

Segmental Relaxations have Macroscopic Consequences in Glassy Polymer Films

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We have investigated the consequences of physical aging in thin spin-coated glassy polystyrene films through detailed dewetting studies. A simultaneous and equally fast exponential decay of dewetting velocity, width, and height of the rim with aging time was observed, which is related to a reduction of residual stresses within such films. The temperature dependence of these decay times followed an Arrhenius behavior, yielding an activation energy of 70 ± 6 kJ/mol, on the same order of magnitude as values for the β -relaxation of polystyrene and for relaxations of surface topographical features. Our results suggest that rearrangements at the level of chain segments are sufficient to partially relax frozen-in out-of-equilibrium local chain conformations, i.e., the cause of residual stresses, and they might also be responsible for macroscopic relaxations at polymer surfaces.

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Thin glassy polymer films often exhibit properties deviating from bulk behavior, as demonstrated by many groups [1–14]. The cause of such deviations has often been attributed to confinement and interfacial effects [1,3–5,11–13]. In addition, the way such polymeric films have been prepared is also believed to have an impact on their properties. In particular, the fast transition from a dilute solution to a dry glass during rapid solvent evaporation upon spin-coating is considered to be crucial. Especially for long chain polymers, the resulting conformations may deviate strongly from an equilibrated melt. The role of nonequilibrated chain conformations as a major source of residual stress, apart from, e.g., stresses induced by a mismatch of thermal expansion, was evidenced by changing molecular weight [5] and solvent quality [15], and found in various experiments [15–19] even for floating films [20]. As a consequence of built-in residual stresses, films may be unstable and eventually rupture, as shown, e.g., by dewetting experiments [15,16,19,20]. Several clear signs [8,11] indicate that thin films of long chain polymers are not in equilibrium and need excessively long times of annealing above the bulk glass transition temperature $T_{g,bulk}$ to reach equilibrium. Interestingly, despite these slow equilibration processes, often at temperatures well below $T_{g,bulk}$, significant and comparatively rapid changes of several film properties have recently been observed [6,13,14]. These experiments rely mostly on height-resolved changes of the surface topography of such films [6,14].

Obviously, nonequilibrated films will evolve towards equilibrium causing a change in film properties with time. However, when films are kept at temperatures below the glass transition, it is not clear whether significant and detectable changes can occur on experimental time scales.

Under such conditions of aging, relaxations on the level of entire chains are not expected. Rather, local motion at the level of chain segments are possible, characterized, e.g., by the β -relaxation [2,21]. This raises the question, whether such segmental relaxations have an impact on static and dynamic properties of polymers observed at a macroscopic level, for example, through changes in film thickness or the dynamics of dewetting. Furthermore, it is not clear whether the presence of residual stresses caused by strong deviations of chain conformations from equilibrium accelerate or slow down relaxations at the segmental level. In this Letter, we focus on the relaxation dynamics during aging of such out-of-equilibrium films, and compare it with literature data for glassy bulk samples which were quenched from an equilibrated melt, as well as to surface measurements. We have employed a macroscopic dewetting approach to detect changes induced by aging below $T_{g,bulk}$ through systematic variations of the duration and temperature of aging. A simultaneous study of different observables (diameter of the dewetting hole, and shape and size of the rim formed during dewetting) enabled us to exclude purely interfacial phenomena and relate the relaxations to changes occurring within the entire film. From these observations, we are able to deduce the relaxation dynamics, i.e., the decay time of residual stresses inside the film as a function of aging temperature.

