University of Nebraska - Lincoln
DigitalCommons@University of Nebraska - Lincoln

Papers in Nanotechnology

Chemical and Biomolecular Engineering Research and Publications

12-29-2003

Solid-like dynamics in ultrathin films of polymeric liquids

Gaurav Singh
Department of Chemical Engineering, Virginia Polytechnic Institute and State Uniuersity, Blacksburg, Virginia 24061

Ravi Saraf
Department of Chemical Engineering, University of Nenraska-Lincoln, rsaraf@unl.edu

Yves Martin
T.J. Watson Research Centre, IBM Corporation, Yorktown Heights, New York 10598

Follow this and additional works at: http://digitalcommons.unl.edu/chemeng_nanotechnology

Part of the Nanoscience and Nanotechnology Commons

Singh, Gaurav; Saraf, Ravi; and Martin, Yves , "Solid-like dynamics in ultrathin films of polymeric liquids" (2003). *Papers in Nanotechnology.* Paper 2.
http://digitalcommons.unl.edu/chemeng_nanotechnology/2

This Article is brought to you for free and open access by the Chemical and Biomolecular Engineering Research and Publications at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Papers in Nanotechnology by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

Solid-like dynamics in ultrathin films of polymeric liquids

Gaurav Singh and Ravi F. Saraf[a)]
Department of Chemical Engineering, Virginia Tech, Blacksburg, Virginia 24061

Yves Martin
T.J. Watson Research Centre, IBM Corporation, Yorktown Heights, New York 10598

(Received 11 April 2003; accepted 6 November 2003)

In this letter, we demonstrate that, at mesoscales, nonferroelectric liquid films of poly(dimethyl siloxane) exhibit significant electrostriction not present in the corresponding bulk state. Remarkably, the observed electrostrictive effect has a response time <20 μs in contrast to >5 ms recorded in conventional bulk (ferroelectric) polymers. The emergence of this fast electrostrictive strain in thin films is explained in terms of the amalgamation of two contrasting dynamic features—the influence of a highly mobile, viscous layer (at the air/film interface) on the less-mobile, but fast responding, solid-like layer at the film/substrate interface. The effect is observed for thickness below 200 nm.
© *2003 American Institute of Physics.* [DOI: 10.1063/1.1637145]

The interfacial structure and properties of soft matter, such as polymers, deviate significantly from the bulk. It is recognized that molecular segments of polymers closer to a "free" surface (i.e., film/air interface) have higher mobility than the bulk. This is beautifully illustrated by orienting molecular chains at the surface by simply rubbing the surface of a vitrified (or crystalline) polymer with a soft material.[1–3] The polymer molecular segments at the film/substrate interface, in contrast to the bulk, experience stronger dispersive forces from the substrate molecules that are more polarizable and/or packed denser. This additional interaction may be modeled as the "tail end" of a van der Waals long-range interaction emanating from the substrate.[4] These stronger interactions lead to densification at the film/substrate interface.[5,6] The densification effect is shown to manifest as a solid-like elastic behavior in <1 Hz dynamic strain experiments by surface force apparatus.[7]

In this letter, we describe a study, where fast dynamics, at >10 kHz, in thin films of polymeric liquids is observed. The dynamic behavior is obtained by deforming the film under oscillating electric field and measuring the electrostrictive strain by the interferometric method. The results indicate elastic-like dynamics with a strong dependence on film thickness. The fast dynamic behavior fades away at a film thickness above 200 nm. The observation is explained by considering a non-Gibbs film where the two interfaces commence to overlap, such that the structure of the intermediate core layer is different from the bulk.[8]

