Onset of Plasticity in Thin Polystyrene Films

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Bekele J. Gurmessa and Andrew B. Croll

Department of Physics, North Dakota State University, Fargo, ND, USA*

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Polymer glasses have numerous advantageous mechanical properties in comparison to other materials. One of the most useful is the high degree of toughness that can be achieved due to significant yield occurring in the material. Remarkably, the onset of plasticity in polymeric materials is very poorly quantified, despite its importance as the ultimate limit of purely elastic behavior. Here we report the results of a novel experiment which is extremely sensitive to the onset of yield and discuss its impact on measurement and elastic theory. In particular, we use an elastic instability to locally bend and impart a *local* tensile stress in a thin, glassy polystyrene film, and directly measure the resulting residual stress caused by the bending. We show that plastic failure is initiated at extremely low strains, of order 10^{-3} for polystyrene. Not only is this critical strain found to be small in comparison to bulk measurement, we show that it is influenced by thin film confinement - leading to an increase in the critical strain for plastic failure as film thickness approaches zero.

Thin polymer films are materials that are uniquely suited for countless goals, finding use in studies ranging from fundamental polymer physics [1, 2], to elasticity [3–10], and glass-phase physics [11–17]. Polystyrene is often used as a model polymeric material because thin films are easily produced and manipulated, they are relatively rigid, and polystyrene is a comprehensively studied glass-forming polymer with well known *bulk* material properties. However, as the thickness of a polymer film is reduced to nanoscopic dimensions it is now well established that the glass transition is altered [11–17], the number of entanglements between chains are reduced [1, 2], and mechanical properties can change [18, 19]. Remarkably few studies have considered how failure processes might be altered in thin films, or how plasticity might alter a films response to other stimuli.

Recent focus has turned towards a surface instability known as wrinkling that occurs when a thin polymer film (modulus $\bar{E}_f$, dimensions $L \times L$ and thickness h) is bound to a stress free elastic substrate (modulus $\bar{E}_f$) and is subjected to a compressive uniaxial stress [4]. When stress is applied, the film is initially compressed in plane but quickly reaches a critical point above which the film buckles out of plane [6, 9]. In the limit of small strain, ϵ, a balance between the energy associated with the bent plate $U_B \sim \epsilon L^2 \bar{E}_f h^3 / \lambda^2$ and the stretched substrate $U_S \sim \epsilon L^2 \bar{E}_S \lambda$ reveals the utility of the system - the pattern is directly related to the thin film material properties (minimization gives $\lambda = 2\pi h (\bar{E}_f / 3 \bar{E}_s)^{2/3}$) [3–7]. This simple analysis was developed for the ill defined 'near threshold' regime, although the analysis seems to be accurate in many situations that are clearly no longer small perturbations [9]. Larger displacements (the far from threshold (FT) regime) currently challenges elastic theory for a solution, which has prompted significant experimental and theoretical efforts [7, 10, 20, 21]. The FT work often investigates aspects of stress focusing [8], deformations in which the stress distributions become strongly heterogeneous and notably similar to material failure (e.g. fracture).

Reaching the FT regime typically requires the application of large stresses. High stress also leads to failure, for example the nucleation of fractures (or shear deformation zones and crazes) in a wrinkled film [18] or the formation of delaminations if the wrinkling energy exceeds the adhesion energy between the film and the substrate [21–23]. More importantly, high stress may push the film beyond the material limits of linear elasticity, where plasticity will affect certain aspects of stress focusing [24]. Therefore, for both practical and fundamental reasons, it is critical to understand where and how plastic deformation occurs in thin polymer films.

In this letter we describe a sensitive measurement of the onset of plasticity in thin polystyrene films, an important material property which has thus far been experimentally overlooked. Explicitly, we monitor the complete position of a polymer film bound to a soft substrate with confocal microscopy during the application and removal of a compressive stress. As the film wrinkles and delaminates, it creates point of high curvature that correspond with high tensile strain on the surface of the film. To determine elastic limits we compare localized regions of damage apparent in relaxed (flat) films with the curvature that preceded them. Not only do we show that the critical strain for onset of plastic deformation, ϵ_p, in a thin polymer film is considerably lower than what is expected from bulk measurements, but we show that the critical point is affected by thin film confinement in a manner that is not related to entanglement density.

