Introduction to mechanical testing of soft solid polymers

Costantino Creton

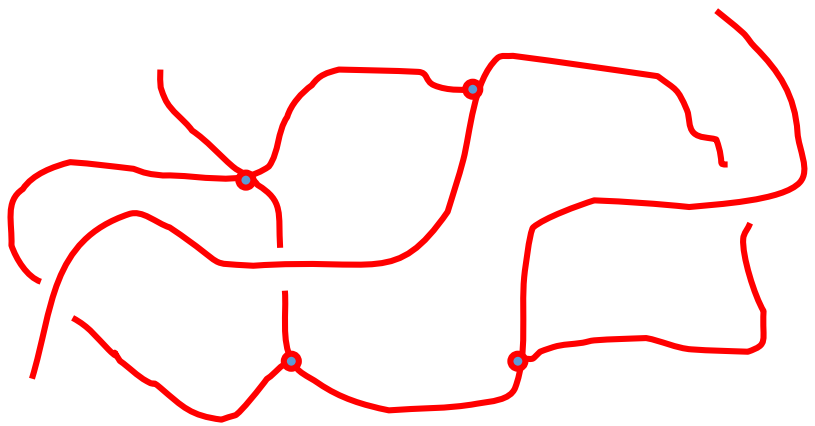
Laboratory of Soft Matter Science and Engineering

ESPCI Paris, (France)

http://ccreton.simm.espci.fr/

Soft Polymer Materials

Mechanical properties dominated by entropic elasticity:



Crosslink points (covalent)

Hydrogen bonds

Specific interactions

Physical crosslinks

Entanglements (relaxing)

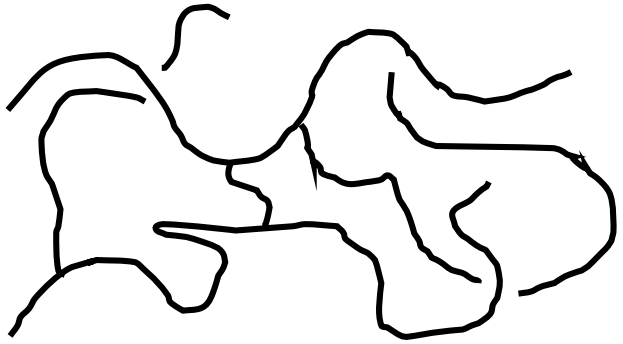
Simple physicist's view: a collection of Gaussian chains , E ~ kT per chain

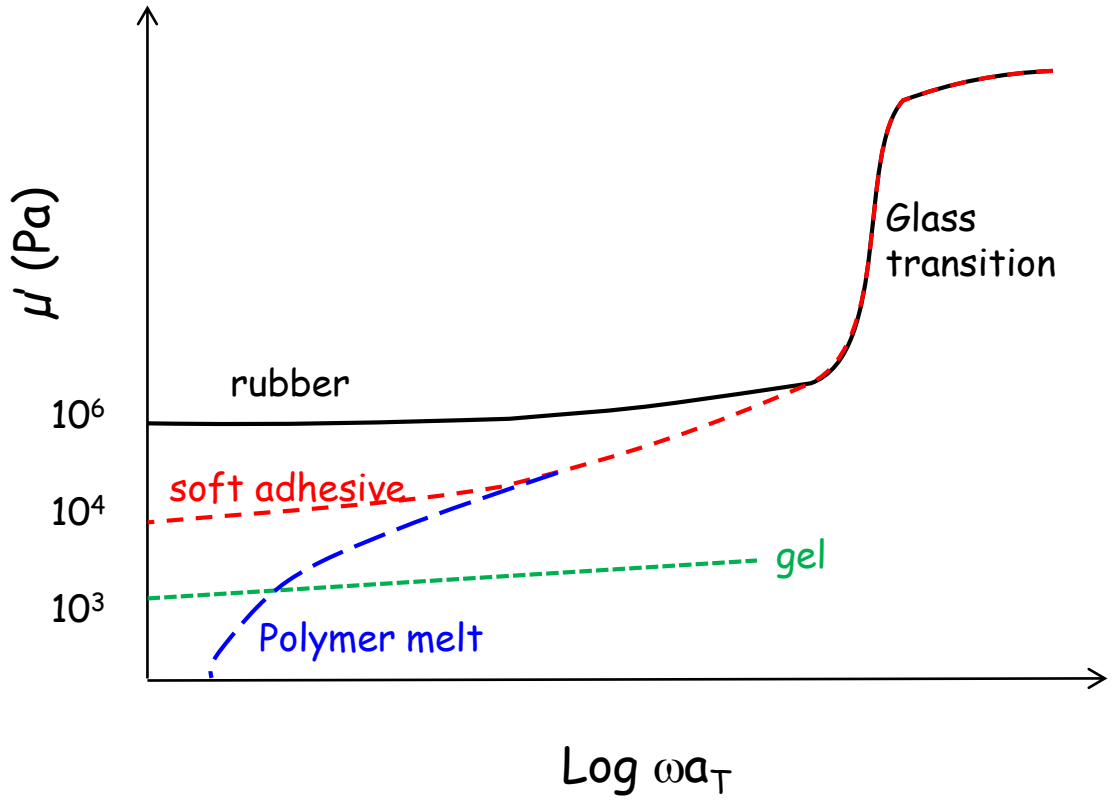
Simple view of a viscoelastic network: The effective number of elastic chains varies due to relaxation (E = f(t))

Complex network with finite extensibility of chains and bonds of variable strength

Moduli are in the range of 1 kPa to 1 Mpa

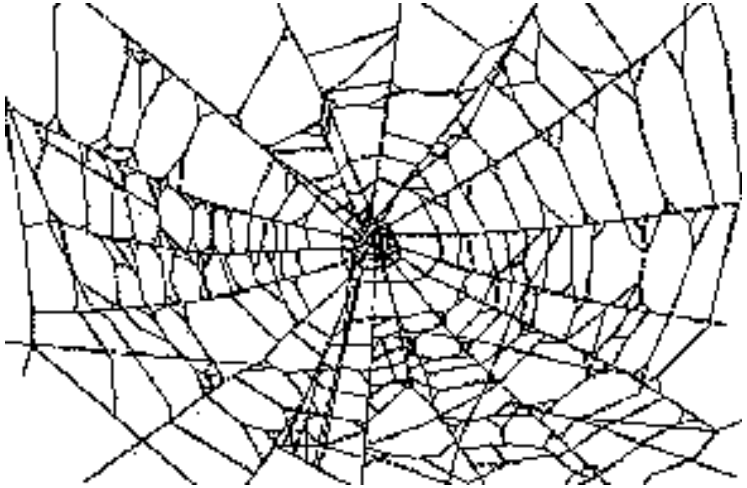
Entanglements can relax the stress while solvent swelling
Reduces the density of elastic chains

