Rate-dependent elastic hysteresis during the peeling of Pressure Sensitive Adhesives

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Collaboration:

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1. FRACTURE OF HARD AND SOFT MATERIALS

2. BASICS OF PSA (PRESSURE SENSITIVE ADHESIVES)

3. HOW TO MODEL THE MECHANICS OF PEELING?

4. SOME NEW KEY EXPERIMENTS:
   1. ROLE OF THE PEELING ANGLE (MODE MIXITY)
   2. ROLE OF NON-LINEAR RHEOLOGY

5. ON THE ROAD AGAIN...
FRACTURE AND ADHESION OF HARD AND SOFT MATERIALS
PHYSICAL SCALES OF DISSIPATION MECHANISMS

Oxide glass
PMMA
PC
PP
Elastomers
Adhesives
Laminated windshield
Fibre composites
Linear Elastic Fracture Mechanics (LEFM)

Hypotheses:
- Linear elasticity (CMM)
- Infinitely sharp crack
- No interaction between lips
- Quasistatic solution

Energy balance:
\[ G = -\frac{dU_{el}}{dA} + \frac{dW}{dA} \geq G_c = w \]

\( G \): strain energy release rate

\[ G_c = \frac{K_{lc}^2}{E'} \]

Fracture energy

Stress field singularity:
\[ \sigma_{ij}(r, \theta) = \frac{K_I}{\sqrt{2\pi r}} \right f_{ij}(\theta) \]

\( K_I \): Stress intensity factor

\[ K_I \geq K_{lc} \]

Toughness
## Materials properties and orders of magnitude

<table>
<thead>
<tr>
<th></th>
<th>Toughness MPa $m^{1/2}$</th>
<th>Fracture Energy J/m²</th>
<th>Surface Energy J/m²</th>
<th>Young Modulus MPa</th>
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<tr>
<td>Glass</td>
<td>0.8</td>
<td>8</td>
<td>0.5</td>
<td>70000</td>
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<td>Polymers: 1-4</td>
<td>100-10000</td>
<td>0.02-0.05</td>
<td>1-3000</td>
<td></td>
</tr>
</tbody>
</table>

\[ w \sim 0.1 \div 10 \text{ J/m}^2 \]

For most materials:

\[
\Gamma = G_c \gg W \quad ! \\
+ \\
\Gamma = G_c = G_c(v) \quad ! \\
+ \\
\text{No healing}
\]

\[
K_{IC} = \sqrt{G_c E'}
\]
Velocity dependence and energy dissipation mechanisms

**Mechanical energy**

Dissipated energy $G_c(v)$

**Surface energy**

Space and time scales of the energy dissipation mechanisms

Sollicitation of a point $(A,B)$ at distance $\delta_P$

Load: $F, X, V$

Crack cavity

Enclave

Crack Tip $v = v(G^*, K^*)$

$t = \frac{\delta_P}{v}$
Three main mechanisms of dissipation $\Gamma(v) > w$

1) Plasticity (Dugdale 1960)
- $\sigma(r) \sim \frac{K}{\sqrt{r}}$
- $r_{zp} \sim \frac{K^2}{\sigma_{zp}^2}$

2) Viscoelasticity (de Gennes 1988)
- $L_1 = v \tau$
- $L_2 = \lambda v \tau$
- $\lambda = \frac{\mu_\infty}{\mu_0}$

3) Elastic Hysteresis (Lake-Thomas 1967)
- Bulk, but linear!
- Large strain, but molecular!

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Material structure and bond types

Oxide glasses

- Dense network of strong bonds

Polymers

- Strong and weak bonds
- Cross-links
- Entanglements
Mechanical properties of polymers are very sensitive to dynamics

- Several tunable length and time scales!
Basics on the fracture of soft elastic materials

LEFM equations:

\[ \sigma(r) \sim \frac{K}{\sqrt{r}} \quad \varepsilon \sim \frac{\sigma}{E} \sim \frac{K}{E \sqrt{r}} \quad u \sim \int \varepsilon dr \sim \frac{K}{E} \sqrt{r} \]

\[ u_y \sim \frac{K}{E} \sqrt{x} \quad x \sim \frac{y^2}{\rho} \quad \rho \sim \frac{K^2}{E^2} \sim \frac{G}{E} \quad \rho_{max} \sim \ell_{ea} \sim \frac{\Gamma}{E} \]

