NANO HIGHLIGHT
Dynamic Heterogeneity and the Behavior of Glass-Forming Materials at the Nanoscale

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Characterization of the viscoelastic response of ultrathin films is important for understanding the glass transition at the nanoscale, and as part of this NIRT, a novel creep test has been developed[1] which relies on the imaging capabilities of the atomic force microscope. In essence, the test is a reduction in size of the classical bubble inflation test. Figure 1 shows a regular array of inflated bubbles in an ultrathin film cast on a substrate having regular spaced channels, with the inset showing an enlarged view of a single inflated bubble. Measurement of the bubble height as a function of time for constant inflation pressure yields the creep compliance. Such linear viscoelastic measurements are shown as a function of time and temperature for films of poly(vinyl acetate) (PVAc) at a thickness of 27.5 nanometers in Figure 2. Comparison of the data with the viscoelastic creep data of Plazek for bulk PVAc[2] suggests that there is little change in the glass temperature based on the viscoelastic response. Interestingly, the value of the rubbery creep compliance appears to strongly depend on film thickness, as shown in the inset in Figure 2. Corroborating the result that the timescales associated with the viscoelastic response in ultrathin films may be very similar to those in the bulk is a viscoelastic contact mechanics analysis[3] of the nanosphere embedding data of Teichroeb and Forrest[4] on ultrathin polystyrene films. The analysis using the bulk properties of polystyrene gives quantitative agreement with the data, indicating little or no depression in the glass transition temperature as measured by the viscoelastic response. The results indicate that a "liquid" surface layer does not exist and also contrast markedly with the results for ultrathin films found using, for example, ellipsometry and calorimetry.

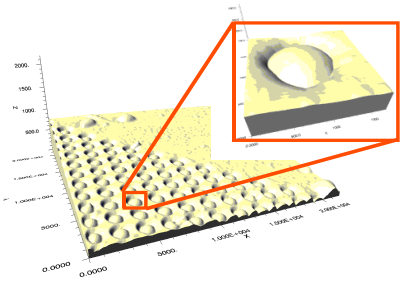

Figure 1: AFM image of a 22 square micron scan showing the regular array of inflated bubbles, with the inset showing an enlarged view of a single bubble.

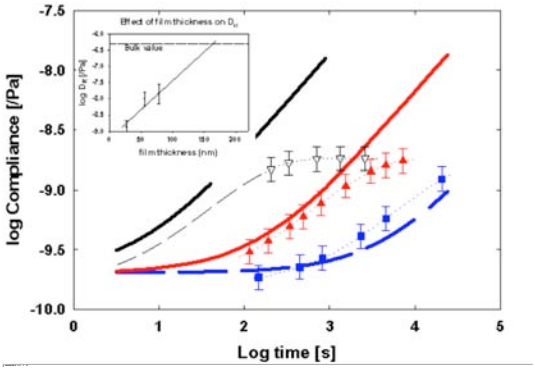

Figure 2: Experimental creep compliance measurements (symbols) and comparison to bulk behavior (lines). The measurement temperature is 25.5 °C (blue), 30 °C (red), and 35 °C (black). The inset shows the logarithm of the rubbery creep compliance as a function of film thickness, with the bulk value indicated by the horizontal line.

References

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2. D. J. Plazek, Journal Of Rheology 24 (6): 907-907 1980.
3. J.H. Teichroeb and J. A. Forrest, Phys. Rev. Lett., 91, 1, 016104-1(2003).
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