468 *Macromolecules* **1994,** *27,* 468–471

Dewetting and Slippage of Microscopic Polymer Films

C. Redon, J. B. Brzoska, and F. Brochard-Wyart*

Section de Physique et Chimie, Institut Curie, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

Received July 7, 1993; Revised Manuscript Received September 21, 1993[●]

ABSTRACT: Films of poly(dimethylsiloxane) deposited on silanized silicon wafers are unstable and dewet by nucleation and growth of dry patches. We have monitored the growth of holes: (i) In thick films (that is, for film thicknesses, e, larger than 10 μm), holes open at constant velocity. The radius of the dry patch, R, grows linearly with time, t. (ii) In microscopic films ($e < 1$ μm), we find $R(t) \sim t^{0.66\pm0.08}$. We interpret this result by a slippage of the polymer chains on the solid surface.

An entangled polymer melt does not flow like the usual liquid. de Gennes[1] predicted that polymers slip on a smooth, passive surface. The slippage is characterized by the extrapolation length b, defined as the distance from the wall at which the velocity extrapolates to zero. For the usual liquids, $b \sim a$, where a is a molecular size. For entangled polymers, $b \sim a(N^3/N_e^2)$ where N is the index of polymerization and N_e the threshold for entanglement. For $N = 10^3$, $N_e \sim 10^2$, $a = 3$ Å, and $b \sim 30$ μm. A pressure gradient parallel to the film induces the usual Poiseuille flow in thick films ($e \gg b$) but plug flow in thin films ($e < b$): the polymer moves like a solid and the viscous dissipation is confined at the liquid/solid interface.

We investigate here the rheology of the polymer melt by monitoring the dynamics of dewetting of poly(dimethylsiloxane) (PDMS) silicone oils deposited on nonwettable silanized silicon wafers. We have studied previously the dewetting of thick films, which are metastable and dewet by nucleation and growth of a dry patch.[2] We found that the hole, surrounded by a rim which collects the liquid removed from the dry region, opens at constant velocity, $V = \mathrm{d}R/\mathrm{d}t$, where $R(t)$ is the radius of the dry spot. We showed both theoretically and experimentally that $V = (1/12(2)^{1/2}L)V^*\theta_e^3$, where θ_e is the equilibrium contact angle, V^* a characteristic velocity ($V^* = \gamma/\eta$, using γ, the liquid surface tension, and η, its viscosity; for example, $V^* = 0.367$ and 0.073 mm/s for PDMS of molecular weights, M_w, 116 500 and 204 000, respectively), and L a logarithmic prefactor describing the divergence of the viscous dissipation in a liquid corner. We noticed a dependence of L upon molecular weight, suggesting a slippage of the polymer, as shown in the discussion.

Our aim here is to study the dewetting of ultrathin polymer films,[3] to see if the polymer chains flow or slip at the solid surface.

The choice and realization of a smooth, grafted silicon surface is one of the keypoints of the present experiments. To prepare extremely high-quality hydrophobic substrates, we have used the results of previous work[4] on temperature-controlled silanization of silicon wafers. The grafting technique is fully described in ref 5: the silicon wafer is thoroughly cleaned in six stages, the last one being photochemical,[6] and then immediately dipped into a 10^{-3} M solution of n-hexadecyltrichlorosilane (HTS) in 20% carbon tetrachloride and 80% tetradecane. The solution is kept at a temperature of 13 °C, which is below the transition temperature T_c of HTS. The reaction is then allowed to proceed for 10 min, at which point the substrate is withdrawn from the reaction bath and stored without

