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Influence of Substrate Properties on the Dewetting Dynamics of Viscoelastic Polymer Films

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Influence of Substrate Properties on the Dewetting Dynamics of Viscoelastic Polymer Films

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We studied the dewetting process of thin polystyrene (PS) films on silicon sub-strates, coated with a thin, irreversibly adsorbed polydimethylsiloxane (PDMS) layer, by optical microscopy and atomic force microscopy. Besides demonstrating the exceptional potential of dewetting for a sensitive characterization of rheological properties of PS thin films, characterized by a stress-relaxation time, τ_1, we focused on the influence of the frictional behaviour (energy dissipation mechanism) at the interface between the PDMS-coated silicon wafer and the PS film on the dewetting process. Our results show that the initial stages of dewetting depend sensitively on the thickness and the way the PDMS layer was adsorbed. The maximum width of the dewetting rim at τ_1 increased with increasing PDMS layer thickness, which can be interpreted as an increase of the effective, velocity-dependent slippage length. Interestingly, τ_1 was found to be almost independent of the substrate properties. Our results demonstrate that dewetting is a really powerful approach for rheological and frictional studies of thin polymer films.

INTRODUCTION

Many phenomena such as wetting, adhesion, and friction are affected by the surface and interface properties [1,2], and consequently, they are significant not only from the scientific point of view but also for applications. Partially driven by their importance in many industrial processes, properties of thin liquid films are the object of numerous theoretical and experimental studies. The roles of thin films in the protection of surfaces, the composition of paintings, or the stability of adhesives represent only a few applications that illustrate the richness and the importance of this field of study. As an example of particular interest in recent years, we mention the deviations of the glass-transition temperature, T_g, from bulk values, which have been reported for thin polymer films [3–12].

Our understanding of the origin of some extraordinary properties of thin polymer films in the nanometer range is still not satisfactory, despite enormous efforts over the past decade. Several approaches were employed to investigate and quantify mechanical, relaxation, and calorimetric properties. A better understanding of the glass transition and other properties of polymer surfaces and interfaces might also come from the dynamic studies such as dewetting. Thus, to get some insight into temporal changes in thin films, we and several other groups have chosen dewetting studies [13–41]. A schematic representation of the dewetting process and geometry is given in Figure 1. Previously, it has been shown that the dewetting behaviour close to the glass transition of the polymer is rather complex [26–30,33–41].
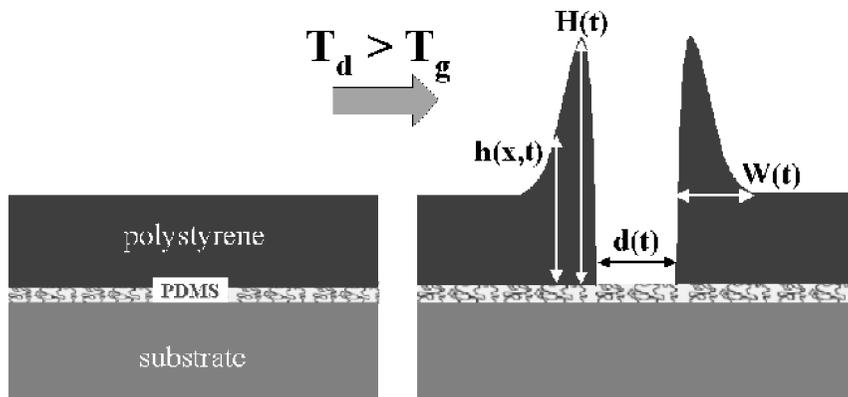
FIGURE 1 Schematic representation of the studied system before (left side) and during (right side) dewetting.

In particular, the shape of the part collecting the removed material (*i.e.*, the rim), the change of this shape with time, and the appearance of several regimes exhibiting different dynamic behaviour have attracted our attention.