Transition to large strain (blunting):

\[ \varepsilon \sim 1 \quad \sigma \sim E \]

\[ \sigma \sim \frac{K}{\sqrt{r}} \quad E \sim \frac{K}{\sqrt{r_b}} \quad r_b \sim \frac{K^2}{E^2} \sim \rho \]

Crack tip stress (Saint Venant):

\[ \sigma \sim \frac{K}{\sqrt{r}} \quad r \geq \rho_b \]

\[ \sigma_{max} \sim E \quad r \leq \rho_b \]

\[ \sigma_{max} \sim \sigma_0 \sqrt{\frac{c}{\rho}} \sim \frac{K}{\sqrt{\rho}} \sim E \]

Hui 2003
Basics on the fracture of soft elastic materials

Elastic blunting of a sharp crack: Inhibition of propagation

Propagation conditions:

\[ \sigma_{tip} \geq \sigma_c \quad G \geq \Gamma \]

\[ E \geq \sigma_c \quad \rho_b \sim \frac{\Gamma}{E} \]

Enthalpic solids (Rigid):

\[ \sigma_c \sim \frac{E_g}{10} \leq E_g \sim 1 \text{GPa} \]

Entropic solids (Soft):

\[ E_c \sim \frac{E_g}{1000} \leq \sigma_c \sim 100 \text{MPa} \]

Need for different failure mechanisms!
Basics of PSA

Définition:
- dry (solvent free)
- aggressively and permanently tacky
- room temperature
- variety of dissimilar substrates
- adhere by simple contact (finger pressure)
- clean removal

Applications
- Paint masking
- Surgical plasters
- Repair torn films
- Fix or assemble films (paper)
- Sealing
- Electrical insulation

Milestones:
1930: Patent by Richard Drew
1959-70: Kaelbles model’s
1969: Dahlquist criteria
1970-80: Stress singularity models
2003: Elastic blunting

Materials
- Rubber and rosin blends
- Advanced polymers (acrylates)
Basics of PSA

Adhesive: very soft polymer (PA, ...)

Typical thickness $a \sim 20\text{-}40 \mu m$

Dahlquist criterion:

$\mu' \sim 10\text{-}100 \text{ kPa} @ 1 \text{ Hz}$ - Very soft for spontaneous adhesion

$\mu'' \sim 10 \text{ kPa} @ 1 \text{ Hz}$ – Fast relaxation under finger pressure

$T_g \sim -40 \degree \text{C}$ - Broad band dissipation during peeling

Weak level of crosslinking – no flow, no residuals on substrate

Backing: glassy semicristalline polymer (PE, PP)

Typical thickness $2h \sim 20 \mu m$

$E \sim \text{GPa}$ – Avoid large stretching, very flexible

Substrate: backing itself, with release coating

Glassy -> no sliding? Relatively weak adhesion
Linear rheology of PSA

\[ \tau' \]

1 GPa

Tg

1 MPa

Elastomer

100 kPa

PSA

10 kPa

Cross-linked

Uncross-linked

Weakly cross-linked

Non-linear rheology

\[ \sigma \]

Cross-linked

Uncross-linked

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The Mechanics of Peeling (basics)

Strain energy release rate:

\[ G = \frac{F}{b} (1 - \cos \theta) + \left( \frac{F}{b} \right)^2 \frac{1}{2(2h)E} \]

Kendall 1957

Adhesion energy (Dupré)

\[ \omega = \gamma_1 + \gamma_2 - \gamma_{12} \]

Adherence energy and dissipated energy:

\[ \Gamma(v) = \omega (1 + \Phi(a_T v)) \gg \omega \]

Gent 1972  Maugis Barquins 1988

Interfacial fracture???
Multiscale Modeling of Peeling

10 cm – 1 m
Straight string model (Kendall)

100 µm – 1 mm
Curved knee model (Bending)

20 µm – 100 µm
Viscoelastic cohesive zone

100 nm – 20 µm
Soft viscoelastic adhesive layer
Fracture mechanisms (shear + fibrils)

1 Å nm – 100 nm
Intermolecular cohesive zone (VdW)
Fracture of confined soft materials

1) Softness: Elastoadhesive length is large!

\[ \rho \sim \ell_{EA} - \frac{\Gamma}{E} \sim \frac{\Gamma(v)}{E(v)} \sim \frac{10 \div 100 J/m^2}{10 \div 100 kPa} \sim 1 mm \gg a \sim 20 \mu m \]

For very thick glue \((a \sim 10 \ mm)\)
elastic blunting at crack tip!