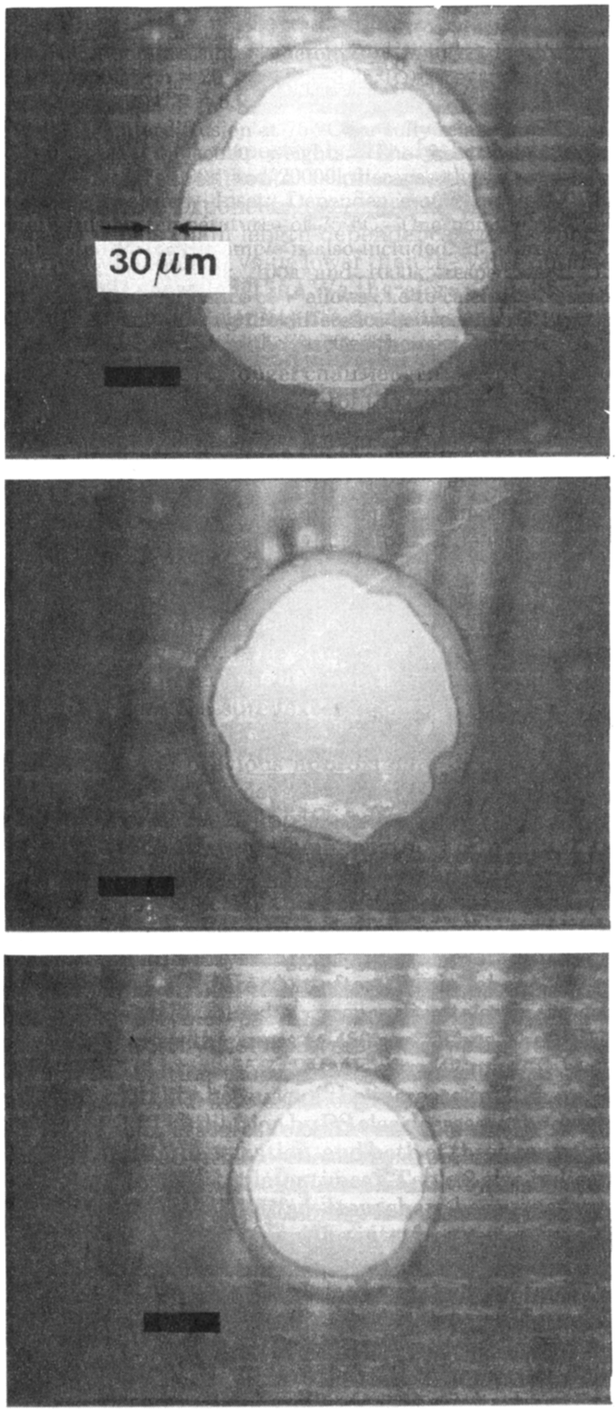

Figure 1. Snapshot of an expanding dry patch in a microscopic film of PDMS of molecular weight 116 500 deposited on a model silanized silicon wafer. The film thickness is about 400 nm.

[●] Abstract published in *Advance ACS Abstracts,* December 1, 1993.