Dewetting experiments represent an attractive possibility because of their simplicity, sensitivity, and rapidity. Dewetting allows one to link molecular and interfacial properties (and variations thereof) with macroscopically observable parameters such as dewetting velocity and shape of the rim. Despite its simplicity with respect to experimental observation—a simple optical microscope often is more than sufficient—it turns out that dewetting is extremely sensitive to even tiniest changes in the studied system. Previously, when analyzing and interpreting dewetting results, the focus has been on the temporal evolution of the dewetted distance. However, several other relevant parameters such as the shape of the rim and its temporal evolution can (and have to) be observed simultaneously, which provides access to additional information in a highly quantitative way.

When dissipation of the invested energy originating from capillary forces is mainly located within the volume of the film, the removed material (proportional to the dewetted distance, d) will be redistributed within the film over a certain distance, Δ_0, which is characterized by film thickness, h_0, and frictional properties [39]:

$$d << \Delta_0 \sim \left(\frac{h_0 \eta}{\zeta}\right)^{1/2} \tag{1}$$

with ζ being the friction coefficient at the interface and η the viscosity of the film. In such a situation, there will be no rim formed next to the dewetted zone. This is, for example, the case for free-standing films or at very early stages of hole opening in supported viscoelastic films.

However, for supported films, as more and more material will be removed in the course of time (*i.e.*, as the hole diameter increases), this material cannot easily be accommodated within the film and a rim will start to appear. At the beginning, the rim has a highly asymmetric shape (see Figures 1 and 2B), with a steep side reaching a height (H) next to the three-phase contact line and an exponential decay on the other side, with a decay length Δ_0. One can also define a width (W) of the rim as the distance between contact line and the position where the height of the rim has reached a value rather close to the initial film thickness h_0. At the earliest stages of dewetting, which can be identified by optical microscopy, experiments showed [26,27,38,41] that both H and W increased approximately linearly with the dewetted distance (d), in contrast to the square-root dependence observed for viscous fluids [17]. At times longer than τ_1, W reached a maximum. Interestingly, also the temporal evolution of both H and W is similar (*i.e.*, logarithmic in time). Correspondingly, the dewetting velocity, defined at the contact line, is decreasing in time.

In this article, we present several experimental results on the dewetting behaviour of thin polymer films on smooth nonwettable substrates. We concentrate in particular on the influence of energy dissipation at the film–substrate interface and show how this affects the dewetting behaviour.
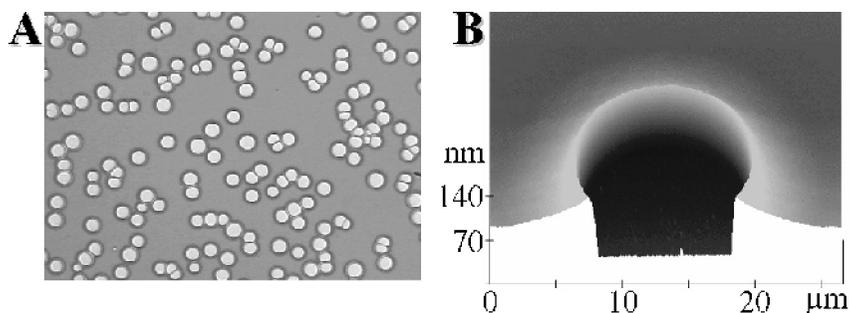
FIGURE 2 a) Typical optical micrograph ($310 \times 230 \, \mu m^2$) of a 40-nm-thick PS film ($M_w = 4840 \, kg/mol$) deposited on a silicon wafer coated with a 6-nm-thick PDMS layer ($M_w = 38 \, kg/mol$, annealed for 5 h at 150°C, PDMS layer thickness after washing: e = 6 ± 0.8 nm). The PS film was aged for 6.5 h at 50°C and then dewetted for 900 s at 125°C. b) One of these holes observed by atomic force microscopy. The asymmetric rim can be clearly seen.

