

Viscoelastic Thin Polymer Films under Transient Residual Stresses: Two-Stage Dewetting on Soft Substrates

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A nonmonotonic, two-stage dewetting behavior was observed for spin coated thin viscoelastic polymer films on soft elastic substrates. At times shorter than the relaxation time of the polymer ($t < \tau_{\text{rep}}$), dewetting generated deep trenches in the soft rubbery substrate which, in turn, almost stopped dewetting. At later stages ($t \gg \tau_{\text{rep}}$), dewetting accelerated, accompanied by an unstable rim. However, holes nucleated at $t < \tau_{\text{rep}}$ showed only this second-stage behavior. Our observations are attributed to large elastic deformations in the substrate caused by transient residual stresses within the film.

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The stability of ultrathin polymer films on various substrates has attracted broad interest due to their ubiquitous applications in numerous fields and the possibility of unveiling molecular processes and the corresponding physics that govern the behavior of polymers under confinement [1–20]. On nonwetable substrates, such ultrathin films (thickness, $h < 100$ nm) may undergo dewetting driven by capillary (intermolecular) forces [1–13] and residual stresses within these films [14–21]. However, only recently the causes and consequences of residual stresses in ultrathin films, generated by the process of spin coating which is often employed for thin film preparation [14,20], were investigated systematically. In a physical aging experiment, residual stresses were found to play a prominent role in controlling nucleation and growth of dewetting holes in the thin viscoelastic films [16]. Theoretically, it was shown that films experiencing lateral stress undergo an instability initiated by an anisotropic diffusion of the polymer molecules which can lead to the formation of dewetting holes [17]. Substantial residual stresses, also dubbed molecular recoiling stresses, were determined by dewetting experiments as a function of molecular weights and film thickness in thin polymer films [16–20].

One of the striking revelations discovered in these recent experiments is the surprisingly large magnitude of the molecular recoiling force, which can amount up to several times the capillary force [18,20]. In the here presented dewetting experiments, we attempt to temporarily store part of the corresponding energy in the form of deformation energy of an elastic substrate and so try to make the magnitude of these stresses visible. In addition, we anticipate that the transient contribution of the molecular recoiling force in dewetting of viscoelastic thin films on deformable soft elastomeric substrates should give rise to a host of remarkable dewetting scenarios. Taking into account knowledge of liquid-liquid dewetting, film-soft substrate interactions [3,5], as well as liquid droplet

spreading on viscoelastic surfaces [22–27], we therefore explore the dewetting behavior based on a strong mechanical coupling between a viscoelastic film and a soft elastic substrate. In particular, we report the first detailed study on how dewetting on a soft substrate depends on the relaxation time of the retracting polymer.

For our experiments, monodisperse, high molecular weight polystyrene (PS) ($M_w = 0.2, 0.4, 0.9, 1, 2,$ and 5 Mg/mol, $M_w/M_n < 1.10$, Pressure Chemicals Company, USA and PSS, Mainz, Germany) were used for the formation of ultrathin viscoelastic films of thickness (h) ranging from 20 to 80 nm. The substrates used for most of the experiments presented here were prepared by spin-coating a heptane or toluene solution of polydimethylsiloxane (PDMS) silicone rubber (Sylgard 182 or Sylgard 184, Dow Corning) onto polished silicon wafers. The resulting thickness (e) ranged from 20 nm to about $2 \mu\text{m}$. The Young's modulus of the silicone cured for 1 h at 150°C was 2 MPa [28]. On top of this silicone layer, we spin coated the ultrathin PS film. We note that the results presented below did not change significantly when the PS film was prepared on a bare silicon wafer, floated off on water and then transferred onto the silicone layer. However, as this transfer process contains the risk of creating many imperfections in the films (stresses, deformations, ripples, folds, weak contact, inclusions of air gaps, etc.), we used such samples only for control experiments. To investigate the effect of substrate softness, we used a Si-wafer coated with a thin monolayer of irreversibly adsorbed PDMS (thickness 10 nm). The film thickness and roughness of the PS films were measured by ellipsometry and atomic force microscopy (AFM). Dewetting was performed in a vacuum oven or on a nitrogen-purged microscopy hot-stage at temperatures ranging from 130°C to 200°C . The dewetted samples were examined under an optical microscope and by AFM (Digital Instruments Nanoscope IIIA/D3100) at ambient conditions.