0024-9297/94/2227-0468$04.50/0

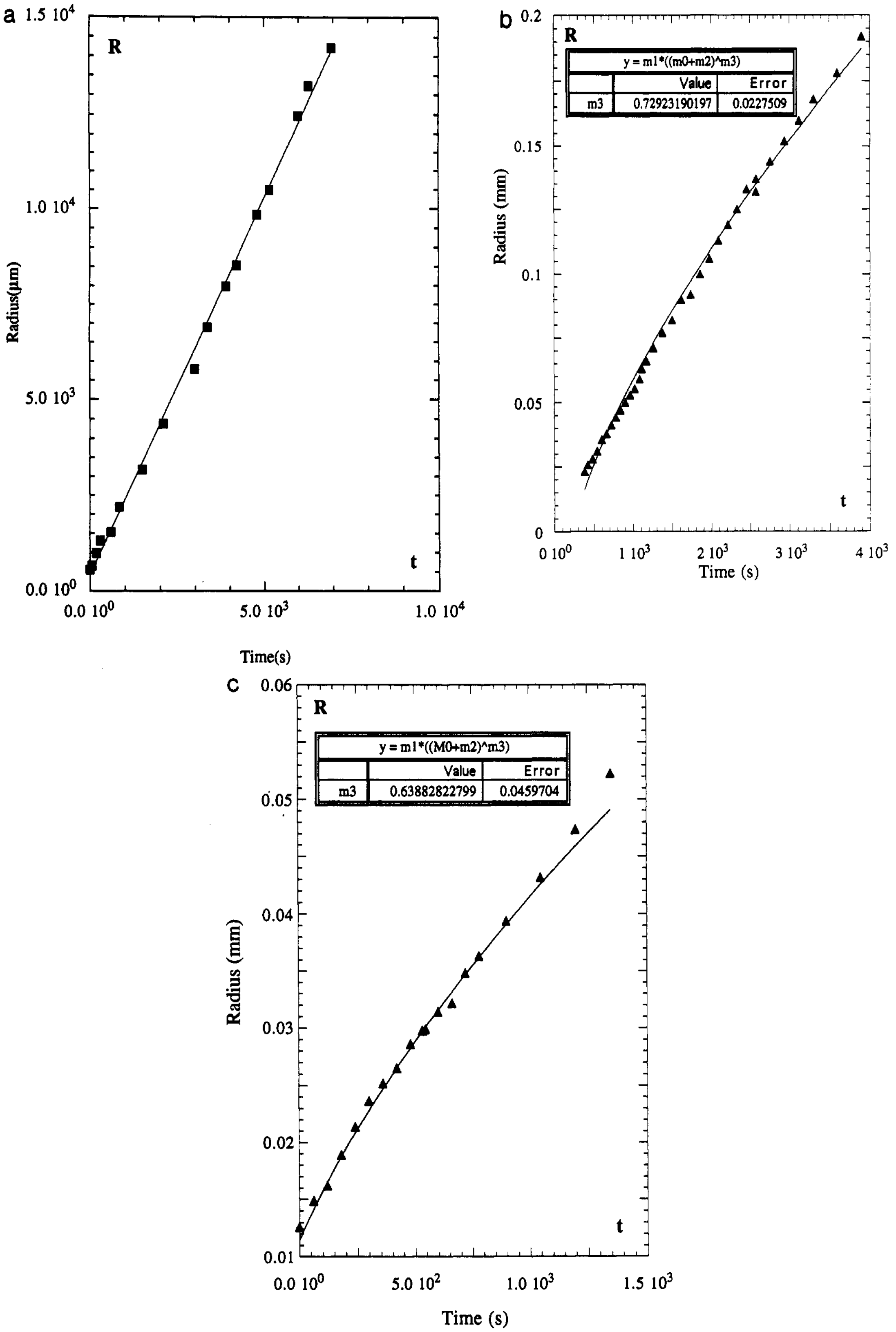

Figure 2. Time dependence of the mean radius R of the dry region: (a) for a thick PDMS film on a fluorinated silicon wafer; (b and c) for thin PDMS films on a silanized support and of molecular weight 116 500 (b) and 204 000 (c).

any further treatment. The modified substrate has a typical γ_c of 20.3 ± 0.4 mN/m and very low hysteresis. For n-PDMS of M_w = 62 700, we have measured $\theta_a = 18°$ and $\theta_r = 16°$, where θ_a (θ_r) is the advancing (receding) contact angle.

PDMS films of uniform thickness, e, are prepared by spin-coating (i) a melt, to achieve macroscopic films ($e \sim$ 20–50 μm) (the thickness is deduced from the weight of the wafer before and after deposition of the film); (ii) a polymer solution in hexane, to achieve microscopic films ($e < 0.5$ μm) (the thickness is then measured by Newton color interferometry).

Thick films are metastable, and the initial hole is created by blowing a dry air jet perpendicular to the surface. Thin films are unstable, and holes open spontaneously. In the late stage of the dewetting process, rims get into contact and break into droplets (Rayleigh instability), arranged in a polygonal pattern as described in ref 8.

Table I. Exponent Values, x_i, and Their Errors, σ_i, for the Fit $R \sim A(t + B)^x$, Using Two Molecular Weights

x	σ
(a) $M_w = 116\,500$	
0.56	0.04
0.73	0.01
(b) $M_w = 204\,000$	
0.67	0.04
0.78	0.08
0.73	0.03
0.57	0.02
0.72	0.02
0.59	0.06

[a] Using these results, one gets $\sum_{i=1}^{6}(x_i/\sigma_i^2) = 4711.60$ and $\sum_{i=1}^{6}(1/\sigma_i^2) = 7132.9$ for the weighted mean value $\mu = 0.66$.

