COMPLEX FLOW OF NANOCONFINED POLYMERS

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N1G 2W1
• instabilities in freely-standing liquid films

• hole growth in freely-standing PS films
  – ideal geometry for probing complex flow
  – shear thinning
  – convective constraint release relaxation mechanism
  – hole growth occurs for $T$ comparable to $T_{g}^{\text{bulk}}$

• hole growth in freely-standing PS/PI/PS trilayer films
  – holes in central PI layer

• summary & conclusions
CURRENT PROJECTS

POLYMERS
• molecular mobility
  – glass transition & hole growth
• instabilities & pattern formation
• biodegradable polymers

BIOPOLYMERS
• polypeptides & proteins – lipid membranes & polymer brushes

BACTERIAL CELLS
• bacterial adhesion & physical properties of bacteria & biofilms
• to measure structure, dynamics, interaction forces, molecular conformations, adsorption kinetics, we use
  – atomic force microscopy
  – ellipsometry
  – surface plasmon resonance
  – quartz crystal microbalance
  – optical tweezers
  – TIRF
  – infrared techniques (PM-IRRAS, ATR-FTIR)
  – surface circular dichroism
  – TEM
  – differential pressure techniques
• thin liquid films occur in everyday life
  – adhesives (superglue)
  – lubricants (on cornea of eye, engine piston)
  – spray coatings (paint, herbicides, fibers)
  – printing (ink on transparency or tape)
  – soap bubbles & films
  – foams (shaving cream, cappuccino)
  – water films (water spotting, hydroplaning)
HOLE GROWTH IN NON-VISCIOUS FILMS

- fluid collects in a rim
- rest of film undisturbed

- hole radius grows linearly with time

\[ R = \frac{2h}{3t} \]

[Culick, J. Appl. Phys. (1960)]
polymers are complex molecules

- different length scales ranging from segment size to overall chain size $R_{EE} \sim M_w^{0.5}$
- different time scales ranging from segmental relaxation to diffusion of entire molecules

- effect of confinement in thin films
  - changes in conformation & dynamics
HOLE GROWTH IN VISCOUS FILMS

- no rim
- film thickens uniformly

- hole radius grows exponentially with time

[Debrégeas et al., PRL (1995)]
FREELY-STANDING FILM PREPARATION

- high molecular weight, monodisperse polymers dissolved in good solvents

spincoat polymer solution onto mica substrate

anneal film under vacuum

capture film on holder containing 4 mm diameter hole

transfer film onto water surface
– plug flow

– driven by surface tension

\[ \sigma = \frac{2\varepsilon}{h} \]  at edge of hole;

\[ \sigma \sim \frac{1}{r^2} \]  into rest of film

– polymer chains become aligned near edge of hole
optical microscopy of freely-standing polystyrene films

- \( M_w = 717k \)
- \( 96 \text{ nm} < h < 372 \text{ nm} \)
- \( T = 115^\circ\text{C} \) (\( T_g^\text{bulk} = 97^\circ\text{C} \))
- exponential hole growth

- decrease in viscosity for increasing strain rate
- consistent with shear thinning

[Dalnoki-Veress et al., PRE 59, 2153 (1999)]
- shear thinning only observed for entangled polymers
- \( \eta \) is \( M_w \)-independent in nonlinear regime
  [Stratton, J. Colloid Interf. Sci. 22, 517 (1966)]

- decrease in viscosity \( \eta \) with increasing shear strain rate \( \dot{\gamma} \)
SHEAR THINNING IN FREELY-STANDING PS FILMS

- different $T$, $M_w$ and $h$
- use growth time $\tau$ to obtain viscosity $\eta$ at edge of hole
- plot $\eta/\eta_0$ versus reduced shear strain rate $\beta$
- results consistent with viscous flow in presence of shear thinning

\[
\beta = \eta_0 \frac{M_w \gamma / \rho R T}{10^{-1}}
\]

[Dalnoki-Veress et al., PRE (1999)]
[DPE]
[Xavier et al., Macro (2004)]

\[
M_w = 2240k
M_w = 717k
M_w = 282k
M_w = 120k
\]

\[
\eta = \eta_0 M_w \gamma / \rho R T.
\]

slope = $-0.75 \pm 0.01$

[Dalnoki-Veress et al., PRE (1999)]
[Xavier et al., Macro (2004)]
FLOW AT SUCH LOW TEMPERATURES?

