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Thomas Vilmin, Elie Raphael, Pascal Damman, Sylvain Gabriele, Severine Sclavons, et al.. The Role of Nonlinear Friction in the Dewetting of Thin Film Polymers. 2005. hal-00004960

HAL Id: hal-00004960

<https://hal.science/hal-00004960>

Preprint submitted on 24 May 2005

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The Role of Nonlinear Friction in the Dewetting of Thin Film Polymers

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(Dated: May 24, 2005)

The study of the dewetting of very thin polymer films has recently revealed many unexpected features (*e.g.* unusual rim morphologies and front velocities) which have been the focus of several theoretical models. Surprisingly, the most striking feature of all, that is a decrease of the rim width with time, have not yet been explained. In the present letter, we show how the combined effects of a non-linear friction between the film and the substrate, and the presence of residual stresses within the film, result in the presence of a maximum in the time evolution of the rim width. In addition, we show how the introduction of a non-linear friction can also simply explain the rapid decrease of the dewetting velocity with time observed experimentally.

PACS numbers: 68.60.-p, 68.15.+e, 61.41.+e, 83.50.-v

Since the use of nano-devices is nowadays getting more and more important, the stability of thin polymer films has become a major scientific and technologic research area [1]. In particular, the dewetting of thin polystyrene (PS) films has been extensively investigated over the last decade [2]. A great interest has been payed to the unusual rim morphology [3, 4, 5] first studied by Reiter [6]. A detailed experimental study of the dewetting dynamic has been published two years ago [7], showing a sharp decrease of the dewetting velocity with time ($V \sim t^{-1}$).

These observed features have been recently explained theoretically in [8]. The principal ingredients allowing to understand the observed asymmetric shape of the rim are the weak friction of the film onto the substrate (grafted or absorbed liquid polydimethylsiloxane (PDMS) monolayer), allowing a plug-flow description, and the ineffectiveness of the surface tension of the liquid at this stage of the dewetting process. The friction dumps the sliding velocity within the film over a distance $\Delta = \sqrt{\eta h_0 / \zeta_0}$ (where η is the viscosity of the liquid, assumed to be Newtonian, h_0 is the initial thickness of the film, and ζ_0 is the friction coefficient between the film and the substrate) [9], leading to an asymmetric rim of width $\sim \Delta$, whereas the height of the rim H increases progressively. Omitting inertia, the dewetting dynamic can be simply solved by balancing the capillary power by the dissipation due to friction: $|S|V \simeq \zeta_0 \Delta V^2$ (where S is the spreading parameter [10], assumed to be neg-

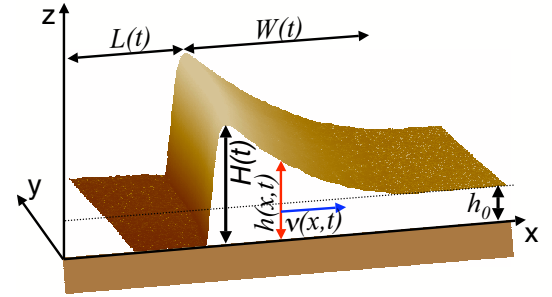


FIG. 1: Film geometry : $h(x,t)$ is the profile of the film, h_0 is the initial height of the film, $H(t)$ is the height of the front, $L(t)$ is the dewetted distance, $W(t)$ is the width of the rim, and $v(x,t)$ is the velocity of the film.