A 2000 g/mol poly(dimethyl siloxane) (PDMS) film is spin casted from hexane solution on a SiO_2/Si wafer with Au electrodes at 30 μm spacing. The radius of gyration R_g is $\sim 6.5\times 10^{-2}$ $M^{0.5}$ nm ~ 3 nm.[9] The wafer is treated in H_2SO_4/H_2O_2 (3:1) solution to produce hydroxyl, Si–OH groups at the surface prior to spin casting.[10] The PDMS is wetting on the surface. The thicknesses of the films are measured by a spectroscopic ellipsometer. The absence of interference fringes at the electrode edge under the Nomarski microscope indicates a negligible meniscus contribution in the film between the 30 μm electrode spacing. An ac electric field, $E(\omega)$, at a frequency ω, is applied via the electrodes. The field, parallel to the film surface, stretches the film parallel to the substrate. The relative angle between the polarization of light and the electric field does not affect the signal. As a result, it shrinks along the thickness direction due to the Poisson effect. The amplitude of thickness modulation, Δd is measured by the differential interferometer setup shown in Fig. 1(a). Interference between phase-modulated "reference" and "sample" beams is measured at the detector. The reference beam is phase modulated at 80 MHz by a Bragg cell. The sample beam is phase modulated at 2ω due to a change in the optical path length caused by (second-order) oscillation in the sample thickness due to the electrostriction effect from the applied field, $E(\omega)$. Figure 1(b) shows the typical signal observed in the spectrum analyzer. The central peak at 80 MHz is due to the carrier frequency from the Bragg cell. The two satellite peaks at 80 MHz$\pm 2\omega$ are due to the phase modulation from the sample. Frequency below 8 kHz is too close to the background from the main peak, and therefore constitutes the lower limit of our measurement. The absence of satellite peaks at 80 MHz$\pm\omega$ indicates that there are no (linear) piezoelectric effects caused by dipole orientation. This is expected, since PDMS is a nonpolar fluid. From the power ratio of the main peak and the (second-order) satellite peak, R, the change in optical path length $\Delta(nd)=R\lambda/\pi$ is obtained, where n is the refractive index of the film.[11] We note that the intensity change (i.e., amplitude modulation) due to the change in reflectivity from the sample due to electric field is well within the noise.

The strain amplitude, $\epsilon=\Delta d/d_0<0$. For $\epsilon<10^{-3}$% (see Fig. 2), with respect to the undeformed state (n_0,d_0), $\Delta(nd)=n_0\Delta d+d_0\Delta n$. The Δn increases due to two primary reasons: (i) increase in density, ρ, caused by the thickness reduction $(\Delta\rho\sim-\Delta d/d_0^2)$, and (ii) orientation of the induced dipole along the field direction. For small strain, in PDMS, it is estimated that by correcting n by $n-0.1$, the effect of refractive index change (i.e., $d_0\Delta n$) can be accounted for as $\Delta(nd)=(n_0-0.1)\Delta d$.[12] For convenience, we report our result as strain magnitude, $|\epsilon|$.

[a)]Electronic mail: rsaraf@vt.edu

 © 2003 American Institute of Physics
Downloaded 02 Sep 2005 to 129.93.70.50. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

