INFLUENCE OF LARGE STRAIN RHEOLOGY ON THE ADHESIVE PERFORMANCES OF PSA

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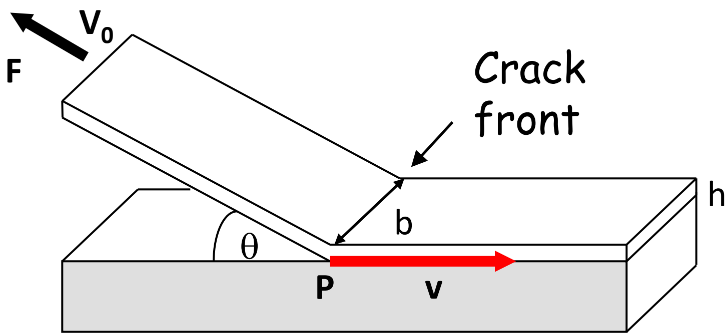
PLOT

1. **HOW TO MODEL THE ADHERENCE IN PEELING?**
2. **SOME NEW KEY EXPERIMENTS:**
    1. **ROLE OF THE PEELING ANGLE (MODE MIXITY)**
    2. **ROLE OF NON-LINEAR RHEOLOGY**
3. **ON THE ROAD AGAIN…**

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

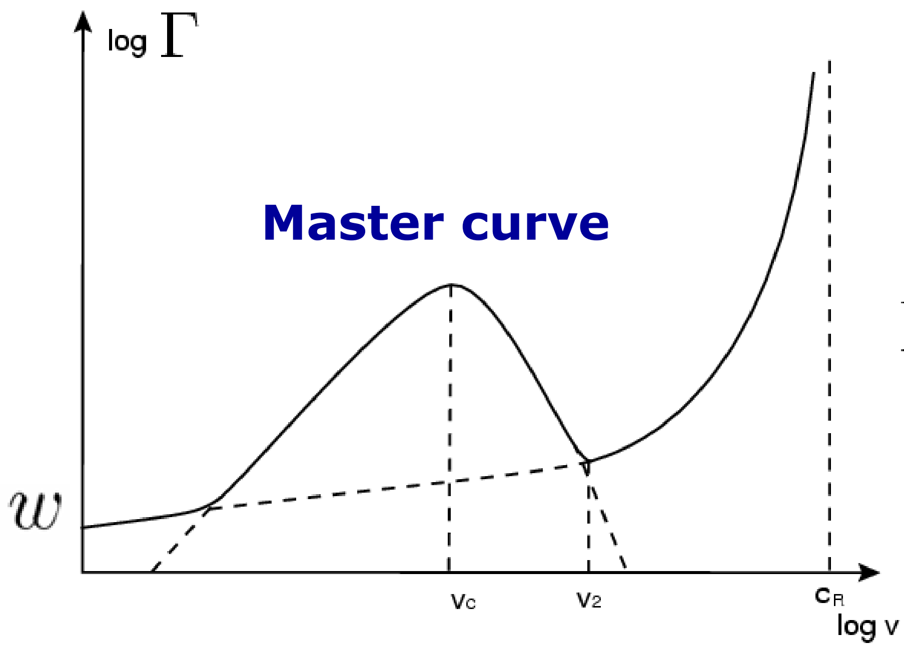
Adhesion energy (Dupré)

$$w = \gamma_1 + \gamma_2 - \gamma_{12}$$

Adherence energy and dissipated energy :

$$\Gamma(v) = w(1 + \Phi(a_T v)) \gg w$$

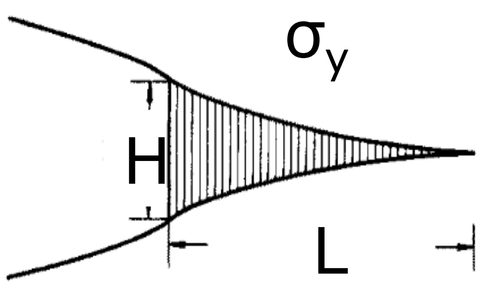
Gent 1972 ***Maugis Barquins 1988***

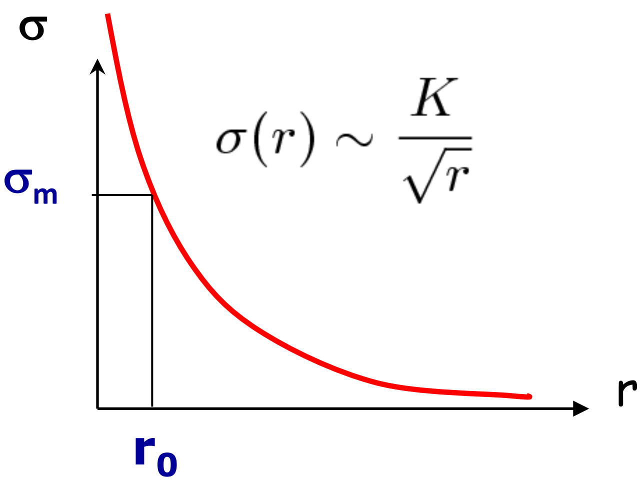


Interfacial fracture???

Three main mechanisms of dissipation $\Gamma(v) > w$

1) Plasticity
(Dugdale 1960)

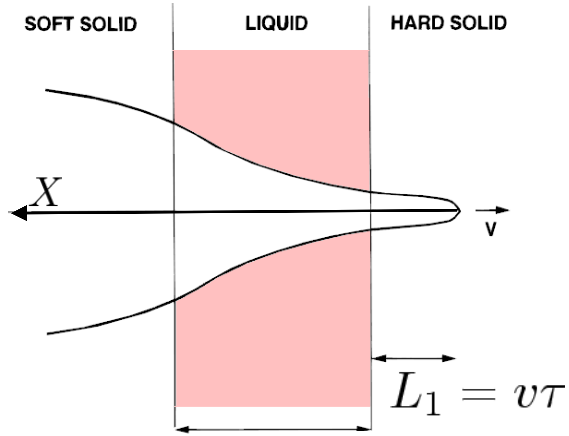




$$\sigma(r) \sim \frac{K}{\sqrt{r}}$$

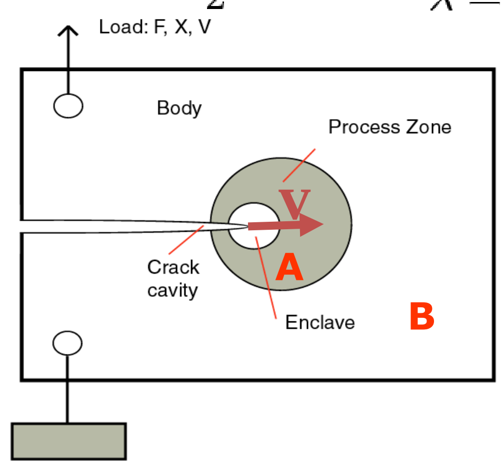
$$r_{ZP} \sim \frac{K^2}{\sigma_{ZP}^2}$$

2) Viscoelasticity
(de Gennes 1988)



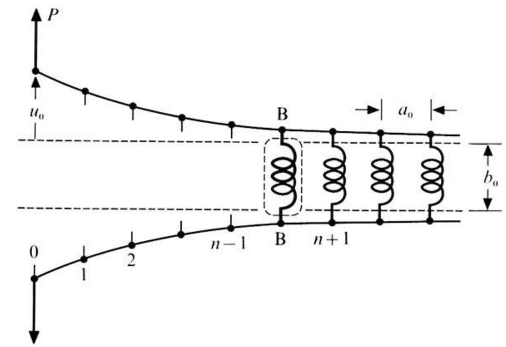
$$L_1 = v\tau$$

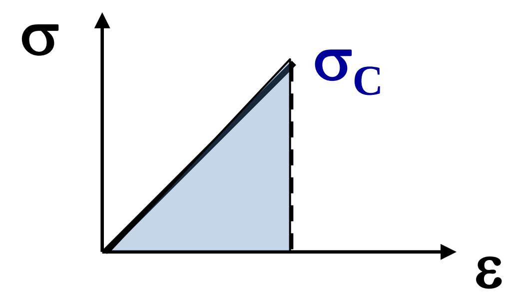
$$L_2 = \lambda v \tau \quad \lambda = \frac{\mu_\infty}{\mu_0}$$



Bulk, but linear!
No large strain!

