera. The position at the maximum brightness gradient in the image data obtained was taken as the gas-liquid interface. The interface profile in the range of 0.1 mm near the contact line was approximated by a polynomial and the contact angle was determined from the gradient on the wall surface. The measurement accuracy of the contact angle using this method is approximately $\pm 1^\circ$. The measurement was performed six times under the same experimental conditions, and the average was determined. The standard deviation of the contact angle in this experiment was $\sim 3^\circ$ since the micro-wrinkle surface has some local inhomogeneity. Table 1 shows the measurement results of arithmetic mean roughness Ra , wavelength of wrinkle λ obtained from the roughness curve, and contact angles for four types of specimen plates with different pre-strains. The dependence of λ on pre-strain was not significant under the conditions of this experiment, and wrinkles with λ of $\sim 10 \mu\text{m}$ were observed. Based on the buckling theory of an elastic body, the wavelength of the wrinkle (Volynskii, et al. 2000) is given by:

$$\lambda = 2\pi h \left[\frac{E_f(1-\nu_s^2)}{3E_s(1-\nu_f^2)} \right]^{\frac{1}{2}} \quad (1)$$

where E , ν , and h are Young's modulus, Poisson's ratio, and film thickness, respectively; f and s indicate film and base polymer, respectively. In this experiment, h was $\sim 100 \text{ nm}$, and λ was calculated from Eq. (1) to give $\sim 4 \mu\text{m}$, which is in the same order as the measured values in Table 1. Although the result gives about half the measured value, the degree of agreement is similar to the results obtained in other literatures (Bowden, et al. 1998). The main cause of the discrepancy may be the increase in elastic

Fig. 3 Experimental apparatus to observe droplet sliding on micro-wrinkled surface.

modulus due to the hardening of the surface of the base material.

Although the receding contact angle shows little anisotropy, the anisotropy of the advancing contact angle tends to increase with increasing pre-strain, and shows $\sim 13^\circ$ at the pre-strain of 35%. Hence the resistance to advancing wetting in the direction perpendicular to the wrinkles tended to increase with the roughness of the wrinkles, as shown in Table 1.

2.2 Critical inclination of plate when droplets start to slide

An experiment of sliding water droplet was conducted using the micro-wrinkled test plate fabricated by the method stated in the previous section. Figure 3 shows an outline of the experimental setup. Droplets with a predetermined volume were placed on a horizontal test plate using a micro-syringe. A predetermined value α was then set for the wrinkle, where α indicates the inclination of the wrinkle as shown in Fig. 4. The inclination φ of the test plate from the horizon was increased with a worm gear, as shown in Fig. 3. To evaluate the anisotropy of drag against the droplet motion by gravity, we measured the critical inclinations φ_P and φ_V at which the droplet starts to slide on the plate with $\alpha = 90^\circ$ and $\alpha = 0^\circ$. Meanwhile, the measurement of the critical inclination angle may have an uncertainty based on the sliding criteria, i.e., with the ambiguous criterion by the visual observation, there should be some uncertainty that an angle somewhat larger than the true value may be measured. In addition, since the sliding velocity may be dependent on the viscosity of the droplet, some deviations may appear between the critical angles for different test liquids. In this experiment, the inclination angle of the plate with the worm gear was increased by 0.5° and the magnified image of the droplet front end was observed for 30 seconds. If the droplet is stretched, the rear end is then observed to see if the contact line continuously moves downward for 30 seconds at a speed of 0.01 mm/s or more. Thus, the motions at the front and rear ends of the droplet were alternately checked several times to determine the critical sliding angle φ as the inclination at which both continuous movements were observed. Hence, the sliding angle can be

Fig. 4 Angle β between the sliding direction of droplet and the gravitational direction

determined independently of the physical properties of the test liquid (Katoh, et al. 2006). The measurement was performed six times under the same experimental conditions for the droplets sliding vertically and horizontally to the wrinkle, and the average was taken as the measured value. The uncertainty of sliding angle is $\pm 1^\circ$

. In addition, the angle β between the sliding direction of the 30- μL droplet and the gravitational direction was measured while changing α from 0 to 90° for every 5° , as shown in Fig. 4. The observation was performed by setting the inclination of the plate approximately 1° larger than the φ_V stated above. The measurement was performed three or more times under each experimental condition, and the average value was determined.