- in bulk, viscosity $\eta_0 \sim 10^{12}$ Pa·s at $T \sim T_g$
  - expect both viscous and elastic effects important
  - late stage hole growth is well-described by viscous flow

- previous studies of crazing of PS films [Berger & Kramer, Macro (1987)]
  - chain scission at low temperatures
  - chain disentanglement at strain rates & higher temps
    - for $M_w = 1800k$: $T > 70^\circ$C for $\dot{\gamma} = 4.1 \times 10^{-6}$ s$^{-1}$
    $T > 90^\circ$C for $\dot{\gamma} \sim 10^{-2}$ s$^{-1}$

- comparable strain rates & temps for hole growth
  $1.5 \times 10^{-4}$ s$^{-1} < \dot{\gamma} < 2 \times 10^{-2}$ s$^{-1}$ for $101^\circ$C < $T < 117^\circ$C
TRANSITION IN HOLE GROWTH

• measure $R(t)$ for single hole using optical microscopy
  – linear growth at early times
    – velocity $v$
  – exponential growth at late times
    – growth time $\tau$
  – range of times for linear growth decreases with
    – increasing $T$
    – decreasing $M_w$

[PS $M_w = 2240k$, $h = 79$ nm at $T = 103^\circ C$]

$R = R_o + vt$

$R = R_o \exp(\frac{t}{\tau})$

[Roth et al., PRE 72, 021802 (2005)]
TRANSIENT BEHAVIOR

- scale axes: $\ln\left(\frac{R(t)}{R(\tau)} \right)$ vs $t/\tau$
  - data sets coincide for $t > \tau$
- isolate transient
  - single exponential decay time $\tau_1$
• measure $R(t)$ for single hole using optical microscopy
  – linear growth at early times
    – velocity $v$
  – exponential growth at late times
    – growth time $\tau$
  – range of times for linear growth decreases with
    – increasing $T$
    – decreasing $M_w$

[Roth et al., PRE 72, 021802 (2005)]
TRANSIENT BEHAVIOR

- **Isolate transient**
  - single exponential decay time $\tau_1$
- **Refer** $t$ to $t_0$ for which $R(t_0) = 0$
- Overlap of data
- Decay time $\tau_1$ scales with $\tau$

**Scale axes:** $\ln\left(\frac{R(t)}{R(\tau)}\right) - \left(\frac{t}{\tau} - 1\right)$ vs $\frac{t}{\tau}$

- **Data sets coincide for** $t > \tau$

**M_w = 717k**

$h = 125$ nm
• empirically, \( R(t) \) data for all times well fit by

- equivalent to time-dependent viscosity \( \eta(t) \)

\[
\eta_\infty = \frac{\varepsilon \tau}{h}
\]

where \( \eta_\infty \) is viscosity for \( t \gg \tau_1 \)

- described by a three-component spring & dashpot model

![Diagram of three-component spring & dashpot model]

single relaxation time
FITS TO $R(t)$ DATA

- 3 fitting parameters:
  - $R_0$: value at start of measurements ($t = 0$)
  - $\tau$: exponential hole growth time
  - $\tau_1$: longest relaxation time

$m_w = 717 \times 10^3$

$h = 90$ nm
**RELATIONSHIP BETWEEN $\tau$ AND $\tau_1$**

- $\tau$ and $\tau_1$ have similar temperature dependence with $\tau_1 \sim \tau/2$

$$[\tau/\tau_1 = 2.2 \pm 1.4]$$
**TUBE MODEL FOR POLYMER DYNAMICS**

<table>
<thead>
<tr>
<th>Shear Rate</th>
<th>Condition</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>$\dot{\gamma} &lt; \tau_d^{-1}$</td>
<td>Reptation + Contour Length Fluctuations (CLF)</td>
</tr>
<tr>
<td>Intermediate</td>
<td>$\tau_d^{-1} &lt; \dot{\gamma} &lt; \tau_R^{-1}$</td>
<td>Convective Constraint Release (CCR)</td>
</tr>
<tr>
<td>High</td>
<td>$\tau_R^{-1} &lt; \dot{\gamma}$</td>
<td>Chain Stretch</td>
</tr>
</tbody>
</table>