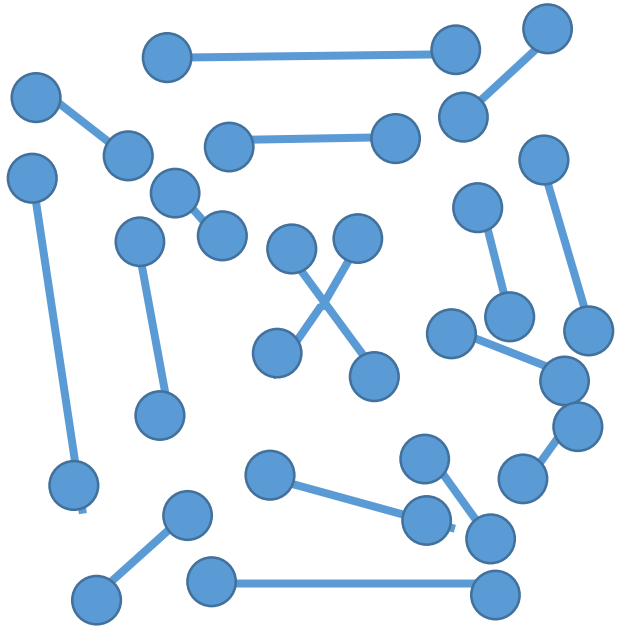




Elasticity of Polymer Networks

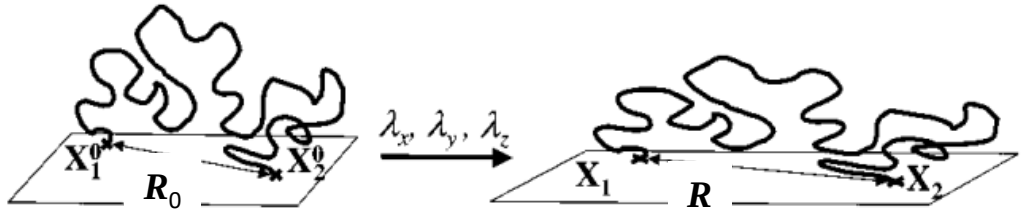
Affine network model





Mean-field models

The strand ends are attached to affinely deformed background



Change of network free energy

$$R_i = \lambda_i R_{0i}$$

$$\Delta F_{aff} = kT \sum_i \left(\frac{3R_i^2}{2b^2 n} - \frac{3R_{i0}^2}{2b^2 n} \right) = \frac{kT}{2} \sum_i \left(\lambda_i^2 - 1 \right) \frac{3R_{i0}^2}{b^2 n} = \frac{kT}{2} \nu V \sum_i \left(\lambda_i^2 - 1 \right)$$

since for random cross-linking $\langle R_{i0} R_{j0} \rangle = \frac{1}{3} b^2 n \delta_{ij}$

Uniaxial network deformation $\lambda_x = \lambda$, $\lambda_y = \lambda_z = \lambda^{-1/2}$. Stress is the derivative $\partial(\Delta F)/\partial L_x$ (force), divided by the cross-sectional area of the sample $L_y L_z$.

$$\sigma = \frac{1}{L_y L_z} \frac{\partial \Delta F}{\partial L_x} = \frac{1}{L_y L_z L_x} \frac{\partial \Delta F}{\partial \lambda} = \frac{1}{V} \frac{\partial \Delta F}{\partial \lambda}$$

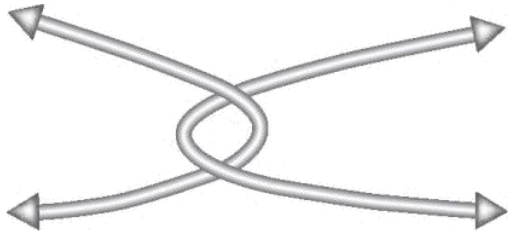
$$\Delta F_{aff} = \frac{kT}{2} \nu V \left(\lambda^2 + \frac{2}{\lambda} - 1 \right) \qquad \sigma = kT\nu \left(\lambda - \frac{1}{\lambda^2} \right) \qquad \sigma_N = G_x \left(\lambda - \frac{1}{\lambda^2} \right)$$

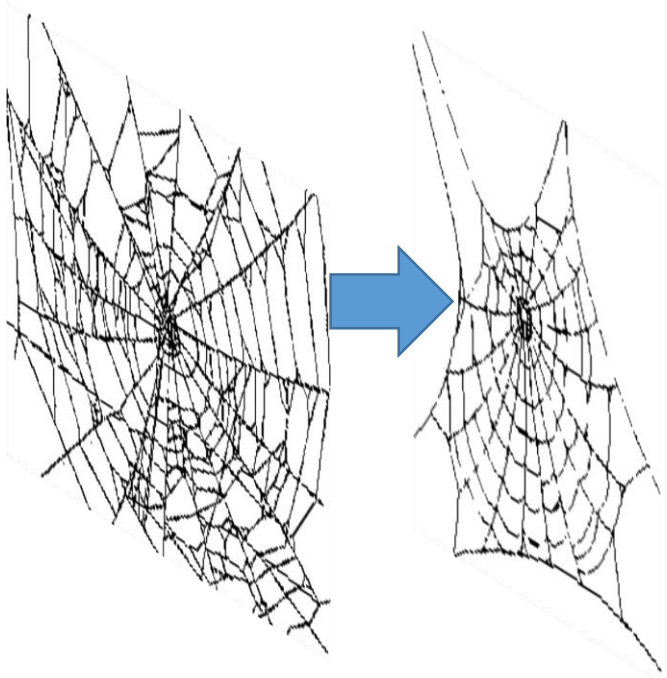
2. Elastic response is nonlinear.

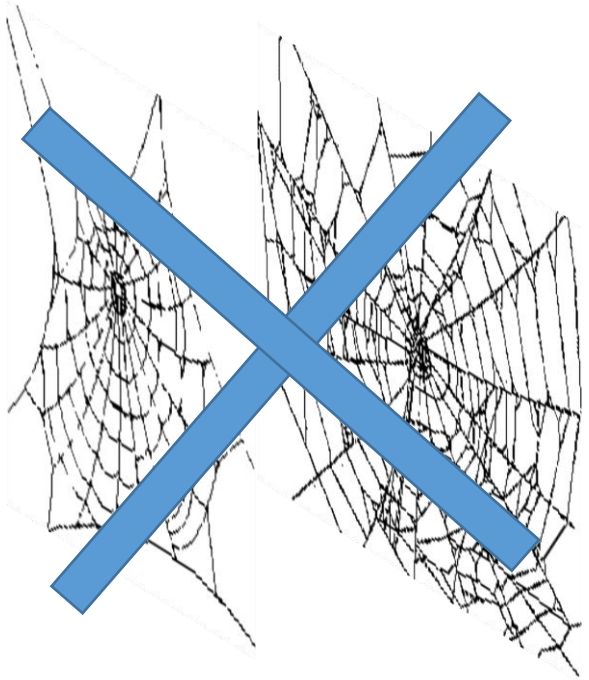
3. Stress is universal, does not depend on the chemical structure of the chain.

Treloar, L. R. G. (1975). The general strain: phenomenological theory. The physics of rubber elasticity. Oxford, Clarendon Press: 210-310.

Two chains cannot pass through each other - ***topological interactions*** known as ***entanglements*** that raise the network modulus







Phenomenological models of entanglements

Free energy is function of deformation invariants

$$I_1 = \lambda_x^2 + \lambda_y^2 + \lambda_z^2, \qquad I_2 = \frac{1}{\lambda_x^2} + \frac{1}{\lambda_y^2} + \frac{1}{\lambda_z^2}$$

Mooney—Rivlin model

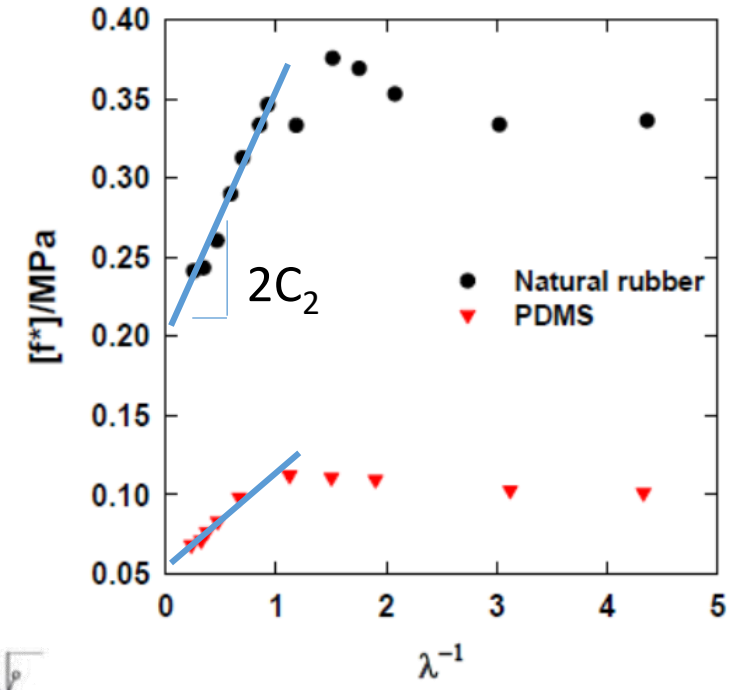
$$\Delta F/V = C_1 (I_1 - 3) + C_2 (I_2 - 3)$$