3. Experimental results of critical sliding angle

3.1 Theoretical discussion

In this section, φ of the droplet is considered theoretically from a simple model to estimate the anisotropy of drag dependent on the moving direction of droplet parallel or perpendicular to the wrinkle. Figure 5 is a schematic diagram of the contact line of the droplet on the wrinkle with $\alpha = 0^\circ$ and the surface tension σ acting on the line element ds of the contact line. The critical sliding angle can be calculated from the force balance between the resultant surface tension obtained from the integration over the contact line C and the gravitational force. The dynamic balance (Dussan and Chow 1983, Katoh, et al. 2018) is expressed as follows:

(a) Surface tension acting on the contact line (b) Droplet movement on wrinkled surface ($\alpha = 0^\circ$)

Fig. 5 Schematic of droplet contact line.

$$\int_C \sigma \cos \theta \times \cos \eta ds = \rho g V \sin \phi \quad (2)$$

where θ is the local contact angle on the contact line C ; η is the azimuthal angle between the outward normal vector of the element ds and the gravitational direction in the plate surface, as shown in Fig. 5(a); ρ and g are density and gravitational acceleration, respectively; and V is the volume of the droplet. Figure 5(b) represents the quasi-static movement of the droplet from the solid line to the broken line. The receding contact angle should appear on the circumference behind the maximum width of the contact line C , since the contact line recedes to make the surface dry. Similarly, the advancing contact angle appears in front of the maximum width. For $\alpha = 0^\circ$, the receding contact angle in Eq. (2) varies from θ_{VR} to θ_{PR} in the range of azimuthal angle $\eta = 0$ to $\eta = \pi/2$ on the contact line C , as shown in Figs. 5(a) and (b). Moreover, the advancing contact angle varies continuously from θ_{PA} to θ_{VA} in the range of $\eta = \pi/2$ to $\eta = \pi$. Assume that the contact angle changes linearly with η , the following distribution can be written for $\alpha = 0^\circ$:

$$0 \leq \eta < \frac{\pi}{2} : \theta = \frac{2(\theta_{PR} - \theta_{VR})}{\pi} \eta + \theta_{VR} \quad (3a)$$

$$\frac{\pi}{2} \leq \eta \leq \pi : \theta = \frac{2(\theta_{VA} - \theta_{PA})}{\pi} \left(\eta - \frac{\pi}{2} \right) + \theta_{PA} \quad (3b)$$

Note that the contact angle from $\eta = \pi$ to 2π varies in the same manner as Eq. (3). When the droplet slides in a direction parallel to the wrinkle ($\alpha = 90^\circ$), the suffixes of the contact angle in the above equations

should be converted as $P \rightarrow V$ and $V \rightarrow P$. Substituting Eqs. (3a) and (3b) into Eq. (2), the resultant surface tension drag F_{VS} corresponding to the left-hand side of Eq. (2) with respect to the direction perpendicular to the wrinkle ($\alpha = 0^\circ$) can be obtained as follows:

