Aging of Thin Polymer Films Cast from a Near-Theta Solvent

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We have examined the aging behavior of spin-cast thin polymer films as a function of their processing history. Films prepared from solutions close to the Θ temperature were aged for varying times at room temperature, followed by a dewetting experiment above the glass transition temperature of the polymer. The characteristic aging time varied strongly with the quality of the solvent, which is attributed to distorted chain conformations in the as-cast films. This is an indication for the nonequilibrium nature of thin polymer films, possibly causing some of their unexplained properties.

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The transition from a solution to a dry melt or glass is believed to have an impact on the behavior of polymeric samples, often resulting in residual stresses due to rapid solvent loss, giving rise to out-of-equilibrium chain conformations [1–3]. These nonequilibrium conformations, in turn, can give rise to changes in the viscoelastic properties of the samples [4]. While experiments have indicated that different ways of sample preparation result in different properties, there are currently no conclusive studies on the mechanism behind these differences.

Numerous groups have shown deviations relative to bulk values in various properties of polymeric samples confined to thin films [5–16]. A lowered softening temperature and decreased interfacial diffusion (employing the same samples) are examples for seemingly contradictory polymer dynamics in thin films [8]. The cause of these deviations is a matter of ongoing debate.

Presently, we do not have an unambiguous relationship between the solution-to-glass or solution-to-melt transition and the resulting mechanical and relaxation properties. Summarizing previous work, it is likely that most high molecular weight polymer films are affected by nonequilibrium chain conformations incurred during their preparation.

Dewetting experiments are useful to provide detailed information about the rheology in thin polymer films. After the initial hole nucleation, the shape of the rim at the hole perimeter provides information about the ratio of surface energy and residual stress to the elastic modulus, providing information about the elastic response of the film to balance the forces present at the rim. The time evolution of the rim and changes in the overall dewetting velocity yield information about the relaxation of residual stresses or changes in modulus and relaxation times in the polymer film. The decreasing hole nucleation rate of films aged below the glass transition is an indication for stress relaxation in glassy polymer films. [17].

This study focuses on the influence of film preparation on the nonequilibrium properties of polystyrene films. Dewetting rim shapes and hole-opening kinetics were compared, yielding the relaxation behavior as a function of the preparation procedure of thin films kept for variable times above (annealing) and below (aging) the glass transition temperature.

Dewetting experiments were performed on high molecular weight polystyrene (PS, 4060 kg/mol, $M_w/M_n = 1.15$) films (ca. 40 nm thick), spin-cast from solutions of two different solvents: toluene, an athermal (very good) solvent for PS and trans-decalin (TD), a PS solvent with a Θ temperature of ca. 21 °C (i.e., a low PS solubility for $T \approx \Theta$) [18]. All films were spun at 4000 rpm. Raising the temperature of the TD solution above the Θ point increases its PS solubility. The variation of the solution temperature thereby provides control over the swelling of PS chains in the solution over a considerable range, given by [19]

$$\frac{1}{c}\left[\frac{14}{3N}(\alpha^3 - \alpha^5) + \frac{2}{3}\frac{\alpha_{\min}^3}{\alpha^3}\right] = \frac{\Theta}{T} - 1, \tag{1}$$

where $\alpha = \sqrt{\langle R^2\rangle/\langle R_0^2\rangle}$ is the amount of swelling, R_0 is the radius of gyration under ideal melt conditions, $\alpha_{\min}$ is the amount of swelling in the fully collapsed state, N is the number of chain segments, Θ is the Θ temperature, T is the temperature, and c is defined as $1 - \Delta S/k_B$, with ΔS the entropic change associated with segment-segment interactions, and k_B Boltzmann's constant. For the M_w of this study, the coil radius changes by ~40% when changing the temperature from 21 to 55 °C. The athermal PS-solvent toluene can be regarded as the extrapolation of the TD solvent to very high temperatures, with an increase in the coil radius by a factor of 2.5 compared to Θ conditions. The question we address here is whether films cast from these varying solutions are affected by these differing coil dimensions.

As in previous experiments [17], dilute solutions were spin-cast onto silicon-supported, grafted polydimethylsiloxane (PDMS) substrates. PDMS provides a rubbery apolar, quasiliquid substrate from which PS readily dewets with high slippage when heated above its glass transition temperature ($T_g \sim 100\,^\circ\mathrm{C}$ in the bulk). Samples were prepared from a range of solutions, simultaneously changing the polymer concentration and solution temperature such that the resulting films were of comparable thickness. PS concentrations ranged from 1.2% at $\approx 21\,^\circ\mathrm{C}$ to 1.0% at $\approx 55\,^\circ\mathrm{C}$. The solutions were placed in a heated bath, while the spin-coater chuck was heated by an incandescent lamp, such that a thermistor placed on the chuck reached equilibrium at the same temperature as the solution. Care was taken during the spin-casting process to minimize the amount of thermal variation that could occur during drawing of the solution into a pipette and spreading it onto the substrate prior to spinning. Dewetting experiments were performed at 125 °C, utilizing a Linkam heating stage and an optical microscope.

