

## Dewetting of Highly Elastic Thin Polymer Films

Günter Reiter

*Institut de Chimie des Surfaces et Interfaces, CNRS, 15, rue Jean Starcky, B.P. 2488, 68057 Mulhouse Cedex, France*

(Received 14 May 2001; published 10 October 2001)

Investigations of the opening of holes in thin, almost glassy polystyrene films deposited onto silicon wafers coated with a polydimethylsiloxane monolayer revealed strong deviations from the behavior of pure liquids. At early stages, these holes grew independent of the molecular weight of the polymer and without the formation of a rim. At later stages, a highly asymmetric rim was built up with the maximum height increasing linearly with the diameter of the hole. As the polymer cannot flow under the conditions of the experiments, our experiments demonstrate that capillary forces are able to provoke plastic deformation on a micron scale in thin quasisolid films.

DOI: 10.1103/PhysRevLett.87.186101

PACS numbers: 68.60.-p, 61.41.+e, 68.55.-a, 83.50.-v

It is well known that capillary forces resulting from intermolecular interactions are capable to retract a purely liquid film from a solid surface [1]. It is, however, less frequent that one encounters a similar dewetting phenomenon for highly viscoelastic films where, on the time scale of the experiment, the material cannot flow like a liquid. Experiments on thin polystyrene (PS) films at temperatures not too far above the glass transition temperature represent such an example [2–5]. Although under such conditions the polymer can by no means be treated as a Newtonian liquid, interpretation of the results so far has not accounted for the highly elastic properties of the polymer film. A quantitative comparison between experiments and existing theory on liquid dewetting has never been presented. Moreover, theoretically it was expected [6] that elastic effects could even stabilize thin films and prevent them from dewetting. The possibility of film rupture and dewetting via surface diffusion [7] or evaporation/condensation [8–10] can be ruled out due to the large number of chemically linked monomers and the practically zero vapor pressure of long chain polymers. One may conclude that dewetting of long chain polymers at temperatures close to their glass transition is not yet fully understood.

Several questions arise: Are capillary forces of the order of 10 mN/m, resulting from the combined action of surface and interfacial tensions, strong enough to provoke detectable morphological changes in highly elastic films? How does the elasticity of the film affect the observed characteristic features of dewetting like the shape of the rim or the temporal evolution of the hole diameter? What are alternative mechanisms as compared to liquid flow to progressively remove elastic material from a growing hole? In order to shed some light onto the phenomenon of dewetting of highly elastic films we followed the process of hole growth in PS films in detail from the very early stages. To accentuate the possible influence of capillary forces we have chosen highly nonwetable substrates.

For our experiments we used, as in many related previous studies [2–5], thin polystyrene films (PS125k: molecular weight  $M_w = 125$  kg/mol, index of polydispersity  $I_p = 1.02$ , and PS3900k:  $M_w = 3900$  kg/mol,

$I_p = 1.05$ , purchased from PSS, Mainz, Germany) of different thicknesses between 10 and 60 nm (as measured by ellipsometry) on top of silicon substrates. Considerable capillary forces were obtained by coating these substrates with polydimethylsiloxane (PDMS) of low wettability, i.e., large negative spreading coefficients ( $S$ ). The coatings were grafted layers (polymer brushes) of end-functionalized PDMS molecules (PDMS78k:  $M_w = 78$  kg/mol,  $I_p = 1.07$ , layer thickness about 20 nm) or layers of adsorbed PDMS (PDMS38k:  $M_w = 38.3$  kg/mol,  $I_p = 2.56$ , layer thickness about 7 nm, and PDMS80k:  $M_w = 80.5$  kg/mol,  $I_p = 2.14$ , layer thickness about 10 nm). The irreversibly adsorbed layers resulted from annealing spin-coated films on hydroxylated (UV-ozone treated) silicon wafers at 150 °C for 5 h under vacuum [11]. PS films were prepared from toluene solution spin coated directly onto the PDMS coated Si wafers.

Dewetting of PS films thinner than 20 nm was followed using only atomic force microscopy (AFM) at room temperature after annealing the samples *ex situ* in a closed hot stage purged with nitrogen. For thicker films, where holes became visible under an optical microscope, real time investigations were performed in addition.