Our experiment is intentionally simple: we apply then remove a compressive stress from thin polystyrene (PS) films bound to an elastomer substrate - in essence a double step strain experiment (see Fig. 1). Under compression, the film buckles forming a wrinkle pattern that evolves to a complex collection of delamination blisters and wrinkles as compression is increased [21, 22]. Upon
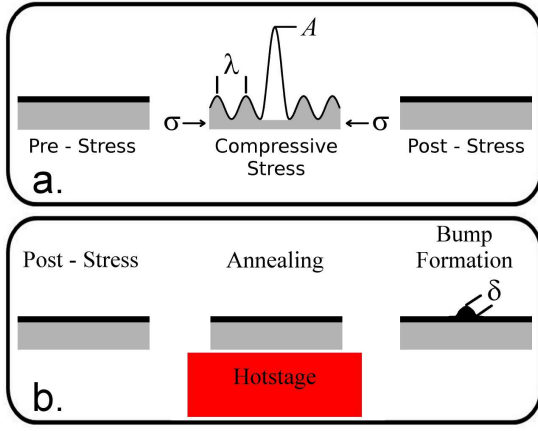
FIG. 1. Schematic of the two stage experiment. (a) Stage 1: a thin PS film is placed on a soft elastomer substrate, uniaxial compression is added and finally removed. The sample is left in a measurably flat state. (b) Stage 2: the sample, after all applied stress has been removed, is placed on a hot-stage and annealed. During annealing, "bumps" form at locations correlated with high curvature during the compression stage of the experiment.
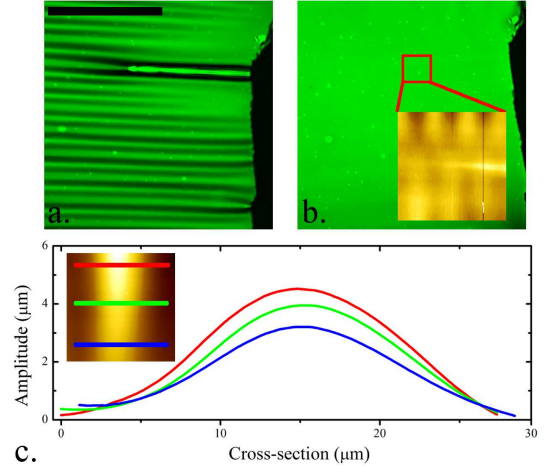

FIG. 2. Typical data from stage 1 of the experiment. a. A confocal microscope image of wrinkles (low curvature) and a delamination (high curvature) near a sample edge. Scale bar indicates 32 μm. b. The same location after removal of stress - there is no optically observable change in the film. The inset shows a 20×20 μm. ASM scan of the flat film and reveals small scale changes in the film (height scale is ~3 nm) c. Cross sections through the delamination illustrating its variable amplitude (inset: an AFM micrograph of a segment of delamination).

release of stress, the topography of regions that were highly curved are measured and found to be flat on the order of the surface roughness (~ 1 nm). There are two possible outcomes from such an experiment: 1) if the deformation is purely elastic the film is returned to its initial (unstressed) configuration or 2) if there is a plastic component to the films response, the film will be left in a higher stress configuration (we remain far below the films glass transition temperature, T_g, during application of step strain). The experimental difficulty lies in determining whether the film is in state 1 or state 2 after the experiment. Here we make this distinction by subsequently annealing the film above its glass transition temperature ($T_g \sim 370$ K for bulk PS) - if the film is in state 1 it will not appreciably change, however if the film has stored stress (state 2) the fluidized film must flow in response. If the plastic stress is uniform and isotropic the response will only appear in the dynamics of the flow [25–27], or as a small change in film thickness. The onset of plastic flow would be difficult to measure in both these schemes. Hence, we add a further refinement to the experiment and use the alternating positive and negative curvature of the wrinkle topography to create a *local* bending stress in the sample (Figs. 2 and 3).