3) Elastic Hysteresis
(Lake-Thomas 1967)

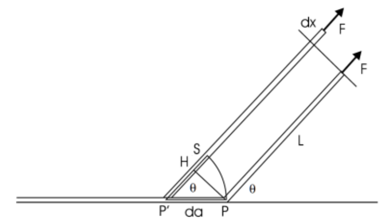




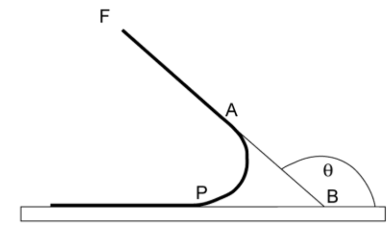
Large strain,
but molecular!

Multiscale Modeling of Peeling

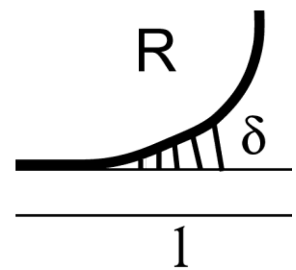
10 cm – 1 m
Straight string model (Kendall)



100 μm – 1 mm
Curved knee model (Bending)

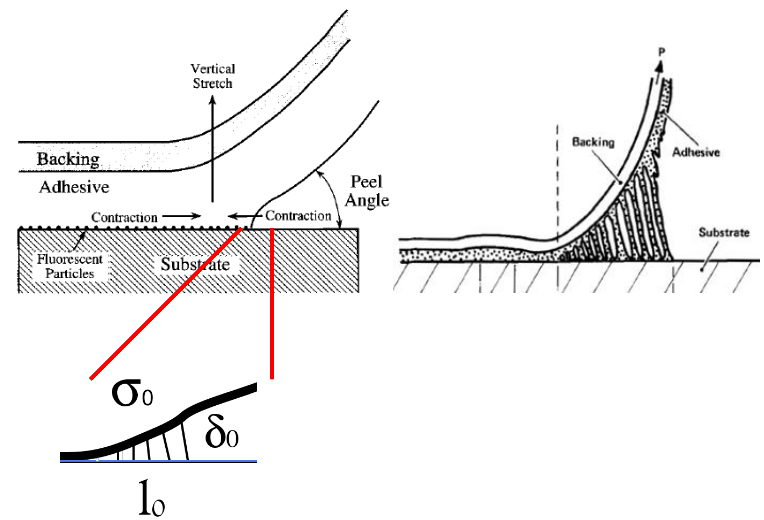


20 μm – 100 μm
Viscoelastic cohesive zone

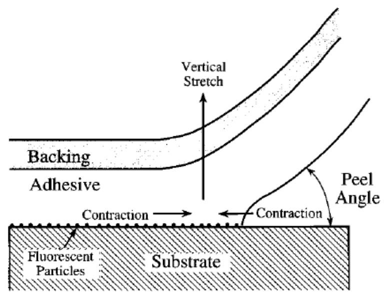


100 nm – 20 μm
Soft viscoelastic adhesive layer
Fracture mechanisms (shear + fibrils)

1 A nm – 100 nm
Intermolecular cohesive zone (VdW)



Basics of PSA



Adhesive: very soft polymer (PA, …)

Typical thickness a ~ 20-40 μm

Dahlquist criterion:

μ′ ~ 10-100 kPa @ 1 Hz - Very soft for spontaneous adhesion
μ″ ~ 10 kPa @ 1 Hz – Fast relaxation under finger pressure
Tg ~ -40 °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* ~ 20 μm

E ~ GPa – Avoid large stretching, very flexible

Substrate : backing itself, with release coating

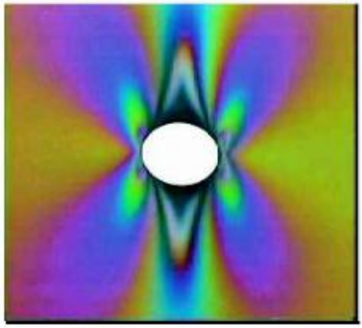
Glassy -> no sliding? Relatively weak adhesion

Fracture of confined soft materials

1) Softness: Elastoadhesive length is large !

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

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



Stress singularity is cut at a distance ℓ_{EA}
and the tip experiences a constant stress ~ *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 :

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

A) Elastoadhesive confinement:

$$\frac{aE}{\Gamma} \ll 1$$

No stress singularity within thickness a
Uniform stress-(large)stretch through thickness

B) Geometric confinement:

$$\frac{a}{b} \ll 1$$

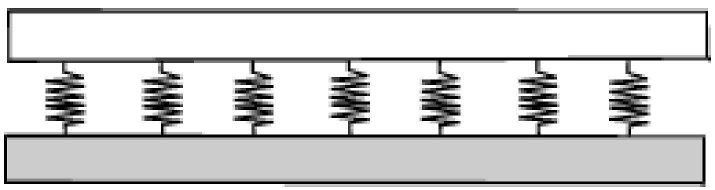
Very stiff oedometric modulus
Strong negative hydrostatic pressure
Tendency to cavitation and stringing

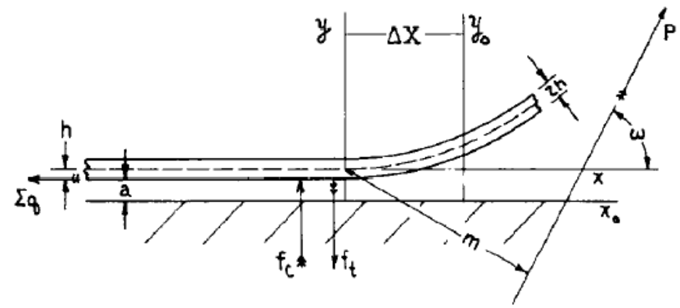
C) Saint-Venant principle:

Lateral variations of (σ,ε) are correlated over distance a

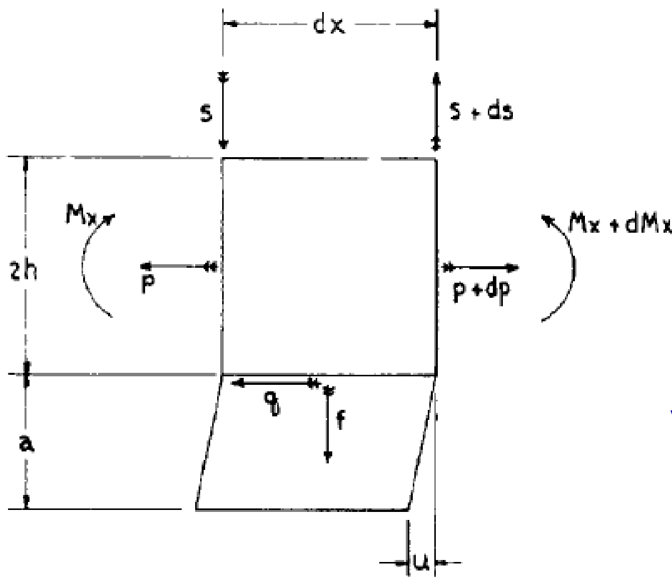
Kaelble's model

Beam on a Winkler elastic foundation?