$\tau_d$ Reptation time

$\tau_R$ Rouse time

Hole growth at $T = 101^\circ C$

- $\tau_d^{-1} \sim 10^{-6} - 10^{-10}$ s$^{-1}$
- $\tau_R^{-1} \sim 10^{-4} - 10^{-7}$ s$^{-1}$
- $\dot{\gamma} \sim 10^{-4}$ s$^{-1}$

- Hole growth at lowest temperatures occurs in the intermediate to high shear rate regimes
  - Relaxation via CCR (no rotation in flow)
  - Since $\dot{\gamma} = 2 / \tau$, expect $\tau_1 \sim \dot{\gamma}^{-1} \sim \tau / 2$
  - Data consistent with CCR

[Graham, Likhtman, McLeish, and Milner, J. Rheol (2003)]
• differential pressure experiment

[Roth et al., RSI 74, 2796 (2003); Roth & Dutcher, PRE 72, 021803 (2005)]

- maintain pressure difference across PS film
- track piston position as a function of time

PS, $M_w = 2240k$, $h = 69$ nm, $T = 98^\circ$C
DPE RESULTS FOR FREELY-STANDING PS FILMS

- temperature dependence of hole growth time $\tau$
  - $M_w = 717k$, 2240k
  - $51 \text{ nm} < h < 98 \text{ nm}$
  - $92^\circ C < T < 105^\circ C$
  - consistent with shear thinning
  - despite large differences in $T_g$, onset temperature for hole formation is comparable to $T_g^{\text{bulk}}$ for all films

[Roth et al., RSI 74, 2796 (2003); Roth & Dutcher, PRE 72, 021803 (2005)]
FREELY-STANDING TRILAYER FILMS

• trilayer films with central fluid layer and solid capping layers
  – periodic lateral morphology forms upon heating due to amplification of thermal fluctuations

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Stress-guided self-assembly in Dutcher films

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Structural evolution and control of Dutcher films

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[C.A. Murray et al., PRE 69, 061612 (2004)]
HOLE GROWTH IN PS/PI/PS TRILAYERS

• hole growth in PS freely-standing films
  – uniform thickening of films
  – absence of rim at edge of hole

• hole growth in PS/PI/PS freely-standing films
  – holes form & grow in central PI layer
  – distinct rim at edge of hole
HOLE GROWTH IN PS/PI/PS TRILAYERS

- presence of rim verified using atomic force microscopy (AFM)

\[ h = 50 \text{ nm}, \quad L = 75 \text{ nm} \]

[C.A. Murray et al. (2006)]
HOLE GROWTH IN PS/PI/PS TRILAYERS

- radius of hole in PI layer measured at fixed temperature $T = 110^\circ$C

$\ln \left( \frac{R}{R_0} \right)$ vs. $t$ for fixed PS thickness $L$ and varying PI thickness $h$

$\ln \left( \frac{R}{R_0} \right)$ vs. $t$ for fixed PI thickness $h$ and varying PS thickness $L$

[C.A. Murray et al. (2006)]
HOLE GROWTH IN PS/PI/PS TRILAYERS

- relevant factors that determine hole growth in PI layer
  - surface & PS/PI interfacial energies
  - bending energy of PS layers
  - dispersion interaction between the PS/air interfaces

- can understand slowing of hole growth with increase in $h$ & $L$
SUMMARY

- hole growth in freely-standing PS films
  - two different experiments
  - shear thinning
  - convective constraint release
  - hole growth occurs at temperatures comparable to $T_g^{\text{bulk}}$

- hole growth in fs PS/PI/PS films
  - qualitatively different hole growth
  - hole growth in PI determined by PS