EXPERIMENT

For the studies presented in this article, we used polystyrene (PS) thin films, which were directly spin-coated from toluene solutions onto polydimethylsiloxane (PDMS)-coated silicon wafers [26,27,38,41]. Dewetting, that is, the retraction of a liquid from a nonwettable substrate covered by spin-coating, is by now a well-studied phenomenon [13–41]. For simple Newtonian fluids on slippery solid surfaces, it was shown that the dewetting dynamics is determined by the dissipation of the capillary energy due to the friction at the solid/fluid interface [13–18]. For viscoelastic polymer fluids, as is the case for PS thin films dewetting at temperatures close to T_g, the situation is, however, more complex [26–30,33–41]. In the present studies, we mainly focused on the early stages of the dewetting process. Dewetting was followed for times shorter than the longest relaxation time of polymer chains in bulk (*i.e.*, the reptation time). During these stages, viscoelasticity dominates the dewetting behaviour.

For the monolayers of adsorbed PDMS, different chain lengths were used: the molecular weight varied from $M_W = 7400$, 38,000, 80,000 up to 139,000 g/mol (ABCR, Karlsruhe, Germany). The PDMS monolayers were formed from comparatively thick films (*ca.* 50 nm) prepared by spin-coating from a heptane solution of PDMS. Solvent evaporation resulted in a thin and uniform film, where the thickness is a function of the concentration of the heptane solution and of the spinning speed. The silicon substrates were properly cleaned by a UV–ozone treatment to remove organic contaminants. The PDMS chains were strongly adsorbed onto the substrate by hydrogen bonds with the silanol groups at the surface of a silicon wafer. The formation of such links was facilitated by annealing the films at elevated temperatures ($T > 100°C$) under vacuum for 5 h. Under these conditions, covalent bonds between the hydroxyl (-OH) groups at the substrate surface and the chain ends may also be formed. Both substrate–PDMS interactions finally led to irreversible adsorption of the PDMS chains. After annealing, the PDMS films were washed in a heptane bath (good solvent for PDMS) for 2 h to eliminate all the chains that did not adsorb to the substrate. Ellipsometric measurements were performed to determine the thickness (e) of the PDMS layer.

Similar to the PDMS films, the PS films ($M_w = 4,840,000$ g/mol, $M_w/M_n = 1.05$, Polymer Standards Service, Mainz, Germany) were prepared by spin-coating a rather dilute toluene solution onto silicon substrates covered with a PDMS monolayer. We obtained a PS film in a vitreous state, which had a characteristic brown interference

colour corresponding to a thickness (h_o) of 40 ± 2 nm as determined by ellipsometry.

Dewetting was induced by heating of the sample on a nitrogen-purged hot stage (Linkam TMS 91, Surrey, UK) above the glass-transition temperature. The temperature was controlled within $\pm 0.5°C$. Real time dewetting was observed by using an optical microscope (Leitz Metallux 3, Wetzlar, Germany).

In Figure 1, we schematically present the morphology of a polystyrene film before and during dewetting at a temperature above the glass-transition temperature, deposited on a PDMS-coated substrate of controlled molecular parameters. The most relevant parameters of dewetting are presented. In Figure 2, we give an example of a typical sample, observed by optical microscopy, showing a somewhat random distribution of many holes. Atomic force microscopy allowed us to determine the shape of the rim around such holes more precisely. In Figure 2B, the asymmetrical shape of the rim around these holes as well as the presence of the dry zone can be clearly observed. In this report, besides focusing on the transition between dewetting regimes defined by the relaxation time, τ_1, we focus in particular on the influence of energy dissipation at the PDMS–PS interface by varying the thickness of the PDMS layer.

RESULTS AND DISCUSSION

In Figure 3, we present a typical series of micrographs showing the growth of a dewetting hole in time (t). We obtained from each micrograph (exploiting line profiles reflecting the interference contrast) precise values of the dewetted distance (d) and the width of the rim (W) (see the scheme in Figure 1 for a definition of d and W). Complementary studies were performed with atomic force microscopy, like the example shown in Figure 2B, to confirm the optical micrographs and to obtain more precise information on the shape of the rim. Complete temporal series of images in the course of dewetting were systematically examined. As an example for such a systematic analysis, we present d(t) and W(t) in Figure 4.