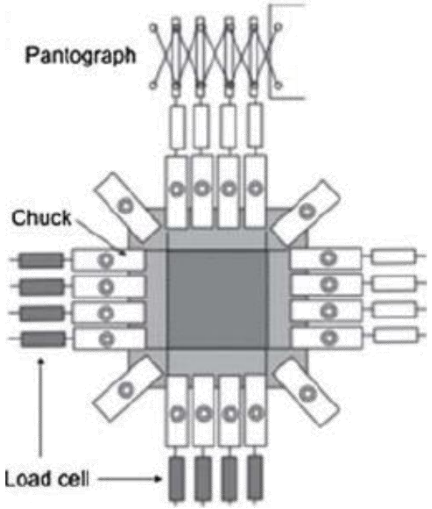
The stress of **uniaxially** deformed network

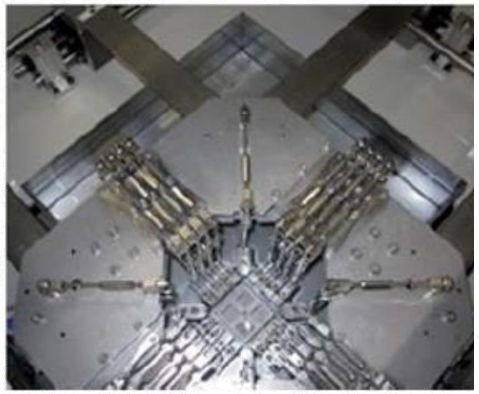
$$\sigma = \left(\lambda^2 - \frac{1}{\lambda}\right) f^*(\lambda),$$
$$f^*(\lambda) = 2C_1 + \frac{2C_2}{\lambda}$$

Biaxially stretched gel –
more complex function

$$\Delta F/V = C_1 (I_1 - 3) + f(I_1, I_2)$$



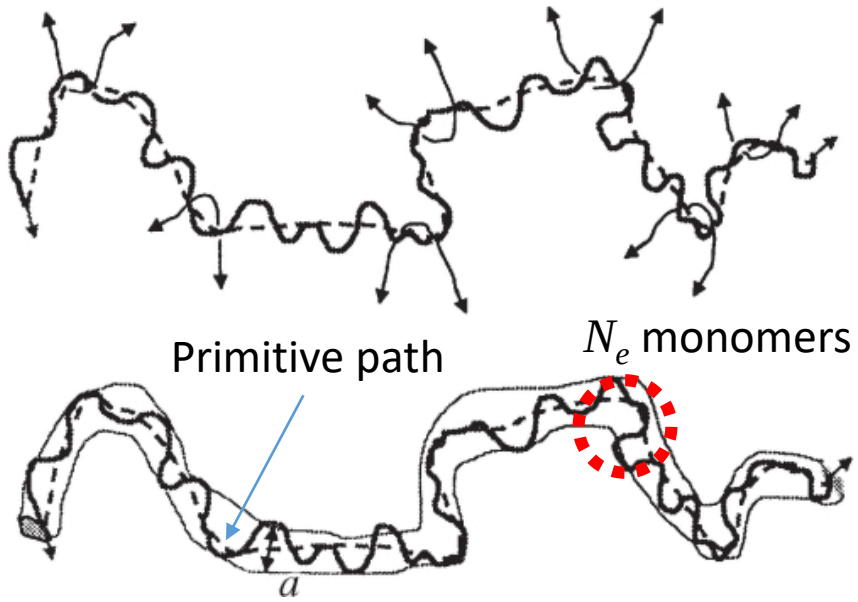




*Mooney, M. (1940). "A Theory of Large Elastic Deformation." Journal of Applied Physics **11**: 582.*

A strand is topologically constrained to a tube-like region by surrounding chains.

Tube diameter $a \simeq bN_e^{1/2}$

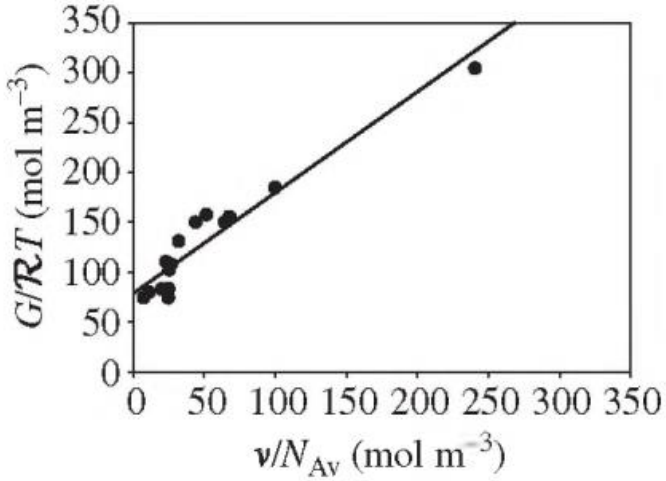


Rubber plateau modulus

$$G_e = \rho kT/M_e$$

The modulus of the entangled polymer network can be approximated as

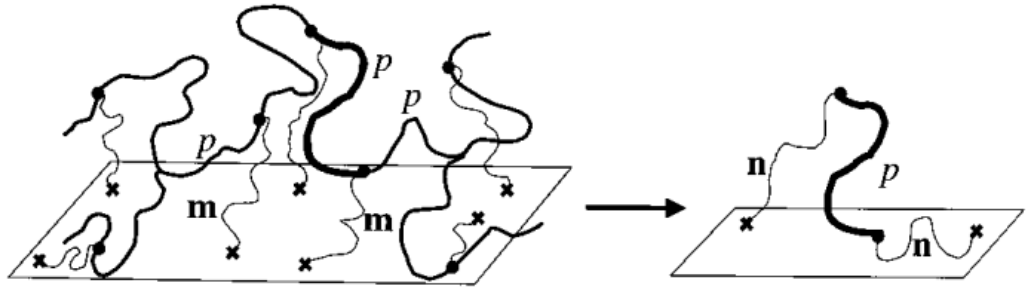
$$G \simeq G_x + G_e \simeq \rho kT \left(\frac{1}{n} + \frac{1}{N_e} \right)$$



Modulus of end-linked PDMS networks with f = 4 at 30°C

Edwards tube model

Every *p*th monomer of a strand (intermediate and thick lines) is connected to the elastic nonfluctuating background by virtual chains with *m* monomers



$n \approx N_e$

Tube diameter does not depend on deformations

$$a \simeq bN_e^{1/2}$$

Nonaffine tube model

Tube diameter depends on deformations

$$a_i \simeq bN_e^{1/2}\lambda_i^{1/2}$$

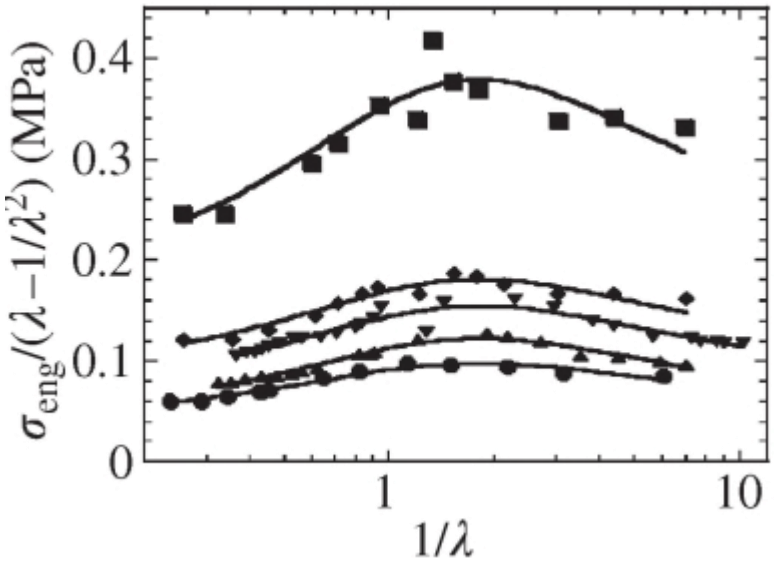
Nonaffine slip-tube model

Slip-links can slide along the network chain, but cannot pass through each other.

