

Slip behavior in polymethylmethacrylate films in dependence of self-assembled monolayer wettability



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ABSTRACT

The slip behavior of polymethylmethacrylate (PMMA) films prepared on self-assembled monolayers (SAM) supported by Si substrate was investigated according to the wettability of the SAM. To this end, the dewetting of thermally annealed PMMA films was measured varying the surface energies of underlying SAM. Total surface energy (γ^t) of SAM increased with increasing UV exposure time. At surface energy of $<31.3 \text{ mJ/m}^2$, the PMMA films showed slip behavior; radius of holes (R) $\propto t^{0.68-0.72}$, where t is dewetting time. The slip behavior seems to be dominated by the viscous friction between the PMMA films and the SAM. As t increased, slip behavior disappeared, $R \propto t^{0.34-0.39}$. At surface energy of $>42.0 \text{ mJ/m}^2$, the PMMA films did not show slip behavior, $R \propto t^{0.45}$. It means that interface effects between PMMA films and SAM layers increase with increasing of γ of SAM layers, and then the molecular interaction in the PMMA films increases. The spreading coefficient (S) of the PMMA films approached positive number for UV exposure times between 0 s and 300 s. We concluded that the stability of the PMMA films can be simply controlled by UV-ozone treatment on the SAM layers.

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1. Introduction

Polymer film dewetting has been studied extensively over the past several decades [1–7]. The polymer films play an important role in industrial and technological applications including bio-membranes [8], patterned technology [9], micro-devices [10], insulating layers [11], and lithography [12].

Reiter's first study of the growth of holes in polystyrene (PS) films ($<100 \text{ nm}$ in thickness) on Si substrates upon annealing above the glass transition temperature (T_g) [13] has been followed by numerous investigations of other systems that can observe polymer films dewetting from underlying substrates [14–16]. Reiter found that films are detached according to steps of (i) holes forming, (ii) hole-growing and rim-forming, and finally (iii) droplet-creating from contacting of holes.

In general, two distinct dewetting behaviors of polymer films have been observed: nucleation and growth dewetting, and spinodal dewetting. The former is initiated by defects or impurities

(heterogeneous nucleation). The latter occurs when capillary waves in the polymer films are spontaneously amplified and intensified, resulting in film breakage, which initiates film dewetting [17–20].

In recent years, the slip kinetics of polymer films during dewetting has been investigated both experimentally and theoretically, which occurs in homopolymer films [21] and polymer films on the SAM [22,23]. The slip length (b) is the distance from the substrate at which the velocity approaches zero. The slip length can be expressed as $b = a(N^3/N_e^2)$, where a , N , and N_e are a monomer size, the index of polymerization, and the threshold for polymer entanglement, respectively [24]. The kinetics of hole growth is determined by the relationship between the radius of holes (R) that form on the polymer film during dewetting, and the dewetting time (t) [25].

The dewetting of thin films is initiated by solvent-induced [26,27] or thermal annealing treatment [28]. As hole growth initiates, R grows as the viscous dissipation ($R \propto \exp(t/\tau)$), where t and τ are the dewetting time and the translational relaxation time of the polymer chain, respectively. As hole growth proceeds, R grows linearly ($R \propto t$), indicative of no-slip behavior. After reaching a transition point, R grows as $t^{2/3}$ ($R \propto t^{2/3}$), indicative of slip behavior as viscous friction.

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The wettability of heterogeneous surfaces can be measured by the contact angle of a water droplet using Cassie's equation. Xu et al. studied the dewetting of PS films on a heterogeneous surface [29]. He studied the slip of PS films on a Si substrate modified with trimethylchlorosilane (TMS). PS films prepared on a surface coated with TMS had a heterogeneous grafting density, in contrast with the homogeneous Si substrate. The complexity of the system including TMS precluded characterization of the PS film slip behavior.

We investigated the dewetting of the PMMA films by controlling the wettability of the underlying SAM layers built up from using octadecyltrichlorosilane (ODTS) on Si substrates [30].

The hydrophilicity of the SAM prepared on Si substrate could be varied systematically by varying the UV exposure time. We monitored the formation of holes and rims in the PMMA film using optical microscopy (OM) with error estimation. In this study, the slip behavior appeared as the first stage of the dewetting process at the lower surface energies.

2. Experimental section

2.1. Materials and films preparation

Polymer thin films were coated onto SAM prepared on the native oxide layer of Si (100) wafers. The Si wafers were cleaned using a piranha solution (70 vol% H₂SO₄ and 30 vol% H₂O₂) for 30 min at 90 °C and were rinsed with distilled water several times. PMMA (Mw 70,000 g/mol, PDI = 1.3, T_g = 119.1 °C) and toluene were purchased from Polymer Source, and Aldrich, respectively. ODTS which was used to prepare the SAM was purchased from Gelest. PMMA films were prepared by spin-coating a toluene solution containing 1 wt% PMMA at 2000 rpm for 60 s onto the SAM supported by the Si wafers. To remove residual solvent, the PMMA films were heated in a vacuum oven for 48 h at 150 °C. The average PMMA film thickness was about 40 ± 1 nm, measured by ellipsometry (VASE, J. A. Woollam Co.). Thermal property was measured using a thermogravimetric analysis (TGA, model TG/DTA-6300). During the measurements, dry nitrogen gas was used for purging with a flow rate of 80 mL/min, and a ramping rate of 10.0 °C/min was employed.

