

Dewetting at the Liquid-Liquid Interface

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The dewetting behavior of a liquid film from a liquid substrate has been studied as a function of the substrate viscosity, using two highly viscous polymers as a model system. The dewetting velocity exhibits a minimum as a function of substrate viscosity. This behavior results from the competition of (1) the mass transport in the substrate, and (2) the retarded deformation of the liquid-liquid interface. Atomic force microscopy is used to image both the liquid-air interfaces and the buried liquid-liquid interface. The shape of the latter changes significantly with increasing substrate viscosity.

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The dewetting of thin liquid films from a flat surface is a common phenomenon with crucial impact on various technological processes. In recent years, the stability of thin liquid films has received considerable scientific interest as well, and a basic understanding of spreading and dewetting has evolved both for simple liquids and complex fluids [1–12]. Thin polymer films with high molecular weights have proven to be ideal model systems in these studies owing to their low vapor pressure and due to the fact that their high viscosity facilitates the study of the dynamic behavior. While most studies so far have dealt with thin liquid films on a solid substrate, the more complex situation of a liquid dewetting from a liquid substrate has received much less attention [12–16]. Brochard-Wyart, Martin, and Redon [12] recently presented a detailed theoretical study suggesting that liquid-liquid dewetting should exhibit a variety of different regimes depending mainly on the relative viscosities of the two liquids, the thicknesses of the respective liquid layers, and the surface and interfacial tensions involved. Martin, Buguin, and Brochard-Wyart [13] showed that the dewetting velocity depends on the viscosity of the substrate and decreases with increasing substrate viscosity. This apparently intuitive result points to the importance of the particular shape of the liquid-liquid interface around the growing hole and suggests that, in contrast to a solid substrate, the rim extends into the underlying liquid. However, so far direct verification of this model has not been possible, as the necessary three-dimensional imaging of the liquid-liquid interface during the dewetting process is a tedious experimental task. As will be shown below, the situation can be even more involved as the amount to which the rim penetrates into the substrate is in itself determined by the relative mobilities in the two liquids.

In this Letter, we present a systematic study of the dewetting process at a polymer/polymer interface for varying molecular weight of the polymeric substrate. It is found that the dewetting velocity initially decreases with increasing substrate molecular weight; however, at large substrate viscosities, the opposite trend is observed. We present a novel technique to image the shapes of both the

growing hole and the interface between the two polymers at any stage of the dewetting process. The shape of the interface changes significantly with substrate viscosity, thereby directly influencing the dewetting velocity. The experimental results are compared to recent theoretical predictions [12].

The system under investigation is a polymeric bilayer of polystyrene (PS) and poly(methylmethacrylate) (PMMA). The viscosity of both materials was varied over a wide range by choosing monodisperse batches of different molecular weights. PMMA films were spin coated from a toluene solution onto polished silicon wafers. The resulting thicknesses were determined by ellipsometry to be 95 ± 2 nm. Subsequently, PS films of two different molecular weights were floated onto the PMMA substrates. The thickness of the PS layers was 91 ± 3 and 124 ± 3 nm for PS($M_w = 95$ kD) and PS($M_w = 177$ kD), respectively. To initiate the dewetting process, the samples were heated to a temperature well above the glass transition temperature ($T_g \approx 100$ °C) under an inert gas atmosphere provided by a constant flow of argon. To ensure reproducibility between different samples, up to seven samples were simultaneously annealed and observed in a single experiment. The dewetting of the PS films was monitored *in situ* through a reflection microscope. “Snapshots” of holes were taken with a charge coupled device camera and stored onto a PC. The shapes of the polymer-air and the polymer-polymer interface were investigated with atomic force microscopy (AFM) by interrupting the dewetting process and rapidly cooling the samples down to room temperature. On each sample, holes of approximately the same size (~ 25 μ m in diameter) were selected. After imaging the free surface of the film the PS top layer was removed by immersing the samples in cyclohexane for 90 sec. After drying, the corresponding area on the remaining PMMA surface was imaged again to obtain information of the former PS/PMMA interface around the holes.