The stress for uniaxial deformation

$$\frac{\sigma}{\lambda - 1/\lambda^2} = G_x + \frac{G_e}{0.74\lambda + 0.61\lambda^{-1/2} - 0.35}$$

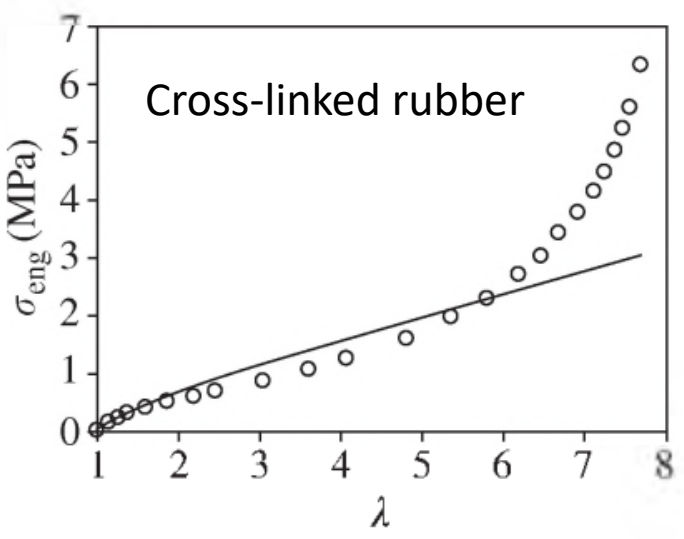
Reduced stress of different rubbers



Rubinstein, M. and S. Panyukov (2002). "Elasticity of polymer networks." Macromolecules ***35: 6670-6886.***

Finite extensibility

Deviations at large λ

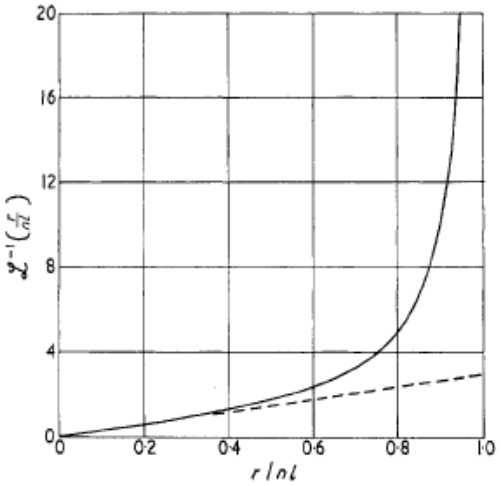


Strain hardening at high deformations λ can be explained by the non-Gaussian statistics of strongly deformed chains:

$$\frac{R}{bn} = \mathcal{L}\left(\frac{fb}{kT}\right) = \coth\frac{fb}{kT} - \frac{kT}{fb}$$

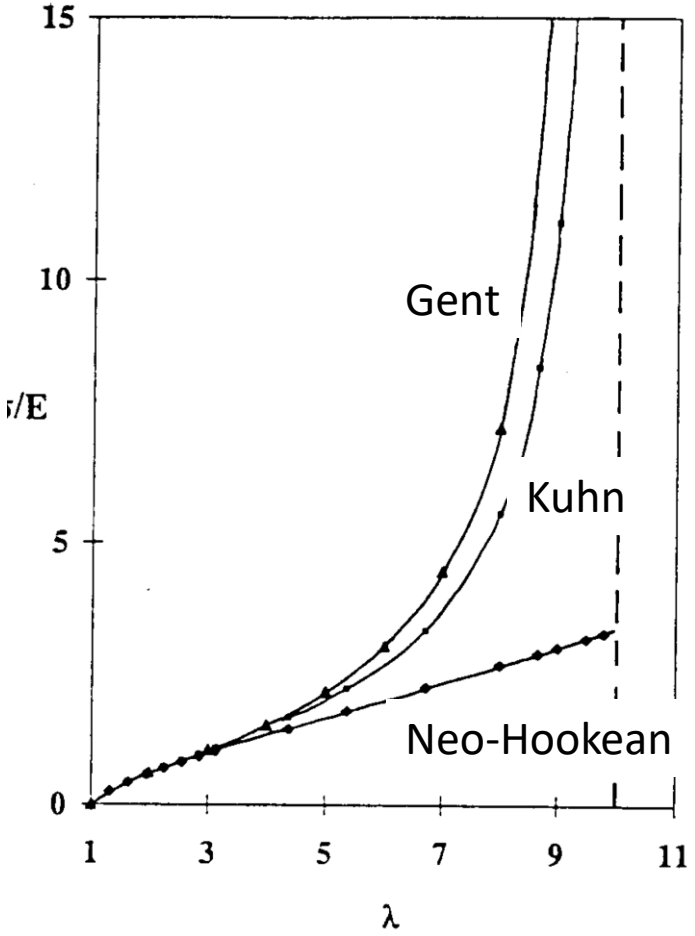
The force ***f*** required to stretch a single chain to an end-to-end distance X can be expressed through the inverse Langevin function:

$$f = \frac{kT}{b}\mathcal{L}^{-1}\left(\frac{R}{bn}\right)$$



This is still entropic but no longer Gaussian

Macroscopic phenomenological 3D model



$$W = -\frac{G_x}{2} J_m ln\left(1 - \frac{J_1}{J_m}\right) \qquad J_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3$$

In uniaxial extension

$$\sigma_N = G_x \left(\frac{\lambda - \frac{1}{\lambda^2}}{1 - \frac{J_1}{Jm}}\right)$$

2 parameters: G_x and J_m

*Gent, A. N. (1996). "A New constitutive relation for rubber." Rubber Chemistry and Technology **69: 59-61.***

Testing methods

Small strain: elastic modulus, linear viscoelastic properties (lecture of Hiroshi Watanabe)

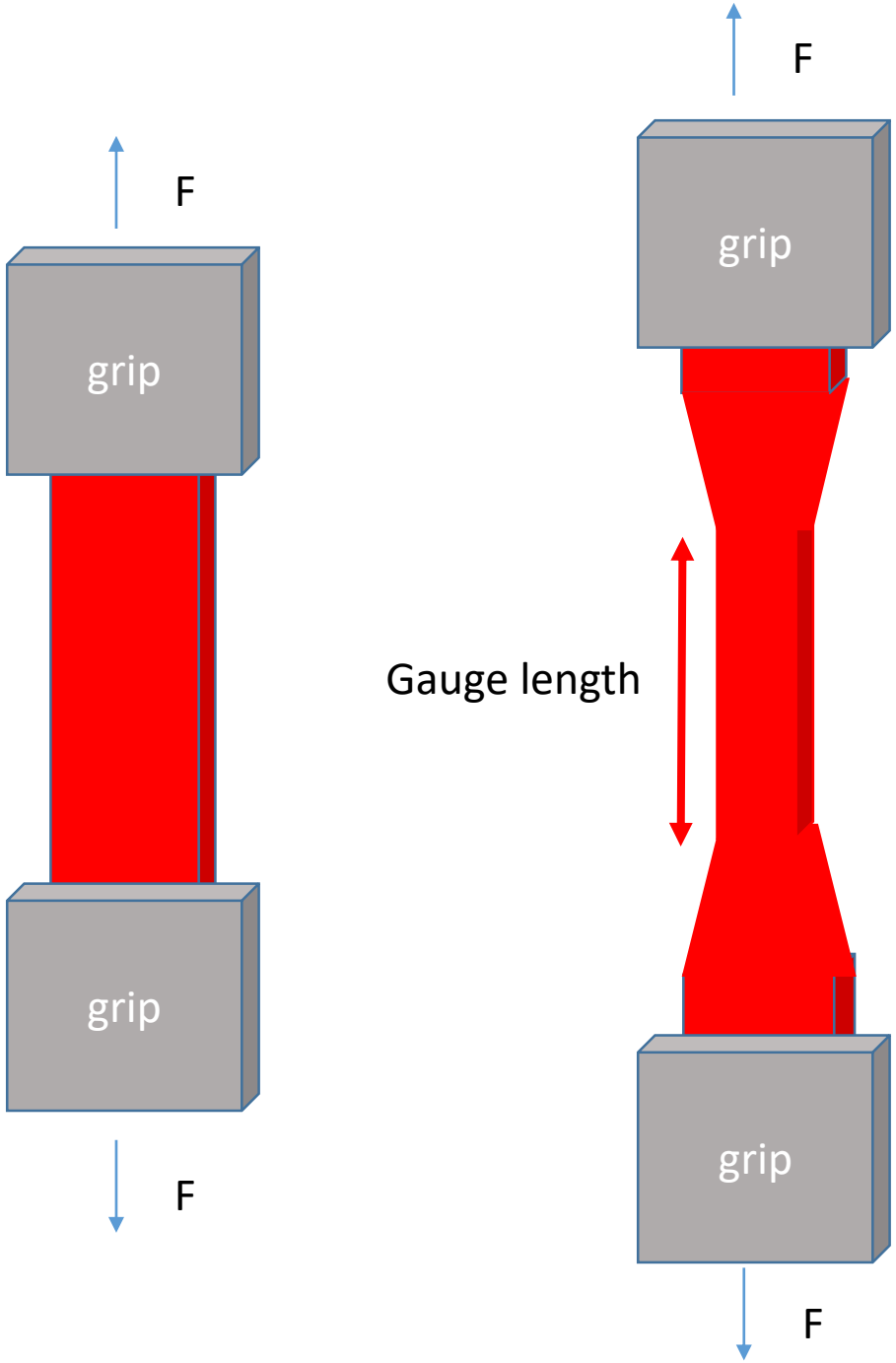
Large strain: Uniaxial, pure shear, biaxial, uniaxial compression