Stress singularity is cut at a distance \(\ell_{EA}\)
and the tip experiences a constant stress \(\sim E\)

Hui 2003

2) Incompressibility

No large volumetric strain without cavitation

Spontaneous cavitation under negative pressure \(-p > E\)

Gent 1972
Fracture of confined soft materials

3) Softness + incompressibility + confinement :

\[ \rho \sim \ell_{EA} = \frac{\Gamma}{E} \sim \frac{\Gamma(v)}{E(v)} \sim \frac{10 \div 100 J/m^2}{10 \div 100 kPa} \sim 1 mm \gg a \sim 20 \mu m \]

A) Elastoadhesive confinement:

\[ \frac{aE}{\Gamma} \ll 1 \]

No stress singularity within thickness \( a \)

Uniform stress-(large)stretch through thickness

B) Geometric confinement:

\[ \frac{a}{b} \ll 1 \]

Very stiff oedometric modulus

Strong negative hydrostatic pressure

Tendency to cavitation and stringing

C) Saint-Venant principle:

Lateral variations of \((\sigma, \varepsilon)\) are correlated over distance \( a \)
Kaelble’s model

Beam on a Winkler elastic foundation?

Backward ($E$)

Adhesive ($Y, \mu$)

Bending + Horizontal stretch

Vertical stretch + Tangent shear

Progressive stress transfer from backing to adhesive
Kaelble’s model (scaling laws)

1) **Uncoupling mode I** (cleavage) and **mode II** (shear), as a function of peeling angle 

2) **Stress concentration** due to elastic stiffness mismatch between adhesive and backing!

$$U_{E_{\text{Ext}}}^B \sim \left( \frac{E}{R^2} \right) \lambda_c \sim \left( \frac{E}{Y} \right)^{1/4} \sim a \left( \frac{E}{Y} \right)^{1/4} \sim 10a \sim 200\mu m$$

$$\sigma_0(\lambda_c b) = F \sin \theta$$

$$U_{A_{\text{Shear}}}^A = \left( \frac{u_0^2}{a^2} \right) \mu \lambda_s$$

$$\lambda_s = \frac{1}{\alpha} \sim \sqrt{\frac{h a E}{\mu}} \sim a \sqrt{\frac{E}{\mu}} \sim 100a \sim 2mm$$

$$\tau_0(\lambda_s b) = F \cos \theta$$
Kaelble’s model (scaling laws)

3) Stress based peel failure criteria:

\[ \sigma_0 \leq \sigma_C \quad \& \quad \tau_0 \leq \tau_C \]

4) Peeling energy:

\[ \Gamma(a, \theta) \sim a \left[ K(\theta) \sqrt{\frac{\sigma_0^2}{Y} + \sqrt{\frac{\tau_0^2}{G}}} \right]^2 \sim a K^2(\theta) \frac{\sigma_c^2}{Y} \sim a K^2(\theta) \mathcal{W}_{el}(\sigma_c) \]

A) \[ \sigma_0 = \sigma_c \quad \tau_0 = \sigma_c \frac{\beta}{\alpha} f(\theta) < \tau_c \quad \text{Strand debonding !} \]

B) \[ \tau_0 = \tau_c \quad \sigma_0 = \tau_c \frac{\alpha}{\beta} \frac{1}{f(\theta)} < \sigma_c \quad \text{Frictional sliding ??} \]

Mode A dominates except at small (and large?) peeling angle

\[ Y \sim 100kPa \quad \sigma_c \sim 10Y \quad K \sim 1 \quad \Gamma \sim 100J/m^2 \implies w \sim 0.1J/m^2 \]
Kaelble’s model (scaling laws)