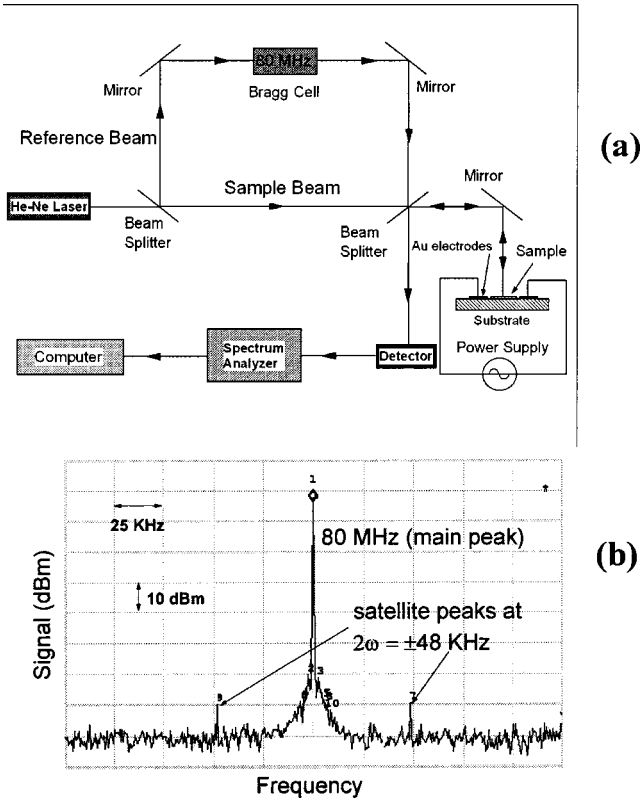

FIG. 1. (a) Differential interferometric setup to measure the amplitude of thickness modulation, Δd due to electric field $Ee^{-i\omega t}$. The interference amplitude measured at the detector is amplified and recorded in a spectrum analyzer connected to a computer for data acquisition. (b) Raw data: the typical power spectrum of the signal in the spectrum analyzer shows the central 80 MHz main peak (No. 1) due to the Bragg cell and two -80.08 and -79.28 dBm satellite peaks (Nos. 9 and 7) at 80 MHz$\pm 2\omega$.

Figure 2 shows the dynamic response of thin films as a function of frequency. The fast response in the 10–64 kHz or 100–16 μs range indicates that the electrostrictive dynamics is primarily elastic. Since the polymer is $\sim$148 °C above its bulk T_g, the film should primarily be liquid except for the "solid-like" layer in the vicinity of the film/substrate interface. The solid-like layer formation is observed under slow (<1 Hz) dynamic mechanical experiments in the polymer thin film confined between two solid surfaces.[7,13] The presence of such an interfacial elastic layer for PDMS on the silica surface is confirmed using quasielastic neutron scattering and nuclear magnetic resonance.[14,15] If the fast, viscoelastic response were exclusively due to the solid-like film/substrate interfacial layer, the Δd measured in Fig. 2 should be independent of d_0, except for inertial damping from the top layer. However, the significant change in the relaxation peaks both in terms of frequency position and intensity suggests the systematic inertial damping effects do not explain the observation.

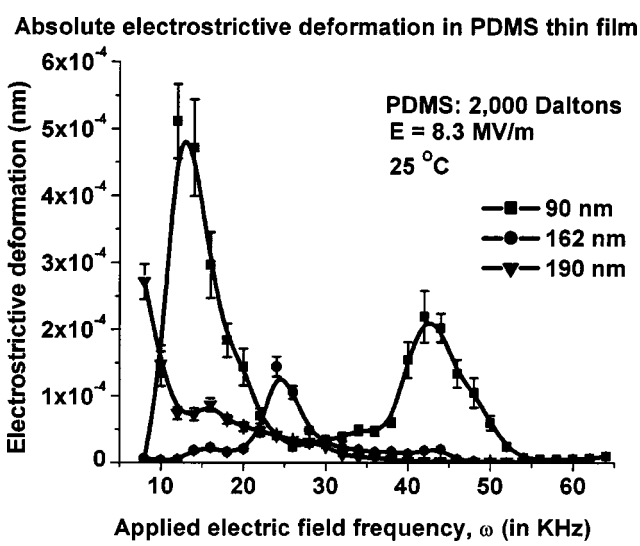

FIG. 2. ω vs Δd response of the PDMS film at the thickness and electric field amplitude indicated. The amplitude of the thickness modulation, Δd, instead of ϵ is plotted for better visualization. The error bars are standard deviation based on 30 data points taken at 0.1 s intervals.