Based also on previous studies [26,27,38,41], the main features of viscoelastic dewetting of such polystyrene films close to the glass-transition temperature can be summarized as follows: At early stages, the dewetted liquid is collected in rims of highly asymmetric shape (See figure 2B), consisting of a steep side towards the dewetted area and a much slower, approximately exponential decay on the rear side. This shape is distinctly different from the one of simple Newtonian fluids, where the rim is rounded as a consequence of the equilibration
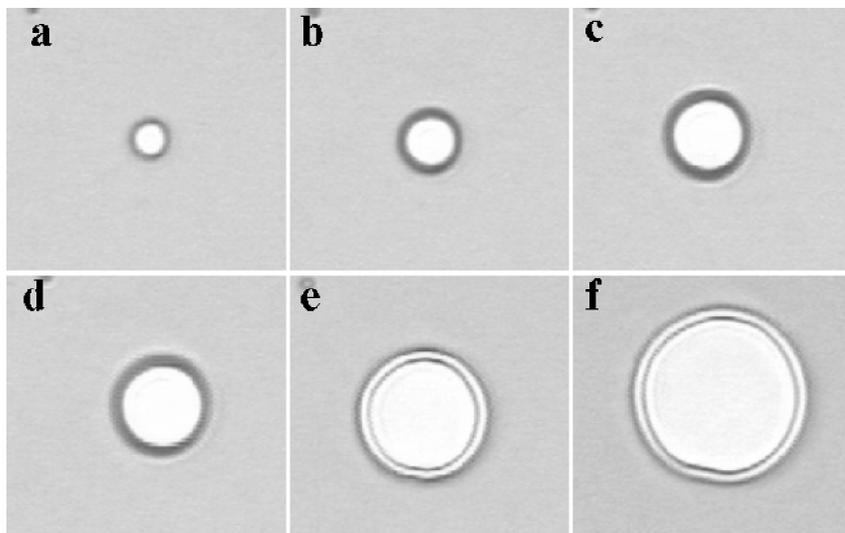
FIGURE 3 Temporal evolution of a hole in a PS film ($M_w = 51.6$ kg/mol, $h_0 = 40$ nm) on a PDMS-coated silicon wafer ($M_w = 38$ kg/mol, annealed for 5 h at 150°C, PDMS layer thickness after washing: e = 6 ± 0.8 nm), dewetting at a temperature of 115°C for a) 180 s, b) 600 s, c) 1200 s, d) 1500 s, e) 2700 s and f) 4800 s, respectively. The size of the optical microscopy images is 22.5×22.5 μm² each.

of Laplace pressure [17,18,39] within the rim. For viscoelastic fluids, the shape of the rim will eventually also be rounded by Laplace pressure. This change in shape sets in at a time τ_1.