$$F_{VS} = \frac{1}{2} \sigma W \left[\left\{ \frac{1}{\frac{2}{\pi}(\theta_{PR} - \theta_{VR}) + 1} - \frac{1}{\frac{2}{\pi}(\theta_{PR} - \theta_{VR}) - 1} \right\} \cos \theta_{PR} - \left\{ \frac{1}{\frac{2}{\pi}(\theta_{PR} - \theta_{VR}) + 1} + \frac{1}{\frac{2}{\pi}(\theta_{PR} - \theta_{VR}) - 1} \right\} \sin \theta_{VR} \right] \\ + \frac{1}{2} \sigma W \left[- \left\{ \frac{1}{\frac{2}{\pi}(\theta_{VA} - \theta_{PA}) - 1} + \frac{1}{\frac{2}{\pi}(\theta_{VA} - \theta_{PA}) + 1} \right\} \sin \theta_{VA} + \left\{ \frac{1}{\frac{2}{\pi}(\theta_{VA} - \theta_{PA}) - 1} - \frac{1}{\frac{2}{\pi}(\theta_{VA} - \theta_{PA}) + 1} \right\} \cos \theta_{PA} \right] \quad (4)$$

where W represents the maximum width of the contact line. The drag F_{PS} in the direction parallel to the wrinkle ($\alpha = 90^\circ$) can be obtained by converting the suffix in Eq. (4) as $P \rightarrow V$ and $V \rightarrow P$. From F_{VS} and F_{PS} , φ_V and φ_P can be calculated as follows:

$$\varphi_V = \sin^{-1} \left[\frac{F_{VS}}{\rho g V} \right] \quad (5)$$

$$\varphi_P = \sin^{-1} \left[\frac{F_{PS}}{\rho g V} \right] \quad (6)$$

Now we consider the surface tension drag in an isotropic surface on which the contact angles are constant in the circumferential direction. Given that $\cos \eta ds = dx$ (where x is the coordinate in span-wise direction) as shown in Fig. 5(a) and assume that the receding contact angle (θ_{VR} or θ_{PR}) is constant in the range of $\eta = 0$ to $\pi/2$ while the advancing contact angle (θ_{VA} or θ_{PA}) is constant in the range of $\eta = \pi/2$ to π , the surface tension drag F_{PS} is given by:

$$F_{PS} = \sigma W (\cos \theta_{PR} - \cos \theta_{PA}) \quad (7)$$

When the droplet slides vertically to the wrinkle, F_{VS} can be obtained by converting P in Eq. (7) to V . From the above equation, φ_V and φ_P can be obtained for the isotropic surface by the following equation (Furmidge 1962, Katoh, et al. 2006):

$$\varphi_V = \sin^{-1} \left[\frac{\sigma W}{\rho g V} (\cos \theta_{VR} - \cos \theta_{VA}) \right] \quad (8)$$

$$\varphi_P = \sin^{-1} \left[\frac{\sigma W}{\rho g V} (\cos \theta_{PR} - \cos \theta_{PA}) \right] \quad (9)$$

The maximum width W of the droplet is required in the calculation of the critical angle in Eqs. (5), (6), (8),

and (9). In this experiment, the test plate was tilted to measure the critical angle after placing droplets of a specified volume on the horizontal surface. For isotropic surfaces, W is kept constant when the plate is tilted from the horizon (Kato, et al. 2006). Therefore, W can be obtained from the profile of an axisymmetric droplet placed in the horizontal plane. The profile of the axisymmetric droplet can be determined from the following Laplace's equation, which represents the force balance between the hydrostatic pressure and the surface tension at the gas-liquid interface (Adamson 1990, Laho, et al. 1996).

$$\sigma \left[-\frac{\frac{d^2 z}{dr^2}}{\left\{1 + \left(\frac{dz}{dr}\right)^2\right\}^{3/2}} - \frac{\frac{dz}{dr}}{r \sqrt{1 + \left(\frac{dz}{dr}\right)^2}} \right] = -\rho g z + \Delta P \quad (10)$$