Boundary conditions: material properties need to be tested in homogeneous deformation

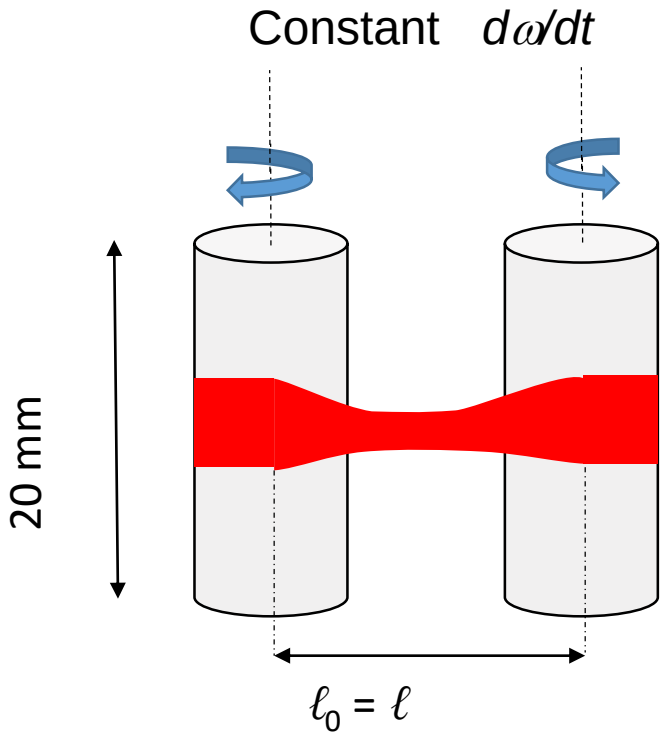
Mechanical testing with heterogeneous deformation

Fracture tests: experimental aspects and interpretations (DIC, strain field, Crack tip structure)