For the systematic aging studies, we used thin (40 nm) spin-coated films of polystyrene (PS) stored in a vacuum oven equipped with an oil free pump, for increasing periods of time ranging from hours to several days at temperatures T_{age} ranging from 25 °C to 90 °C, below $T_{g,bulk} \approx 105$ °C. All experiments were performed using high molecular weight PS ($M_w = 4060$ kg/mol and

4840 kg/mol, $M_w/M_n = 1.15$), spin-cast from solutions of toluene, which is an athermal solvent for PS. All the films were spun at 3000 rpm onto Si (100) substrates, which were coated with a thin, irreversibly adsorbed layer of polydimethylsiloxane ($M_w = 139$ kg/mol; layer thickness ca. 15 nm) before PS film deposition [16]. The polydimethylsiloxane coating provides a well-controlled surface and acts as a nonwetable liquid-like layer, enabling strong slippage and thus, facilitating dewetting of the PS films. The changes upon aging were detected in dewetting experiments, induced by heating the films to $T_{\text{dew}} = 125$ °C. We note that the same dewetting behavior was found for films heated directly from T_{age} to T_{dew} or by first cooling the film to room temperature and only then performing the dewetting experiment by subsequently heating the film to T_{dew} . The temporal evolution at the early stages of the dewetting hole formation (changes in the size of the hole, and shape and width of the rim surrounding the hole) was followed in real time by optical microscopy for ca. 1 hour. Finally, after quenching the dewetted films to room temperature, height profiles of the rim were measured by atomic force microscopy (AFM). We note that only holes detectable immediately after initiating dewetting were investigated. Thus, the opening of all holes was subject to the same residual stress (cf., Ref. [15] for a recent study of holes that form at later times).

Figure 1 displays typical images characteristic for the influence of aging on the dewetting dynamics, obtained by optical microscopy and AFM. For a fixed dewetting time $t_{\text{dew}} \approx 1$ hour, the hole radius R , the width W , and the height H of the rim decreased upon physical aging at 80 °C with increasing aging times. As shown in more detail in Fig. 2, the variation of R decreased with increasing aging time. This effect was more pronounced at high aging temperatures. For the rim width measurements t_{dew} was usually chosen to be the characteristic time τ_w where W reaches a maximum W_{max} [5,7,16], a dewetting time of

several thousand seconds irrespective of aging. Note that τ_w is drastically shorter than the longest relaxation time (the reptation time, $\tau_{\text{rep}} \approx 65$ years for 4060 kg/mol PS at 125 °C) of the polymer in an equilibrated bulk, and hence, τ_w has been attributed to the relaxation of residual stresses inside the film caused by out-of-equilibrium chain conformations induced by the spin-coating process [5,7,16].

To quantify the changes induced by aging, we measured R , W_{max} , and H for a given dewetting time as a function of t_{age} . As shown in Fig. 3, all three quantities $Q = R, W_{\text{max}}, H$ showed a decay with aging time that could be fitted by a single exponential,

$$Q(t_{\text{age}}) = Q(t_{\text{age}} = \infty) + \Delta Q \exp(-t_{\text{age}}/\tau_A^Q). \quad (1)$$

In this way, three sets of characteristic relaxation times as a function of aging temperature were obtained, denoted as τ_A^R , τ_A^W and τ_A^H , respectively. Interestingly, although these three parameters are controlled by differing physical processes and although we have measured these parameters after various dewetting times t_{dew} , the resulting decay times were very similar. This decrease in dewetting dynamics reflects a reduction of the driving forces for dewetting and strongly suggests a decrease in the amount of residual stress within the film caused by physical aging.

Recently, the influence of residual stresses on the dynamics of dewetting of slipping visco-elastic polymer films has been investigated theoretically in detail [22,23]. After nucleation and during the very early stages of growth, dissipation processes at the substrate-film interface cause the formation of a rim surrounding the dewetting hole. The shape of the rim is asymmetric, characterized by an exponential decay towards the unperturbed film of height h_0 , with a decay length $\Delta = \sqrt{b h_0}$, where $b = \eta_0/\zeta$ is the slippage length, η_0 is the viscosity, and ζ is a friction coefficient [24].

