WATER AT POLYMER INTERFACES

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Environment impacts adhesive strength

RH = 78 %

Adhesive

Joint failure

RH = 19 %

No problems

What are the origins of this adhesion failure at a molecular level?

Can we engineer strategies to overcome this?
Why worry about adhesives?

- More than 50,000 rivets to hold together
- Reduce rivets by replacing with adhesive
  - Decrease maintenance costs!
- Changing environmental conditions – how does this effect the adhesive strength?
Interfaces and composite systems

Problem: disordered system with multiple length scales

How to obtain fundamental understanding of moisture in these systems?

Idealized interface = thin film

Highly filled composite polymer systems intrinsically high interfacial area
Adhesion measurements using shaft loaded blister test

\[ G = \frac{Eh}{16} \left( \frac{w}{a} \right)^4 \]

*Eh*: Film Stiffness (modulus, \( E \), · thickness, \( h \))

But this is a bulk measurement, how to understand mechanisms?
Moisture influence: Bulk versus interface contributions

Moisture exposure

Bulk swelling
Decreased cohesive strength
Stress development in polymer

Interfacial moisture
Decreased contact area
Stress development in polymer

Which effect controls adhesive failure?
Contrast control through isotopic substitution

**X-ray Reflectivity (XR)**

- Water ‘looks’ like polymer (similar density)

- Measure thickness change due to moisture absorption
- Mass density profile

**Neutron Reflectivity (NR)**

- Water visible (Heavy water, D<sub>2</sub>O)
- Isotopic sensitivity (¹H vs ²H)
- Measure water distribution within film

Use NR to directly observe water distribution in film
Quantifying moisture distribution: X-ray and neutron reflectivity

Information:
- thickness $D$
- density profile, $Q_c^2$, $\rho(z)$
- interfacial roughness

X-rays or neutrons

$Q_c^2 \implies \rho$

$D \approx 2\pi/\Delta Q$

log $(R)$

fringe persistence $\implies$ surface roughness
Examining water at polymer interface

Thick polyimide on silicon wafer

No well defined interferences due to relative thicknesses
Shift in critical edge and change in decay only differences
Fit suggests D$_2$O accumulates at interface

from the interface, the $Q_c^2$ value and thickness of an intermediate layer which might be present, and the thickness of both transition zones, i.e., between PI and the intermediate layer, and between PI and Si of intermediate layer. The resulting potential energy profiles, expressed in $Q_c^2$ vs. distance from the Si surface for both the dry (lower curve) and the wet (upper curve) samples are given in Fig. 3. The origin on the dis-

Wen-Li Wu, William J. Orts, Charl

Minima in reflectivity not fit without excess at interface

Improved sensitivity to interface by decreasing film thickness

$Q_c^2 = 0.79 \times 10^{-4} \text{ Å}^2$

$h = 80 \text{ nm}$

$Q_c^2 = 1.6 \times 10^{-4} \text{ Å}^2$

$h = 2 \text{ nm}$

$Q_c^2 = 1.06 \times 10^{-4} \text{ Å}^2$

$h = 2 \text{ mm}$

Effect of polymer on interfacial concentration

Convert SLD profile to vol. frac.

\[ \varphi_w(x) = \frac{Q_c^2(x) - Q_c^2_{\text{poly}}}{Q_c^2(D_2O) - Q_c^2_{\text{poly}}} \]

This can be extended to multiple phase systems

Concentration profile near substrate independent of polymer

\textbf{J. Mater. Sci. 1996 31} 927-927
\textbf{Langmuir 2004} 20(4) 1453-1458
\textbf{J. Microlitho. Microfab. 2005} 4(1) 013003

Can we further increase sensitivity?
Crosslinked polyacrylate on sputtered alumina