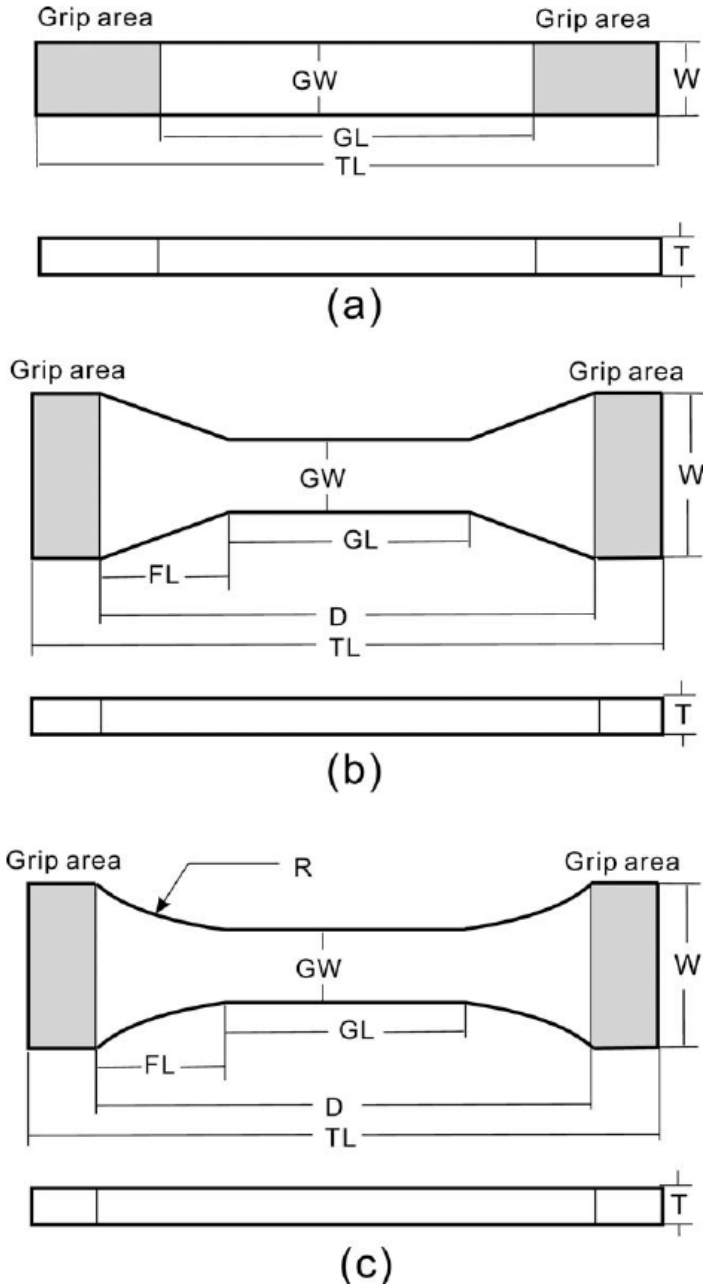
Sticky thin films: how to test adhesion



Tensile tests: practical aspects

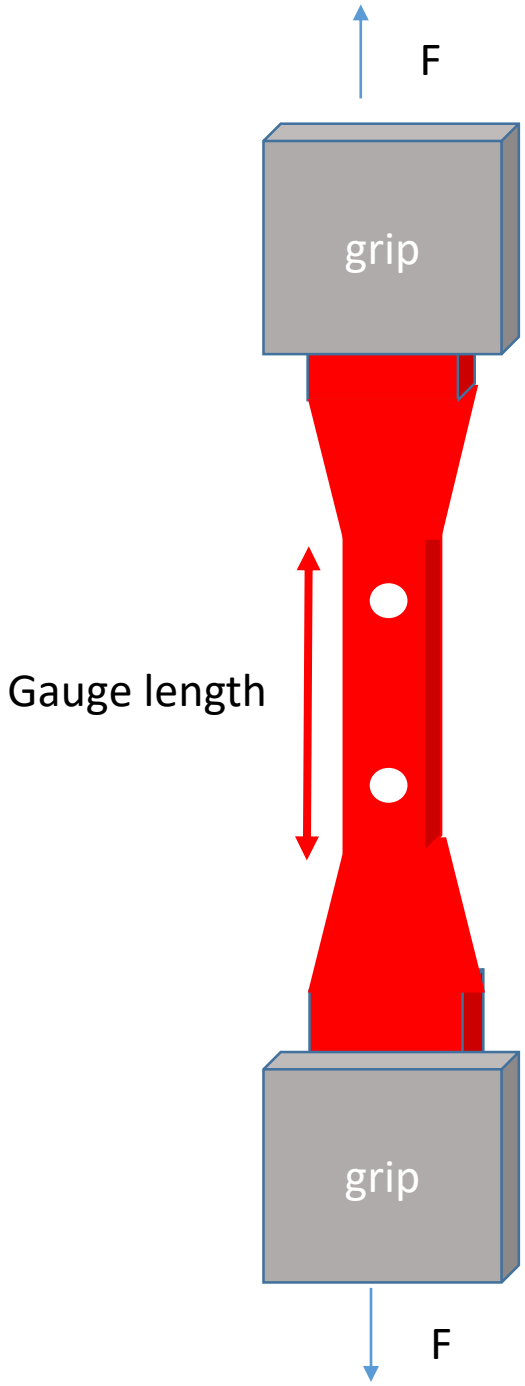


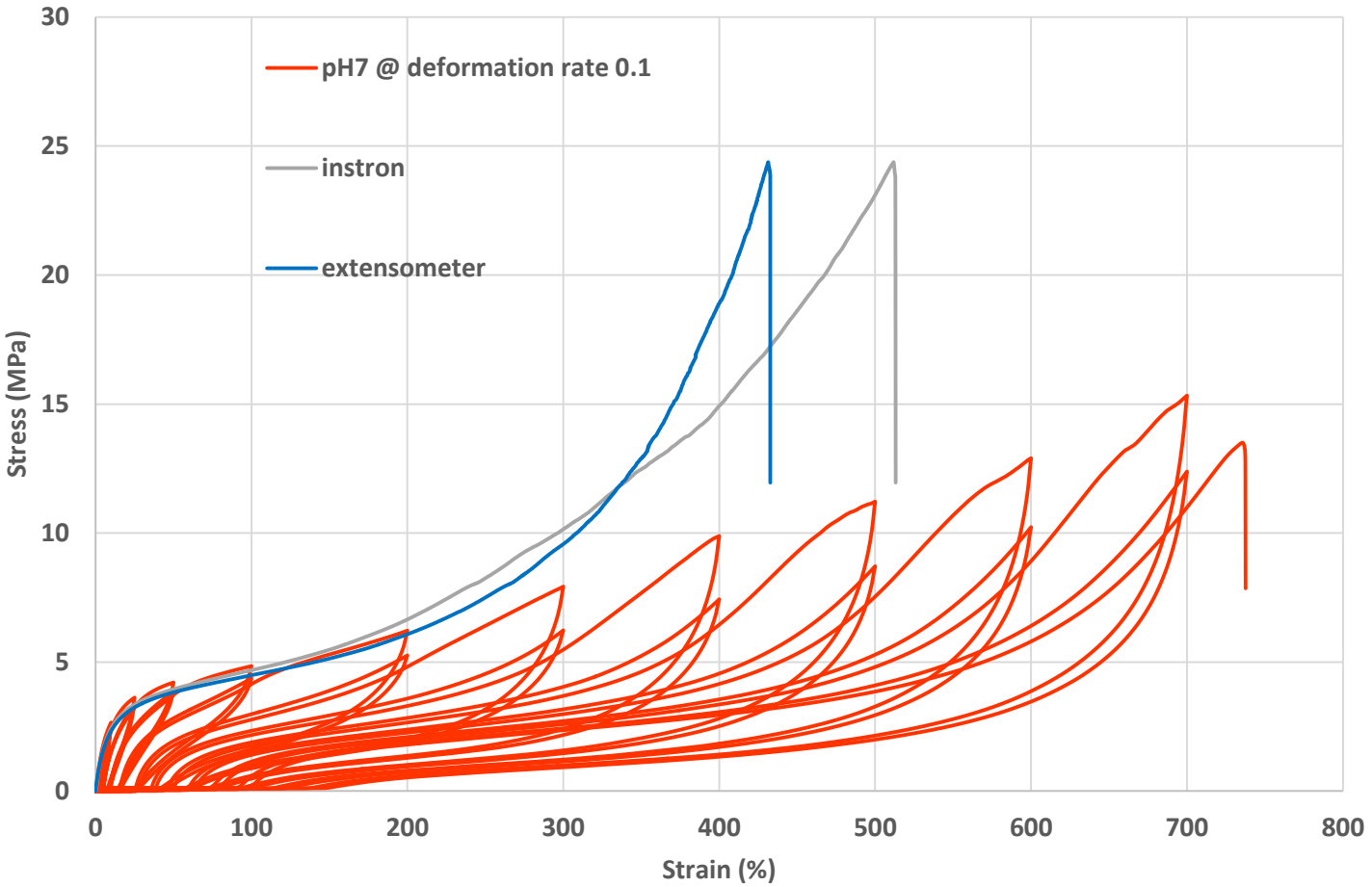
Sentmanat, M. L.,
Rheologica Acta ***2004, 43 (6), 657-669.***

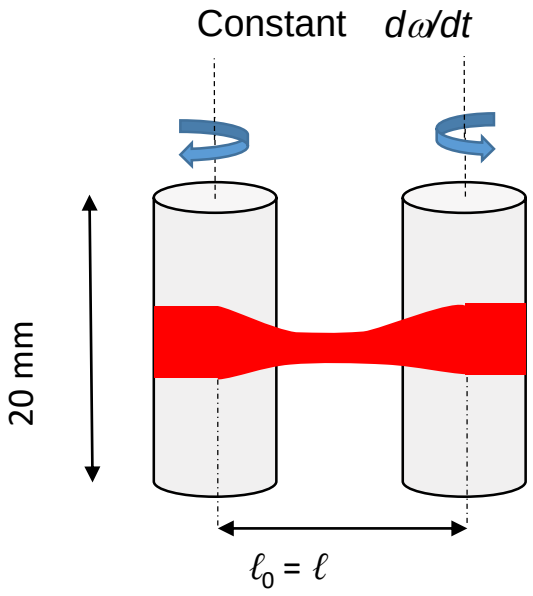


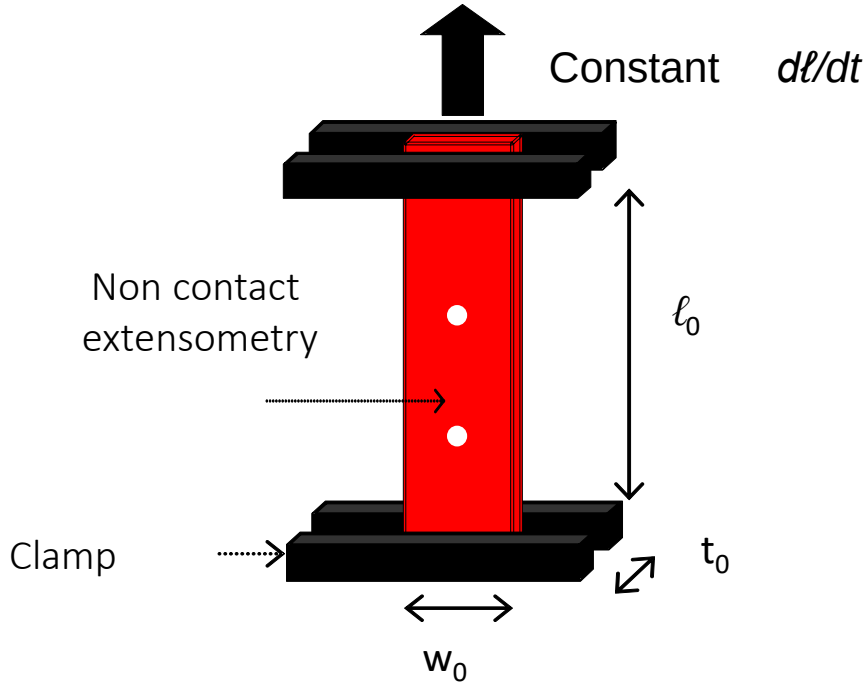
Stress concentration

Feng, L.; Jasiuk, I., *Journal of Biomedical Materials Research Part A* ***2010, 95A (2), 580-587.***