Backing (*E*)



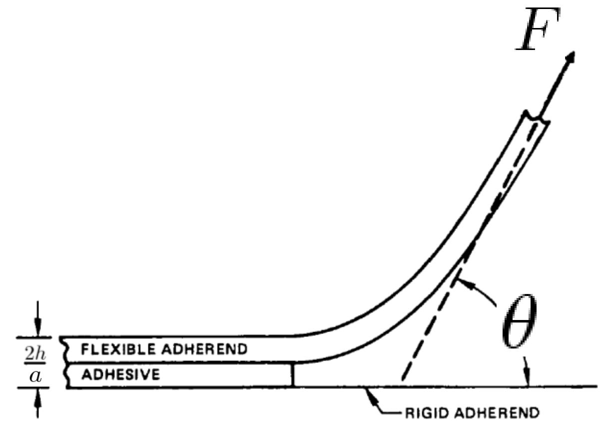
Bending + Stretch

Adhesive (*Y*,*μ*)

Vertical stretch + Tangent shear

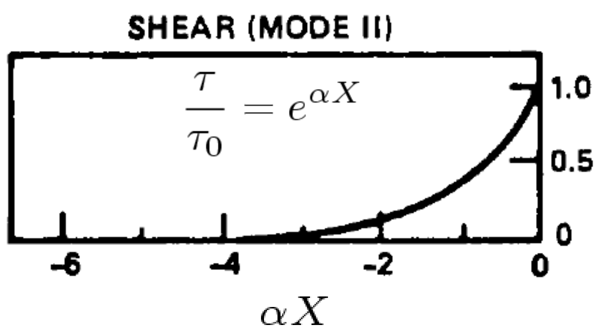
Progressive stress transfer from backing to adhesive

Kaelble's model (scaling laws)



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

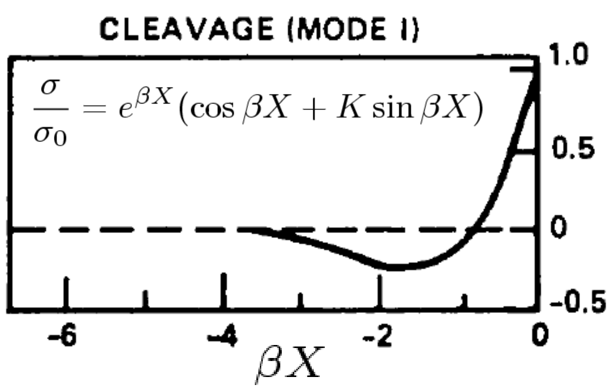
2) **Stress concentration** due to elastic stiffness mismatch between adhesive and backing!



$$U^B_{Ext} \sim \left(E\frac{u_0^2}{\lambda_s^2}\right) hb\lambda_s \sim U^A_{Shear} = \left(\mu\frac{u_0^2}{a^2}\right) ab\lambda_s$$

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

$$\tau_0(\lambda_s b) = F\cos\theta$$

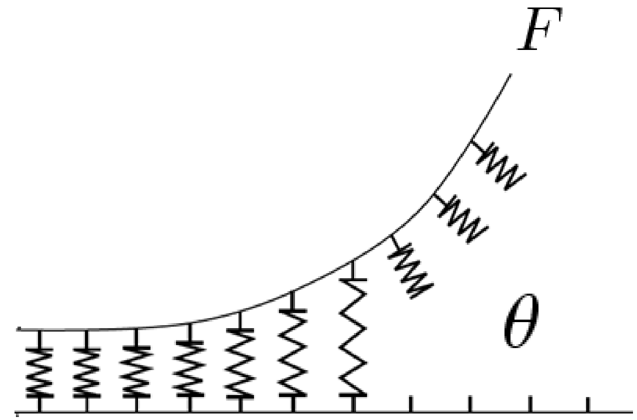


$$U^B_{Bend} \sim \left(\frac{EI}{R^2}\right)\lambda_c \sim \left(\frac{EIy_0^2}{\lambda_c^4}\right) \sim U^A_{Ext} = \left(Y\frac{y_0^2}{a^2}\right) ab\lambda_c$$

$$\lambda_c = \frac{1}{\beta} \sim \left(\frac{EIa}{Yb}\right)^{1/4} \sim a\left(\frac{E}{Y}\right)^{1/4} \sim 10a \sim 200\mu m$$

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

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**:

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

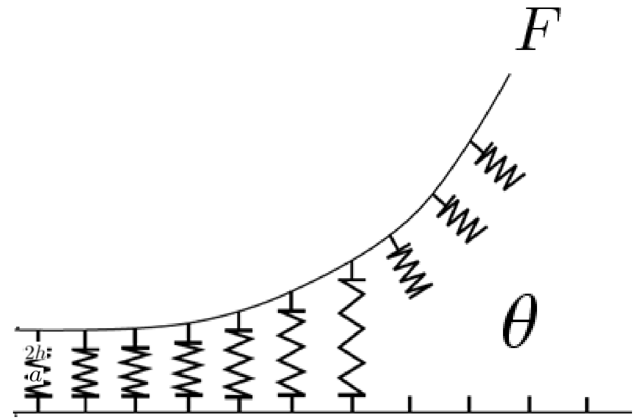
A) $\sigma_0 = \sigma_c \qquad \tau_0 = \sigma_c \frac{\beta}{\alpha} f(\theta) < \tau_c$ Strand debonding !

B) $\tau_0 = \tau_c \qquad \sigma_0 = \tau_c \frac{\alpha}{\beta} \frac{1}{f(\theta)} < \sigma_c$ Frictional sliding ??

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

$$Y \sim 100kPa \quad \sigma_c \sim 10Y \quad K \sim 1 \quad \Gamma \sim 100J/m^2 \gg w \sim 0.1J/m^2$$

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**:

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

Dissipation by Elastic Histeresis !!!

A) $\sigma_0 = \sigma_c$ … nd debonding !

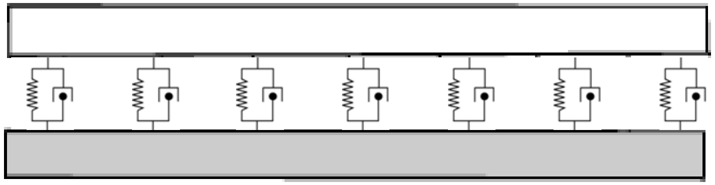
B) $\tau_0 = \tau_c$ … Fric…nal sliding ??

Mode A dom… small (and large?) peeling angle

$$Y \sim 100kPa \quad \sigma_c \sim 10Y \quad K \sim 1 \quad \Gamma \sim 100J/m^2 \gg w \sim 0.1J/m^2$$

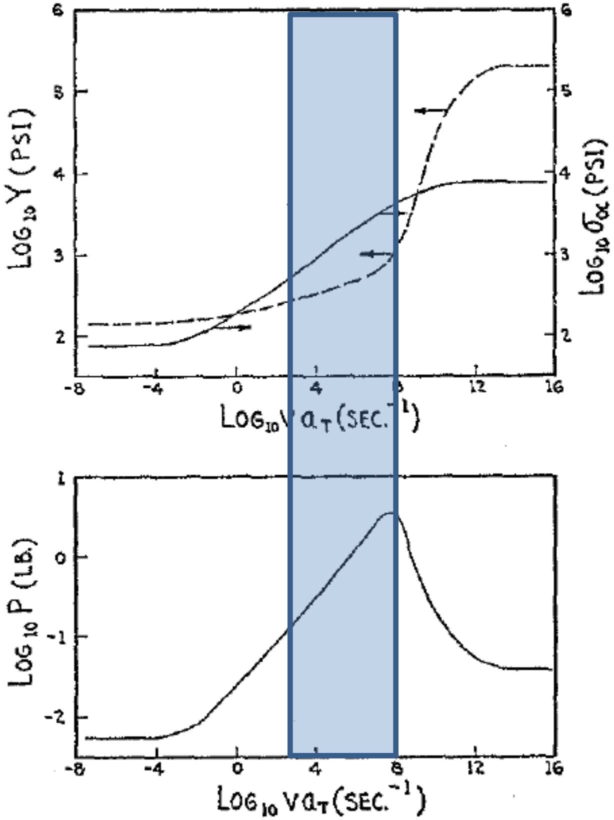
The role of viscoelastic dissipation

Viscoelastic Winkler foundation



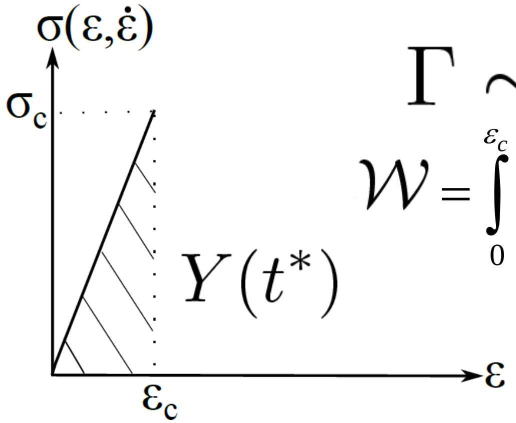
Linear viscoelasticity

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



Kaelble 1964

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:

$$t^* \sim \frac{\lambda_\beta}{V}$$

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

Effective work of debonding :