As indicated in Figure 4, the evolution of d and W exhibits two regimes separated by τ_1. For $t < \tau_1$, W and d both increase approximately logarithmically in time (consequently, the dewetting velocity, V, decreases in time, $V \sim t^{-1}$). During this stage, the rim maintains an asymmetric shape [26,27]. For $t > \tau_1$, the shape of the rim starts to change noticeably, which is clearly manifested by W remaining almost constant while d still increases (however, at a different rate). In fact, the Laplace pressure begins to overcome the elastic effects. Thus, relaxations of the rim towards the more symmetric equilibrium shape set in. τ_1 represents an adequate measure of relaxation processes within thin films and can easily be determined from the temporal evolution of W. Based on this analysis, we can interpret dewetting experiments as a rheological study of nanoscopic polymer films. However, in addition to the rheological properties of the dewetting polymer film, the frictional behaviour (energy dissipation mechanism) at the substrate
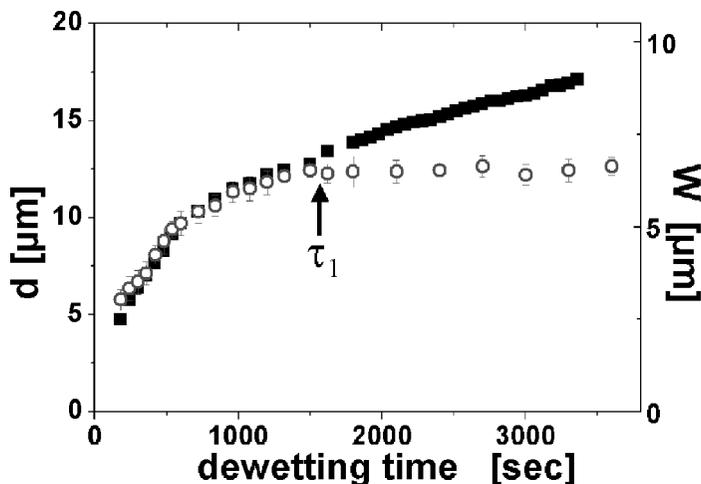
FIGURE 4 Temporal evolution of hole diameter (squares) and the width of the rim (circles) in a PS film ($M_w = 4840\,kg/mol$, $h_0 = 40\,nm$) on a PDMS ($M_w = 80\,kg/mol$, annealed for 5 h at 175°C, PDMS layer thickness after washing: $e = 11.3 \pm 1\,nm$) coated Si-wafer, dewetting at a temperature of 125°C. The characteristic time, τ_1, is given by the time when the width of the rim reaches a maximum value (W_{max}), which, for the high molecular weight used here, stays constant for a rather long time, while the dewetted distance still increases.

to polymer interface (between the PDMS-coated silicon wafer and the PS film) also significantly affects the dewetting process. Thus, in the following, we focus mainly on the influence of the substrate properties on the dewetting process. In particular, we are interested in how the dewetting dynamics change for different PDMS coatings, and we were asking if the relaxation time τ_1 is affected by the substrate properties.

To be able to easily compare the dewetting behaviour of different samples, we kept the parameters affecting the polystyrene film constant (concentration of the toluene solution, *i.e.*, the thickness of the PS film, the spin-coating process, the age of the sample) and only varied parameters affecting the PDMS coating. In a first series of experiments, we increased the thickness of the PDMS coating by increasing the chain length of the adsorbed PMDS molecules. Details are given in Table 1. The annealing procedure for adsorbing the PDMS layer was kept constant and was the same for all samples: 5 h at 150°C. During annealing, the PDMS molecules were adsorbed progressively more strongly by gradually bringing more segments per chain to the

TABLE 1 Thickness of the Adsorbed PDMS Layers for Different Molecular Weights and Annealing Temperatures

M_w PDMS (kDa)	e_{PDMS} (nm) $(T_{ann} = 105°C)$	e_{PDMS} (nm) $(T_{ann} = 150°C)$	e_{PDMS} (nm) $(T_{ann} = 175°C)$
7.4		3 ± 1	
38		6 ± 0.75	
80	6.7 ± 1	10 ± 1.5	11.3 ± 1.5
139		16 ± 2	

substrate where these segments could form hydrogen bonds with the hydroxyl groups of the substrate. As an alternative way to increase the thickness of the PDMS coating of the irreversibly adsorbed PDMS layer, we studied the influence of the annealing temperature (the annealing time was kept constant at 5 h). The thickness of the PDMS layer increased with annealing temperature (see Table 1). Probably, this thickness increase is due to an increase in the number of chemically end-grafted PDMS chains per unit area.