3) **Stress based peel failure criteria:**

\[ \sigma_0 \leq \sigma_C \quad \& \quad \tau_0 \leq \tau_C \]

4) **Peeling energy:**

\[ \Gamma(a, \theta) \sim a \left[ \frac{K(\theta)}{\sqrt{\sqrt{2}}} \right] \sqrt{\frac{\sigma_c^2}{\sqrt{\sqrt{2}}}} \sim aK^2(\theta)\mathcal{W}_{el}(\sigma_c) \]

A) \( \sigma_0 = \sigma_c \) and debonding!

B) \( \tau_0 = \tau_c \) and frictional sliding ??

Mode A dominates at small (and large?) peeling angle

\[ Y \sim 100kPa \quad \sigma_c \sim 10Y \quad K \sim 1 \quad \Gamma \sim 100J/m^2 \Rightarrow w \sim 0.1J/m^2 \]
The role of viscoelastic dissipation

Viscoelastic Winkler foundation

Effective work of debonding:

\[ \Gamma \sim a \mathcal{W} \]
\[ \mathcal{W} = \int_0^{\varepsilon_c} \sigma(\varepsilon, \dot{\varepsilon}) d\varepsilon \]

Link with linear viscoelasticity:

\[ t^* \sim \frac{\lambda_\beta}{V} \]

Linear viscoelasticity

\[ \Gamma(a, \theta, v) \sim a K^2(\theta) \frac{\sigma_c(v)^2}{Y(v)} \]

Kaelble 1964
The role of non-linear viscoelastic rheology
Gent and Petrich model

Effective work of debonding:

\[ \Gamma(v) = \int_0^{\sigma_c} \sigma(\varepsilon, \dot{\varepsilon}) \, d\delta \]

\[ \Gamma(v) = \int_0^{\sigma_c} \sigma(\varepsilon\{\delta(t)\}, \dot{\varepsilon}\{\delta(t)\}) \, d\delta \, dt \]

\[ \Gamma(v) = a \int_0^{\sigma_c} \sigma(\varepsilon, \dot{\varepsilon}) \, d\varepsilon \simeq a \, W(\varepsilon_c(\sigma_c), \dot{\varepsilon}) \]

Pertinent strain rate:

\[ \dot{\varepsilon} = \frac{d(\delta/\alpha)}{dx} \frac{dx}{dt} = \frac{d(\delta)}{dx} \frac{v}{\alpha} \]
The three complementary experimental setups

1) Low velocity (1-100 µm/s)
   Imposed force and angle

2) Intermediate velocity
   (10-1500 µm/s)
   Imposed velocity and angle

3) High velocity (1 mm/s - 4 m/s)
   Imposed velocity and angle
**Bond formation**

1) Lay down a first adhesive layer on the flat bar  
   (the finger is covered with a glove and pressure is gently applied through another backing)

2) Lay down a second adhesive layer and wait 10 minutes before peeling  
   (no significant aging, results are consistent with peeling from roller!)

**Microscopic investigation of the debonding region**

1) Side view  
2) Bottom view
1) Dependence of the adherence energy on the peeling angle

Scotch 3M 600 "Crystal"

Separability!

\[ G(\theta, V) = f(\theta) h(V) \]

Peak velocity \( V_c \) Increases with the angle!


Peeling angle dependence

\[ \Gamma = a W K' (\xi) \]
\[ W = \frac{\sigma_c^2}{2Y} \]
\[ K'(\xi) = \frac{2}{\xi} \left( 1 - \sqrt{1 + \xi} \right) \]
\[ \xi = \xi_0 \left( \frac{\sin \theta - h \beta \cos \theta}{1 - \cos \theta} \right) \]
\[ \xi_0 = 4a \frac{\sigma_c}{Y} \beta \quad \beta \propto Y^{1/4} \]
\[ \Gamma \approx f(\theta, \sigma_c/Y) h(V) \]
\[ \xi_0 = 1.7 \quad \sigma_c/Y \sim 3.5 - 4 \]