The significant thickness effects suggests that the film cannot be considered a simple Gibbs layer where the excess thermodynamic properties are the sum of the air/film interface (top layer), bulk (middle layer), and film/substrate interface (bottom layer). In the non-Gibbs thin film, the top and bottom layers overlap to form a modified middle layer that is different compared to the bulk of a conventional Gibbs film.[8] An alternate description would be that the bulk layer is influenced by the long-range van der Waals interaction due to the dense, highly polarizable substrate, leading to disjoining pressure (Π) in the overlap region.[4]

The Π may alter the effective electromechanical response as follows. Neglecting gravitational effects and assuming the long-range attraction to be simply the van der Waals interaction tail $\sim 1/d^m$, (where m=2 for nonretarded case), the disjoining pressure $\Pi \sim A/(6\pi \mathrm{d})$.[16] Where, A (>0) is the difference in the Hamaker constant for the substrate–liquid and liquid–liquid interactions. The $\Pi>0$ implies that the disjoining pressure is acting opposite to hydrostatic pressure and tends to thicken the film. Thus, due to Π, the film will have a "bounce-back" effect as the electric field decreases the thickness. For small deformation (as is the case with $\epsilon < 10^{-3}\%$) the restoring force is $\sim 1/d^2$. Thus, a faster response is expected due to Π in thinner films. This is consistent with Fig. 2, where in the high-frequency part of the spectra, more activity is observed for thinner films.

The response likely from the middle, overlap layer, as mentioned above, is influenced by Π. Analogous to the dynamic mechanical behavior,[17] the "relaxation" peaks suggest that the behavior is viscoelastic, which may be considered an amalgamation of the high-mobility and viscous top interface, and the fast-responsive and elastic bottom interface.

Interestingly, the dynamic character of the overlap region does not change, as seen by the relatively invariant relaxation peaks at 14, 24, and 44 kHz. However, the relative magnitude changes significantly with thickness. One way to interpret the observation is by considering the intermediate layer as a "two-phase" structure composed of a more ordered mesomorphic structure that is elastic, and the "constrained" amorphous structure that is viscous and less elastic. The 90 nm film presumably is mostly mesomorphic with essentially the two relaxation peaks at 44 and 14 kHz. As the thickness increases, the overlap decreases making the structure more disordered. Thus, the 162 nm film has a more "constrained" amorphous phase giving rise to a strong 24 kHz peak (absent in the 90 nm film) and a small amount of a mesomorphic phase, as seen by the weak relaxation peaks/

Downloaded 02 Sep 2005 to 129.93.70.50. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

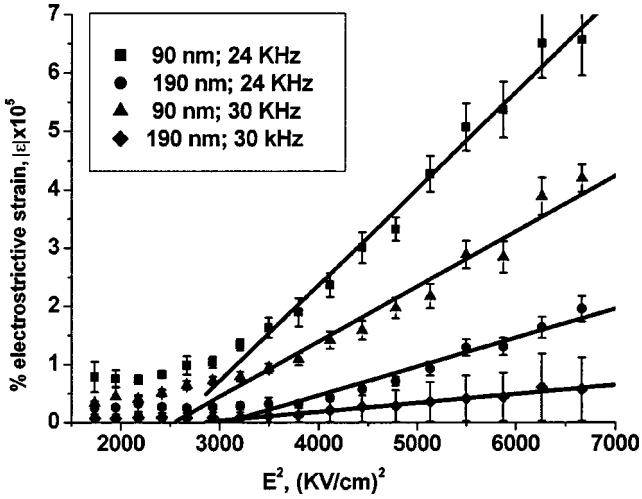

FIG. 3. Linear behavior fitness (including the error bars) range from 0.98 to 0.99. The slopes, $\nu\beta$ in descending order are 165, 95, 50, and 15 $(\mathrm{pm/V})^2$. This is expectedly small. However, the β is significant, considering no electrostrictive response is reported for bulk films.

shoulders at 14 and 44 kHz. Eventually, at 190 nm, the film is closer to the classical Gibbs layer where the overlap region is small, as manifested by weak peaks due to the mesomorphic (14 kHz) and constrained amorphous (24 kHz) phases. Beyond 200 nm, no electrostriction is observed, indicating that the top interface (and the bulk) is too slow (i.e., viscous), and the elastic bottom interface is too rigid (i.e., low mobility) or too thin.