The influence of substrates with different PDMS coatings on the results of the opening of holes in time are shown in Figures 5 and 6. As can be clearly seen, the curves are qualitatively similar but differ significantly in the initial dewetting velocity (the d values increase much faster for the thicker PDMS layers) and the maximum value of the rim width (W_{max}). In principle, the increase in W_{max} can be due to several factors. According to the theoretical work by Vilmin and Raphaël [39], the width of the rim is controlled by the driving forces (capillary forces and residual stresses within the film) and the friction at the interface between the PDMS layer and the PS film [40]. Previous results on the same systems strongly support the concept of a nonlinear friction force, f_r, per unit surface for velocities, v, higher than a certain velocity, v_α, characterized by the friction exponent, α

$$f_r = \zeta v_\alpha \left(\frac{v}{v_\alpha}\right)^{1-\alpha} \qquad (2)$$

There, dissipation of energy at the film/substrate interface can be related to an effective friction coefficient between film and substrate that takes into account a nonlinear velocity dependence of the friction force [40].

Theoretically, taking into account Eq. (2), the maximum width of the rim is predicted to be [40]

$$\Delta_m \cong \Delta_{\alpha1} \left(1 + \frac{h_o \sigma_o}{|S|}\right)^{\alpha/(2-\alpha)} \qquad (3)$$
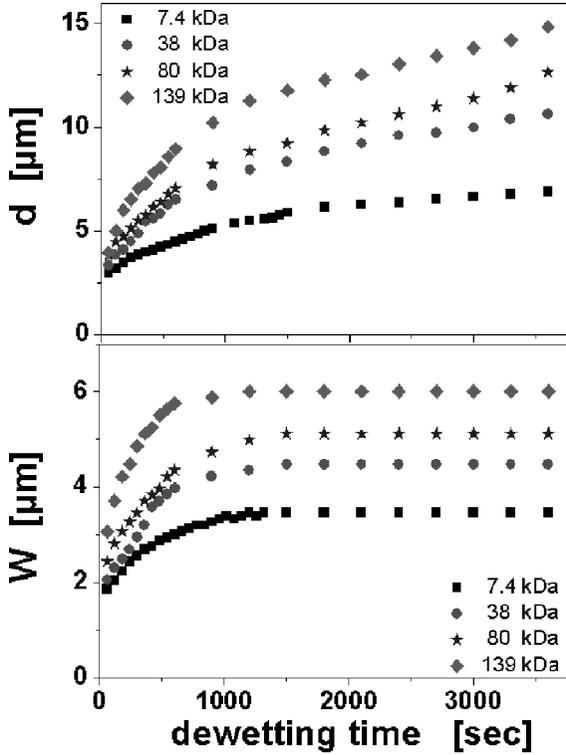
FIGURE 5 Influence of the molecular weight of the PDMS coating of the silicon wafers (M_w indicated in the figure, more details are given in Table 1) on the dewetted distance (d) and the width of the rim (W) as a function of dewetting time for a PS film ($M_w = 4840 \, \text{kg/mol}$, $h_0 = 40 \, \text{nm}$), dewetting at a temperature of 125°C.

with

$$\Delta_{\alpha 1} = \left[\frac{2-\alpha}{2} \left(\frac{V_1}{v_\alpha} \right)^\alpha \right]^{1/(2-\alpha)} \tag{4}$$

and

$$V_1 = \frac{|S|}{(\eta_1 h_o \zeta)^{1/2}}. \tag{5}$$

Here, h_o is the thickness of the PS film, σ_o represents the residual stresses within the PS film, $|S|$ is the absolute value of the spreading parameter, ζ is a friction coefficient, and η_1 is the viscosity of the PS film.
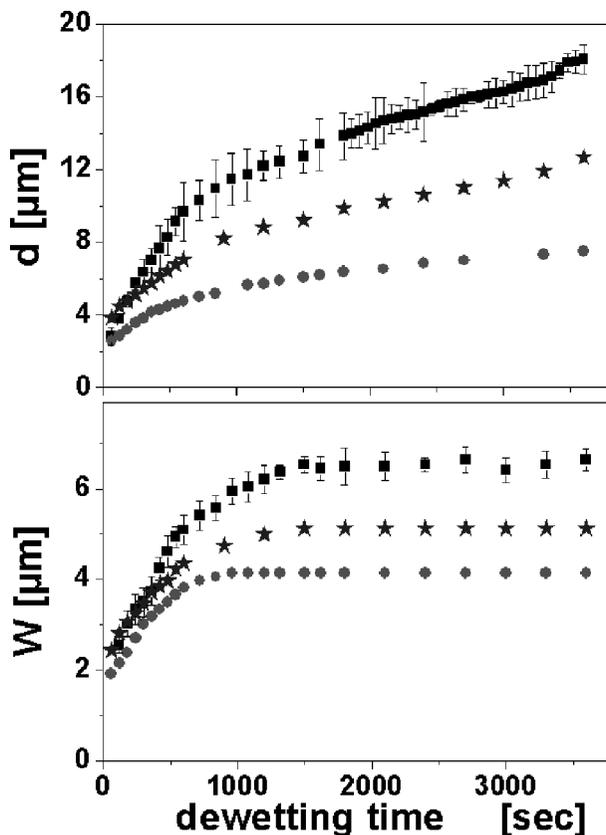
FIGURE 6 Influence of the annealing temperature of the PDMS coating of the silicon wafers ($M_w = 80\,kg/mol$) on the dewetted distance (d) and the width of the rim (W) as a function of dewetting time for a PS film ($M_w = 4840\,kg/mol$, $h_0 = 40\,nm$), dewetting at a temperature of $125°C$. The PDMS coating was annealed for $5\,h$ at $105°C$ (circles), $150°C$ (stars), and $175°C$ (squares), respectively.

As we used the same PS film for all our samples in Figures 5 and 6 and studied dewetting at the constant temperature of $125°C$, we can assume that the values of σ_o, η_1, and h_o are constant. The surface tension of the PDMS layer is also not expected to change significantly with the molecular weight and the thickness of the PDMS layer, consistent with previous experiments [42], and thus $|S|$ is expected to be about the same for all samples studied. Consequently, only changes in the friction coefficient, ζ, and/or the friction exponent, α, can cause variations in Δ_m.

In Figure 7a, W_{max} increases with the thickness of the PDMS layer. Based on these considerations, such an increase may be explained by a decrease of the velocity dependence of the friction force acting at the PDMS–PS interface in the course of dewetting. Interestingly, according to the theoretical predictions, a decrease of α will cause a decrease in the initial dewetting velocity, as observed in experiments.

Based on Eqs. (2)–(5), an increase in W_{max} by a factor of 2 can easily be achieved by a small increase in α, for values of α rather close to 1
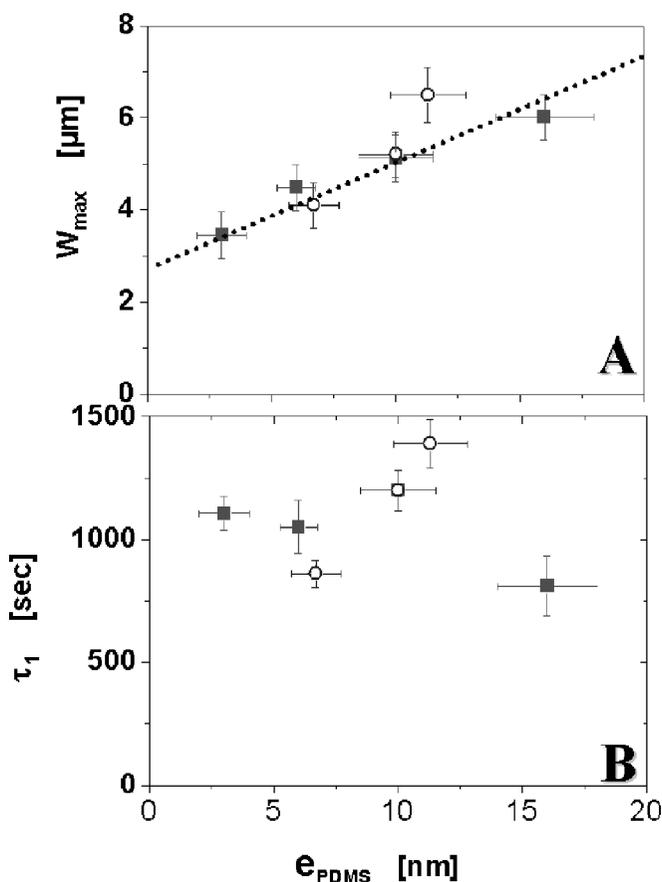
FIGURE 7 a) Maximum width of the rim (W_{max}) and b) relaxation time of residual stress (τ_1) as a function of the thickness of the adsorbed PDMS layer. This thickness was varied by using PDMS of different molecular weights ranging from $M_w = 7.4$ to $139\,kg/mol$ (squares) and by adsorbing the PDMS ($M_w = 80\,kg/mol$) at different temperatures (circles). The dotted line in a) serves as a guide to the eye.