$$\text{Boundary condition: } r = 0: z = 0, \frac{dz}{dr} = 0 \quad (11)$$

where r is the radial coordinate, z is the vertical coordinate with $z = 0$ at the top of the droplet, and ΔP represents the pressure inside the droplet at $z = 0$. Assume an appropriate value for ΔP , the solution $z(r)$ of Eq. (10) under the boundary condition of Eq. (11) can be obtained using Runge–Kutta method. Meanwhile, the droplet was placed by a syringe to ensure a predetermined volume. Since the contact line spreads on the solid surface, the advancing contact angle θ_A appears on the wall. The volume integration of the droplet is performed from $z = 0$ using the solutions of Eqs. (10) and (11). The angle of the gas-liquid interface to the horizon should be the advancing angle θ_A at the z -coordinate where the prescribed volume V is reached. Hence, ΔP can be determined using Newton's method, to satisfy the above condition. From the solutions of Eq. (10) and ΔP , W can be obtained from the radius at the z -coordinate where $\theta = \theta_A$ is satisfied. Since the contact angle is anisotropic in this experiment, the above method cannot be used directly. However, the difference between θ_{VA} and θ_{PA} is small, as given in Table 1. Thus, the droplet width for each θ_{VA} and θ_{PA} was obtained by the method described above, and their average was used as W . The observed droplet width is almost consistent with the calculated value, with an error of $\sim 10\%$. When the pre-strain is large (35%), however, the discrepancy becomes $\sim 15\%$, which gives a noticeable influence on the theoretical value of ϕ . In the following section, we will discuss the uncertainty of the sliding angle affected by the droplet width.

3.2 Experimental results and discussion

The droplet sliding angle for $\alpha = 0^\circ$ and 90° was measured with various droplet volumes. Figure 6 shows a summary of the results for two kinds of specimen plates. The results obtained from Eqs. (5), (6),

(8), and (9) are drawn together in each figure for comparison. The φ_V (red plot: droplets slide vertically to the wrinkle) is greater than φ_P (blue plot: droplets slide in parallel to the wrinkle). Although φ_P differs by only several degrees from φ_V for pre-strain 16.7% as shown in Fig. 6(a), φ_V for strain 35% is larger than φ_P by more than 10° , as shown in Fig. 6(b). Thus, the surface tension drag is strongly dependent on the direction of the droplet movement to the wrinkle. When the theoretical results are compared with the experimental results, the measurement results of φ_V in both figures are almost consistent with the result of Eq. (5), based on contact angle distribution around the contact line. On the other hand, the measured results for φ_P are close to the values obtained from Eq. (9) where constant contact angles were assumed.

(a) Specimen S17 (pre- train 16.7%)

(b) Specimen S35 (pre- strain 35%)

Fig. 6 Critical inclination angle when the droplet starts to slide on a surface with micro-wrinkle (red plots: $\alpha = 0^\circ$, blue plots: $\alpha = 90^\circ$. Solid lines indicate theoretical results with variable contact angles stated by Eqs. (5) and (6). Broken lines indicate theoretical results with constant contact angle stated by Eqs. (7) and (8))

Fig. 7 Photomicrograph of contact line of droplet (pre-strain 35%. Contact lines are highlighted by blue and red solid lines in each figure).

Note in Fig. 6(b) that the results of Eq. (9), where the practically observed droplet width W was used instead of the theoretical width stated in the previous section, are also shown. When the strain was increased, the maximum width when the droplet starts to slide at the critical angle was slightly smaller than the width initially set on the horizontal plate. The droplet may be strongly restrained in the groove (wrinkle) direction when the droplets slide on the surface with large roughness. In this case the measured sliding angles are consistent with Eq. (9) where the measured W was used, as shown in Fig. 6(b). The experimental results of φ_V and φ_P for other specimens (pre-strain 18.5% and 30.8%) also agree with the theoretical results in a similar manner as in Fig. 6 although the measurement results of φ_V are slightly smaller than the results obtained from Eq. (5).

