Shear modulation microscopy as an ultra-sensitive probe of nonlinear response: stick-to-slide transitions and viscoplastic deformations of polymers

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INTRODUCTION

Dynamic, oscillatory methods in scanning force microscopy have enabled nanoscale research in rheology and viscoelasticity on polymeric systems.1-5 Among such techniques, scanning shear modulation microscopy has been used to probe the stick-to-sliding transition with increasing drive amplitude,2 and the near-surface glass transition with increasing temperature.6 The commonly adopted approach is to measure the dynamic, torsional forces on the tip via amplitude and phase outputs of a lock-in amplifier, to quantify the response to sinusoidal shear movements (of sample or tip) at frequencies in the kilohertz regime.4-5 Lost in this approach are the details of real-time response that may reveal highly nonlinear interactions, i.e. strongly anharmonic distortions due to sliding or plastic yield, or intrinsically nonlinear viscoelastic responses.

Given that fundamentally important material responses are being probed, it is important to understand the phenomenology of oscillatory shear measurements at a fundamental level. To this end we have embarked on research to examine the nonlinear character of the tip-sample interaction using Fourier analysis of the real-time response. Here we report on two studies, one in which a stick-to-sliding transition is being probed, and the other in which plastic yield is being probed. The first study examines autophobically dewetted, ultrathin polyvinyl alcohol films on mica, contrasting the nonlinear response on the first, strongly adsorbed layer from that of a discontinuous second layer with bulk-like characteristics. The second study examines polystyrene films cast on silicon and ranging in molecular weight (MW), revealing a time evolution of nonlinearity under repeated shear modulation that is strongly dependent on entanglement (and thus MW). This evolution derives from increasing indentation under creep or increasing plowing via plastic yield, depending on the shear modulation amplitude. The latter case includes void generation at the highest MW’s explored.

EXPERIMENTAL

Materials. Atactic polyvinyl alcohol (Aldrich, 99% hydrolyzed, Mw=85,000-146,000) was dissolved in distilled/deionized water (DW) at 1 wt% concentration by heating to 90°C for two hours under stirring, diluted to 10-3 wt%, then cast onto cleaved mica from a drop over several hours as the water slowly evaporated. Films were imaged as prepared the next day, and repeatedly over a period of months with negligible change in morphology or properties. High-force scanning procedures determined a variable film thickness of 1-4 nm depending on surface location. Low-polydispersity polystyrene (Mw/Mn < 1.1, Aldrich) films were prepared by spin-coating a 2% solution of polymer into toluene onto a Si substrate previously cleaned with an H2O2/H2SO4 (piranha) mixture. The films were annealed at 150°C in vacuum for 10-20 hours before use. Film thicknesses were 120-180 nm as determined by raster-scan abrasion to substrate at temperatures above Tg.

Instrumentation. Two Molecular Imaging PicoSPMs were used for all force microscopy: the polyvinyl alcohol study was conducted using a PicoSPM controlled by a Molecular Imaging PicoScan (configuration #1), whereas the polystyrene study was conducted using a PicoSPM controlled by a Digital Instruments Nanoscope III (configuration #2). Configuration #1 enabled the simultaneous collection of up to six data channels of information: height, vertical cantilever deflection, torsional cantilever response, X-driving signal, relative humidity inside of the Molecular Imaging PicoApex environmental chamber, and sample temperature (Molecular Imaging sample heating stage). In configuration #2, shear modulation drive and response signals were collected with a National Instruments LabView system interfaced to a Digital Instruments Signal Access Module and using a LabView program developed in-house. The X-modulation signal was added to the X voltage with a home-built adder circuit. In both configurations the X-modulation signal was provided using a commercial, virtual function generator program running in LabView. Oscillation frequencies ranged from 1-100 Hz and amplitudes from 0.25-60 nm. All experiments reported here were conducted at room temperature, with variable relative humidity (5-80%) in configuration #1 and constant relative humidity of 5% in configuration #2.