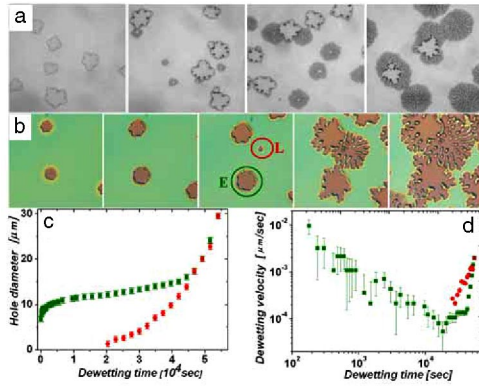


FIG. 1 (color online). Optical micrographs showing dewetting of (a) of different samples of a 40 nm PS film ($M_w = 0.9$ Mg/mol) on a $2 \mu\text{m}$ PDMS layer at 170°C ($\tau_{\text{rep}} = 2700$ sec) for (from left to right) 5360 480 and 540 min (size of images: $206 \times 206 \mu\text{m}^2$) and (b) a time series from a single 40 nm PS film ($M_w = 1.0$ Mg/mol) on a 200 nm PDMS layer at 180°C ($\tau_{\text{rep}} = 1200$ sec) for (from left to right) 2, 110, 380, 800, and 900 min (size of images: $58 \times 58 \mu\text{m}^2$). (c) Hole diameter (for uneven holes, a mean diameter of the enveloping perimeter of the hole was taken), and (d) dewetting velocity for the holes labeled by **E** (squares) and **L** (circles) in panel (b).

Previous experiments (e.g., [2,7,10]) on nondeformable, nonwetable substrates showed the appearance of many holes, randomly distributed across a thin polymer film which was heated above its glass transition. A distinct rim was associated with each hole and typically these holes grew until they eventually coalesced and formed polygon ridges which ultimately disintegrated into droplets via a Rayleigh instability [10,29]. However, in the here presented experiments a different behavior was observed (Fig. 1). Initial holes grew rapidly at the beginning, but subsequently slowed down significantly and came to an apparent standstill. In contrast, holes nucleated at later stages [for example, after several hours at 170°C in Fig. 1(a) and 1(b)] did not show such a slowing down but rather exhibited rim instabilities and an acceleration of the dewetting velocity. With the early formed holes remaining almost stationary, these later ones grew so rapidly that they eventually covered almost the whole film. Interestingly, at about the same time as these secondary unstable holes appeared, the early stage holes also slowly restarted to grow in diameter and developed fingers.

Such a difference in dewetting behavior between early and late holes, but also the possibility to nucleate holes in thin films after many hours of annealing, was never observed on hard substrates. Thus, we examined the influence of the soft substrate by systematically varying the thickness (e) of the rubbery PDMS layer. From Fig. 2, it becomes quite obvious that, with respect to hard substrates, dewetting on soft substrates was slowed down significantly. For example, at annealing times longer than about 10^4 sec, a quasistatic hole diameter was observed which did not depend significantly on the dewetting temperature [see

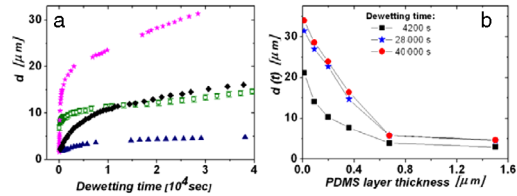


FIG. 2 (color online). (a) Hole diameter (d) as a function of dewetting time (for uneven holes, a mean diameter of the enveloping perimeter of the hole was taken) for a 55 nm PS film ($M_w = 1.0$ Mg/mol) dewetting at 130°C ($\tau_{\text{rep}} = 1.2106$ sec) on a 10 nm monolayer of irreversibly adsorbed PDMS molecules (stars), a 360 nm thick (lozenges) and a $2 \mu\text{m}$ thick cross-linked PDMS layer (triangles). For comparison, the data from hole “**E**” of Fig. 1 (open squares) are replotted (b) Hole diameter as a function of the thickness of the soft rubbery PDMS layer for a 55 nm PS film ($M_w = 1.0$ Mg/mol) dewetting at 130°C measured after different dewetting times as indicated in the figure.

the 360 nm thick PDMS layer in Fig. 2(a)]. Solely, at the significantly higher temperature of 180°C , this diameter was reached much faster. From Fig. 2(b), one can conclude that the hole diameter decreased with increasing PDMS layer thickness. In contrast to the behavior on a hard substrate (compare with the results on Si-wafer coated with a PDMS monolayer), dewetting holes created on a cross-linked PDMS layer of $1.5 \mu\text{m}$ did not grow beyond a diameter of about $5 \mu\text{m}$, even after long annealing times (but shorter than the bulk reptation time (τ_{rep}) of the polymer at that dewetting temperature [30]). We conclude that dewetting of PS films on thick enough soft substrates seems to be confronted with a limiting diameter of the opening holes.