As stated above, the sliding angle shows different behaviors between $\alpha = 0^\circ$ and 90° . To examine the differences in the behavior when the droplet starts to slide, the profile of contact line was observed by photomicrography. Figure 7 shows an example for specimen S35 (pre-strain 35%). When the droplet slides vertically to the wrinkle, the contact line shows a wavy pattern, as shown in Fig. 7(a). On the other hand, when the droplet slides in parallel to the wrinkle as shown in Fig. 7 (b), the contact line has a profile with sharp steps for each wavelength of the wrinkle. The movement of the contact line is strongly restrained by the groove, and each contact line element exclusively moves along the groove, as shown in Fig. 7(b). Since the surface tension acts normal to each contact line element, φ may be close to the results obtained from Eq. (9), where the receding and advancing contact angles are fixed as θ_{PR} and θ_{PA} parallel to the groove. On the other hand, the distribution of the contact angle in Fig. 7(a) may appear in the circumferential direction of the contact line. Hence, φ_V approaches the value estimated by Eq. (5) in which the contact angle distribution was assumed.

4. Sliding direction of droplets

4.1 Theoretical consideration

A droplet with 30 μL was set on the surface with various angles α , and the droplet deflection angle β

from the gravitational direction was measured, as shown in Fig. 4. Meanwhile, we consider a simple theoretical model to predict the deflection before showing the experimental results. In the previous section, the drag caused by surface tension shows that the anisotropy is dependent on whether the droplet slides vertically or parallel to the wrinkle. When the droplet is set on the surface with inclined wrinkles, it may slide in the direction where the work of droplet is minimized, i.e., the sum of work against the surface tension drag and the decrease of gravitational potential energy is minimized. Here it is assumed that the drag F_{VS} in the direction perpendicular to the wrinkle and F_{PS} in the direction parallel to the wrinkle are obtained from Eqs. (4) and (7), respectively.

Figure 8 is a schematic of the contact line movement on a surface with wrinkles. The wrinkle is inclined at α and the droplet slides in a direction β deflected from the gravitational direction. The overall movement of the contact line $\vec{AC}$ is considered to be a combination of movement of the lines $\vec{AB}$ and $\vec{BC}$ in directions parallel and perpendicular to the groove of the wrinkle, respectively; as shown in Fig. 8. The work W_S related to the surface tension drag can be estimated from F_{VS} and F_{PS} . If we consider the scalar product between the drag in lines $\vec{AB}$ or $\vec{BC}$ and the moving direction of contact line; and also consider the length of each vector, the W_S per unit length movement of the contact line can be obtained by the following relation:

Fig. 8 Schematic of contact line movement inclined β from gravitational direction on surface with micro-wrinkle.

$$W_s = F_{VS} \cos^2(\alpha + \beta) + F_{PS} \sin^2(\alpha + \beta) = F_{VS} + (F_{PS} - F_{VS}) \sin^2(\alpha + \beta) \quad (12)$$

On the other hand, E_P of the potential energy change of the droplet can be evaluated by the following equation:

$$E_P = -\rho g V \sin(\varphi_V + \Delta\varphi) \cos \beta \quad (13)$$

where φ_V indicates the critical sliding angle perpendicular to the wrinkle. $\Delta\varphi$ was set at 1° in this experiment, as described in Section 2. The sum of Eqs. (12) and (13) gives the total energy change E when the droplet travels a unit length on the test plate, given as:

$$E = F_{VS} + (F_{PS} - F_{VS}) \sin^2(\alpha + \beta) - \rho g V (\varphi_V + \Delta\varphi) \cos \beta \quad (14)$$

The deflection angle β is obtained by minimizing E in Eq. (14) as:

$$\frac{\partial E}{\partial \beta} = (F_{PS} - F_{VS}) \sin 2(\alpha + \beta) + \rho g V \sin(\varphi_V + \Delta\varphi) \sin \beta = 0 \quad (15)$$

Thus, β obtained from the above equation was compared with the experimental results.