In a first experiment, the shape of the rim that forms upon hole formation was analyzed. Figure 1 shows that the rim-shape bounding holes with $\approx 7\ \mu$m radii depends on the solvent from which the film was cast.

The rim shape of a dewetting hole is dependent on the viscoelastic properties and energy dissipation mechanisms of the film in which it grows. Strongly asymmetric rim shapes with a gradual monotonic decay to the unperturbed film are observed for times much shorter than the reptation time τ_r. For the case where a stored in-plane stress dominates dewetting, the rim height

$$H \sim h_0 + \frac{|S|}{E} + \frac{h_0\sigma_0}{E} \tag{2}$$

is constant, governed by the ratio of the stored stress in the film σ_0 to the elastic modulus E [20]. h_0 is the undeformed film thickness and S is the spreading coefficient.

After the stored stress has relaxed (for $t \sim \tau_r$) the films are purely viscous, with a height increasing proportional to $t^{1/3}$ controlled by spreading coefficient, viscosity, and slippage length [12].

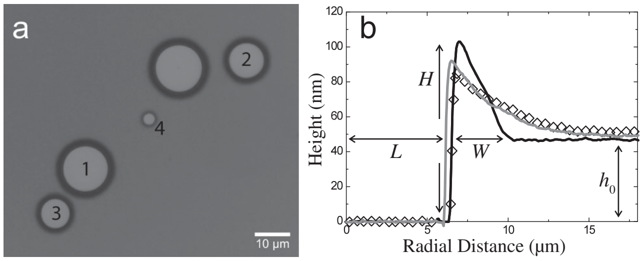

FIG. 1. (a) Optical micrograph of a typical film cast from TD at 23 °C, aged for 3 h, after heating for 1 h at 125 °C. Smaller holes were nucleated after longer incubation times compared to bigger holes. (b) AFM rim profiles of holes growing in films spun from toluene (diamonds) and TD at 25 °C (black line) and 55 °C (gray line). The films were heated immediately after preparation.

A more detailed viscoelastic model incorporating possible nonlinear friction requires a numeric solution of the constitutive equations [4]. Residual stresses in the film lead to a rapid initial hole opening, causing a large rim height and width. Once this initial stress decays, viscous effects dominate and the rim height and width may decrease for an intermediate time period—accommodated by a shape change—before increasing again for long enough times [20]. Since $t \ll \tau_r$ for the data reported here, Eq. (2) is a good approximation for the data of Fig. 1.

The comparison of films prepared from solvents of varying quality for PS in Fig. 1(b) clearly shows differences in the rim shape. While films prepared from good (TD at 55 °C), athermal (toluene), and near-Θ (TD at 25 °C) solvents show very asymmetric rims at short times, only holes formed in films cast from a fairly good solvent display a characteristic exponential decay of the rim after opening up a hole with $L \approx 6\ \mu$m [20]. Films of similar thickness and thermal treatment spin-cast from near-Θ conditions exhibit a much taller peak height and a much more rapid decay towards the film. In terms of Eq. (2), an increased height signifies either a higher stress in the film or a smaller modulus. The difference in these parameters can only arise from nonequilibrium states of the molecules caused by differences in film preparation.

The nonequilibrium properties of spin-cast polymer films manifest themselves also in the hole-opening kinetics. While purely viscous liquids exhibit a $t^{2/3}$ increase in the hole radius with time (in the case of slippery substrates), deviation from this time evolution is a signature of stored stresses in the film, a change in the rheological boundary condition, or in the effective viscosity. Because the effects of film preparation may change with time, special care must be taken when conducting hole-opening experiments: (1) since PS films are known to change their properties when stored at room temperature (aging), the time elapsed between film preparation and the beginning of the dewetting experiment must be taken into account; (2) when brought to $T = 125\,^\circ\mathrm{C} > T_g$, holes nucleate at various times during annealing. Since the thermal history of films may have an impact on the hole-opening kinetics, it is important to keep track of the hole nucleation time.

Because holes in the film nucleate at various times, as seen in Fig. 1(a), it is possible to simultaneously follow the temporal evolution of rim profiles of several holes. At a fixed temperature, holes that nucleated at different times grow in parts of the film that have been annealed at $T = 125\,^\circ\mathrm{C}$ for different periods of time. The time for hole nucleation is therefore defined as the incubation time in annealing studies.