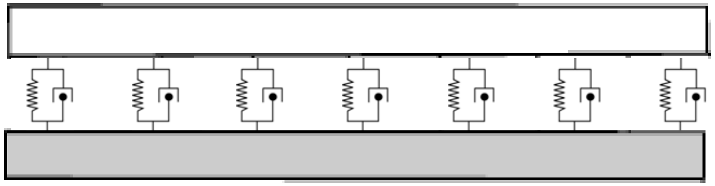
$$\Gamma(v) = \int_0^{\sigma_c} \sigma(\varepsilon, \dot{\varepsilon}) d\delta$$

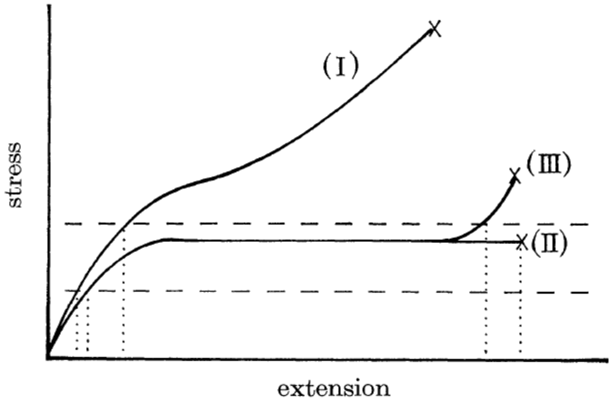
$$\Gamma(v) = \int_0^{\sigma_c} \sigma(\varepsilon\{\delta(t)\}, \dot{\varepsilon}\{\delta(t)\}) \dot{\delta} dt$$

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

Pertinent strain rate :

$$\dot{\varepsilon} = \frac{d(\delta/a)}{dx}\frac{dx}{dt} = \frac{d(\delta)}{dx}\frac{v}{a}$$



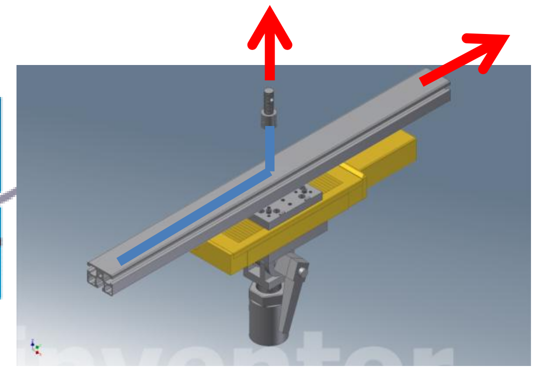


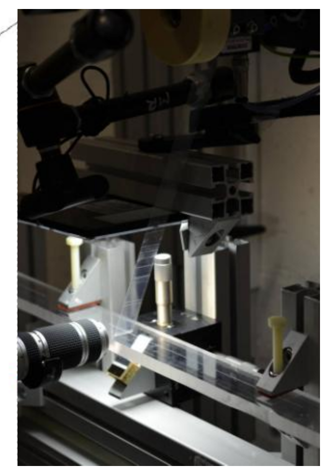
Gent & Petrich 1969

The three complementary experimental setups

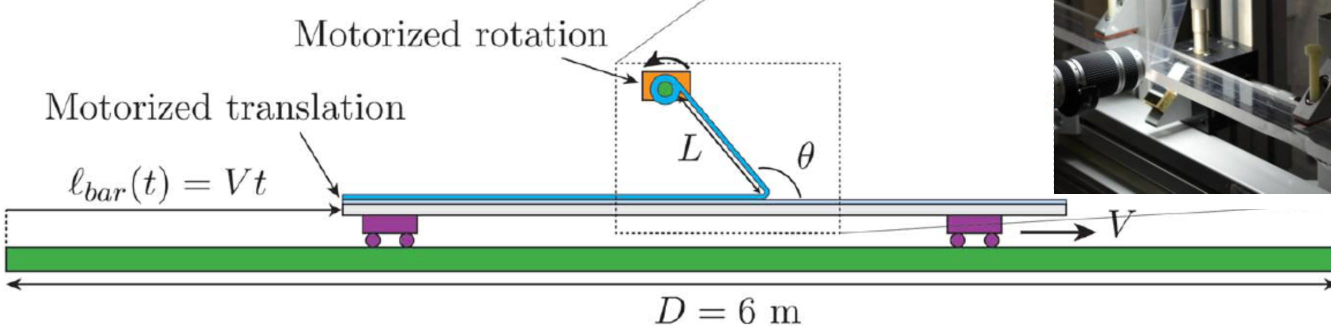
1) Low velocity (1-100 μm/s)
   Imposed force and angle

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





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



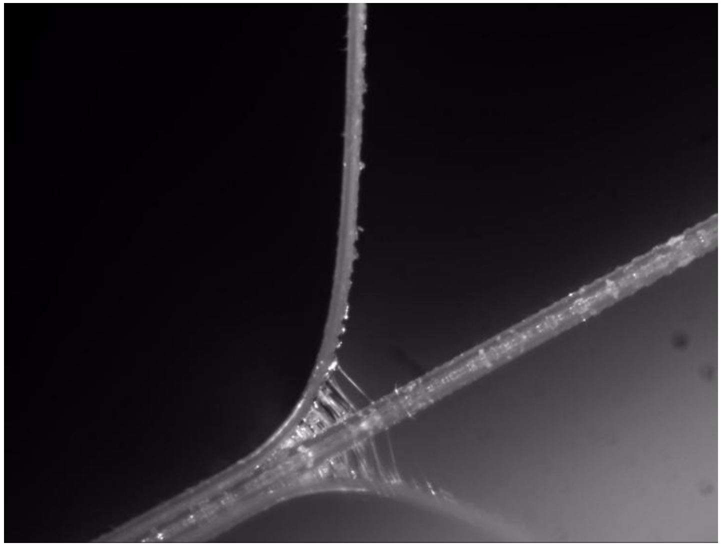
Bond formation

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)

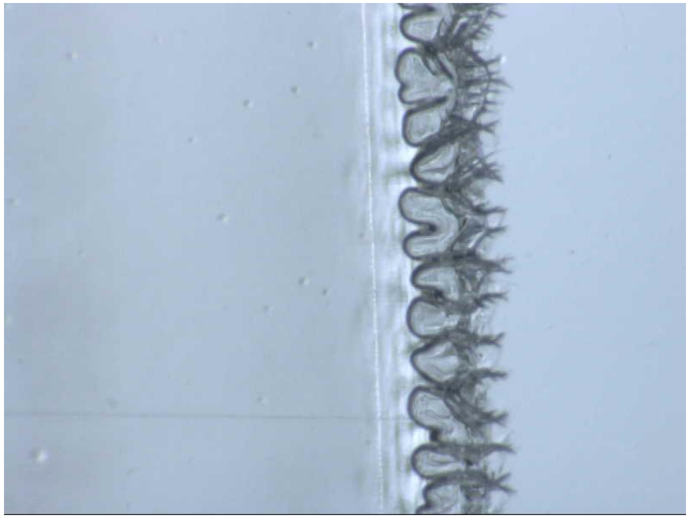
2) Lay down a second adhesive layer and wait 10 minutes before peeling
   (no significant aging, results are consistent with peeling from roller!)