We use 3 mm × 12 mm × 70 mm substrates of crosslinked polydimethylsiloxane (PDMS). Curing agent and PDMS prepolymer (Dow chemical Corning, Sylgard 184) are typically mixed in a 1:30 weight ratio. After degassing, the polymer mixture is poured into a petri dish, cured at 85 °C for two hours and then left in the vacuum oven for the next 12-15 hours. PS films are prepared by spin casting various concentrations of PS and toluene

mixtures onto a freshly cleaved mica substrate. We use PS of several molecular weights (1.3 Mg/mol, 120 kg/mol Polymer Source, 106 kg/mol Fisher Scientific) and one polystyrene - b - poly(2-vinyl pyridine) molecule (symmetric diblock copolymer, 104 kg/mol, Polymer Source). Finally, the prepared thin film is transferred to a clean deionized water surface (Milli-Q) and transferred to a PDMS substrate on a home built strain stage. Samples are subsequently compressed and then relaxed as described above. While the exact strain rate of the surface of the delamination was not measured, we estimate it to be $\sim 2 \times 10^{-3}$ s^{-1} from the total time and the deformed geometry. In all cases the films were imaged with Laser Scanning Confocal Microscopy (LSCM - Olympus Fluoview 1000) or with Atomic Force Microscopy (AFM - DI Dimension 2100).

Fig 2 b. shows a single LSCM optical section of a typical sample while under compression ($h = 71$ nm). The sample shows wrinkles (center), cracks (edge) and delamination (brightest wrinkle peak) [21]. From such an image the wrinkle wavelength can easily be measured, but more importantly, through optical sectioning we also determine the height of each pixel. Primarily, we use the reflection from the surface of the polymer (the highest intensity is recorded when the focal point of the lens is centered on the film surface allowing sub-Rayleigh resolution in the out of plane dimension). Secondly, we verify the measurements by loading the film with a typical
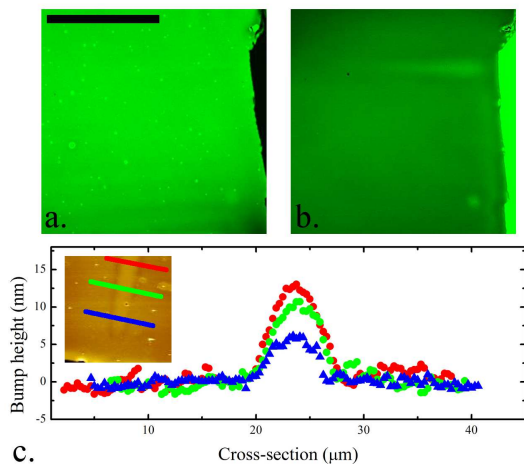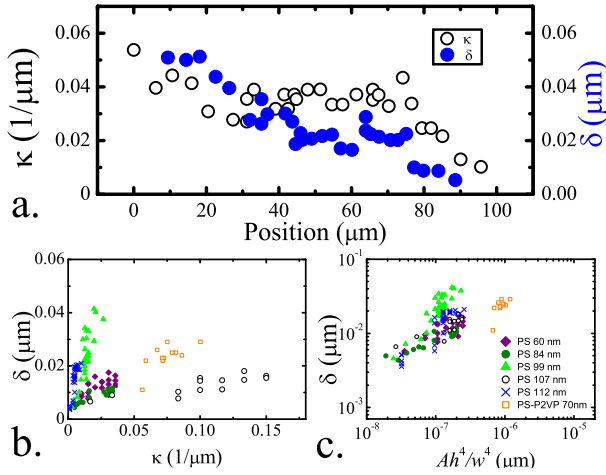
FIG. 4. (a) curvature and bump height as a function of position, illustrating the high degree of correlation between the two variables. (b) Correlation plot of δ vs κ showing several polymer films. (c) Scaling plot showing collapse of the data.

[29–31]. Our measurement, to the best of our knowledge, represents the first accurate measurement of the yield point in a thin polymer film [32].