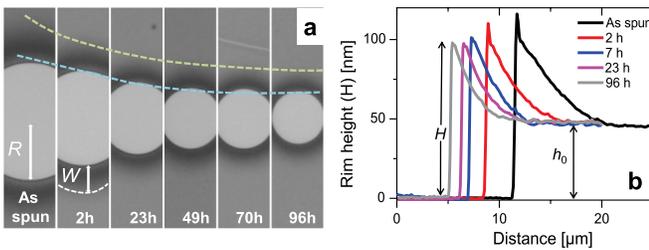


FIG. 1 (color online). (a) Section of dewetting holes in nominally identical PS films (thickness 40 ± 2 nm, $M_w = 4060$ kg/mol) that have been aged at 80 °C for varying periods ranging from 2 hours to 96 hours, taken after dewetting at 125 °C for ca. 1 hour. The size of the optical micrographs is ca. $14 \times 60 \mu\text{m}^2$ each. (b) AFM height profiles of the rims surrounding these holes after one hour of dewetting, formed in films aged for different times at 80 °C. The distance is measured from the center of the holes.

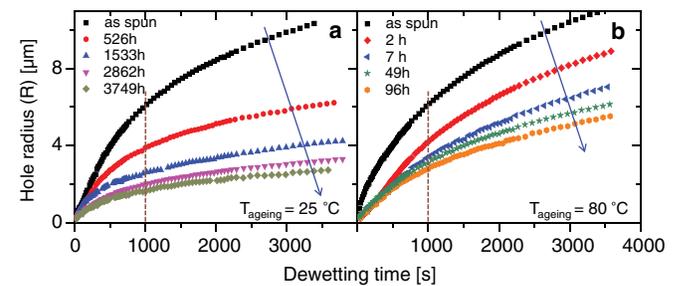


FIG. 2 (color online). Temporal evolution of the radius of dewetting holes, nucleated immediately upon heating to 125 °C in PS films (40 ± 2 nm, 4060 kg/mol) that have been aged at (a) 25 °C, (b) 80 °C. At any fixed dewetting time (the dashed vertical lines indicate 1000 secs of dewetting), both the hole radius and its growth velocity (derivative of the radius with respect to dewetting time) exhibited a decrease with aging time. The arrows indicate increasing aging time.

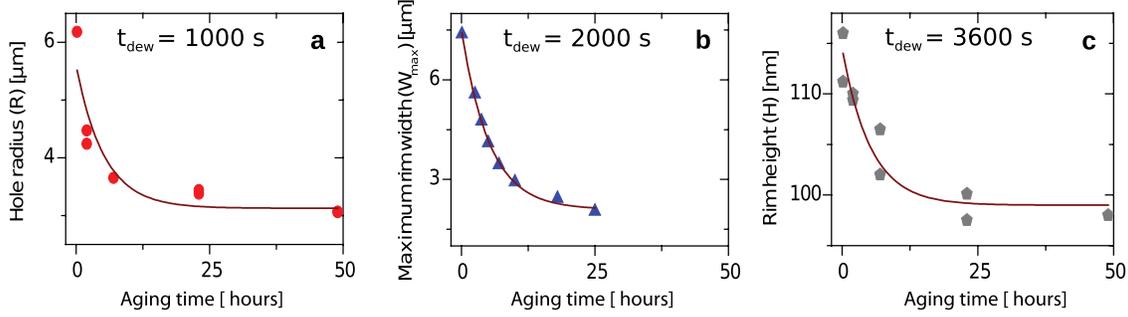


FIG. 3 (color online). (a) Hole radius, (b) maximum width of the rim, and (c) height of the rim after dewetting, as a function of aging time at 80 °C. All these quantities follow an exponential decay as a function of aging time, defining characteristic relaxation times τ_A^Q which for all three quantities are ca. 5 hours. Solid lines represent fits to Eq. (1). PS films of 40 ± 2 nm, $M_w = 4060$, and 4840 kg/mol.