The PDMS layer on top of the Si wafer “screened” all heterogeneities of the solid substrates and thus represented an ideally homogeneous surface of low surface tension which cannot be wetted by PS. In addition, there is no adsorption between PS and PDMS. Thus, faster dewetting velocities than observed on most other nonwetable substrates were possible. There is also a technical advantage. As PDMS is liquid at room temperature while PS is glassy, AFM in the tapping mode can clearly distinguish the two polymers, allowing for an unambiguous detection of full thickness holes in PS films. This is important at the early stages of hole formation when shallow depressions become deeper and eventually rupture the film.

As found previously [2,4,5], all PS films on such substrates turned out to be metastable and ruptured upon annealing at elevated temperatures. The number density of holes increased rapidly with decreasing film thickness.

Here we concentrate on the shape of these holes and its evolution with time at temperatures above 103 °C. Preliminary experiments indicated, however, that hole formation was also possible at lower temperatures. As described in Ref. [12], hole formation may be due to the relaxation of internal tensions induced during sample preparation and caused by confining the polymers to films thinner than the size of the unperturbed coil.

In Fig. 1 we present typical AFM results from the thinnest films investigated which show the early stages of hole formation. Such thin films were used to ensure that several holes could be detected within one AFM image. These films allow one to observe that almost all holes were formed within a narrow time interval at the very beginning. However, a high number density of holes causes the coalescence of holes at early stages and thus prevents the hole opening to follow at late stages. We note that the material displaced from the dewetted areas did not form visible rims around these areas but was distributed almost evenly within the whole film in between the holes. Thus, imposing mass conservation, the film thickness between the holes had to increase. A comparison between the thicknesses before annealing as measured by ellipsometry and the depth of the holes measured by AFM is shown in Figs. 1g and 1h. Taking into account that, e.g., x-ray reflectometry averages over

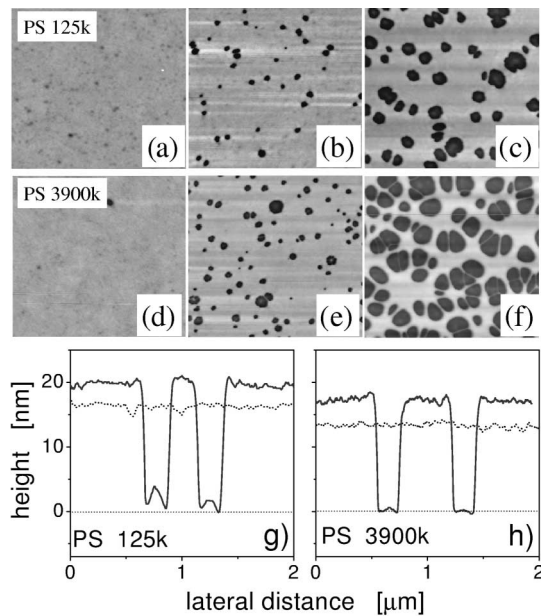


FIG. 1. Typical atomic force micrographs showing the formation of holes in thin PS films on PDMS coated Si wafers. Two different molecular weights are compared as indicated in the figure. First row: 16 nm PS125k on PDMS38k; second row: 13 nm PS3900k on PDMS38k. (a),(d) show the as-prepared samples. (b),(e) and (c),(f) were measured after annealing for 1 and 10 min at 105 °C, respectively. (g),(h) show cross sections of the as-prepared samples (dotted line) and after annealing for 10 min at 105 °C (full line). The size of the images in (a)–(f) is  $3 \times 3 \mu\text{m}^2$ .

areas of many  $\mu\text{m}^2$ , such measurements will observe an apparent thickening of the film at the onset of dewetting without detecting significant roughness [13].

Although we used two very different molecular weights of PS, both samples showed about the same dewetting behavior. This demonstrates that the viscosity of the polymer, which varied by several orders of magnitude, does NOT play a significant role in determining the rate at which the holes open. Furthermore, this indicates that the plateau shear modulus of PS, which does not depend significantly on chain length, may be the essential control parameter for the growth rate.