Microscopic investigation of the debonding region

1) Side view

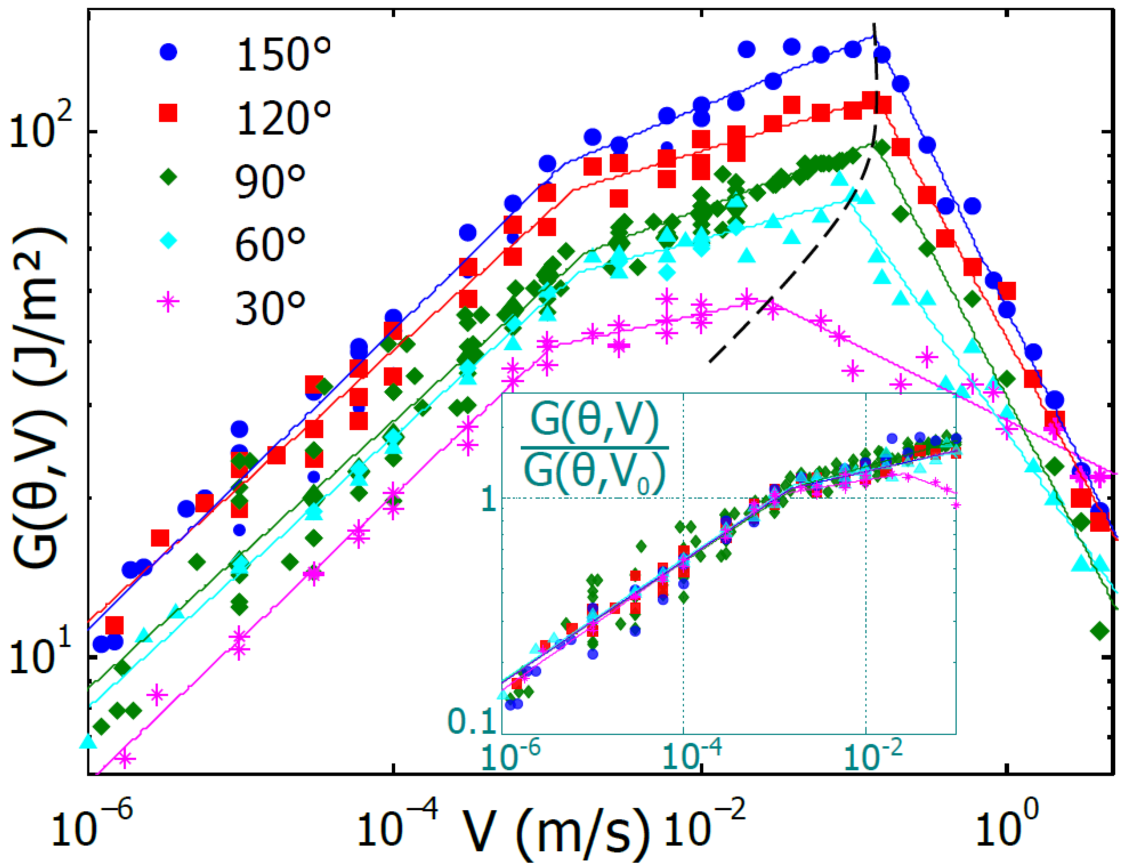


2) Bottom view



1) Dependence of the adherence energy on the peeling angle

Scotch 3M 600 ''Crystal''



Separability !

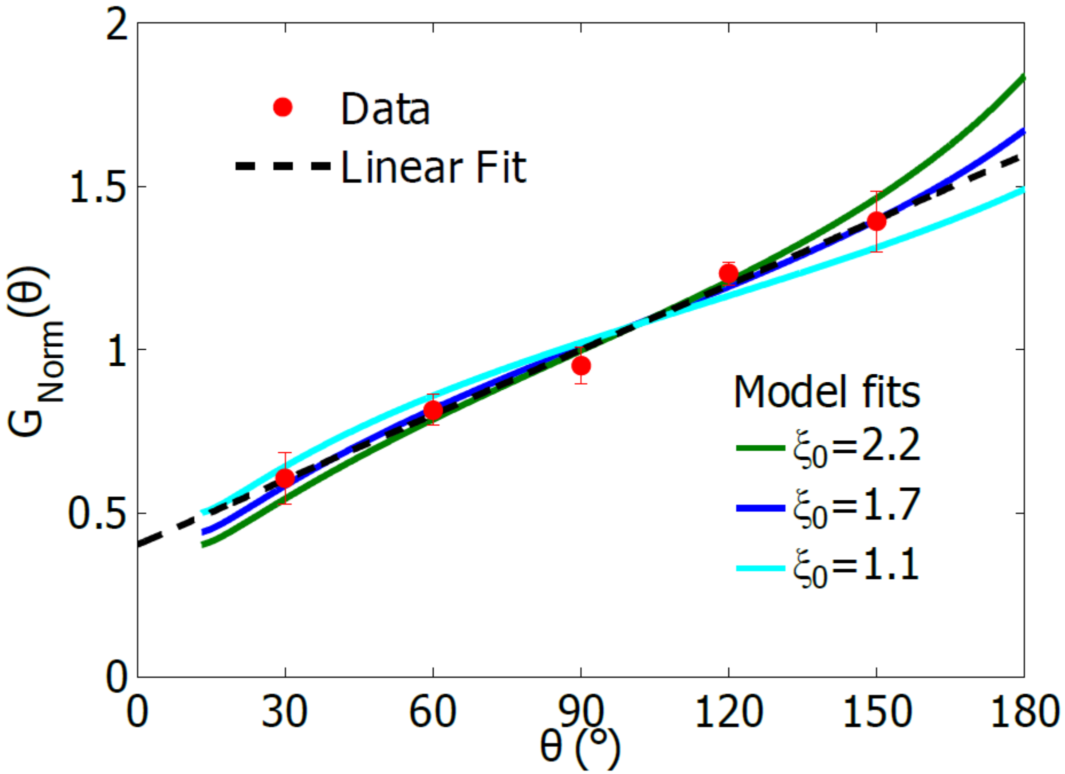
$$G(\theta, V) = f(\theta)h(V)$$

Peak velocity Vc Increases with the angle !

En accord avec
Dalbe et al. Soft Matter (2014)

Villey et al, Soft Matter (2015)

Peeling angle dependence



Average of $\frac{G(\theta)}{G(90°)}$ over the 1 µm/s-1 m/s range

$$\Gamma = a\mathcal{W}K'^2(\xi)$$

$$\mathcal{W} = \frac{\sigma_c^2}{2Y}$$

$$K'(\xi) = \frac{2}{\xi}\left(1 - \sqrt{1+\xi}\right)$$

$$\xi = \xi_0\left(\frac{\sin\theta - h\beta\cos\theta}{1-\cos\theta}\right)$$

$$\xi_0 = 4a\frac{\sigma_c}{Y}\beta \qquad \beta \propto Y^{1/4}$$

$$\Gamma \approx f(\theta, \sigma_c/Y)h(V)$$

Villey et al, Soft Matter (2015)

$$\xi_0 = 1.7 \qquad \sigma_c/Y \sim 3.5 - 4$$

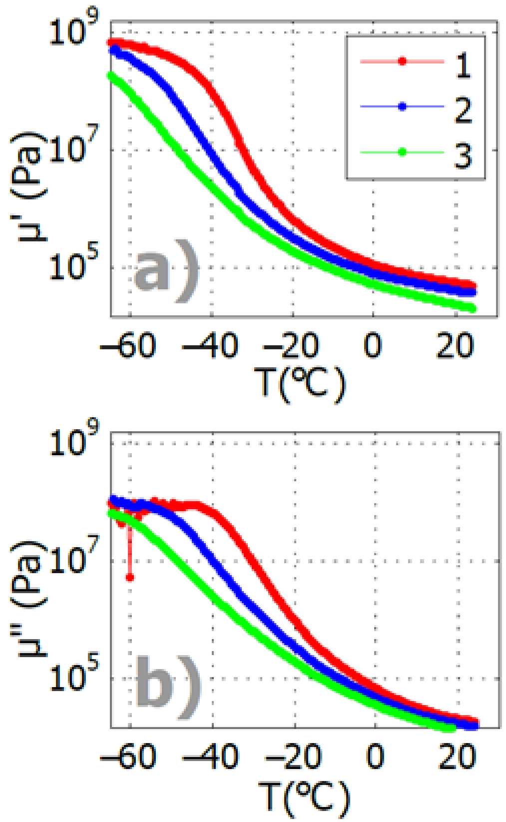
2) Dependence on linear and non-linear rheology

6 different formulations supplied by 3M©

Main polymer: 2-ethyl hexyl acrylate (EHA)