We start our discussion with the results on the dewetting velocity. A series of samples with PS molecular weight $M_{w,PS} = 95$ kD and varying PMMA molecular

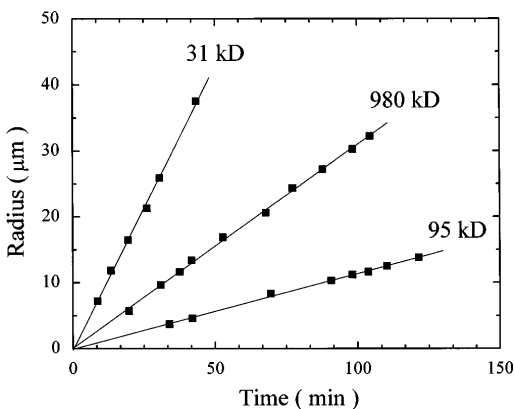


FIG. 1. Radii of holes in the PS layer as a function of time t for various molecular weights of the PMMA substrates ($M_{w,PS} = 95$ kD, $T = 170$ °C).

weight was annealed at $T = 170$ °C and monitored simultaneously. Upon annealing, circular holes are formed spontaneously in the PS top layer [17], which are found to grow as a function of annealing time. The radius of these holes is determined by a straightforward numerical analysis of the digitized images. Over the times accessible in the experiment, a linear growth is observed in all cases, indicating a constant dewetting velocity $v = dR/dt$ (Fig. 1). In Fig. 2, this dewetting velocity is plotted as a function of the molecular weight of the PMMA underlayer. For low PMMA molecular weights, the dewetting velocity is indeed found to decrease with increasing PMMA molecular weight. However, in contrast to the results of Ref. [13], the dewetting velocity exhibits a minimum at around $M_{w,PMMA} = 90$ kD, and starts increasing again as the PMMA molecular weight is further increased. We have repeated the experiment with a different PS molecular weight ($M_{w,PS} = 177$ kD) and somewhat thicker PS films. The results of this series are included in Fig. 2 as well. The same general behavior is observed, with the minimum of the dewetting velocity being shifted to higher PMMA molecular weight around 170 kD.

For the following discussion it is useful to distinguish two regimes in substrate viscosity. For small PMMA viscosity (regime I) the dewetting velocity is rapidly decreasing. As outlined briefly above, the rapid decrease of dewetting velocity with decreasing substrate mobility

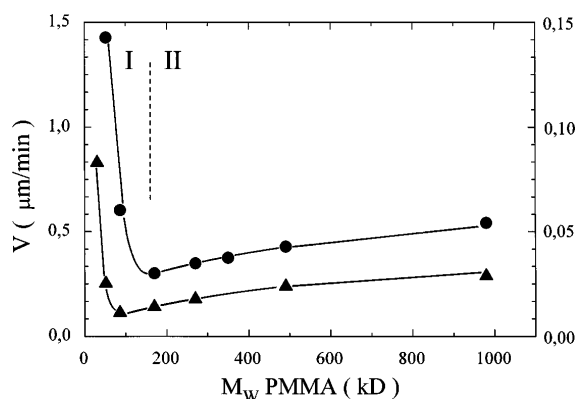


FIG. 2. Dewetting velocity $v = dR/dt$ of thin PS films from a thin PMMA underlayer as a function of the molecular weight of the PMMA. Triangles: $M_{w,PS} = 95$ kD, $T = 170$ °C (left scale); circles: $M_{w,PS} = 177$ kD, $T = 180$ °C (right scale). The solid lines are guides to the eye.

can be reasoned by assuming that the rim around the growing holes extends considerably into the substrate layer. To test this hypothesis experimentally, we have imaged portions of holes with AFM before and after removal of the PS top layer with cyclohexane (Fig. 3). The two images were taken at the same spot. In Fig. 3(b) the curved shape of the bottom part of the rim clearly shows that the PS trim extends considerably into the PMMA underlayer. Apparently, dissolving one of the components provides a good means of imaging the polymer-polymer interface.

The AFM results obtained in regime I confirm the notion that the lower portion of the rim leads to a hydrodynamic resistance against the growth of the holes. However, the different behavior in regime II, where we observe an *increase* in dewetting velocity with decreasing substrate mobility, suggests that this resistance is decreased for large PMMA molecular weights. We propose that with decreasing substrate mobility, the deformation of the PMMA layer necessary for rim penetration cannot be accomplished fast enough during the dewetting process. In the extreme case of very high PMMA molecular weight the PS overlayer dewets from an effectively flat PMMA underlayer with the finite (but small) interdigitation of polymer chains at the interface, being the only hindrance against slippage [18].