In Fig. 2 we present a quantitative comparison of our results of the early stages for hole growth. Almost all tiny holes (with a diameter  $D$  of about 70 nm) were already formed after annealing for 1 min. (The number density did not change significantly upon further annealing.) This implies an average opening velocity  $\dot{D}$  of these holes of about 70 nm/min and an average shear rate  $\dot{\gamma} = \dot{D}/D$  of about  $0.7 \text{ min}^{-1}$ . Comparing  $1/\dot{\gamma}$  with the reptation time ( $t_{\text{rep}}$ ) of PS close to the glass transition temperature (for the conditions of the experiments shown in Fig. 1,  $t_{\text{rep}}$  is larger than one year [14]) demonstrates that on the time scale of the experiments we cannot expect viscous flow of the polymer. Thus, the gain in interfacial energy has to be balanced mostly by other dissipation mechanisms like plastic deformation of the quasisolid PS film. Probably some energy can also be dissipated at the PS/PDMS interface by deformation of the PDMS layer.

Upon further annealing for up to about 5 min no significant growth was observed. Only later on, the holes became significantly larger. Our limited data allow us to fit the growth of the holes at their earliest stages to an exponential function, similar to what was expected theoretically [15] for the first stage of hole growth in viscoelastic films when

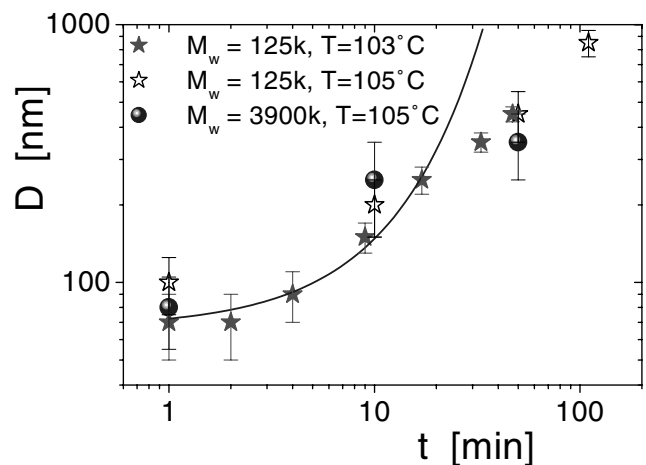


FIG. 2. Hole diameter ( $D$ ) as a function of annealing time ( $t$ ) for PS films of Fig. 1 annealed at 103 °C and 105 °C. Note that the molecular weight does not seem to have an influence on the growth rate. The solid line represents an exponential fit to the early stages yielding  $D[\text{nm}] = 67[\text{nm}] \exp(t/12.6[\text{min}])$ .

no rim is formed. However, as we used rather thin films, the many holes per unit area started to coalesce already as their diameter became larger than about 200 nm, which has an influence on the growth rates. Complementary measurements, also on thicker films, indicated that after an initial (most likely) exponential regime, growth seems to pass over to a power-law behavior, already at hole diameters below  $1\ \mu\text{m}$ . This regime coincides with the appearance of a rim. At even later stages, when the hole diameters were about  $10\ \mu\text{m}$ , the dewetting velocity slowed down drastically. Although all experiments show qualitatively this behavior, quantitative differences between samples exist, probably due to slight differences in the properties of the PDMS coating [16]. The exact functional dependence of  $D(\text{time})$  will be the subject of a future publication.

In Figs. 3 and 4 we give examples for the behavior of extended annealing using slightly thicker films where, on average, holes were separated by several microns. Again, at the very beginning of hole formation (for hole diameters less than about  $1\ \mu\text{m}$ ), no rim could be detected (see the smallest holes in Fig. 4a). However, at later stages one could clearly observe the formation of a rim. The optical micrographs resemble very much previously published examples on similar systems [2,4,5]. The shape of the rim, however, is highly asymmetric with an extremely steep side towards the interior of the hole and a much slower decay on the rear side (see Figs. 3c and 4a). This has to be contrasted to the more symmetric shapes expected theoretically [18] and observed experimentally [4,17,19,20] for dewetting of viscous liquids. The decay on the rear side can be fitted to an exponential function ( $y = A \exp[(x - x_0)/\kappa] + y_0$  with amplitude  $A$  and offsets  $x_0$  and  $y_0$ ). Interestingly, the characteristic decay length  $\kappa$  did not vary with annealing time. Fits to the profiles shown in Fig. 4a resulted all in  $\kappa \approx 0.5\ \mu\text{m}$ . We note, however, that  $\kappa$  could vary between 0.3 and several  $\mu\text{m}$  for samples with slightly varying thicknesses of the PDMS coating. The hole opening velocity was faster for larger  $\kappa$ .