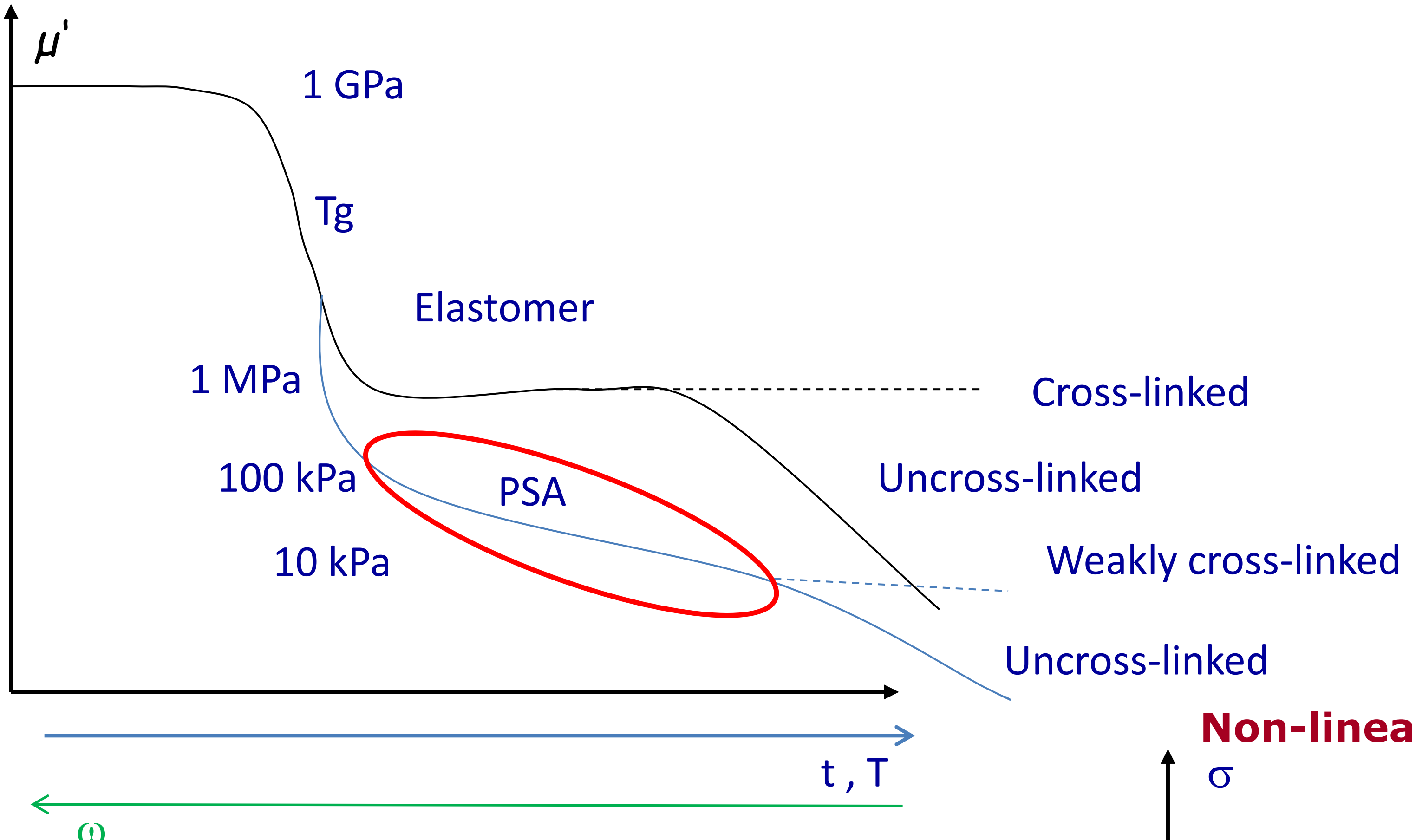
3 levels of methacrylate (MA) : Decrease Tg

2 levels of crosslinker (A,B) : Decrease ε_c

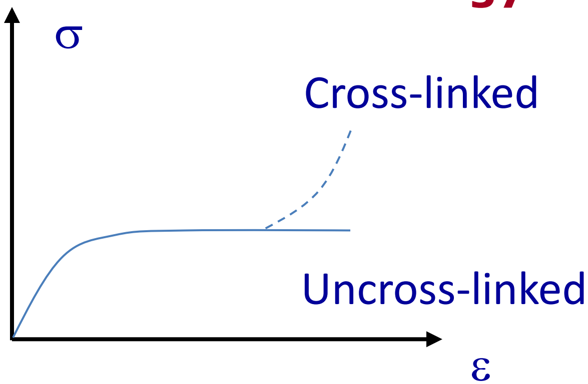


Name	EHA	MA	AA	Cross-Linker	T_g
1A	70%	25%	5%	0.2%	-34 ± 4 °C
1B	70%	25%	5%	0.4%	-34 ± 4 °C
2A	85%	10%	5%	0.2%	-43 ± 5 °C
2B	85%	10%	5%	0.4%	-43 ± 5 °C
3A	95%	0%	5%	0.2%	-53.5 ± 8 °C
3B	95%	0%	5%	0.4%	-53.5 ± 8 °C