ative). For a Newtonian liquid, this balance gives a constant dewetting velocity $V = |S|/\zeta_0 \Delta$ [9]. The decrease with time of the velocity observed experimentally is explained by the viscoelastic properties of the polymer film, *i.e.* by the fact that the liquid behaves like a low viscosity (η_0) Newtonian liquid at very short times ($t < \tau_0 = \eta_0/G$), like an elastic solid (of elastic modulus G) in an intermediate time regime ($\tau_0 < t < \tau_1 = \eta_1/G$), and like a very viscous Newtonian liquid (with a viscosity $\eta_1 \gg \eta_0$, where η_1 is related to the molecular weight of the polymer) at long times ($t > \tau_1$) [11]. During the short and long times regimes [12], the film dewetts like a Newtonian liquid, with the respective constant velocities $V_0 = |S|/\zeta_0 \Delta_0$ ($t < \tau_0$, $\Delta_0 = \sqrt{\eta_0 h_0 / \zeta_0}$) and $V_1 = |S|/\zeta_0 \Delta_1$ ($t > \tau_1$, $\Delta_1 = \sqrt{\eta_1 h_0 / \zeta_0} \gg \Delta_0$). In the intermediate regime (which concerns an important part of the experiments, for which the temperature is close

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to the glass transition temperature) the increase of the height of the rim is slowed down by elastic forces, resulting in a linear relation between the width of the rim W and the dewetted distance L . The energy balance thus reads $|S|V \simeq \zeta_0 h_0 G L V^2 / |S|$ which gives a decrease of the velocity like $t^{-\frac{1}{2}}$. The more rapid decrease ($V \sim t^{-1}$) observed experimentally [7] is obtained by including a positive horizontal stress σ_0 within the film at the beginning of the dewetting process; the existence of σ_0 is attributed to the spin-coating of the PS solution, which is followed by a fast evaporation of the solvent, letting the PS molecules in a non-equilibrium frozen-in state [13].

Until now, little attention has been paid to the time evolution of the rim width reported in [7], though it is most unexpected. Indeed, after logarithmically increasing, the rim width reaches a maximum, and then slowly goes down. One can show that such a decrease of the rim width with time is impossible in a classical dewetting situation where surface tension rounds the rim. In the theoretical model described above [8], despite the fact that surface tension is ineffective, the rim width of a viscoelastic film increases with time during the elastic regime ($W \sim L$), while reaching a constant value in the long time Newtonian regime: $W = \Delta_1 = \sqrt{\eta_1 h_0 / \zeta_0}$, therefore showing no decrease with time of the rim width. However, at the sight of the latter expression of W , we can anticipate that W could decrease at the condition that the friction parameter ζ_0 increases with time.

A non-constant friction parameter is possible in the case where the friction force does not increase linearly with the sliding velocity. These cases are quite common in polymer physics. The friction of a PDMS elastomer on grafted or absorbed PDMS surfaces has been shown to increase only very slowly with the velocity: Casoli *et al.* found a friction force increasing proportionally to $V^{\frac{1}{3}}$ on absorbed brushes, and a friction force increasing only like $V^{\frac{1}{6}}$ on dense grafted brushes, for sliding velocities being between $10 \mu\text{m.s}^{-1}$ and 5mm.s^{-1} [14]. More recently Bureau *et al.* showed a $V^{\frac{1}{3}}$ dependence of the friction force between an elastomer and a grafted brush, for sliding velocities ranging from $300 \mu\text{m.s}^{-1}$ down to $0.01 \mu\text{m.s}^{-1}$ [15], which is the velocity range of the dewetting experiments.

A general expression of the friction force by surface unit is [16]:

$$f_r = \zeta_0 V_\alpha \left(\frac{v}{V_\alpha} \right)^{1-\alpha} \quad (1)$$

where α is a shear-thinning exponent smaller than one. According to the reported friction experiments, α could range between $2/3$ and $5/6$. The effective friction coefficient is then a decreasing function of v : $\zeta = \zeta_0 (V_\alpha/v)^\alpha$, where V_α is the velocity below which the friction coefficient remains equal to ζ_0 correspondingly to a linear friction. Hereafter, we assume V_α to be small enough for us to omit the linear friction regime. For a Newtonian fluid, such a friction force would bring, as an equilibrium

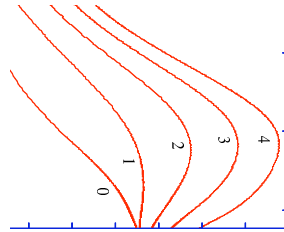


FIG. 2: Numerical calculations of the evolution of the rim width for $h_0 \sigma_0 / |S| = 0, 1, 2, 3,$ and 4 , with a friction exponent $\alpha = 2/3$, and a ratio $\tau_1 / \tau_0 = 100$.