The growth of the holes marked 1–4 in Fig. 1(a) were followed with time. Figure 2(a) shows the result of increasing incubation times. The data show a significant slowing

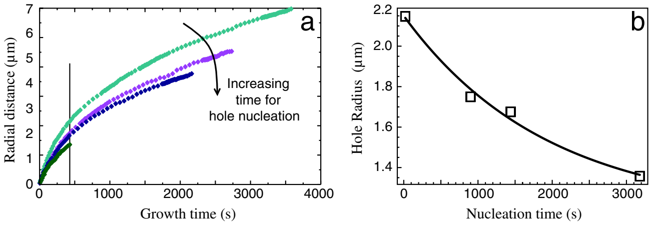

FIG. 2 (color online). (a) Growth of the four holes marked 1–4 in Fig. 1(a), which were nucleated 20, 900, 1440, and 3180 s after the film was brought to 125 °C. The ordinate is the time that each hole has grown since it was nucleated, rather than the time elapsed since the film reached $T = 125\,^\circ\mathrm{C}$. (b) Plot of the hole radii of the four films after a growth time of 430 s [vertical line in (a)], showing an exponential decay with a time constant of ≈ 1930 s.

down of the hole-opening rate with time, faster than for purely viscous films, which is indicative of a viscoelastic rheology [4]. Holes that nucleated at increasing times after the film temperature was raised to 125 °C exhibit a clear decrease in growth velocity with increasing incubation time. A comparison of the hole radius of the four samples after a hole-opening time of 430 s in Fig. 2(b) indicates an exponential relaxation, yielding a decay time of ca. 30 min for the hole-opening driving force. In terms of Eq. (2), the initial σ_0/E ratio contributes nearly 50% to the hole-opening kinetics. This supports the hypothesis that the chains in the films, which were initially out of equilibrium, equilibrate during annealing. Note that the relaxation time of Fig. 2(b) is much smaller than the bulk reptation time for the high molecular weight PS used here at 125 °C ($\approx 2 \times 10^8$ s) [12].

In a second series of experiments, films were spin cast from TD at 25 °C, then stored (aged) at room temperature for different periods of time, followed by dewetting experiments above T_g. Figure 3(a) displays the resulting hole-opening kinetics for films with increasing aging time, for holes that nucleated immediately upon heating the film to 125 °C. A decrease in dewetting velocity with increased aging time was observed, which is indicative of a decaying stress or an increasing modulus with aging time of the sample. The hole radii of the six samples at three fixed hole-opening times in Fig. 3(b) show a very similar exponential decay, defining a characteristic relaxation time of the film of 43 ± 9 h, in Fig. 3(b). A comparison between samples aged in ambient atmosphere and in vacuum showed no difference in dewetting behavior, excluding an effect of residual solvent in the film.

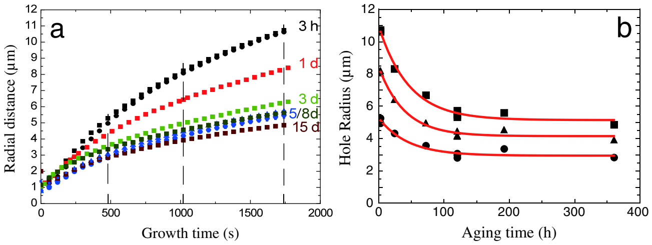

FIG. 3 (color online). Growth of dewetting holes nucleated immediately upon heating to 125 °C in films cast from TD at 25 °C that have been aged at room temperature, exhibiting decreasing growth velocities with increasing aging time. (b) Hole radii taken at three constant times [480 s, circles; 1020 s, triangles; 1740 s, squares; dashed lines in (a)] follow an exponential decay with a characteristic time of 43 ± 9 h.

Finally, the experiment of Fig. 3 was repeated, analyzing a large number of holes in films that were spin-cast from TD at four different temperatures, and the characteristic relaxation times for aging at room temperature was determined for all four sample series. Varying the temperature of the spin-coating solution in Fig. 4(a) has a substantial effect on the room temperature relaxation times of the TD-spun films, with a change in relaxation times by a factor of 4. Films cast from toluene had a relaxation time of ~700 h at room temperature, in agreement with the extrapolation of Fig. 4 to the athermal limit (i.e., a relative coil diameter of 2.5)