Detailed inspection of the dewetting hole topography by atomic force microscopy (Fig. 3) unveiled that the depth of the holes could be much deeper than the film thickness. This indicated that significant substrate deformations incurred by dewetting, manifesting a strong mechanical coupling between visco-elastic film and soft substrate. The deformation of the substrate proved to be elastic and was fully recoverable as verified by removing the PS film via a solvent rinse. Large deformations in the PDMS layer occurred only during stages of dewetting when the PS film was deformed elastically, i.e., at times shorter than τ_{rep} . Consequently, for experiments at low temperatures close to the glass transition the influence of film elasticity persisted for longer times. Pushed aside by the opening forces, the material from within the dewetted hole generated a visible rim at the hole perimeter, and simultaneously a similar rim on the substrate side, which we call an “elastic trench” as it deformed the rubbery PDMS layer underneath. Most importantly, this substrate deformation engendered an elastic restoring force which counteracted the driving capillary and molecular recoiling forces in the film. The existence of a trench also caused an increase in frictional resistance for the opening of the hole by augmenting significantly the

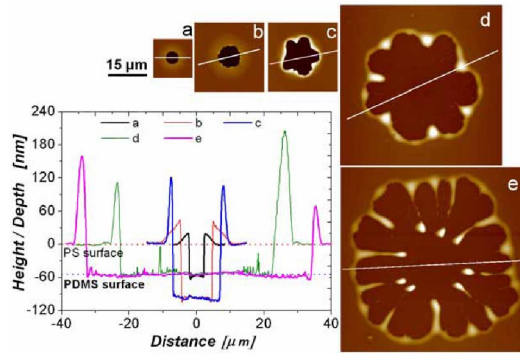


FIG. 3 (color online). Atomic force microscopy cross section through dewetted holes, indicated by white lines in the corresponding full 2D topography AFM images next to the graph, in a 55 nm PS film ($M_w = 1.0$ Mg/mol) on a 360 nm PDMS layer, dewetting at 140 °C ($\tau_{\text{rep}} = 160000$ sec) for (a) 300, (b) 1500, (c) 20 000, (d) 800 000, and (e) 950 000 sec, respectively. The surface of the unperturbed PS film has been set to zero height or depth level. Accordingly, the level of the unperturbed PDMS surfaces is at -55 nm. Traces *b* and *c* represent the transient depression in the soft substrate.

contact area between PS and PDMS which is proportional to the perimeter of the trench. The shape of the dewetting hole and the depression in the PDMS layer thus have to be related to the balance of the driving dewetting forces in the viscoelastic film, the frictional resistance at the film-substrate interface, and the counteracting elastic substrate deformation. All together caused the slowing down of dewetting with the increase of the thickness of the deformable soft PDMS layer and ultimately allowed only the formation of comparatively small quasistatic holes.

The deformation of the cross-linked rubbery substrate did not disappear once the residual stresses had relaxed which, based on previous experiments [16,19], occurred at a time significantly shorter than τ_{rep} . In fact, the apparent standstill of hole propagation after only few minutes of annealing at 180 °C (Figs. 1) is believed to be strongly influenced by a rapidly decreasing contribution of residual stresses to the forces driving dewetting while, by contrast, the forces resisting dewetting due to the elastic deformation of the substrate (the trench) still remained. However, the lifetime of the trench is not infinite. The elastic trench could be removed by polymer diffusion and viscous flow driven by capillary forces (Laplace pressure) which had to compete with interfacial friction between PS and PDMS at the level of the trench, an equilibration process needing relatively long times, longer than τ_{rep} . After full equilibration, only a much shallower “viscous trench” caused by the normal component of the capillary force (i.e., $\gamma \sin\theta$, with γ being the surface tension of PS and θ being the contact angle [23]) was left. At that point, most resistance due to deformation of the rubbery PDMS film was removed and the PS film slipped on the PDMS substrate. Consequently, the dewetting rim became unstable due to a dewetting velocity which now depended on the width of

the rim [31]. This rim instability [31,32] generated finger-like threads of PS which eventually decomposed into droplets.