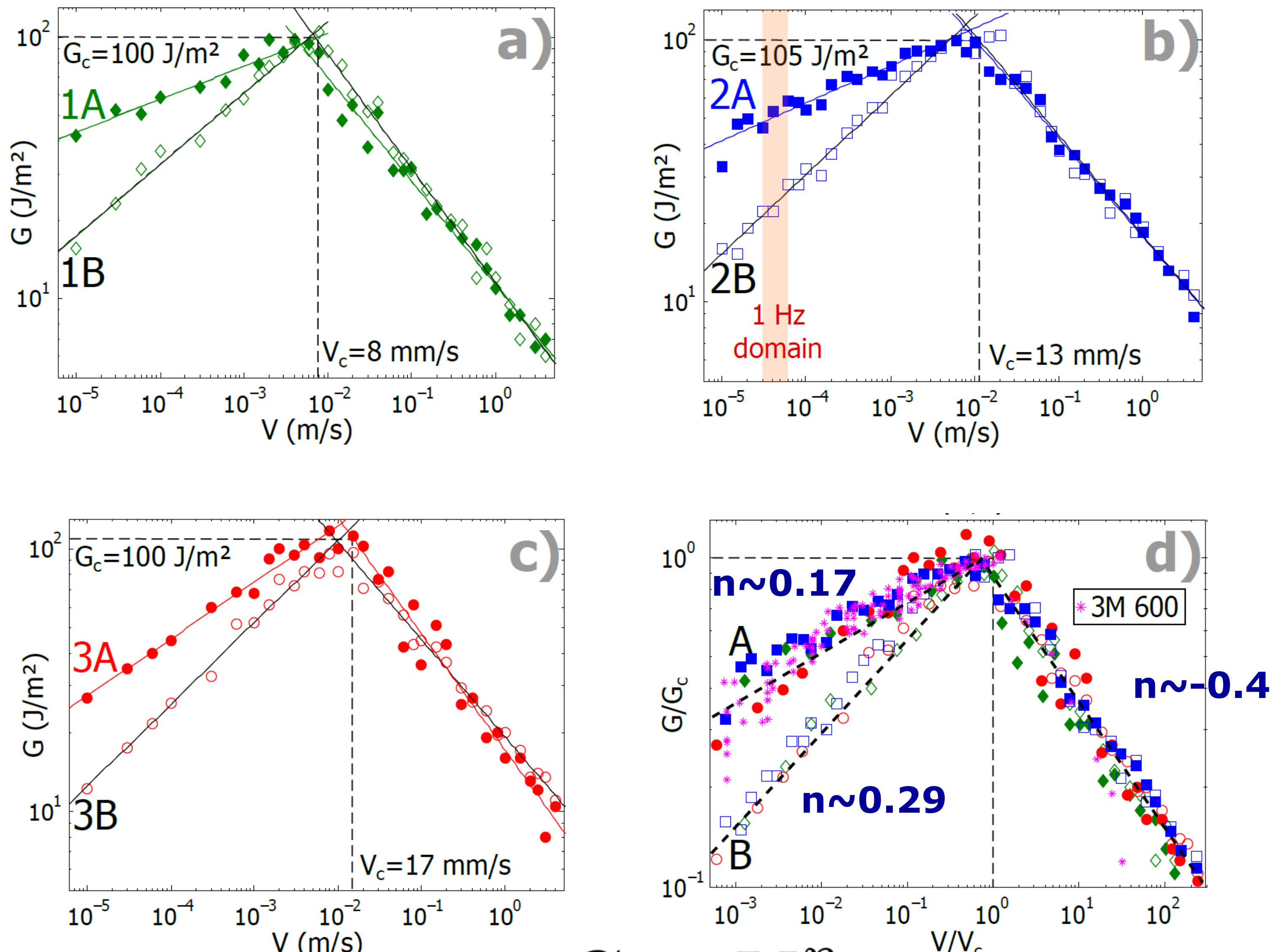
Linear rheology of PSA



Non-linear rheology



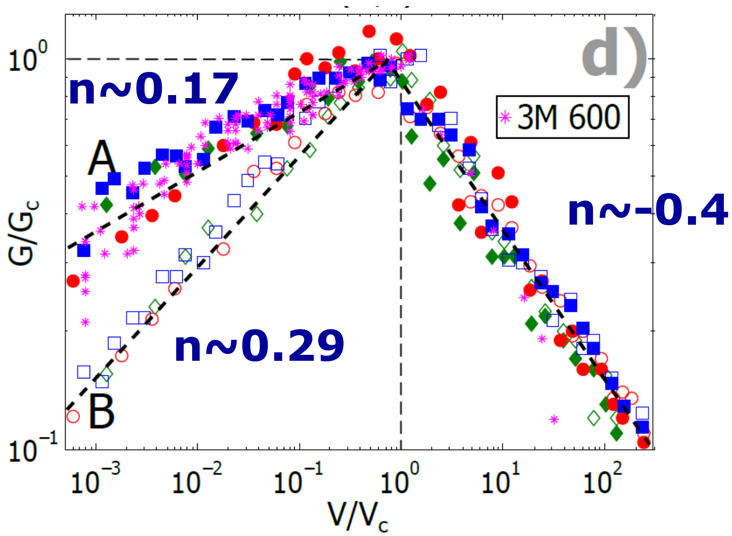
Distinct effect of non-linear rheology!



$$G \propto V^n$$

Villey et al, Soft Matter (2015)

Distinct effect of non-linear rheology!



$$G \propto V^n$$

1. Effect of change of Tg

G_c ~ 100 J/m² ~ cst

V_c ~ Arrhenius shift factors

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

ΔH ~ 40-50 kJ/mol

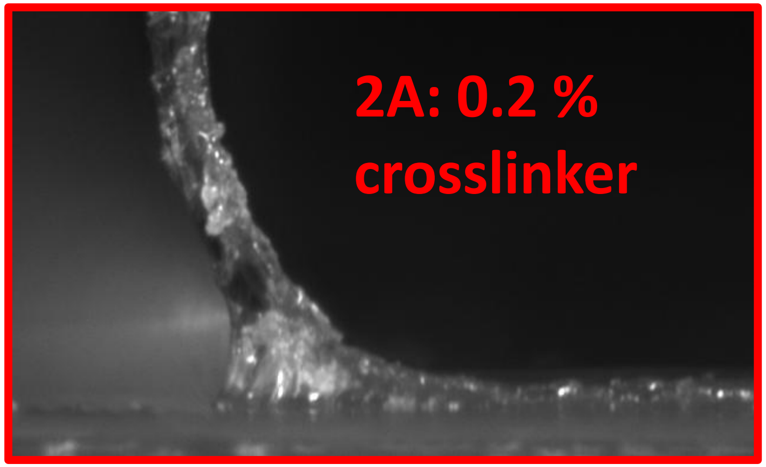
(literature: 60-80 kJ/mol)
Cailles et al, Polymer, 2015

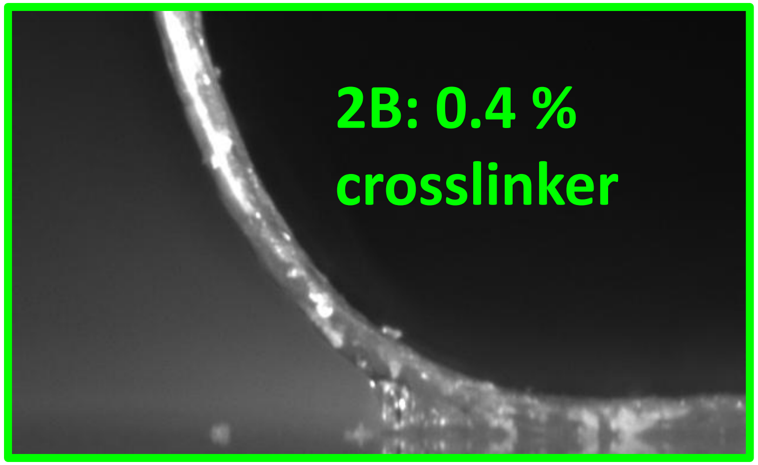
2. Effect of crosslink density

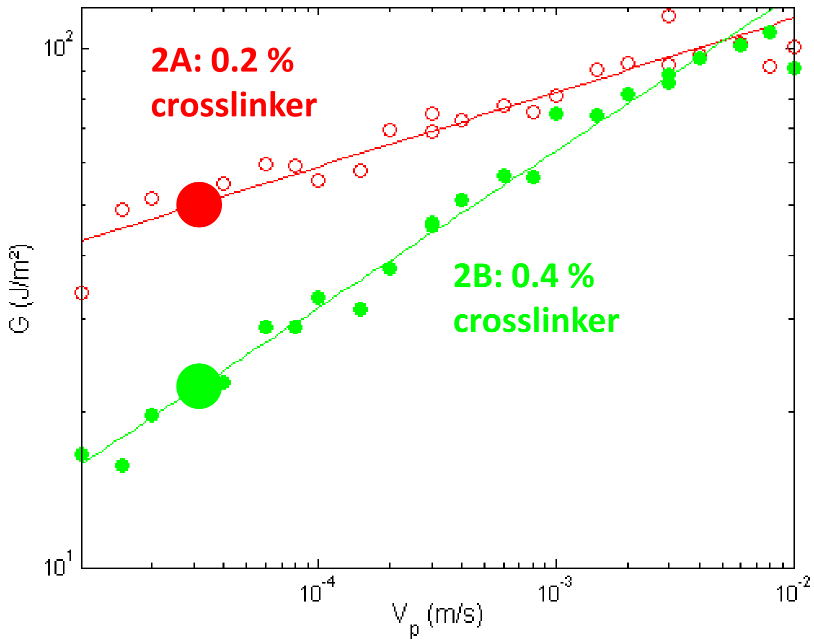
An increase in the density of crosslinks, has the effect of reducing the maximum extensibility of the fibrils, and thus the adherence energy

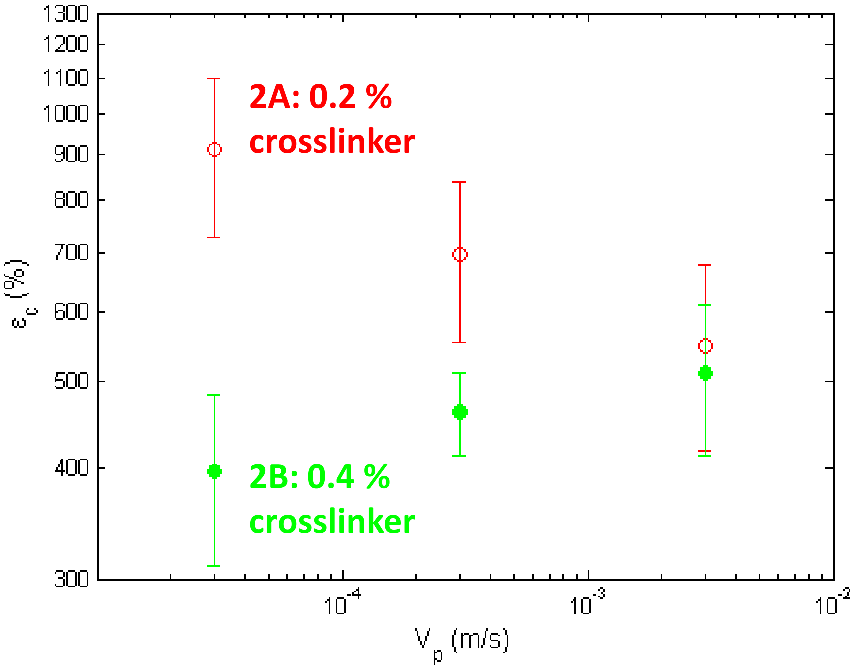
This effect is reduced when increasing the crack velocity and disappears at the peak, where the maximum extensibility is governed by the entanglement network