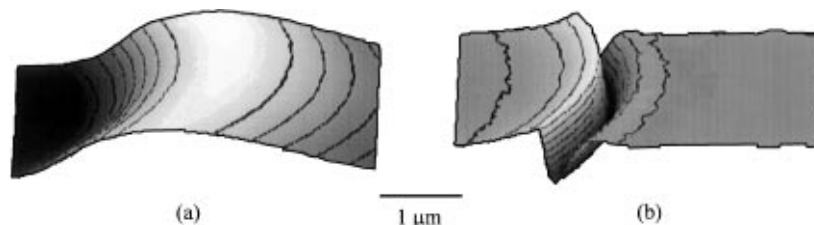


FIG. 3. AFM images of the right edge of a 25 μm wide hole before (a) and after (b) removal of the PS top layer using a selective solvent ($M_{w,PS} = 95$ kD, $M_{w,PMMA} = 31$ kD; $T = 180$ °C). Black contour lines are included for clarity. These lines connect points of equal height; since raw data are shown without any smoothing, the lines appear somewhat fuzzy in areas of small surface slope.

To investigate the role of the interface deformation we extended the AFM investigations to higher substrate viscosities and examined the effect of the PMMA molecular weight on the shape of the polymer-polymer interface. In Fig. 4 single traces of AFM scans are shown for rims of holes with increasing PMMA molecular weight. The bottom part of the rim of 31k PMMA forms a clear "trench," which is much less developed for 56k PMMA and which is absent for PMMA molecular weights above 126k. This finding supports our hypothesis that the shape of the bottom part of the rim is responsible for the observed behavior of regime II. It should be emphasized that the observed flattening of the lower portion of the rim is a dynamic effect resulting solely from a competition of the different mobilities in the two liquids. This interpretation is corroborated by the shift of the minimum in dewetting velocity to larger PMMA molecular weight as the viscosity (mobility) of the dewetting PS layer is increased (decreased; see Fig. 2). With higher PS viscosity, the dewetting slows down and the effective time for rim penetration is increased. Consequently, the effect of rim flattening should become relevant only at higher PMMA molecular weights. As a matter of fact, the equilibrium contact angles determined by the surface and interfacial energies of the two polymers, do *not* vary significantly with PMMA molecular weight. This fact was established experimentally by investigating the interfacial shape in droplets formed during the late stage of dewetting.

In the following, we shall compare the experimental findings with the theoretical predictions put forward in Ref. [12]. The AFM images of the polymer-polymer interfaces indicate that we establish a transition from substrate liquid behavior to a substrate solid behavior with increasing PMMA molecular weight. This transition is expected to occur at $\eta_{\text{PMMA}} \cong \eta_{\text{PS}}/\Theta_E$ with η_{PMMA} , η_{PS} , and Θ_E being the viscosities of the two polymers and the equilibrium contact angle, respectively. Given that the latter does not significantly depend on molecular weight for the polymers studied here, the transition should occur at higher PMMA weight, when the PS molecular weight is increased. This effect is observed qualitatively in Fig. 2, where we show that the location of the minimum dewetting velocity is shifted to higher PMMA viscosities as we increase the PS molecular weight. In regime I, a linear growth of the holes is expected for underlayer thicknesses L comparable to the lateral size l of the rim, while for very thin underlayers ($l \ll L$), the holes are expected to grow as $t^{2/3}$ [12]. In our experiments, the PMMA underlayer thickness is rather small and one may expect the $t^{2/3}$ -thin substrate behavior. In contrast, the experimental results indicate a constant dewetting velocity. For a comparison to the theoretical predictions, it needs to be emphasized, though, that the overall shape of the rims for low molecular weight PMMA differs significantly from the model presented in Ref. [12]. In contrast to the theoretical model, the interface deformation