4.2 Experimental results of deflection angle

The deflection angle β was measured for four types of specimens shown in Table 1. The results are shown in Fig. 9, where the theoretical results obtained from Eq. (15) are drawn by solid curves as well as experimental plots. However, the results of only three kinds of specimens are shown in the figure as there

Fig. 9 Deflection angle from gravitational direction for a droplet sliding on surface with micro-wrinkles (Strains: 16.7%, 18.5%, and 30.8%)

was little difference between the experimental and theoretical results for pre-strains 30.8% and 35%. When specimens with pre-strain 30.8% and 35% are compared, the difference in the surface tension drags ($F_{PS}-F_{VS}$) for pre-strain 35% in Eqs. (14) and (15) is larger by $\sim 10\%$. On the other hand, the gravitational potential $\rho g V \sin(\varphi_v + \Delta\varphi_v)$ is larger for pre-strain 35% by $\sim 10\%$ such that β is equal for both specimens. Since the drag and gravitational potential increase by almost the same ratio from 30.8% to 35% strain, no difference may be observed in the deflection angle.

As shown in Fig. 9, β increases with the strain while the experimental results exhibit a maximum β between $\alpha = 40^\circ$ and 60° . In the range of this experiment, it is possible to deflect the sliding direction of droplets to $\sim 20^\circ$ from the gravitational direction on a surface with micro-wrinkles.

When the theoretical values obtained in the previous section are compared with the experimental results, it is possible to roughly estimate the deflection angle from the proposed model, although some deviation may exist from the experimental results. The maximum β appears at a smaller α in the theoretical model than in the experimental results. In the theoretical model, horizontal and vertical drags of surface tension were simply added to obtain the work of drag. However, in the actual system, the movement of contact line may be more strongly restricted in the parallel direction to the wrinkles. Hence, the maximum β may appear at a larger α in the experimental results than in the theoretical model. However, since the values of maximum β in each strain roughly agrees with the calculated results, the droplet slides in the direction where the work of the contact line (i.e., the work of the drag and the gravitational potential) is minimized.

5. Summary

The tensile strain in the range 16.7–35% was applied to the base polymer (PVC) and a micro-wrinkled surface with wavelength 8–12 μm was manufactured, based on the buckling phenomenon of PVK film spin-coated on the base polymer. The advancing contact angle parallel and perpendicular to the wrinkle showed an anisotropy of $\sim 10^\circ$ or more.

The critical sliding angles of the droplets in the direction parallel and perpendicular to the wrinkle were measured experimentally. The sliding angle in the direction perpendicular to the wrinkle can be determined from the force balance between surface tension and gravitational force where azimuthal distribution of the contact angle was assumed. On the other hand, the sliding angle in the parallel direction to the wrinkle can be obtained by the model where the contact angle is assumed to be constant.

When the droplet was set on the surface with inclined wrinkle, it could be deflected in the moving direction from the gravitational direction by a maximum of $\sim 20^\circ$. The deflection could be determined from the condition of minimum work of the contact line movement.

Nomenclature

Roman symbols

E : Energy change of droplet per unit length [J/m];
 E_P : Potential energy change of droplet per unit length [J/m];
 F_{PS} : Drag of surface tension parallel to wrinkle [N];
 F_{VS} : Drag of surface tension perpendicular to wrinkle [N];
 g : Gravitational acceleration [m/s²];
 r : Coordinate in radial direction;
 Ra : Arithmetic average roughness [m];
 s : Coordinate along contact line [m];
 V : Liquid volume [m³];
 W : Droplet width [m];
 z : Coordinate in the upward direction from top of droplet [m].

Greek symbols

α : Oblique angle of micro-wrinkle [°];
 β : Deflection angle of moving droplet [°];
 η : Azimuthal angle on contact line [°];
 θ : Local contact angle [°];
 ρ : Liquid density [kg/m³];
 σ : Surface tension [N/m];
 φ : Critical sliding angle of droplet [°].

Subscripts

A: Advancing;
P: Parallel to wrinkle;
V: Perpendicular to wrinkle;
R: Receding.

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