Reflectivity

$Q_c^2 = 3.21 \times 10^{-4} \text{ Å}^{-2}$

$h = 1.5 \mu\text{m}$

$Q_c^2 = 0.79 \times 10^{-4} \text{ Å}^{-2}$

$h = 35 \text{ nm}$

$Q_c^2 = 2.4 \times 10^{-4} \text{ Å}^{-2}$

$h = 2 \text{ mm}$


Interference fringes from thin alumina

Shift due to contrast change from $D_2O$ sorption

Improved sensitivity to interface
Moisture accumulation for polyacrylate on alumina

XR – measure film swelling

Vary cure condition to change $\text{H}_2\text{O}$ solubility

Bulk solubility does not influence moisture content at alumina / polymer interface

Design of system to maximize sensitivity

- Relatively thin polymer coating (< 150 nm)
- High contrast oxide layer (10-30 nm)
- D₂O as probe

![Graphs showing reflectivity vs. q (Å⁻¹)]

\[
Q_c^2 = 0.79 \times 10^{-4} \text{ Å}^{-2} \\
h = 85 \text{ nm}
\]

\[
Q_c^2 = 2.4 \times 10^{-4} \text{ Å}^{-2} \\
h = 35 \text{ nm}
\]

\[
Q_c^2 = 1.06 \times 10^{-4} \text{ Å}^{-2} \\
h = 2 \text{ mm}
\]

Vogt et al., *Langmuir* 2005, 21, 2460

Multiple interferences yields added sensitivity to buried interface contrast
Water accumulates at interface

• Does this accumulation directly impact adhesion?
• Can this accumulation be controlled?
• What are critical factors?
Critical relative humidity

Is the interface to blame for failure at high humidity?

Cohesive failure

Adhesive failure

Tan et al., *Langmuir* 2008, 24, 9189

\[ Q_c^2 = 0.79 \times 10^{-4} \, \text{Å}^{-2} \]
\[ h = 85 \, \text{nm} \]

\[ Q_c^2 = 1.6 \times 10^{-4} \, \text{Å}^{-2} \]
\[ h = 15 \, \text{nm} \]

\[ Q_c^2 = 1.06 \times 10^{-4} \, \text{Å}^{-2} \]
\[ h = 2 \, \text{mm} \]
Impact of humidity on interfacial properties

What’s driving the failure?

Tan et al., Langmuir 2008, 24, 9189
Comparison of interface and bulk

No discontinuity at interface
So is moisture at interface important?

Tan et al., *Langmuir* 2008, 24, 9189
Influence of substrate on moisture accumulation

Moisture accumulation at interface dependent upon surface chemistry.
Correlating interfacial moisture and adhesion for PMMA

Interplay between dry adhesion and moisture accumulation
Intermediate surface energy for best wet adhesion

Interfacial water matters!

Change in the interface at the critical humidity

Interfacial moisture broadens at the critical humidity
Is this responsible for the failure?

Tan et al., *Langmuir* 2008, 24, 9189
How could this change in the profile impact adhesion?

Only the average in plane distribution of water is determined from neutron reflectivity. Distribution is not uniform!

Dry surface

Ultrathin film (15 nm)

Water drop on surface

Hydrophilic interface (catastrophic adhesion loss)

Hydrophobic interface (minimal adhesion loss)
Proposed model for critical relative humidity

1. Initial accumulation at the interface only mildly perturbs the contact area – adhesive energy still greater than cohesive energy
2. This grows, but does not significantly stress the interface
3. When the bulk concentration increases significantly at the critical humidity, it causes shear stress accumulation near the interface due to the decreased contact area
4. This stress forces the additional water accumulating at the interface to be pushed into the film
5. This additional water at the interface causes a large stress normal to the film surface leading to adhesive failure
How to test model?

- Stress accumulation should be important

Water causes normal stress in adhesive?