The shape of the rim stays asymmetric for times up to the disentanglement time when the polymer starts to behave like a viscous liquid. For the long polymer chains and the dewetting temperature of this study, this final stage is reached only after many years. Hence, during the investigated period of dewetting, we can consider the polymer film as a mainly elastic body. The deformation is then given by the applied stress σ divided by the elastic modulus E . Hence, after the initial period of rim formation, H has an approximately constant value

$$H = h_0 \left(1 + \frac{\sigma_{\text{tot}}}{E} \right) \quad \text{or} \quad \frac{H - h_0}{h_0} = \frac{\sigma_{\text{tot}}}{E}. \quad (2)$$

Here, $\sigma_{\text{tot}} = \sigma_{\text{cap}} + \sigma_{\text{res}} = \frac{|S|}{h_0} + \sigma_{\text{res}}$ is the total stress acting on the film, consisting of the capillary stress σ_{cap} and the residual stress σ_{res} in the film.

The other two observables, W and R , are correlated by volume conservation: $W(H - h_0) \sim h_0 R$. With constant H , $W \propto R$ in this regime. Consequently, W and R exhibit the same time dependence. In addition to the influence of the visco-elastic properties of the film, W , R , and the velocity $V = \frac{dR}{dt}$ depend on the frictional properties of the film-substrate interface, characterized (for linear friction) by $V \propto 1/\sqrt{\zeta}$ [22,24]. In contrast, H is only governed by $\frac{\sigma_{\text{tot}}}{E}$ and is consequently, not affected by interfacial friction, cf., Eq. (2).

The temperature dependence of the characteristic relaxation times upon aging as extracted from the dynamics of R , W_{max} , and H is shown in Fig. 4(a), demonstrating that all three observables yielded quantitatively similar behavior. These results clearly indicate that the dynamics of all dewetting observables is governed by the same physical parameters. As changes in interfacial properties (friction with the substrate) are not expected to cause a change in H , the similar decay of *all three quantities* strongly points to a relaxation process occurring within the entire film and the only dewetting parameter which affects all three quantities in a similar way is the ratio $\frac{\sigma_{\text{tot}}}{E}$.

According to Eq. (2), the relative decay of H during aging can either be due to a decay of residual stress (assuming that the capillary stress is constant and interfacial tensions do not significantly change with aging), or be caused by an increase in the elastic modulus [5,22]. The latter requires, however, the formation of a significant number of new entanglements during the course of aging. Below the glass transition temperature T_g , chain reptation is suppressed and entanglement formation is extremely unlikely. Intrachain segmental motions are however possible even for $T < T_g$. Thus, the simultaneous and

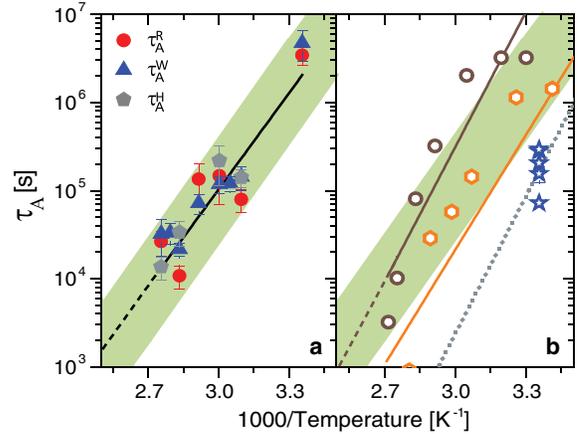


FIG. 4 (color online). (a) Relaxation times of the hole radius (τ_A^R), the maximal rim width (τ_A^W), and the rim height (τ_A^H) vs. inverse aging temperature, of nominally identical PS films ($M_w = 4060$ and 4840 kg/mol) prepared by spin-coating from toluene. The solid line is an Arrhenius fit of all relaxation times, yielding an activation energy $E_a = 70 \pm 6$ kJ/mol. The highlighted area encompassing all data points and their error bars gives rise to a range in E_a values between 50 kJ/mol and 107 kJ/mol. (b) Comparison of the results of (a) (shaded area) with reported relaxation times derived from the surface relaxations of i) nano deformations (open hexagons) [6] and ii) nano bumps (open circles) [14], including Arrhenius fits to these data (solid lines). The dotted line represents results from dye probe reorientation measurements [12] and the stars show relaxation times for PS films spun from trans-decalin [15].

equally fast decay of all three observables Q can only be attributed to a decay of residual stress, and consequently, to relaxations at a segmental level.