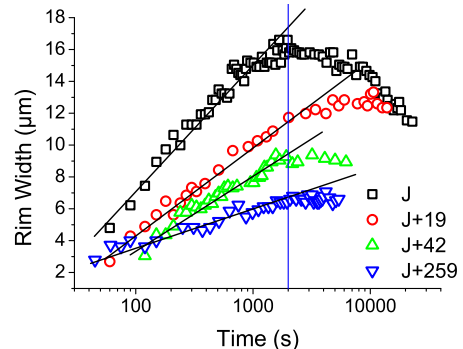


FIG. 3: Width of the rim as a function of dewetting time for films ($h_0 = 57 \text{nm}$, $M_w = 233 \text{kg/mol}$, and $T = 125^\circ \text{C}$) aged at room temperature for days indicated in the figure.

relation between friction and viscous forces within a film dewetting toward the x direction:

$$\zeta_0 V_\alpha \left(\frac{v}{V_\alpha} \right)^{1-\alpha} = \eta_0 \frac{\partial}{\partial x} \left(h \frac{\partial v}{\partial x} \right) \quad (2)$$

As long as h remains of the order of h_0 , the solution of Eq.(2), is simply given by

$$v(x, t) = V_{0\alpha} \left(1 - \frac{x - V_{0\alpha} t}{\Delta_{0\alpha}} \right)^{\frac{2}{\alpha}} \quad (3)$$

when $x - V_{0\alpha} t < \Delta_{0\alpha}$, and $v(x, t) = 0$ elsewhere. Here, the dewetting velocity $V_{0\alpha} = \left(\left(\frac{2-\alpha}{2} \right) V_0^2 / V_\alpha^\alpha \right)^{\frac{1}{2-\alpha}}$ is constant in time, as well as the rim width $\Delta_{0\alpha} = \frac{2}{\alpha} \left(\left(\frac{2-\alpha}{2} \right) V_0^\alpha / V_\alpha^\alpha \right)^{\frac{1}{2-\alpha}} \Delta_0$ [17]. These analytical results have been confirmed by numerically solving Eq.(2) combined with the volume conservation equation and the condition of stress continuity at the front of the film.

As expected, when the friction force is a non-linear function of the velocity, the rim width is a function of the amplitude of the dewetting driving forces (*i.e.* the capillary forces in usual cases: $\Delta_{0\alpha} \sim |S|^{\frac{\alpha}{2-\alpha}}$). A decrease of the rim width can thus be expected if the driving forces

decrease during the dewetting process. That is, in fact, what happens when a viscoelastic film presents residual stresses at the onset of the dewetting. Indeed, the residual positive stresses are part of the driving forces, but they decrease with time, as the film undertakes internal relaxation toward an equilibrated state [8, 13].

An equilibrated viscoelastic film would start ($t < \tau_0$) dewetting with a velocity $V_{0\alpha} \simeq (V_0/V_\alpha)^{\frac{\alpha}{2-\alpha}}$, and a rim width $\Delta_{0\alpha} \simeq (V_0/V_\alpha)^{\frac{\alpha}{2-\alpha}} \Delta_0$, and then ($\tau_0 < t < \tau_1$) slow down to $V_{1\alpha} \simeq (V_1/V_\alpha)^{\frac{\alpha}{2-\alpha}}$, ending with a rim width $\Delta_{1\alpha} \simeq (V_1/V_\alpha)^{\frac{\alpha}{2-\alpha}} \Delta_1$ at long times ($\tau_1 < t$). When a horizontal positive stress σ_0 is initially present, the film starts dewetting with a velocity $V_i = V_{0\alpha} (1 + h_0 \sigma_0 / |S|)^{\frac{\alpha}{2-\alpha}}$ and a rim width $\Delta_i = \Delta_{0\alpha} (1 + h_0 \sigma_0 / |S|)^{\frac{\alpha}{2-\alpha}}$. During the elastic regime ($\tau_0 < t < \tau_1$), the residual stress has not yet relaxed much, and the rim width increases up to its maximum value:

$$\Delta_m \simeq \Delta_{1\alpha} \left(1 + \frac{h_0 \sigma_0}{|S|} \right)^{\frac{\alpha}{2-\alpha}} \quad (4)$$