We follow the growth of one single hole, using a microscope and a videocamera. Each frame is acquired in $^1/_{24}$ s with a spatial resolution of 10 μm. Figure 1 shows the birth and growth of a hole in a microscopic film of PDMS of molecular weight 116 500. The hole appears circular, and the liquid removed from the dry patch accumulates into a visible rim. We have plotted in Figure 2 the radius $R(t)$ of the dry patch for a thick film of PDMS ($M_w = 116\,500$) deposited on a modified fluorinated silicon wafter ($\gamma_c < 15$ mN/m) (Figure 2a) and also the radius $R(t)$ for microscopic films deposited on model grafted silanized silicon wafers (Figure 2b,c), using two molecular weights: $M_w = 116\,500$ and $M_w = 204\,000$. We clearly see on Figure 2a that R grows linearly with time over a large time scale. The radii range varies from 0.1 to 20 mm; the growth velocity is about $V_1 = 1.8$ μm/s for a large equilibrium contact angle of about 50°. (It is interesting to remark that the same macroscopic film of the same 116 500 M_w PDMS, deposited on our silanized silicon wafer, dewets with a constant velocity $V_2 = 54 \pm 3$ nm/s for an equilibrium contact angle of 16°. These results are in perfect agreement with our previous work[2] since $V_1/V_2 = (\theta_1/\theta_2)^3$). On the contrary, for microscopic films, the $R(t)$ curve can no longer be fitted by a straight line but corresponds with a very good precision to a power law of the form $R(t) = a(t + t_0)^x$ where $x = 0.73 \pm 0.01$ in case b and $x = 0.67 \pm 0.04$ in case c. The holes open spontaneously, and the initial time $t = 0$ is not known; it is thus called t_0 in the fit. Table 1 shows the different values obtained for x, using these two polymer molecular weights. The mean value is then $x = 0.66 \pm 0.08$.

Drying is controlled by a competition between capillary forces and viscous flows,[1] and the dewetting of thick films is well described by hydrodynamic theories, which assume no slip at the solid/liquid interface. We extend these models to the case of a strong polymer slippage. The motion of the moving rim (Figure 3a) of size $l = x_A - x_B$ (where A and B are the two contact lines which limit the rim) can be derived from a balance between the driving capillary forces F_d

$$F_d = \gamma_{sl} + \gamma - \gamma_{so} = \frac{1}{2}\gamma\theta_e^{\,2} \qquad (1)$$

where γ_{ij} are the solid/liquid, liquid/gas, and solid/gas interfacial tensions, and the friction force exerted by the solid on the moving liquid. Using the viscous stress $\sigma_{xz}(0)$, one gets

$$F_v = \int_{x_A}^{x_B} \sigma_{xz}(0)\,\mathrm{d}x \qquad (2)$$

In the lubrication approximation,[7] the flow $v_x(z)$ of the rim of contour $\zeta(x)$, moving at uniform velocity V, is a Poiseuille flow which satisfies the conditions

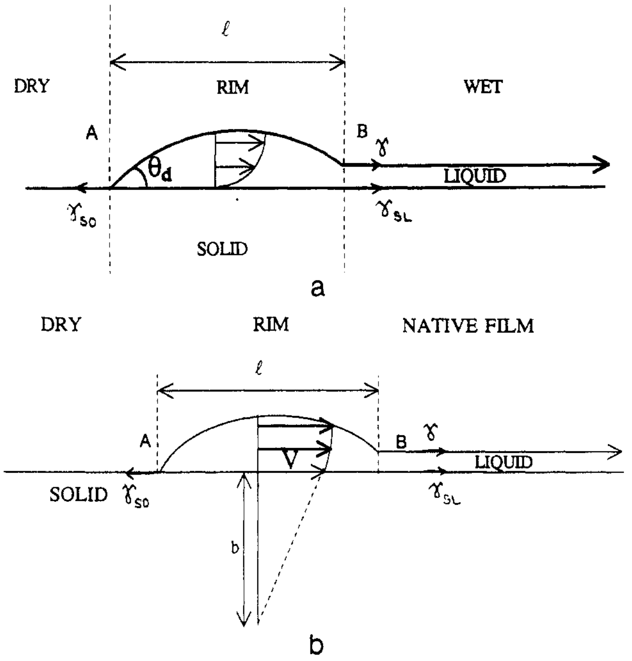

Figure 3. Opening of a microscopic hole in a film of native thickness e: the flows in the moving rim are represented for films thicker (a) or thinner (b) than the extrapolation length b. In case a, the contact angle is θ_d. It is related to the velocity V through the Tanner law.[7] In case b, the viscous dissipation is confined at the solid/liquid interface. The contact angle in A is now the equilibrium contact angle θ_e.

$$\int_0^{\zeta} v_x(z)\,\mathrm{d}z = \zeta V \qquad \text{(uniform motion)}$$

$$\left(\frac{\partial v_x}{\partial z}\right)_{z=\zeta} = 0, \qquad \left(\frac{\partial v_x}{\partial z}\right)_{z=0} = \frac{v_x(0)}{b} \qquad \text{(slip)}$$

It leads to

$$v_x(z) = \frac{3V}{1 + 3b/\zeta}\left[\frac{-z^2}{2\zeta^2} + \frac{z}{\zeta} + \frac{b}{\zeta}\right] \qquad (3)$$

The viscous stress $\sigma_{xz}(0)$ is then

$$\sigma_{xz}(0) = \eta\frac{V}{\zeta/3 + b} \qquad (4)$$

and the balance $F_v = F_d$ gives

$$\int_{x_A}^{x_B} \eta\frac{V}{\zeta/3 + b}\,\mathrm{d}x = \frac{1}{2}\gamma\theta_e^{\,2} \qquad (5)$$

Thick Rims. Usual Poiseuille Flows (Figure 3a). If the maximum thickness of the rim, $\theta_e{*}l$ is larger than b, the dissipation is dominated in the two liquid wedges near A and B contact lines. If θ_d is the dynamical contact angle, the profile near the wedges is $\zeta = \theta_d{*}x$, and eq 5 leads to

$$6\eta\frac{V}{\theta_d}\left|\,\log(\theta_d x + 3b)\right|_{x=0}^{x=l/2} = \frac{1}{2}\gamma\theta_e^{\,2} \qquad (6)$$

As shown in ref 2, $\theta_d = \theta_e/2^{1/2}$ and the velocity V of the rim is

$$V = \frac{V^*}{12(2)^{1/2}}\theta_e^{\,3}\frac{1}{\ln(\theta_e l/b)} \qquad (7)$$

The rim moves at the velocity V, constant in time. The slippage effect enters only in the logarithmic term and is a small effect. However, it explains why we previously found that the slope of the curve V/V^* versus θ_e^3 depends upon molecular weight. As the molecular weight M_w grows, the extrapolation length, b, grows and the L factor slows down, as observed experimentally.[2]

Thin Rims. Plug Flows (Figure 3b). In the limit $\zeta \ll b$, eq 5 can be written simply as

$$kVl = \frac{1}{2}\gamma\theta_e^2 \tag{8}$$

where $k = \eta/b$ is a monomer/solid friction coefficient. The velocity decreases with time, because the friction is now proportionnel to the width l of the rim and can be calculated from eq 8 and the liquid conservation equation. The liquid from the dry patch is collected in the rim, and this leads to

$$l \sim (Re/\theta_e)^{1/2} \tag{9}$$

From eqs 8 and 9, we find

$$R \sim (V^*)^{2/3}\theta_e^{5/3}(b^{2/3}/e^{1/3})t^{2/3} \tag{10}$$

Our experimental data give $R \sim t^x$, with $x = 0.66 \pm 0.08$ in good agreement with the theoretical exponent $x = {}^2/_3$.

To summarize, we are able to probe the rheology of polymer melts via the growth of holes in microscopic films of polymer. At this point, it is fair to mention recent, direct measurements of the local velocity of a sheared polymer melt within the first 100 nm from the solid/liquid interface.[9] This is based on evanescent wave induced fluorescence (EWIF) and fringe pattern fluorescence recovery after photobleaching (FPFRAP). Our indirect technique is less powerful but easy to set up and may be useful to test the smoothness of modified solid surfaces.

Acknowledgment. We thank P.-G. de Gennes for a critical reading of the manuscript.

References and Notes

(1) de Gennes, P.-G. *C. R. Acad. Sci. Paris* **1979**, Série B, 219.
(2) Redon, C.; Brochard-Wyart, F.; Rondelez, F. *Phys. Rev. Lett.* **1991**, *66*, 715.
(3) Brochard-Wyart, F.; Redon, C.; Sykes, C. *C. R. Acad. Sci. Paris* **1992**, Série II, *314*, 19.
(4) Brzoska, J. B.; Brochard-Wyart, F.; Rondelez, F. *Langmuir*, to be published.
(5) Brzoska, J. B.; Shahidzadeh, N.; Rondelez, F. *Nature* **1992**, 360.
(6) Vig, J. R. *J. Vac. Sci. Technol., A* **1985**, *3*, 1027.
(7) de Gennes, P.-G. *Rev. Mod. Phys.* **1985**, *57*, 827.
(8) Reiter, G. *Phys. Rev. Lett.* **1992**, *68*, 75.
(9) Migler, K. B.; Hervet, H.; Leger, L. *Phys. Rev. Lett.*, in press.