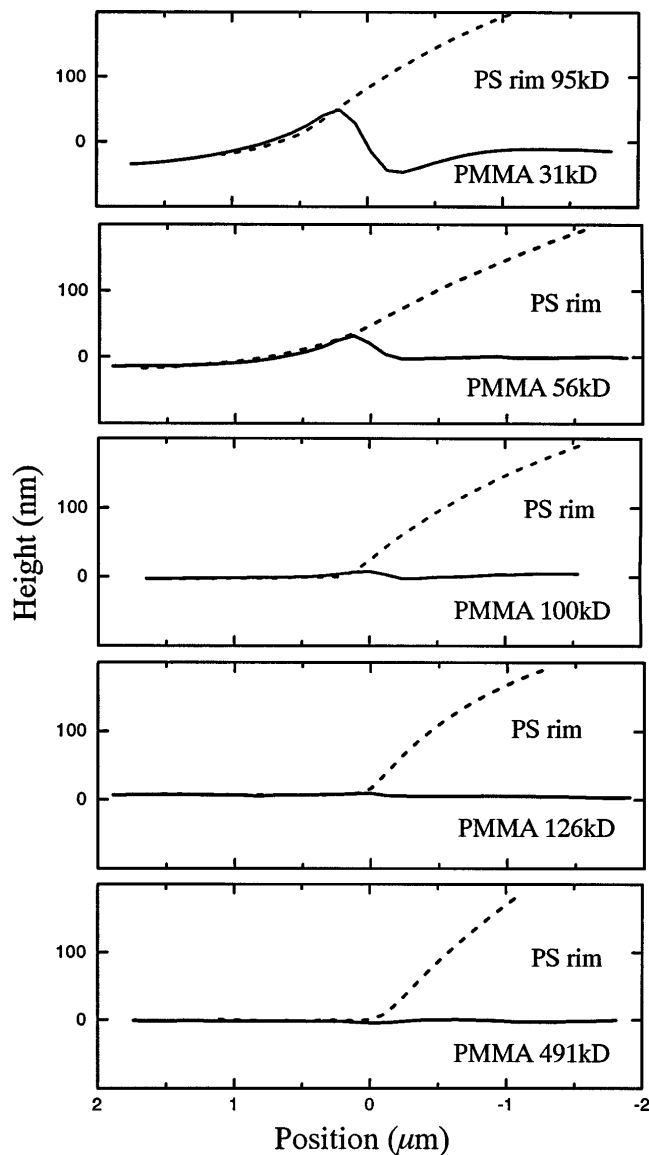


FIG. 4. Cross sections through AFM images taken at the same holes before (dashed line) and after (solid line) removal of the PS top layer for different PMMA molecular weights. ($M_{w,\text{PS}} = 95 \text{ kD}$; $M_{w,\text{PMMA}} = 31k, 56k, 100k, 126k, \text{ and } 491k$).

is localized close to the contact line and its lateral extension l' is significantly smaller than the total size of the rim. Therefore, the experiments do not clearly fall in the thin substrate regime ($l' \ll L$), but rather in a transition regime between thin and bulky substrates. To further explore this problem, we have repeated the same set of experiments for PMMA thickness around 30 nm and have found no qualitative difference in the observed interfacial structure and growth characteristics. For film thicknesses considerably thinner than 100 nm, however, a strong decrease of the dewetting velocity with decreasing PMMA thickness is observed. Here, the mobility of the PMMA substrate layer may well be influenced by the presence of the silicon surface. While this issue shall be the subject of a forthcoming publication [19], we conclude

that the data shown in the present paper are consistent with a constant dewetting velocity decreasing as η_{PMMA}^{-1} as expected for a bulk substrate. This finding certainly points to the importance of the particular interfacial shape for the dewetting behavior. In regime II, the experimental finding of a constant dewetting velocity is in agreement with the theoretical prediction for dewetting from a solid substrate given that nonslip conditions prevail. While the large PMMA viscosity at high PMMA molecular weights establishes a literally solid surface, it is the finite interpenetration of polymer chains at the PS/PMMA interface that prevents the PS from slippage.

Finally, we offer a tentative explanation for the observed elevation of the contact line. Given that our substrates are liquid, during the dynamic process of dewetting the normal component of the surface tension pulls on and elevates the triple line. This reduces the free energy of the system in much the same way that a fluid on a viscoelastic solid raises the contact line [20]. However, given that the effect of contact line elevation is most pronounced at low PMMA viscosities, it can be attributed to flow rather than to viscoelastic effects. This reasoning is confirmed by additional experiments showing that an even more pronounced rim elevation is observed if the relative viscosity of the PMMA substrate is further decreased. It is interesting to note that, *in equilibrium*, PS droplets on thin PMMA films also exhibit a lifting of the triple line while those on thick films do not. In both cases the system tries to increase the area of the (low interfacial energy) PS-PMMA interface at the expense of the (tenfold higher interfacial energy) PS-air interface, thereby reducing the total free energy. In the thick film case, however, the droplet can sink into the film and lower the total surface areas without having to raise the contact line. We conclude that during dewetting the PS cannot sink into the PMMA layer fast enough, thereby assuming its equilibrium shape due to hydrodynamic flow beneath the droplet.

In conclusion, we have shown that the dewetting velocity of thin liquid films from liquid substrates exhibits a complex dependence on the substrate viscosity in qualitative agreement with recent theoretical predictions. The use of a polymeric model system together with selective dissolution of one of the polymers enabled us to directly image the liquid-liquid interface during the dewetting process. The shape of the interface is shown to vary with the substrate viscosity, thereby strongly influencing the dewetting process. The results indicate that care must be taken with assumptions on the interfacial shape during liquid-liquid dewetting. Besides this, the

technique of interface imaging via selective dissolution of one of the polymers could prove to be a valuable tool applicable to a much wider class of interfacial problems.

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