F
grip
Gauge length
grip
F

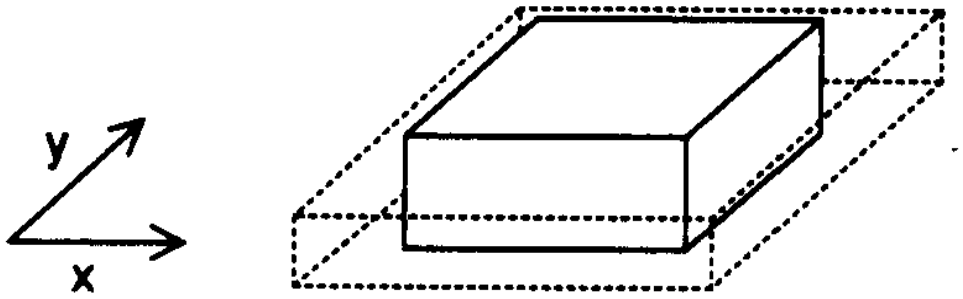

pH7 @ deformation rate 0.1
instron
extensometer
Stress (MPa)
Strain (%)
0
5
10
15
20
25
30
0
100
200
300
400
500
600
700
800

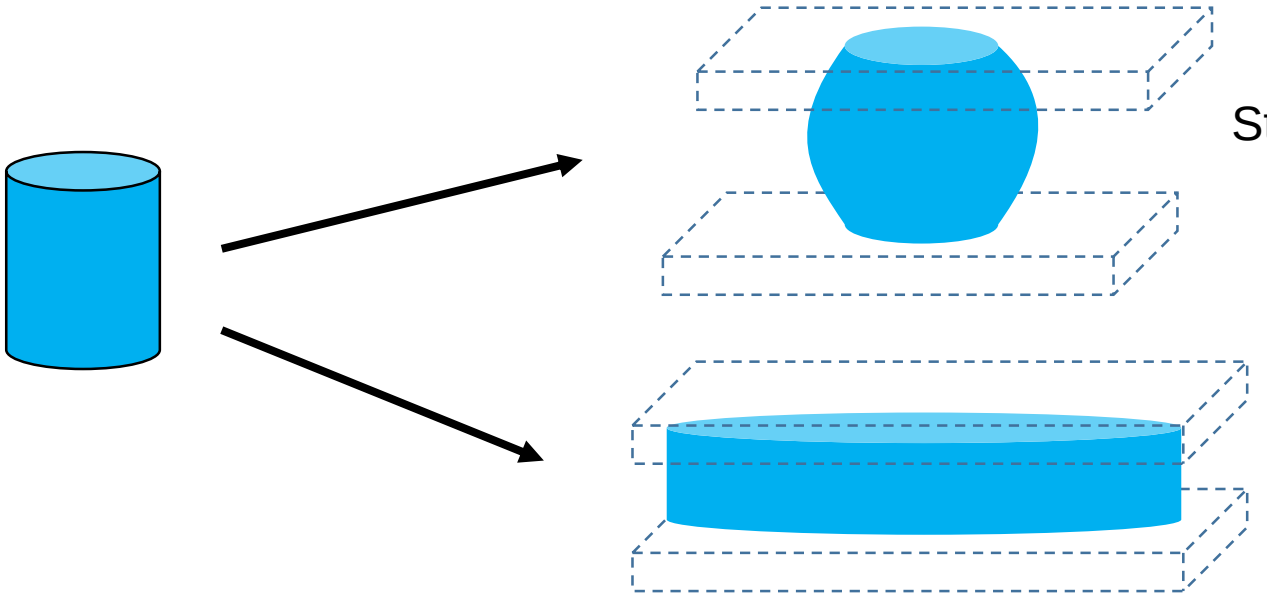




In viscoelastic materials, strain rate history matters

Compression tests: boundary conditions





Sticky wall (β = 0)

Slippery wall (β = ∞)

$$v_s(r,h) = \beta \tau_{zr}(r,h)$$

$$E_{sq} = 3G\left[1 + \frac{1}{2(H/R)^2(1+5\beta G/H)}\right].$$

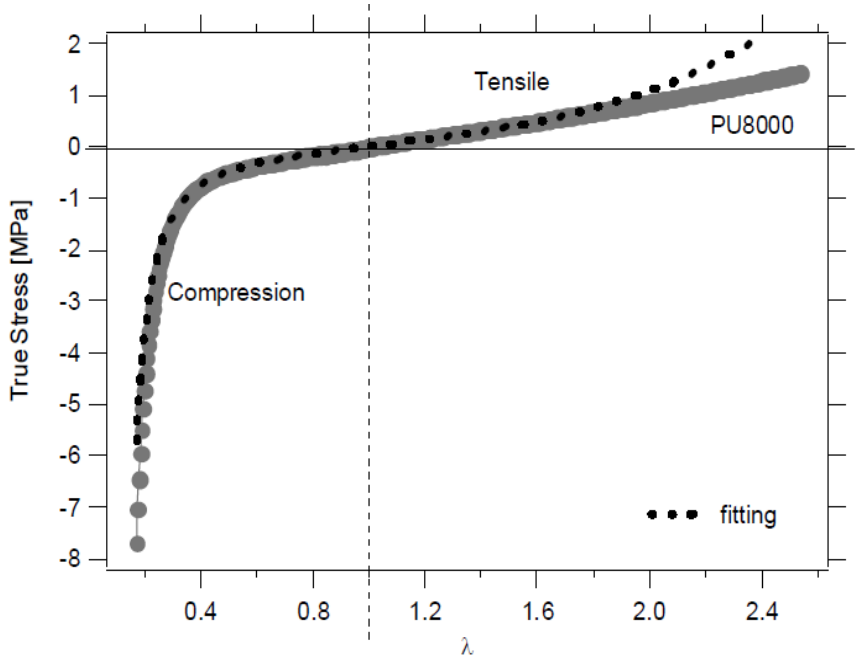
Laun, H. M.; Rady, M.; Hassager, O., *J Non-newton Fluid* ***1999, 81, 1-15.***

Nominal stress – True Stress

$$\sigma_N = \frac{F}{A_0}$$ Constant volume

$$\sigma_T = \frac{F}{A} \qquad \frac{A}{A_0} = \frac{\ell_0}{\ell} = \frac{1}{\lambda}$$

$$\sigma_T = \lambda \sigma_N$$

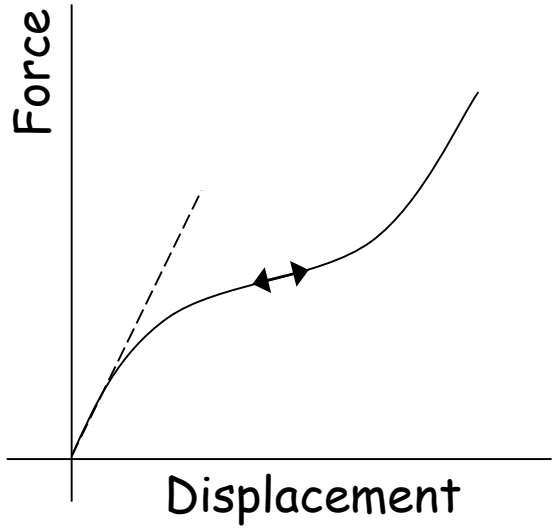


In tension: $|\sigma_T| \gg |\sigma_N|$

In compression: $|\sigma_T| \ll |\sigma_N|$

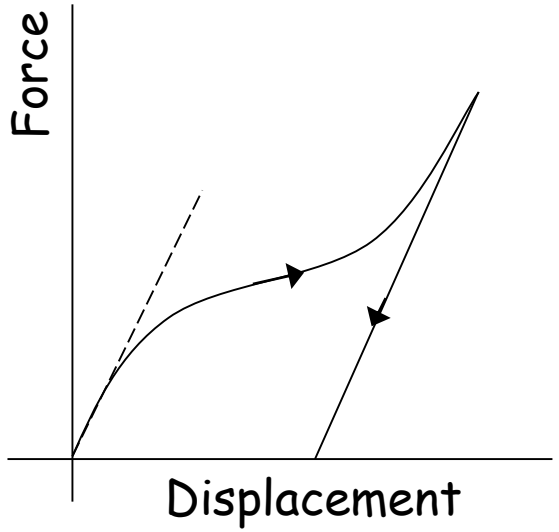
Some definitions

Elasticity



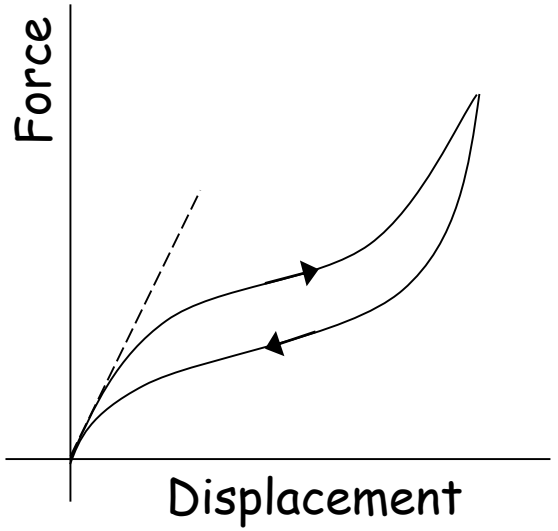
reversible deformation, dissipates no energy