The dewetted volume  $D^2\pi e$  is proportional to  $2\pi DH\kappa$  ( $e$  is the film thickness). As a consequence of  $\kappa$  being time invariant, the maximum height  $H$  of the rim had to grow at the same speed as the diameter of the hole ( $H \sim D$ ).

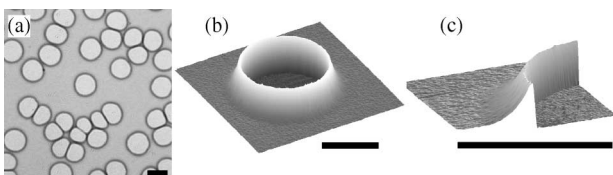


FIG. 3. Typical examples for holes and the corresponding rim formed in a 24 nm thick PS film. This film is thick enough so that the holes are on average separated by several  $\mu\text{m}$ . (a) Optical micrograph after annealing for 80 min at  $120^\circ\text{C}$ . AFM images (b) and (c) focus on the asymmetric shape of the rim. The length of the bar represents  $5\ \mu\text{m}$  in each case.

This has been checked in Fig. 4b. Such a linear relation between  $H$  and  $D$  strongly hints (as does the highly asymmetric shape of the rim) that the polymer is not flowing like a liquid. Otherwise, we would expect that equilibration of the Laplace pressure within the rim leads to a more symmetric shape, the rim should grow both in height and width simultaneously, and consequently  $H \sim D^{1/2}$ . Besides several preliminary ideas [21], there exists no theory which can explain this particular shape of the rim and why  $\kappa$  should be constant.

In our experiments at temperatures close to the glass transition the polymer was highly elastic and thus viscous flow could not be responsible for the observed phenomenon. Consequently, the driving capillary forces must have been sufficiently strong to *plastically* deform the thin and almost glassy polymer films. A simple comparison of the acting stress  $\sigma$  due to capillary forces [ $\sigma = S/e$  [15] (with  $S \approx -20\ \text{mN/m}$  and  $e = 20\ \text{nm}$ :  $\sigma \approx 10^6\ \text{N/m}^2$ )] with the plateau modulus ( $G$ ) of PS ( $G \approx 10^6\ \text{N/m}^2$ ) supports our hypothesis. This dewetting behavior may be analogous to removing snow in winter. There, similar to the capillary

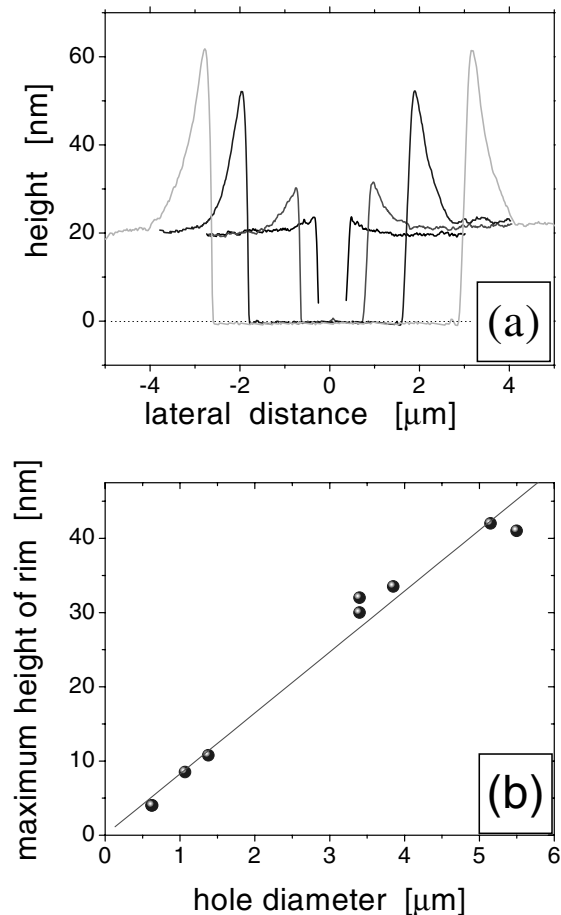


FIG. 4. (a) Cross sections through holes in a 20 nm thick PS film after annealing for 1, 5, 40, and 80 min at  $120^\circ\text{C}$ , respectively. Note the highly asymmetric shape of the rim. (b) The maximum height of the rim can be represented by a linear function (full line) of the diameter of the hole.

forces pushing the thin film away from the dewetted area, a layer of snow of certain thickness is pushed with a shovel, resulting in the buildup of a rim in front of the shovel. Also the slowing down of dewetting with growing size of the rim finds an analogy. As more and more snow is removed, the rim in front of the shovel gets larger, making pushing harder. Eventually the human force may be too weak to push the snow any farther. One may expect that the same physical laws describe the two phenomena.