Casting a film from a solution involves the rapid increase in polymer concentration from a (semi-)dilute solution to a melt or glass. In a quasistatic fashion (where the system is close to its thermodynamic equilibrium at any time), this requires the continuous increase in entanglements per chain to reach a value of $(N/N_e)^{3/2}$ in the melt (N_e: number of monomers between entanglements). Because of the large reptation time for high polymer concentrations, spin-coating leads to coils that get trapped in less-entangled states in the film, leading to moduli, viscosities, and stored stresses in the film that differ substantially from the bulk. This is schematically shown in Fig. 4(b), indicating qualitatively the main factors influencing the pathways for the different spin-coating temperatures in Fig. 4(a). While the coil diameter changes only little as the solution is increasingly concentrated, the coil volume is increasingly interpenetrated by other chains. The segmental mobility is, however, simultaneously reduced and is completely arrested when the solution reaches the glass transition temperature. With a lack of segmental mobility,

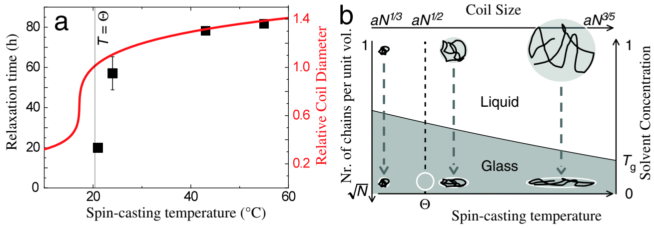

FIG. 4 (color online). (a) Relaxation times as a function of temperature of the solution from which the films were spun. The curve is the result of Eq. (1) with c as a fitting parameter. (b) Schematic of polymer coil conformations upon spin-coating for temperatures above and below $T = \Theta$. The open circle indicates a fully entangled chain in equilibrium.

further solvent evaporation leads to a collapse of the chains onto themselves. In a thin film, this collapse is restricted to one dimension, resulting in oblate coil structures. The deformation of the coil structure gives rise to an in-plane stress, while the reduction in entanglements lower the elastic modulus and the melt viscosity [14].

The two main factors determining the final chain conformations are indicated in Fig. 4(b). Conceptually, the final state must depend on the chain size in solution, which is determined by the solvent quality. Second, chain deformation must depend on the solvent concentration φ_s at which the solution turns glassy. Both quantities are temperature dependent. The former is determined by Eq. (1), while the latter is given by the Fox equation [21]

$$\frac{1}{T_{g_s}} = \frac{\varphi_s}{T_m} + \frac{1-\varphi_s}{T_g}, \tag{3}$$

with T_{g_s} the glass transition temperature of the solution and $T_m = -35\,^\circ\mathrm{C}$ the melting temperature of TD. φ_s varies from ≈ 0.5 at the TD Θ temperature to ≈ 0.25 at $55\,^\circ\mathrm{C}$, schematically indicated in Fig. 4(b).

Other factors include the variation in evaporation rate (and therefore film formation time) with temperature and a possible temperature dependence of the residual solvent in the film influencing the aging behavior. Importantly, however, all effects other than the solvent quality are expected to exhibit a continuous (near-linear) behavior over the investigated temperature range. The rapid decay of relaxation times as the spin-coating temperature approaches $T = \Theta$ is evidence for the dominating role of the solvent quality. Figure 4(b) qualitatively elucidates this effect: (1) the larger the swollen coil size, the stronger the deformation of the coils in the film, the higher the in-plane tensile stress in the film; (2) the more compact the chain in solution, the lower its number of entanglements with other chains, the lower the film modulus. A comparison with Fig. 1(b) suggests that the latter effect is dominant. A more highly entangled coil conformation (arising from the deposition from a good solvent) gives rise to a higher modulus (and therefore lower rim height) as well as to slower aging. The exclusive action of a higher stress (at constant modulus), on the other hand, while also leading to slower melt relaxation is incompatible with the lower rim height of Fig. 1(b).

In summary, we demonstrate the role of the quality of the solvent from which polymer films are cast on the nonequilibrium conformation of the chains in the film. Our data of film aging at room temperature of Fig. 4(a) are supported by the rim-shape analysis of Fig. 1, suggesting a variation of quenched chain entanglements with the quality of the solvent from which the film was cast. Interestingly, the aging time increases with improving solvent quality, with the strongest effect observed for the athermal solvent. The faster near-Θ stress relaxation does, however, not necessarily imply a faster overall equilibration of the chains. The full equilibration of the high M_w chains is likely to take many months even for temperatures above T_g [14].

Finally, the strong dependence of film preparation conditions on the aging behavior of thin films far below T_g sheds a new light on the low temperature softening of thin polymer films (aka their lowered glass transition temperature). While the deformation of polymer coils as a whole should not modify the solidification temperature of the film, which is dominated by the segmental dynamics, our aging experiments indicate that spin-coating perturbs the polymer coils down to the segmental length scale. While this needs further experimental verification, our experiments point towards an explanation for the ‘‘abnormal’’ glass transition temperature in thin films in terms of nonequilibrium chain conformations caused by film preparation.

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