2) Dependence on linear and non-linear rheology

6 different formulations supplied by 3M©

Main polymer: 2-ethyl hexyl acrylate (EHA)
3 levels of methacrylate (MA) : Decrease Tg
2 levels of crosslinker (A,B) : Decrease $\mathcal{E}_C$

<table>
<thead>
<tr>
<th>Name</th>
<th>EHA</th>
<th>MA</th>
<th>AA</th>
<th>Cross-Linker</th>
<th>$T_g$</th>
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</thead>
<tbody>
<tr>
<td>1A</td>
<td>70%</td>
<td>25%</td>
<td>5%</td>
<td>0.2%</td>
<td>$-34 \pm 4 , ^\circ C$</td>
</tr>
<tr>
<td>1B</td>
<td>70%</td>
<td>25%</td>
<td>5%</td>
<td>0.4%</td>
<td>$-34 \pm 4 , ^\circ C$</td>
</tr>
<tr>
<td>2A</td>
<td>85%</td>
<td>10%</td>
<td>5%</td>
<td>0.2%</td>
<td>$-43 \pm 5 , ^\circ C$</td>
</tr>
<tr>
<td>2B</td>
<td>85%</td>
<td>10%</td>
<td>5%</td>
<td>0.4%</td>
<td>$-43 \pm 5 , ^\circ C$</td>
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<tr>
<td>3A</td>
<td>95%</td>
<td>0%</td>
<td>5%</td>
<td>0.2%</td>
<td>$-53.5 \pm 8 , ^\circ C$</td>
</tr>
<tr>
<td>3B</td>
<td>95%</td>
<td>0%</td>
<td>5%</td>
<td>0.4%</td>
<td>$-53.5 \pm 8 , ^\circ C$</td>
</tr>
</tbody>
</table>
Linear rheology of PSA

\[ \mu' \]

1 GPa

1 MPa

100 kPa

10 kPa

\( T_g \)

Elastomer

PSA

Cross-linked

Uncross-linked

Weakly cross-linked

Uncross-linked

\[ \sigma \]

Non-linear rheology

Cross-linked

Uncross-linked

\[ \varepsilon \]
Distinct effect of non-linear rheology!

\[ G \propto V^n \]

Distinct effect of non-linear rheology!

1. Effect of change of $T_g$

$G_c \sim 100 \text{ J/m}^2 \sim \text{ cst}$

$V_c \sim \text{ Arrhenius shift factors}$

$$\log a_T = \log \frac{V_{ref}}{V} = \frac{\Delta H}{R} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right)$$

$\Delta H \sim 40-50 \text{ kJ/mol}$

(literature: 60-80 kJ/mol)

*Cailles et al, Polymer, 2015*

2. Effect of crosslink density

An increase in the density of crosslinks, has the effect of reducing the maximum extensibility of the fibrils, and thus the adherence energy

This effect is reduced when increasing the crack velocity and disappears at the peak, where the maximum extensibility is governed by the entanglement network.
Confirmation by microscopic analysis

2A: 0.2% crosslinker

2B: 0.4% crosslinker

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Interpretation of the adherence curve $\Gamma(V)$
Main conclusions

1. The bond stress distribution is essential to understand the dependence of the adherence energy on the geometry of loading (adhesive thickness and peeling angle).

2. The occurrence of large deformations is essential to reach high values of $\Gamma$ by rate dependent elastic hysteresis. The large strain rheology must then be taken into account for quantitative predictions of the adherence energy.

3. The strong confinement of the soft uncompressible adhesive is a key feature to reach these large deformations through cavitation and stringing and to develop hysteretic dissipation.
Open questions

Full role of non-linear rheology
(large strain, finite extensibility, entanglement network)

Criterion of fibril debonding
(stress, strain, strain energy density, total strain energy)

What determines the position of the instability?
(peak in the adherence, change to brittle failure, …)

Role of the substrate
(relating adhesion energy $w$ and debonding stress $\sigma_c$?)

Boundary condition on the substrate
(sliding permitted?)
Perspective: the role of fibril mechanisms

While acknowledging fibril formation, most authors keep referring to bulk rheology of the adhesive!

A more realistic average behavior of fibrilled adhesive can be obtained by comparing with tack measurements!