STUDY 1: RESULTS AND DISCUSSION

Figure 1 contains a 1x1-µm sliding friction force image acquired in conventional contact mode on a polyvinyl alcohol film, contrasting low friction (dark) on the strongly adsorbed first layer from high friction on the bulk-like second layer. At right are representative time dependent shear responses for each region under a 2.5-nm amplitude, 100-Hz driving signal at RH=28%. The response on the second layer (green) is nearly sinusoidal indicating linear response, whereas on the first layer the sine wave is “clipped” (blue), i.e. nonlinear response.

Figure 1. (left) Sliding friction force image, brighter corresponding to higher force. (right) Representative time dependences of small-amplitude shear-modulation response on corresponding regions at left.

Similar measurements were acquired over a range of drive amplitudes. In each case the real-time response was collected for approximately 5000 cycles and Fourier transformed every 25 cycles (a single line in “image” mode), then the 200 transforms averaged. The amplitude of first (circles) and third (triangles) harmonic response is plotted in Figure 2 for each film component, first layer in blue and second layer in green. The increase and turnover of the first harmonic amplitude embodies a transition from stick to partial sliding. The latter causes the first harmonic amplitude to decrease as the third harmonic increases. At the largest drive amplitude (7.5 nm) the ratio of third-harmonic response amplitudes on the two film components is nearly the same as the ratio of sliding friction forces rendered in image form in Figure 1 (left). Important note is that the ratio of the first harmonic amplitude reaches a maximum is different by a factor of two on the two film components, but as the drive amplitude tends to zero.
we find a consistent slope of the first harmonic plots (dashed line), indicating consistent shear stiffness. Thus it is a 2:1 difference in the “resistance to sliding” that translates into the approximately 2:1 ratio of sliding friction force, i.e. the latter seemingly has no connection to shear stiffness. Presumably a lack of conformational freedom on strongly adsorbed PVA translates into a lesser capacity to absorb shear strain energy viscoelastically, such that the tip begins to slip upon a smaller shear stress. Sliding friction images thus appear to be sensitive to intrinsic lossiness, in turn related to the level of molecular freedom. In conclusion, the Fourier analysis of nonlinear response under shear modulation sheds new light on the factors underpinning sliding frictional behavior.

**STUDY 2: RESULTS AND DISCUSSION**

Perhaps a simpler quantification of nonlinearity is to compute the ratio of third to first harmonics, which we call S (“nonlinear shear parameter”). Whereas on polyvinyl alcohol S holds constant under repeated shear modulation at a single location during the measurement interval, we find that on polystyrene S evolves over the course of many tens of oscillation cycles as exemplified in Figure 3. We further analyzed this time evolution by numerically fitting to the form $S = A + B[1-\exp(-t/\tau)]$. The determined value of $B$ weights the magnitude of time dependent response. $B$ can be negative (at relatively small drive amplitudes) or positive (at larger drive amplitudes). Subsequent topographic images reveal that negative values of $B$ correspond to plastic indentation (creep) without lateral buildup of polymer, whereas positive values of $B$ correspond to ploughing, i.e. lateral movement and buildup of polymer outside of the 1D shear-modulation “track” (lateral wear).

We further find that the drive amplitude at which $B$ transitions from negative to positive (18 nm in Figure 3) is a function of molecular weight, and that ploughing (positive $B$) generates excess film volume, i.e. voids, only at larger molecular weights. A summary plot of this behavior is shown in Figure 4. Here we plot the drive amplitude that corresponds to a negative-to-positive transition of $B$ versus molecular weight, after normalizing this transitional drive amplitude to the estimated contact diameter (in the JKR adhesive contact model). The contact diameter was varied by examining a range of loads, but normalizing collapses the results onto a single plot (Figure 4). An apparent cusp in the plot in the vicinity of the entanglement molecular weight ($M_c$) is similar to the well-known behavior of viscosity and other polymeric properties.

In conclusion, our findings suggest that entanglement is critical in determining characteristic types of plastic deformation during shear modulation experiments. Our results exemplify the importance of analyzing real-time shear-modulation responses, together with topographic images of modified polystyrene morphology, in order to make correct interpretations about molecular motions during shear modulation measurements.

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**REFERENCES**