Around the characteristic time τ_1 , the residual stress has decreased significantly, leaving the capillary forces as the only driving forces. Consequently, the rim width decreases down to $\Delta_{1\alpha}$ simultaneously with the increase of the dewetting distance. Once again, we confirmed these results by numerical resolutions of the equations of the flow (see Fig. (2)). We notice that Δ_m is higher than $\Delta_{1\alpha}$ only if the exponent α is not nil. The combination of non-linear friction together with residual stresses is thus necessary to explain the decrease of the rim width with time. Interestingly, the residual stresses σ_0 can come off from the relation between the initial dewetting velocity V_i and the maximum rim width Δ_m :

$$V_i = V_\alpha \left(\frac{\zeta_0}{h_0} \right)^{\frac{1}{\alpha}} \left(\frac{\eta_1^{2(1-\alpha)}}{\eta_0} \right)^{\frac{1}{2-\alpha}} \Delta_m^{\frac{2}{\alpha}} \quad (5)$$

The exponent α could thus be deduced from a Log-Log plot of V_i as a function of Δ_m , for dewetting experiments with various values of the residual stress. Furthermore, we notice a weak dependance of $V_i / \Delta_m^{\frac{2}{\alpha}}$ on the viscosity η_1 , and thus on the molecular weight of the polymer, when α is close to unity. Then, several Log-Log plots, corresponding to different molecular weights, can be superposed in order to measure α .

At the same time, we have conducted new experiments on the aging of thin PS films deposited onto a PDMS mono-layer. The consequences of up to three hundred days of aging, just below the glass transition, on the dewetting have been systematically investigated. We observed a slowing down of the dewetting, as well as a decrease of the maximum rim width, when increasing the aging time (see Fig. (3) and (4)). Eventually, at the longest aging time, no maximum rim width was observed. We interpreted these results as a manifestation of the very slow relaxation of the residual stresses

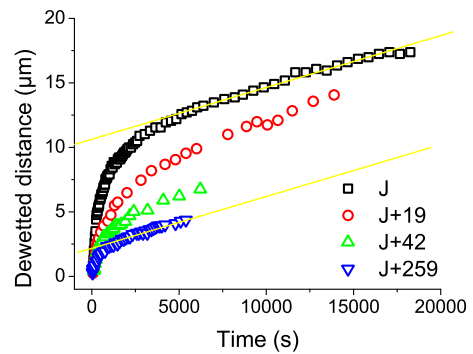


FIG. 4: Dewetted distance as a function of dewetting time for films ($h_0 = 57nm$, $M_w = 233kg/mol$, and $T = 125^\circ C$) aged at room temperature for days indicated in the figure.

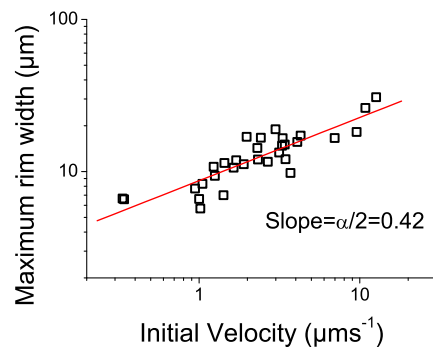


FIG. 5: Evolution of the maximum rim with as a function of the initial dewetting velocity for several aging times and PS molecular weights ranging from 35K to 600K.