Model: poly(n-alkyl methacrylate)

<table>
<thead>
<tr>
<th></th>
<th>PMMA</th>
<th>PEMA</th>
<th>PnPMA</th>
<th>PnBMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_f$</td>
<td>$3.15 \pm 0.07$ GPa</td>
<td>$1.91 \pm 0.1$ GPa</td>
<td>$1.20 \pm 0.06$ GPa</td>
<td>$&lt; 100$ MPa</td>
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<tr>
<td>$T_g$</td>
<td>$105 \degree C$</td>
<td>$65 \degree C$</td>
<td>$36 \degree C$</td>
<td>$15 \degree C$</td>
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<tr>
<td>$n$</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
</tbody>
</table>

Torres et al., ACS Nano 2009, 3, 2677
Impact on changing the model adhesive

PMMA

PEMA

PnBMA

Glassy

Glassy

Rubbery

Low modulus PnBMA does not exhibit critical relative humidity
What about moisture uptake?

Near saturation – less water in PnBMA than PMMA

Longer alkyl chain leads to more hydrophobic model adhesive
Is the interface impacted?

Different at high humidity?
Does low modulus lead to decrease in moisture?

Low modulus appears to lead to suppression of moisture accumulation at interface (rubbery polymers)

Karul et al., Polymer 2009, 50, 3234
Simple Model for Thickness Dependent Swelling

Bulk Swelling

Excess Swelling

Shaded area is excess thickness

\[ \frac{h}{h_0} = 1 + \frac{\Delta t_{eq}(h_0) + t_{\text{excess}}}{h_0} \]

\[ \phi_{eq} = \frac{t_f - t_i}{t_f} \]

\[ t_{\text{excess}} = \int_0^T (\phi_w(x) - \overline{\phi}) dx \]

Vogt et al., *Langmuir* 2005, 21, 2460
Thickness dependent swelling

Model corresponds well with thickness dependent swelling

Vogt et al., *Langmuir* 2005, 21, 2460
Is there always an excess at the interface?

No thickness dependence for films on native oxide
HMDS treated substrate leads to decrease in absorption for thin films

Vogt et al., Polymer 2005, 46, 1635
What about aqueous solutions?

- **Hydrophilic** interface relative to bulk polymer
  \(\Rightarrow\) interfacial excess & enhanced thin film swelling
- **Hydrophobic** interface relative to bulk polymer
  \(\Rightarrow\) interfacial depletion & suppressed thin film swelling

We obtain similar information about the interfaces immersed in D\(_2\)O.
What about salts?

Addition of salt increases fracture energy for failure

Does this correlate with the interfacial water content?
Developing system with high sensitivity

Note that SLD for aluminum is very close to silicon.
**Impact of salt on water distribution**

Comparison of profiles with saturated NaCl and D$_2$O

- Sharper interface between epoxy and aluminum oxide in case of salt
- Less bulk swelling in case of salt as well

Is this due to salt incorporation into the film?
Examination of NaCl in film

No evidence of salt accumulation within polymer

\[ Q_c^2 = 1.04 \times 10^{-4} \text{ Å}^{-2} \text{ for NaCl} \]

Can we directly visualize salt ion distribution?

Prabhu et al., *Langmuir* 2005, 21, 6647
- Contrast match solvent to the dry film (not much reflectivity)
- $d_{12}$-TMAH uptake increases contrast (more reflectivity)
- Base uptake observed
d$_{12}$-TMA profile within ultrathin PNBHFA

- **Direct measurement** of base profile within thin solid polyelectrolyte films
- TMA$^+$ concentration within film enhanced with increasing base concentration
- Non-uniform profile within the film; reduced near the substrate
- Diffuse counterion profile at free surface

Prabhu et al., *Langmuir* 2005, 21, 6647
Combining contrasts

Can measure excess ion concentration that extends into solution from charging of polymer film

*Prabhu et al., Langmuir 2005, 21, 6647*
Conclusions

• Water accumulates at polymer/substrate interface
• Concentration at interface
  • Independent of bulk solubility
  • Dependent on substrate chemistry
• Water accumulation correlates with adhesion loss
• Mechanism for critical relative humidity appears to be stress concentration due to moisture accumulation
• Salts can increase or decrease water uptake in films
• Contrast match provides facile route to visualize ion distribution
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