(*i.e.*, close to solid-like friction). Formally, we may define an effective friction coefficient, $\zeta_{eff}(v)$, valid for velocities v larger than v_α:

$$\zeta_{eff}(v) = \zeta \left(\frac{v_\alpha}{v}\right)^\alpha \tag{6}$$

ζ_{eff} is a decreasing function of the dewetting velocity, v. This allows us to define a velocity dependent slippage length, b(v):

$$\mathrm{b}(v) = \frac{\eta_1}{\zeta_{eff}(v)}. \tag{7}$$

Equations (2)–(7) allow us to interpret an increase of W_{max} by a decrease of the effective friction coefficient, which is equivalent to an increase of the new velocity-dependent slippage length, b(v). Accordingly, thicker PDMS coatings are more slippery.

We have previously shown that the characteristic stress relaxation time, τ_1, is independent of the level of residual stresses induced by the spin-coating process [38]. One may also ask the question if differences in the frictional properties at the film/substrate interface have an effect on the way the residual stresses relax in the PS films. We can get the answer to this question by determining the characteristic time, τ_1. The results for the samples presented in Figures 5 and 6 are shown in Figure 7b. Taking into account the error bars, one may conclude that the changes of τ_1 are not very large. Both the thickness of the PDMS layer and the way it was prepared did not create any clear trends for τ_1. This approximate constancy of τ_1 can be seen directly from Figures 5 and 6. There, the changes in behaviour of the temporal evolution of the rim—from an initially strong increase in W to a rather constant value of W at later stages—occur for all curves at almost the same time. The fact that τ_1 is independent of the substrate may reflect the huge difference in the glass-transition temperatures of the PDMS and the PS molecules. Of course, if the PS chains would be adsorbed onto the substrate, their relaxation properties would have changed. However, due to the strong incompatibility between PDMS and PS (this is a major reason why this pair of polymers was chosen in first place) and the corresponding interfacial tension between them, the PDMS substrate can be considered as a highly nonwettable and nonpenetrable substrate for PS. Therefore, the substrate does not significantly affect the relaxation processes of PS chains. In contrast to the rather small variations in τ_1, the differences in the W_{max} values can be considered to be fairly important however.

CONCLUSION

In summary, besides their exceptional potential for an insightful characterization of rheological properties of polystyrene thin films (*e.g.*, the stress relaxation time, τ_1), dewetting experiments have also been shown to represent a highly sensitive tool for determining frictional properties of polymer/substrate interfaces. In combination with theoretical predictions, we were able to illuminate the influence of the energy-dissipation mechanism at the interface between the PDMS-coated silicon wafer and the PS film on the dewetting process. The initial opening velocity of holes increased with the thickness of the PDMS layer. Whereas τ_1 did not change much by varying the substrate properties (*via* changes of the PDMS coating), the maximum width of the dewetting rim increased significantly with PDMS layer thickness, indicating an increase of an effective, velocity-dependent slippage length. Keeping constant the parameters that characterize the dewetting film (*i.e.*, its thickness and mechanical properties), systematic studies on variously coated substrates will certainly allow one to exploit the full potential of dewetting for studies of interfacial properties such as friction and adhesion at polymer–polymer interfaces.

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