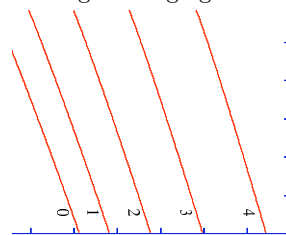


FIG. 6: Numerical calculations of the evolution of the dewetted distance for $h_0 \sigma_0 / |S| = 0, 1, 2, 3$, and 4, with the friction exponent $\alpha = 2/3$, and a ratio $\tau_1 / \tau_0 = 100$.

within the film with aging time. The Log-Log plot of the maximum rim with as a function of the initial dewetting velocity for several aging times and several PS molecular weight revealed a friction exponent $\alpha = 0.84 \pm 0.1$ (see Fig. (5)). The time corresponding to the maximum rim width should correspond to the characteristic relaxation time of elastic constraints τ_1 within the film. We notice that this time is significantly shorter than the corresponding relaxation time in bulk (*i.e.* the bulk reptation

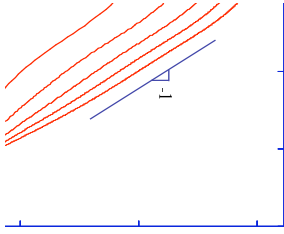


FIG. 7: Numerical calculations of the evolution of the dewetting velocity for $h_0\sigma_0/|S| = 0, 1, 2, 3,$ and 4 , with the friction exponent $\alpha = 2/3$, and a ratio $\tau_1/\tau_0 = 100$.

tion time of the polymer chains), which is consistent with the fact that the entanglement length should be longer in thin films [18]. Other structural relaxation mechanisms related to the proximity of the glass transition might also be involved.

Another interesting result, which reinforces the implication of non-linear friction in dewetting, is that, even though the initial dewetting velocity V_i decreases with the aging time, the power-law evolution of the velocity during the dewetting process remains the same ($V \simeq t^{-1}$). This observation is in contradiction with the predictions of the theoretical model developed in [8], where a t^{-1} law was predicted for high residual stresses, but where the decrease of the velocity should tend toward a $t^{-\frac{1}{2}}$ law for low residual stresses. On the other hand, this observation is coherent with the model we developed here. Indeed, the dewetting velocity of an equilibrated viscoelastic film goes from $V_{0\alpha}$ down to $V_{1\alpha}$ during the elastic regime. The power law of this decrease can be obtained from the energy balance, which reads $|S|V \simeq \zeta_0 h_0 G V_\alpha^\alpha L V^{2-\alpha} / |S|$. The later relation gives:

$$V = V_{1\alpha} \left(\frac{t}{\tau_1} \right)^{-\frac{1}{2-\alpha}} \quad (6)$$

for $\tau_0 < t < \tau_1$, which is not far from $V \sim t^{-1}$ if α is close to unity, as deduced from the plot of W_m as a function of V_i (see Fig. (5)). Thus, the dewetting velocity has always a power law close to t^{-1} , which is made more rapid around the relaxation time τ_1 by the presence of residual stresses. This latter result is in complete agreement with our experiments (see also [7, 19]). We have also confirmed these analytical prediction by numerical solutions (see Fig. (6) and (7)).

In conclusion, the non-linearity of the friction force between the substrate and the film, together with the initial presence of residual stress within the dewetting liquid, are necessary to explain the observed decrease of the rim width with time. Coincidentally, the non-linear friction leads to a rapid decrease of the dewetting velocity of a viscoelastic film, which fits the experiments better than the velocity decrease predicted by the formers models. The good agreement of the predictions on both the rim width evolution and the dewetting velocity makes us confident about the validity of our model. Finally, the Log-Log plot of the initial dewetting velocities as a function of the maximum rim width allows to determine the exponent α characterizing the friction between the film and the substrate. Our study clarifies the role played by the friction and the residual stresses, both ingredients that may be of great importance in other polymer thin film situations. A major challenge for the future would be to understand the processes involved in the relaxation of the residual stresses below the glass transition.

Acknowledgments

Pascal Damman is a Research Associate of the Belgian National Funds for Scientific Research (FNRS). This work was supported by the FNRS, the Walloon Region and the European Social Fund.

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