Confirmation by microscopic analysis

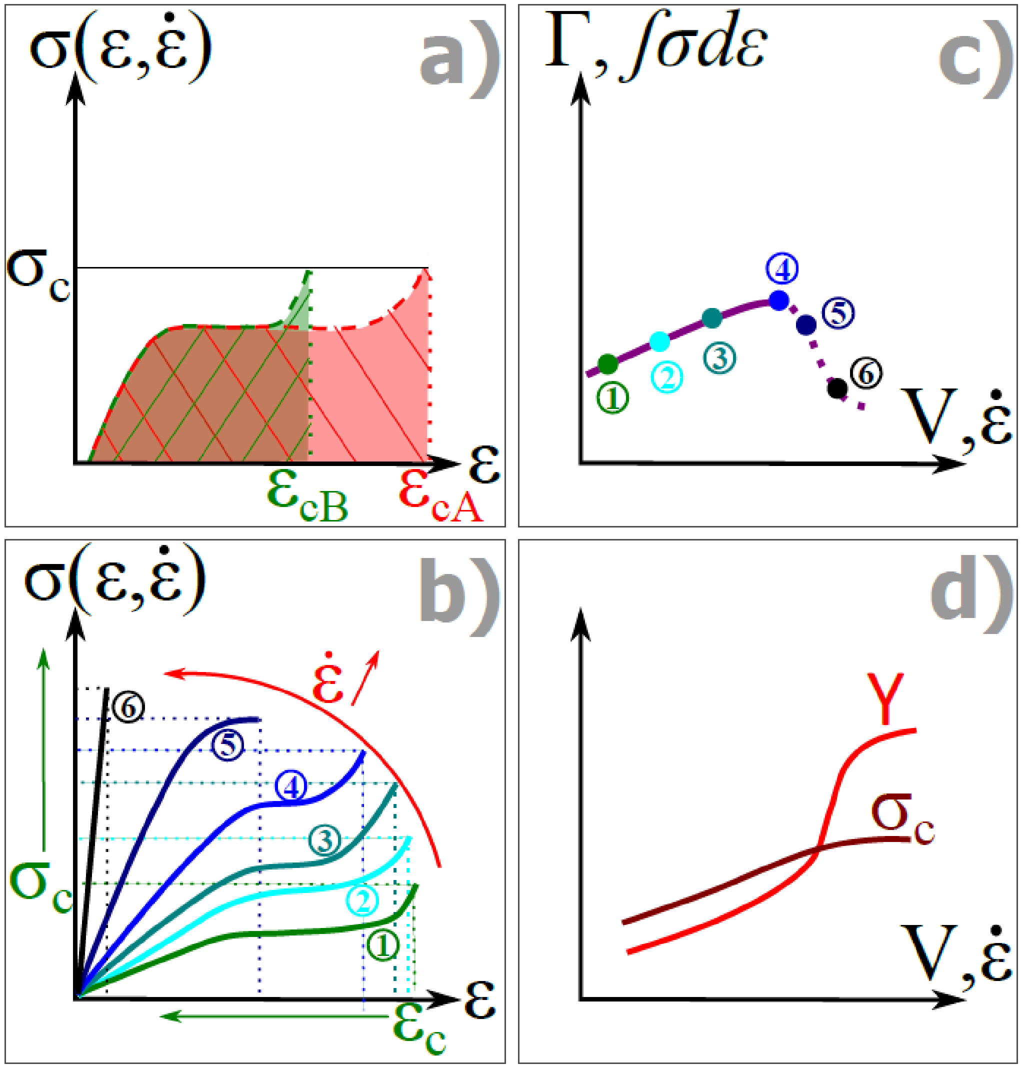








Interpretation of the adherence curve Γ(V)



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 Γ 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, …)

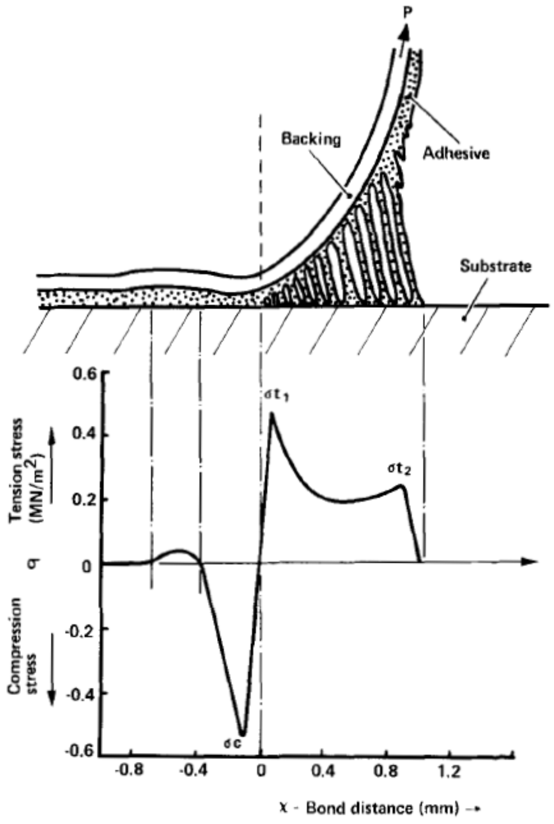
Role of the substrate
(relating adhesion energy *w* and debonding stress σ_c?)

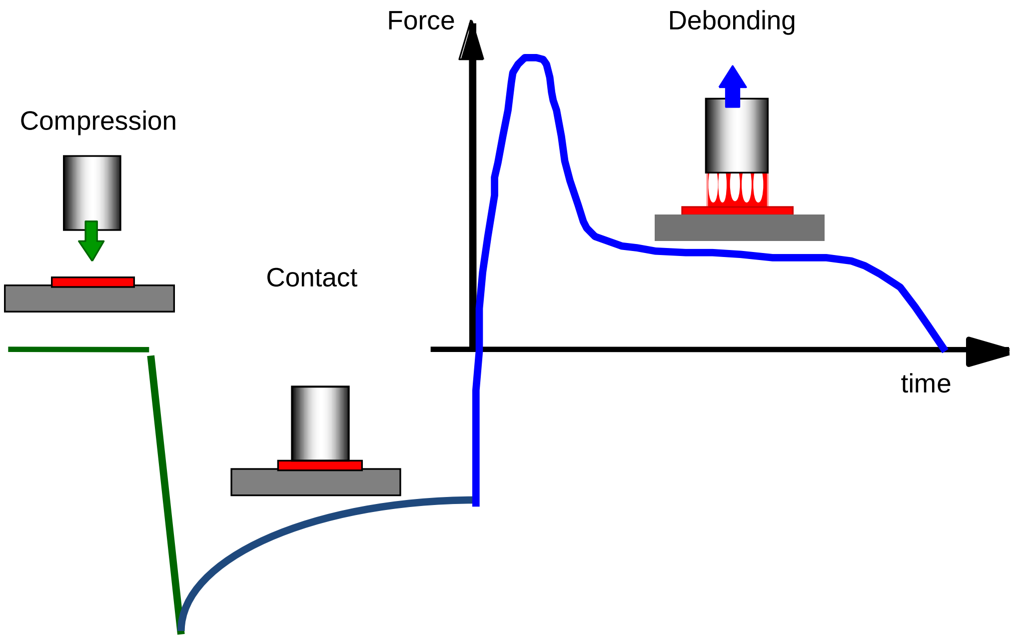
Boundary condition on the substrate
(sliding permitted?)

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!





Thanks for your attention!

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