The electrostriction coefficient, β (a tensor) is defined as the proportionality constant between the strain, ϵ, and E^2. For isotropic system with uniaxial E, β is a scalar quantity. In our study, E is parallel to the film plane and the strain is measured along the thickness plain [see Fig. 1(a)]. Thus, $\epsilon = \Delta d/d_0 = \nu\beta E^2$, where ν is the Poisson ratio of the polymer. Figure 3 shows a typical $|\epsilon|$ vs E^2 behavior in the relatively "flat" portion of the frequency response (see Fig. 2). The (expected) linearity is observed, but beyond a threshold E of ~53 kV/cm. The threshold field cannot be attributed to the experimental measurement limit since the lines do not converge at (0,0) but [~2800 $(\mathrm{kV/cm})^2$, 0]. A possible explanation may be an activation barrier to commence the long-range segmental motion. For example, at small fields, small polarization may cause only local orientation, while at large fields significant polarization may lead to (cooperative) long-range chain orientation causing larger deformation, and hence, larger β.

One of the authors (R.F.S.) thanks the Office of Naval Research (Grant No. N00014-01-1-0977), and Jeffress Memorial Trust, VA, for financial support; and Jayan Krishnaswami for data acquisition automation.

[1] J. C. Wittmann and P. Smith, Nature (London) **352**, 414 (1991).
[2] M. F. Tony, T. P. Russell, J. A. Logan, H. Kikuchi, J. M. Sands, and S. K. Kumar, Nature (London) **374**, 709 (1995).
[3] A. M. Higgins and R. A. L. Jones, Nature (London) **404**, 476 (2000).
[4] P. G. de Gennes, Rev. Mod. Phys. **57**, 827 (1985).
[5] D. N. Theodorou, *Physics of Polymer Surfaces and Interfaces* (Butterworth-Heinemann, Boston, MA, 1992), p. 139.
[6] S. K. Kumar, M. Vacatello, and D. Y. Yoon, Macromolecules **23**, 2189 (1990).
[7] S. Granick, Science **258**, 1374 (1991).
[8] B. V. Derjaguin, N. V. Churaev, and V. M. Muller, *Surface Forces* (Consultants Bureau, New York, 1987), p. 26.
[9] *Polymer Handbook*, 2nd ed., edited by J. Brandrup and E. H. Immergut (Wiley, New York, 1975), p. IV-48.
[10] G. Evmenenko, S. W. Dugan, J. Kmetko, and P. Durra, Langmuir **17**, 4021 (2001).
[11] P. G. Charlette, lan. W. Hunter, and C. J. H. Brenan, Rev. Sci. Instrum. **63**, 241 (1992).
[12] $\Delta nd = [n - (N_{Av}\alpha\rho/3\epsilon_0 M)[(n^2+2)^2/6n] - SG]\Delta d$, where the first term is from $n\Delta d$, the second term is from densification, and the third term due to orientation is simply stress optical coefficient S time modulus G. Where $\rho \sim 1$ g/cm^3, electronic polarizability, $\alpha \sim 5.08\times 10^{-39}$ C^{2}m^2/J, $M = 2000$ Daltons, $n \sim 1.45$, estimated $S \sim 3.7\times 10^{-11}$ m^2/N (based on Ref. 7, pp. 380 and 382), and G~1 MPa. Thus, the third term $\sim 10^{-5}$ is negligible compared to second term of ~0.1. Thus, the correction is simply, $\Delta nd = (n_0 - 0.1)\Delta d$, where the correction to n_0 is independent of d.
[13] H.-W. Hu and S. Granick, Science **258**, 1339 (1992).
[14] V. Arrighi, J. S. Higgins, A. H. Burgess, and G. Floudas, Polymer **39**, 6369 (1998).
[15] V. M. Litvinov, H. Barthel, and J. Weis, Macromolecules **35**, 4356 (2002).
[16] F. Brochard Wyart and J. Daillant, Can. J. Phys. **68**, 1084 (1990).
[17] J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd ed. (Wiley, New York, 1980).

Downloaded 02 Sep 2005 to 129.93.70.50. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp