Notes

Dewetting of Supported Viscoelastic Polymer Films: Birth of Rims

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Received June 28, 1996
Revised Manuscript Received November 12, 1996

I. Introduction

We have recently studied the growth of a hole in freely suspended films of long-chain polymers.[1] We found that the liquid from the hole is not collected into a rim, as it is in soap films. The liquid spreads out with a flow field $V(r) \propto \dot{R}(R/r)$, where R is the radius of the hole and r is the distance to the center of the hole; this velocity field was monitored by the motion of glass spheres floating at the liquid free surface. We found that $R(t)$ grows exponentially with time

$$R(t) = R_0 e^{t/\tau} \tag{1}$$

where $\tau = 0.7(e/V^*)$ ($V^* = \gamma/\eta$ is a capillary velocity of the liquid, γ is its surface tension, and η is its dynamic viscosity). We have interpreted these features by a viscoelastic model (presented below).

Our aim here is to study the bursting of a highly viscous polymer film, not suspended in air, but deposited on a nonwettable, smooth, solid substrate; for instance a silanated silicon wafer. de Gennes predicted[2] that polymers slip on solid substrates if the surface is *smooth* and *passive* (i.e. does not bind the polymer). The slippage is characterized by the hydrodynamic extrapolation length b, which can be very large, up to millimeters. The theoretical value $b = a(N^3/N_e^2)$ (where a is a monomer size, N is the polymerization index of the polymer, and N_e is the threshold for entanglements). This has been confirmed by direct measurements of the liquid velocity at the wall, through a new nanovelocimetry technique.[3]

Another (easier) way to achieve a strong slippage is to cover the solid substrate with a lubricant film of small thickness e_0 and low viscosity η_0. In that case, $b = e_0(\eta/\eta_0)$ can be very large. For $e_0 = 1\ \mu$m, $\eta/\eta_0 = 10^4$, one expects $b \cong 1$ cm.

If the film thickness e is much larger than b, the polymer behaves like a usual liquid. But if $e \ll b$, we expect plug flows: the flow field in a thin supported film is then very similar to the flow in suspended films. However, for supported films, we must include in the discussion the viscous friction at the S/L interface.

We discuss here the growth of a hole, including the viscoelastic properties of the polymer film and the friction at the wall.

In section II, we recapitulate the model of the “soft balloon” described in ref 1 for the bursting of suspended films. We then show that supported films should behave like suspended viscoelastic films when the radius of the hole is less than a certain threshold value R_c.

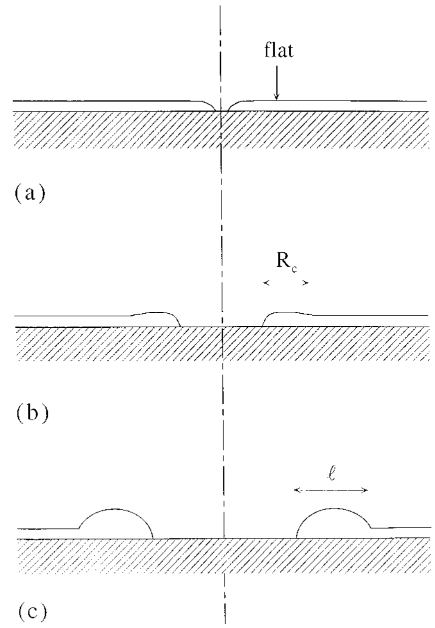

Figure 1. Onset of a rim surrounding an opening hole in a thin liquid film (thickness e < the hydrodynamic extrapolation length b) deposited on a low-energy, defect-free, solid surface (a) For $R < R_c = (eb)^{1/2}$, the film behaves like a suspended film and remains flat. (b) for $R_c < R < R_c' = b$, we get into a crossover regime of birth of a rim limited to a corona R_c around the hole. For $R > R'_c$ all the liquid from the hole is collected into a mature rim of size l.

In section III, we describe the onset of a rim surrounding the hole when the friction with the solid substrate becomes dominant ($R > R_c$). In this crossover regime, the viscoelasticity of the film and the slippage at the wall are both important.

In section IV, we show that above another critical radius R_c' we should get into a classical viscous regime where the liquid of the hole is collected into a rim. The motion of the rim can be derived simply from the balance between the capillary driving force and a simple friction force since the rim slips at velocity $V = dR/dt$ on the solid substrate.

II. Absence of a Rim: $R < R_c$ (Figure 1a)

A thin polymer film deposited on a nonwettable substrate (spreading coefficient $S = \gamma_{S_0} - (\gamma_{SL} + \gamma)$, where γ_i are respectively the surface tensions of the solid, of the solid/liquid interface, and of the liquid) is unstable below a critical thickness $e_c = 2K^{-1} \sin(\theta_e/2)$, where θ_e is the S/L contact angle and $K^{-1} = (\gamma/\rho g)^{1/2}$ is the the capillary length (ρ is the liquid density and g is the gravitational constant). This film can be achieved by spin coating a polymer solution on a silanated silicon wafer. To ensure $e \ll b$, we are interested in film thicknesses e ranging from 10 nm up to a few microns. At time $t = 0$, a hole is created in the film, spontaneously for unstable ultrathin films or nucleated by capillary suction (or by blowing an air jet) for metastable thicker films.

Let us first assume that dissipation at the S/L interface can be neglected. The film then behaves like a suspended film.[1] To interpret the absence of a rim collecting the liquid and the instantaneous thickening of the film far from the hole, we have developed a model based on the viscoelastic behavior of the polymer melt. At short times the melt behaves like a rubber, with an elastic modulus μ ($\mu \approx kT/N_e a^3 \cong 10^6$ Pa). At long times (above the reptation time T_{rep}) the film flows like a liquid. As the hole opens, the whole film is elastically deformed by the capillary forces $\gamma + \gamma_{SL} - \gamma_{S_0} = S$ acting at the hole periphery. This gives rise to a Laplace pressure S/e at the edge of the hole. The stress σ_{rr} is transmitted at velocity c up to a distance $L_d = cT_{rep}$, where c is the shear wave velocity in the rubber. With $c = 100$ m/s and $T_{rep} = 0.01$ s, $L_d = 1$ m. Above L_d, the elastic waves are damped. We assume here that L_d is larger than the sample. The radial stress which satisfies the boundary conditions $\sigma_{rr}(R) = S/e$ and $\sigma_{rr}(\infty) = 0$ is given by

$$\sigma_{rr}(r) = \frac{S}{e}\left(\frac{R}{r}\right)^2 \tag{2}$$

As σ_{rr} varies with a characteristic frequency $\dot{R}/R = \tau^{-1} \ll T_{rep}{}^{-1}$ the flow induced in the film corresponds to a zero-frequency viscous response given by

$$\sigma_{rr} = 2\eta\frac{\partial V}{\partial r} \tag{3}$$

i.e., using (2)

$$V = \frac{SR^2}{2\eta e r} \tag{4}$$

Writing $V(r{=}R) = \dot{R}$, we get for $R(t)$ the exponential growth of eq 1.

For our supported film, the viscous dissipation F_d associated with the flow field (4) is composed of two terms:

(a) inside the film

$$F_d^{film} = \int_R^\infty \left(2\pi r e\ dr\ 2\eta\left[\left(\frac{\partial V}{\partial r}\right)^2 + \left(\frac{V}{r}\right)^2\right]\right) = 4\pi\eta e\dot{R}^2 \tag{5}$$

(b) at the S/L interface

$$F_d^{slip} = \int_R^\infty kV^2(2\pi r)\ dr = 2\pi k\dot{R}^2R^2 \log\frac{L}{R} \tag{6}$$

where $k = \eta_0/a$ is a monomer friction coefficient related to the extrapolation length by $k = \eta/b$ and L is an upper cutoff discussed in section III.

Equating the dissipation to the surface energy gained per unit time, one finds the growth law

$$F_d^{film} + F_d^{slip} = 2\pi R\dot{R}|S| \tag{7}$$

The suspended film behavior is valid as long as $F_d^{slip} \ll F_d^{film}$, i.e. for $R < R_c$ given by

$$R_c{}^2 \approx be \tag{8}$$

(we ignore the log factor in eq 6)

Conclusion: for $R < (be)^{1/2}$, the hole has an exponential growth and we expect no rim.

III. Birth of the Rim: $R_c < R < R_c'$ (Figure 1b)

As soon as $R > R_c$, the viscous dissipation is dominated by F_d^{slip}.
Equation 7 becomes

$$kR\dot{R}\log\left(\frac{L}{R}\right) = S \tag{9}$$

We have to discuss now the upper cut-off in the logarithmic divergence, L. As shown in the appendix, the transverse sound waves in the transient rubber are damped by the friction of the rubber on the solid surface. The flows induced by the elastic stress are limited to a corona around the hole, of width R_c. Setting $L = R + R_c$ in (9), we find

$$kR\dot{R}\log\left(1 + \frac{R_c}{R}\right) = |S| \tag{10}$$

i.e. for $R \gg R_c$

$$\dot{R} \approx \frac{|S|}{\eta}\left(\frac{b}{e}\right)^{1/2} \tag{11}$$

In this crossover regime representing the birth of the rim, the dewetting velocity is constant.

The screening of the flow, limited to a corona, leads to an accumulation of liquid at the periphery of the hole. This corresponds to the birth of the rim. Born at $R = R_c$, the rim is achieved when all the liquid of the hole is collected in the corona. If l is the width of the rim, volume conservation leads to

$$2\pi R\theta_e l^2 \approx \pi R^2 e$$

i.e.

$$l \approx (Re)^{1/2} \tag{12}$$

The rim is fully established when $l \geq R_c$. The condition $l = R_c$ corresponds to the second threshold R_c':

$$R_c' = b \tag{13}$$

IV. Mature Rim: $R > R_c'$ (Figure 1c)

For $R > b$, all the liquid of the hole is collected in the rim. The motion of the rim is simply derived from a global balance of forces: (i) the driving force S per unit length of the rim; (ii) the resisting friction force klV (per unit area)

$$klV = S \tag{14}$$

where l is given by eq 12. This leads to

$$\dot{R}(Re)^{1/2} = \frac{S}{\eta}b \tag{15}$$

i.e.

$$R^{3/2} = \frac{S}{\eta}\frac{b}{e^{1/2}}t \tag{16}$$

Above, R_c', the velocity of the rim decreases because the driving force is constant, but the friction increases with the size of the rim. The law $R(t) \approx t^{2/3}$ has indeed been

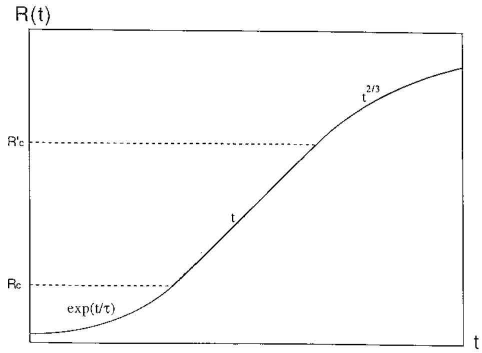

Figure 2. Radius R of a hole versus time t. For $R < R_c = (eb)^{1/2}$, the hole increases exponentially with time. For $R_c < R < R_c' = b$, the velocity is constant. Finally, for $R > R_c'$, $R(t)$ varies as $t^{2/3}$.

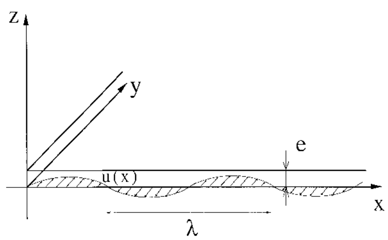

Figure 3. Transverse elastic waves in a thin polymer film deposited on a smooth solid substrate. u refers to the displacement of the rubber in the y direction while the wave propagates in the x direction.

observed by Redon[4] for very viscous liquids deposited on silanated silicon wafers.

V. Concluding Remarks

With an ideal solid surface the hydrodynamic extrapolation length can be extremely large (up to a millimeter for molten polyethylene[5]). On real surfaces slippage is very often achieved only above a threshold velocity V*.[3] This is usually explained by postulating that a few chains from the melt are bound to surface sites. Thus the experiments which we discuss here would require an almost perfect surface: either a silanated silicon wafer of high quality, giving very little hysteresis in the contact angles, or a surface covered with a lubricant film, which is strictly not miscible with the polymer. Experiments using ultraviscous poly(dimethylsiloxane) oil deposited on glass covered by a suitable lubricant are underway.

For microscopic films, the formation of the rim could be monitored by atomic force microscopy; for thicker films, by optical interferometry. We expect (Figure 2) that, for $R < (eb)^{1/2}$, the growth velocity $V(R) = dR/dt$ for the growth of the hole increases exponentially, reaches a plateau for $(eb)^{1/2} < R < b$, and ultimately decreases for $R > b$. The long-time limit ($R(t) \approx t^{2/3}$) has been observed previously: in her experiments, Redon noticed that a certain time was necessary to observe the formation of the rim and that the curve $R(t)$ was very flat at short times. Very recently, Composto[6] observed an exponential growth of holes in the liquid/liquid dewetting of a polymer liquid film deposited on a wet solid substrate. These qualitative features are encouraging, but we shall need accurate experiments to investigate the dynamics of "young holes", their growth, and how rims are formed.

Appendix: Damping of Elastic Waves (Figure 3)

We study here the elastic modes of the thin polymer film deposited on a smooth solid substrate. Our aim is to describe the damping of the elastic waves, induced by the friction at the S/L interface.

The polymer film behaves like a rubber of elastic modulus μ at high frequency and like a liquid of viscosity η at low frequency. η is related to μ by the scaling relationship $\eta = \mu\, T_{rep}$. In a simple model, assuming one relaxation time, one can describe the viscoelastic behavior by an imaginary modulus $\mu(\omega)$ given by

$$\mu(\omega) = \frac{i\omega\eta_p}{1 + i\omega T_{rep}} \qquad (A1)$$

We study then transversal elastic waves in the thin rubberlike material. The wave vector q is in the plane of the layer and we consider the long-wave length limit ($qe < 1$). If u refers to the displacement of the rubber in the y direction, the balance of inertial, elastic, and friction forces per unit area can be written as

$$\rho e\frac{\partial^2 u}{\partial t^2} = \mu e\frac{\partial^2 u}{\partial x^2} - k\frac{\partial u}{\partial t} \qquad (A2)$$

where k is the friction coefficient at the S/L interface. We look for a solution $u = u_q e^{iqx}e^{i\omega t}$. The dispersion relation derived from eqs A1 and A2 is

$$\omega^2 = \frac{i\omega\eta_p}{\rho(1 + i\omega T_{rep})}q^2 + \frac{i\omega k}{\rho e} \qquad (A3)$$

We focus on the elastic waves; i.e. we assume $\omega T_{rep} \gg 1$. Equation A3 can be written in this limit as

$$\omega^2 = c^2q^2\left(1 + \frac{i}{qL_d}\right) + i\omega\frac{\eta}{\rho}q_c^{\ 2} \qquad (A4)$$

where c is the sound wave ($c = (\mu/\rho)^{1/2}$), $L_d = cT_{rep}$, and $q_c = (eb)^{-1/2}$. In the following, we assume $L_d \gg q^{-1}$. From eq A4, we expect two regimes: (i) propagative modes ($\omega = \pm cq$), at high frequency $\omega > \omega_c = (\eta/\rho)q_c^2$; (ii) overdamped modes at $\omega < \omega_c$:

$$\omega = i\frac{\mu}{\eta}\frac{q^2}{q_c^{\ 2}} \qquad (A5)$$

The wave vectors of the damped elastic waves range between an upper value $q = q_c[cT_{rep}/(eb)^{1/2}]$ (corresponding to $\omega = \omega_c$) and a lower limit $q = q_c$ (corresponding to $\omega = 1/T_{rep}$). This means that the slowest elastic waves ($\omega = 1/T_{rep}$) are damped on a length $R_c = (eb)^{1/2}$. This explains why the corona, i.e. the region elastically deformed, has a width limited by R_c. Above this distance, all elastic shears induced by the opening of the hole are damped. At low frequency $\omega\, T_{rep} < 1$, i.e. $q < q_c$, the polymer film has a pure liquid behavior.

References and Notes

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MA960929X