We summarize the critical strain measurements by plotting ϵ_p as a function of film thickness in Fig. 5. In addition to an overall small value of ϵ_p, measurements show the critical strain *increases* in films of thicknesses below 100 nm. While anomalous effects have often been measured in polymer films of this same thickness range [11, 12, 14–18, 25], our measurement is novel in several respects. First, this is a change in a heretofore untested material property relevant to failure, elastic theory and the basic sample preparation used in countless thin film experiments. Secondly, this observation is a unique window on the behavior of confined polymer systems from a mechanical perspective. Thirdly, our experiments are independent of thermal strain (common to many thin film experiments) and because we observe no wrinkles after laminating the PS film to the PDMS substrate we can explicitly state a limit on any strain occurring due to the lamination of the thin film to the substrate (below $\sim 0.5\%$).

The change we observe could be related to a reduction of inter-chain entanglements [1, 2], or to a change in the glass transition temperature of the film[11–15, 19]. Bending gives the opportunity to make a clear distinction between the two possibilities as it preferentially probes a film's free surface and the applied strains can be accurately measured in the vanishingly small strain limit. Small strain ensures that the network of polymer chains is not deformed significantly, and therefore the entanglements themselves cannot play a role in the overall effect (this is not common in most failure measurements [2, 18], or in many simulations [33, 34]). As evidence for this we duplicate the experiment with PS films of an order
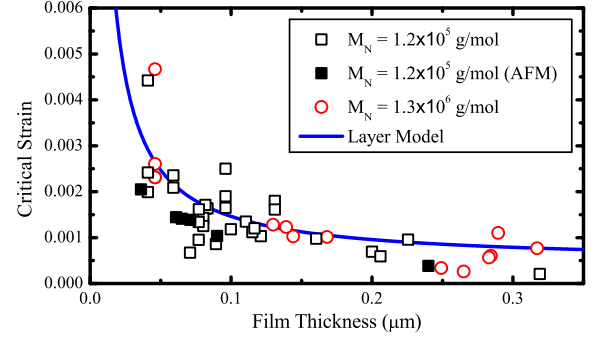

FIG. 5. Critical yield strain as a function of film thickness. The figure shows data from two molecular weights differing by an order of magnitude and a fit to the layer model described in the text. Also shown (solid squares) is data generated by direct measurement before annealing (see supplementary file)

of magnitude larger molecular weight. Fig. 5 shows no observable effect of molecular weight on the location or magnitude of the upturn. We tentatively conclude that the critical strain for the onset of plastic deformation must then be related to the same mechanism behind reductions in the glass transition. While suggested by the simulations of Böhme and de Pablo, the relationship between the glass transition depression and plasticity has not yet been examined. Qualitatively, the glass transition is reduced due to a region of increased mobility near the free surface of the polymer film (operating over a lengthscale of ~ 10 nm). In this region a larger strain is needed before stress can be stored as stress can more easily relax away. A trivial layered model can be written as $\epsilon_p(h) = (\ell/h)(\epsilon_p - \epsilon_p^0) + \epsilon_p^0$, where ℓ is the size of the soft layer and ϵ_p, ϵ_p^0 refer to the surface and bulk respectively. A fit to our data in Fig. 5, assuming a typical lengthscale $\ell = 10$ nm, gives find $\epsilon_p = .017 \pm .002$ and $\epsilon_p^0 = .001 \pm .001$.

In conclusion, we have developed a sensitive new method to generate *local* strain in thin polymer films and have used it to measure the onset of yield in polystyrene. Our measurements show that the onset of yield occurs at much lower strains than are measurable in the bulk. Furthermore, the critical strain shows significant increases in films thinner than 100 nm. The confinement induced increases are independent of molecular weight, suggesting that they are related to changes in the glass transition temperature rather than changes in underlying inter-chain entanglement network. Our measurement has implications for many current experimental investigations of the elastic properties of thin polymer films, particularly in experiments attempting to probe the far from threshold elastic behavior.

out some pertinent literature.

* andrew.croll@ndsu.edu

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