In summary, our experiments demonstrate that a thin film does not need to be purely liquid in order to allow for dewetting. Intermolecular interactions responsible for capillary forces may be sufficiently strong to deform even quasisolid films. Moreover, one may anticipate a similar phenomenon for any other thin solid films of low elastic modulus and large deformability. Furthermore, our results imply that phenomena like changes in film morphology or apparent thickening may also occur *below* the glass transition temperature ( $T_g$ ) and can therefore not be taken as a criterion for determining  $T_g$ . Further experiments and new theoretical concepts are needed to advance our understanding of this intriguing phenomenon of dewetting of quasisolid films.

We are indebted to Philippe Auroy for providing us with the end-functionalized PDMS molecules. The help of Rajesh Khanna with experiments is highly appreciated. Very fruitful discussions with Françoise Brochard and Pierre-Gilles de Gennes are gratefully acknowledged.

- 
- [1] C. Redon, F. Brochard-Wyart, and F. Rondelez, *Phys. Rev. Lett.* **66**, 715 (1991).  
 [2] G. Reiter, *Phys. Rev. Lett.* **68**, 75 (1992); *Langmuir* **9**, 1344 (1993).

- [3] P. Lambooy, K. C. Phelan, O. Haugg, and G. Krausch, *Phys. Rev. Lett.* **76**, 1110 (1996).  
 [4] T. G. Stange, D. F. Evans, and W. A. Hendrickson, *Langmuir* **13**, 4459 (1997).  
 [5] K. Jacobs, S. Herminghaus, and K. R. Mecke, *Langmuir* **14**, 965 (1998).  
 [6] S. A. Safran and J. Klein, *J. Phys. II (France)* **3**, 749 (1993).  
 [7] D. J. Srolovitz and S. A. Safran, *J. Appl. Phys.* **60**, 247 (1986).  
 [8] D. J. Srolovitz and S. A. Safran, *J. Appl. Phys.* **60**, 255 (1986).  
 [9] A. Sharma, *J. Colloid Interface Sci.* **199**, 212 (1998).  
 [10] A. Oron and S. G. Bankoff, *J. Colloid Interface Sci.* **218**, 152 (1999).  
 [11] A. Casoli, M. Brendlé, J. Schultz, P. Auroy, and G. Reiter, *Langmuir* **17**, 388 (2001).  
 [12] G. Reiter and P. G. de Gennes, *Eur. Phys. J. E* (to be published).  
 [13] W. J. Orts, J. H. Van Zanten, W. L. Wu, and S. K. Satija, *Phys. Rev. Lett.* **71**, 867 (1993).  
 [14] G. Reiter and U. Steiner, *J. Phys. II (France)* **1**, 659 (1991).  
 [15] F. Brochard-Wyart, G. Debrégeas, R. Fondecave, and P. Martin, *Macromolecules* **30**, 1211 (1997); G. Debrégeas, P. Martin, and F. Brochard-Wyart, *Phys. Rev. Lett.* **75**, 3886 (1995).  
 [16] Dewetting experiments of thin PDMS films on such PDMS coatings have demonstrated the sensitive dependence on properties of the coating [17].  
 [17] G. Reiter and R. Khanna, *Phys. Rev. Lett.* **85**, 2753 (2000); *Langmuir* **16**, 6351 (2000).  
 [18] F. Brochard-Wyart, P. G. de Gennes, H. Hervert, and C. Redon, *Langmuir* **10**, 1566 (1994).  
 [19] Q. Pan, K. I. Winey, H. H. Hu, and R. J. Composto, *Langmuir* **13**, 1758 (1997).  
 [20] R. Limary and P. F. Green, *Langmuir* **15**, 5617 (1999).  
 [21] P. G. de Gennes (to be published).