The results of Fig. 4(a) suggest an Arrhenius behavior for the relaxation time

$$\tau_A = A_0 \exp\left(\frac{E_a}{k_B T}\right), \quad (3)$$

where A_0 is a constant, k_B is the Boltzmann constant, and E_a is the activation energy of the underlying relaxation process. Fitting our results to Eq. (3) yields $E_a = 70 \pm 6$ kJ/mol.

It is instructive to compare this value—derived from a macroscopic dewetting study—to the β -relaxation process, which is believed to involve noncooperative motions at the segmental level of the polymer chain [2,21]. In the literature, values of 150 ± 80 kJ/mol for the β -relaxation in thin film and bulk PS can be found [2,9,21,25,26].

Several studies on thin polymer films also indicated a sub- T_g Arrhenius-type relaxation process, which was related to the motion within a distinct surface layer of higher mobility or to increased heterogeneity [2,12,13,21,27], yielding $E_a \approx 100$ kJ/mol [12,13] and $E_a = 185 \pm 3$ kJ/mol [9]. Lateral force microscopy measurements on thin PS films [2] found a thickness dependent surface β -relaxation process, with $E_a \approx 55$ kJ/mol for a 65 nm thick film. Fast sub- T_g -relaxations at surfaces of thin polymer films were measured by AFM, including the relaxation of surface dimples ($E_a = 83 \pm 16$ kJ/mol) [6] and the reduction in the height of surface bumps in water ($E_a = 98 \pm 17$ kJ/mol) [14].

Interestingly, within the scatter of the data, our results exhibit the same order of magnitude in relaxation time as these surface relaxation processes, cf., Fig. 4(b). Dewetting is, however, not a surface sensitive technique. In particular, the height of the rim is not controlled by a possible high mobility surface layer. Dewetting involves the displacement of whole polymer chains and takes place across the entire film thickness. Moreover, at the used dewetting temperature, the film behaved like an elastic body, as demonstrated by the asymmetric shape of the rim. Stress relaxation could therefore, only occur by motion on the level of chain segments.

Finally, it is illuminating to compare room temperature relaxation times of aging films spun from different solvents, cf., the stars in Fig. 4(b) [15]. A reduction in solvent quality gave rise to a decrease in relaxation times, indicating that the state of polymer chain entanglement in solution was transferred to the dried film [15]. The change from a good solvent (toluene) to a near-theta solvent (trans-decalin, $T_\theta = 21$ °C) corresponds to a decrease in chain swelling (radius of gyration) in solution, leading to reduced chain overlap and thus, to a decrease in observed relaxation times. These results indicate that the segmental relaxation times depend on the local chain environment, which is

strongly affected by preparation conditions such as solvent quality and film deposition technique. The varying published E_a values are, therefore, likely to reflect differences in the local chain environment, which can be altered by details of the film preparation protocol, such as pre-annealing thin polymer films above T_g . The low E_a value found here (compared to most other published data) possibly reflects the high residual stresses in the thin films of unusually high M_w PS.

In conclusion, the experiments presented here suggest that motion on the level of chain segments is sufficient to partially relax frozen-in out-of-equilibrium local chain conformations, which are the cause of residual stresses in thin polymer films. These relaxations are not expected to fully equilibrate the polymer film, which would require reptation of entire chains. It is also unlikely that segmental rearrangements lead to a homogeneous system on a nanometer length-scale. It is interesting and surprising to discover that changes in PS surface topography and the here studied influence of aging on dewetting exhibit similar relaxation times and rather similar activation energies. This might indicate that segmental relaxations are responsible for both observations. However, further studies are needed to answer the question whether local changes at the level of chain segments are responsible for changes in the surface topography on length-scales which are several orders of magnitude larger than the relaxing segments. In film dewetting, however, such local rearrangements have a dramatic influence, revealing the effect of submolecular (segmental) processes on macroscopic length-scales.

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