2.2. SAM preparation

SAM layers were prepared on the Si substrate as follows. A beaker charged with anhydrous toluene was placed in a chamber at room temperature. Si wafers were introduced into the beaker. 10 mM ODTS solution dissolved in anhydrous toluene (Aldrich) was added to the beaker, and SAM layers were allowed to self-assemble on the Si wafers over a period of 3 h under nitrogen. The Si wafers were removed from the ODTS solution, rinsed with toluene and ethanol twice, and then baked in a vacuum oven at 120 °C for 20 min. After baking, the substrates were cleaned by ultrasonication in toluene and ethanol. The SAM thicknesses were about 14–18 Å, measured by ellipsometry. SAM layers were then exposed to UV light (AH1700, Ahtech LTS Co.) for varying exposure times. The various PMMA films (0–300) are labeled according to the UV exposure time. For example, PMMA0 denotes the SAM layers not exposed to UV light, and PMMA100 denotes the SAM layers exposed to UV-ozone treatment for 100 s.

2.3. Wettability of the SAM

To determine the wettability of the SAM, the each surface energy (γ) of the SAM was calculated using the "Owens–Wendt equation", using both the contact angles of droplets of diiodomethane (DIM) and distilled water (DI) on the SAM.

2.4. Thermal dewetting of thin films

Dewetting of the PMMA films on the SAM did not occur spontaneously at room temperature. Thus, thermal annealing at 250 °C was applied to initiate dewetting. PMMA films were placed on an OM sample stage and thermally annealed at 250 °C using a temperature controller. An OM (Leitz Wetzlar) with a digital CCD camera was used to observe the changes in the morphologies of the PMMA films in situ as a function of the dewetting time. After acquisition of the images, image analysis was performed to determine R and W using the Photoshop CS3 software. These values were transformed into real dimensions using a scale bar.

3. Results and discussion

Fig. 1 shows images of the DI droplets on the variously treated SAM. The contact angles of a DI droplet (≈ 1.00 mg) after UV-ozone treatment of 0, 60, 100, 180, and 300 s were 108°, 93°, 86°, 73°, and 61°, respectively. The hydrophilicity of the SAM surfaces increased with UV exposure time, which induced oxidation of the $-\text{CH}_3$ groups to $-\text{COOH}$ groups in the SAM layers [31]. Total surface energies (γ^t) calculated from the DIM and DI contact angles on the SAM, are shown in Table 1. The values of γ^t for the SAM surfaces increased with increasing the UV exposure time. γ^t is the sum of the dispersive (γ^d) and polar (γ^p) components. As the UV exposure time increased, γ^d increased from 26.1 to 38.9 mJ/m², and γ^p increased from 0.0 to 11.9 mJ/m², respectively. In previous study, we found by XPS measurement that the relative atomic percent of O1s increases with increasing the surface energy. UV-ozone treatment onto the SAM layers is a good method for stabilizing the PMMA films by improving the wettability of the SAM.

Fig. 2 shows OM images of the PMMA films on the SAM as a function of thermal annealing time. PMMA0 films couldn't be deposited on the SAM due to the hydrophobicity of the $-\text{CH}_3$ groups of SAM layers. Fig. 2a–c shows the morphologies of the surface of PMMA60. Fig. 2a shows the surface of the PMMA film without thermal annealing. As dewetting of the films proceeded, the formation of the holes was formed and enlarged as shown in Fig. 2b and c. Similar properties were observed for PMMA100 and

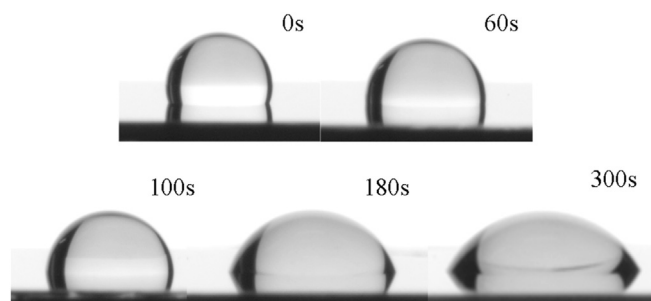


Fig. 1. Images of DI droplets upon the SAM of various hydrophilicities: DI droplet (1.00 mg) on the SAM surface with UV exposure times of 0, 60, 100, 180, and 300 s, respectively.

Table 1

Total surface energy of the SAM as a function of the UV-ozone treatment.

| UV exposure time (s) | γ^t (mJ/m ²) | γ^d (mJ/m ²) | γ^p (mJ/m ²) |
|----------------------|---------------------------------|---------------------------------|---------------------------------|
| 0 | 26.1 | 26.1 | 0 |
| 60 | 31.3 | 29.8 | 1.5 |
| 100 | 34.8 | 31.7 | 3.1 |
| 180 | 42.0 | 34.8 | 7.2 |
| 300 | 50.8 | 38.9 | 11.9 |

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