It was already demonstrated previously [13,18,20] that residual stresses resulting from film preparation can be significantly larger than capillary forces and, at times shorter than τ_{rep} , are responsible for the formation of highly asymmetric rims in elastically deformed polymer films. These rims were much larger than ones generated by capillary forces alone [15,16]. As a first approximation, the substrate depression (D), measured inside the hole (see Fig. 3), can be considered as a direct indicator of the local strain in the PDMS layer inside the hole, from which the total dewetting force exerted on the film can be estimated [15–20]. As shown in Fig. 4, the systematic analysis of D made it clear that D reached a maximum value within relatively short time. Later on, D slowly started to decrease. The late stage dewetting process, characterized by a renewed increase in hole diameter and the nucleation of rapidly growing 2nd-stage holes, set-in when the substrate depression decreased substantially. However, in Fig. 4 this stage was only reached for the shorter polymer where the dewetting time exceeded τ_{rep} . It is quite revealing that for $t < \tau_{\text{rep}}$ the hole diameter for both samples in Fig. 4(b) (differing in chain length by a factor of 5) reached about the same quasistatic value of approximately 20 μm . The vanishing of the depression in the soft substrate reflects both the decrease of the residual stresses and the transition to a viscous behavior at times longer than τ_{rep} , causing a transition from the initial elastic trench [Fig. 4(c)] to the

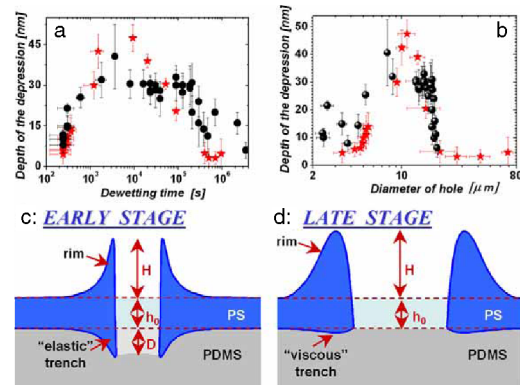


FIG. 4 (color online). Depth of the depression within the hole (a) versus dewetting time and (b) versus the diameter of the holes for the samples of Fig. 3 (stars) and a 55 nm PS film ($M_w = 5.0$ Mg/mol) on a 360 nm PDMS layer, dewetting at 130 °C (spheres, $\tau_{\text{rep}} = 2.910^8$ sec). (c),(d): Schematic representation of the shape of the rim and the trench of a dewetting hole in a PS film deforming the soft rubbery PDMS layer underneath. Because of elastic deformation of the PS film at early stages the corresponding elastic trench is digging into the soft PDMS under-layer quite deeply. At late stages, after the relaxation time τ_{rep} , only a small deformation (viscous trench) due to the normal component of the capillary force at the three phase contact line is left in the PDMS layer.

final viscous trench [Fig. 4(d)]. Holes which were nucleated only after the relaxation of residual stresses were never surrounded by large rims and correspondingly never caused large deformations of the soft substrate. Therefore, equilibration of the trench was fast and the transition to a viscous dewetting behavior occurred soon after hole nucleation.

In conclusion, a novel dewetting behavior of thin polymer films on soft substrates exhibiting two distinctly different stages was revealed. The transition from early to late stage dewetting was found to be governed by relaxation processes in the dewetting viscoelastic film. At times shorter than τ_{rep} , due to elastic deformation of the dewetting film amplified by residual stresses [15,16,19], a considerable trench was induced in the deformable substrate. The size of the trench was much larger than what capillary forces alone could have achieved. If such an elastic deformation could be maintained indefinitely, holes would never grow beyond a maximum diameter determined by the balance of forces driving dewetting and the counteracting elastic force resulting from the induced elastic deformation of the rubbery substrate. However, the elastic behavior of the dewetting film vanished at times longer than τ_{rep} and thus the elastic trench disappeared. At this stage, the polymer behaved like a viscous fluid and dewetting was controlled by slippage, which induced a Rayleigh-type rim-instability [31,32] and led to droplet formation. Consequently, by using deformable substrates, long-lasting metastable films containing only tiny holes can be achieved for times shorter than τ_{rep} . In potential applications, one may take advantage of the often very long relaxation times of polymers. In such cases, one can obtain almost stable films for extended periods of time by simply using soft instead of rigid substrates.

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