Plasticity, Damage



irreversible deformation, dissipates energy

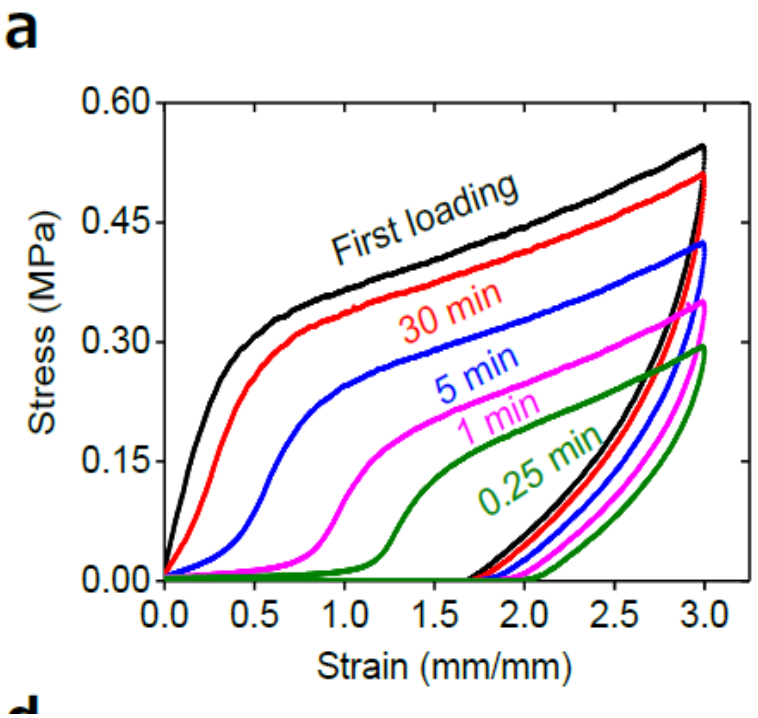
Viscoelasticity



dissipates energy

More complex behavior

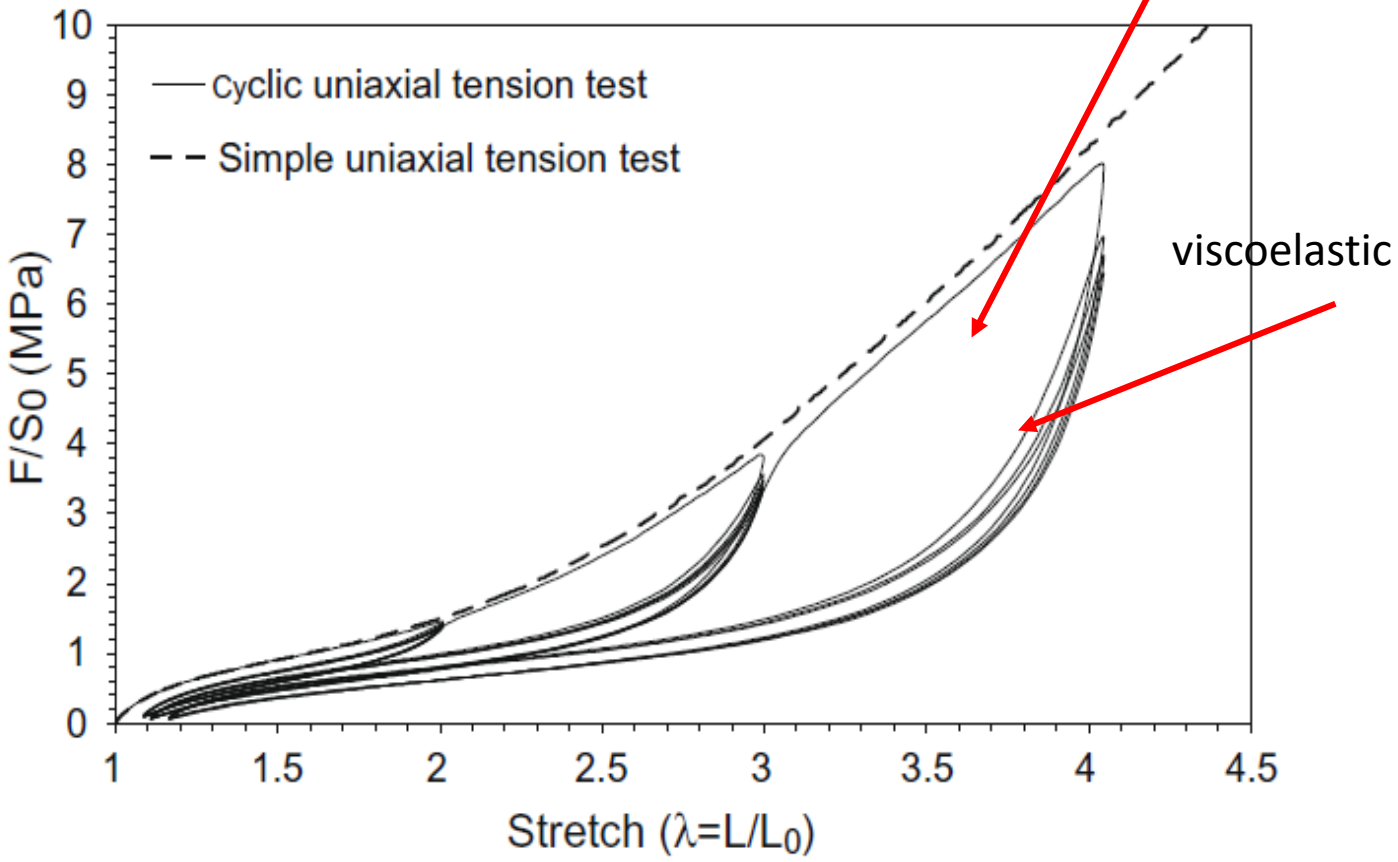
Recoverable damage



1st cycle hysteresis/Mullins effect

damage

viscoelastic

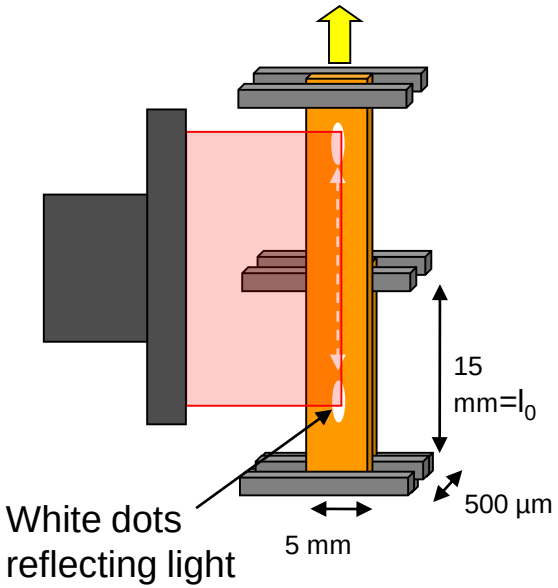


Change/breakage of internal structure

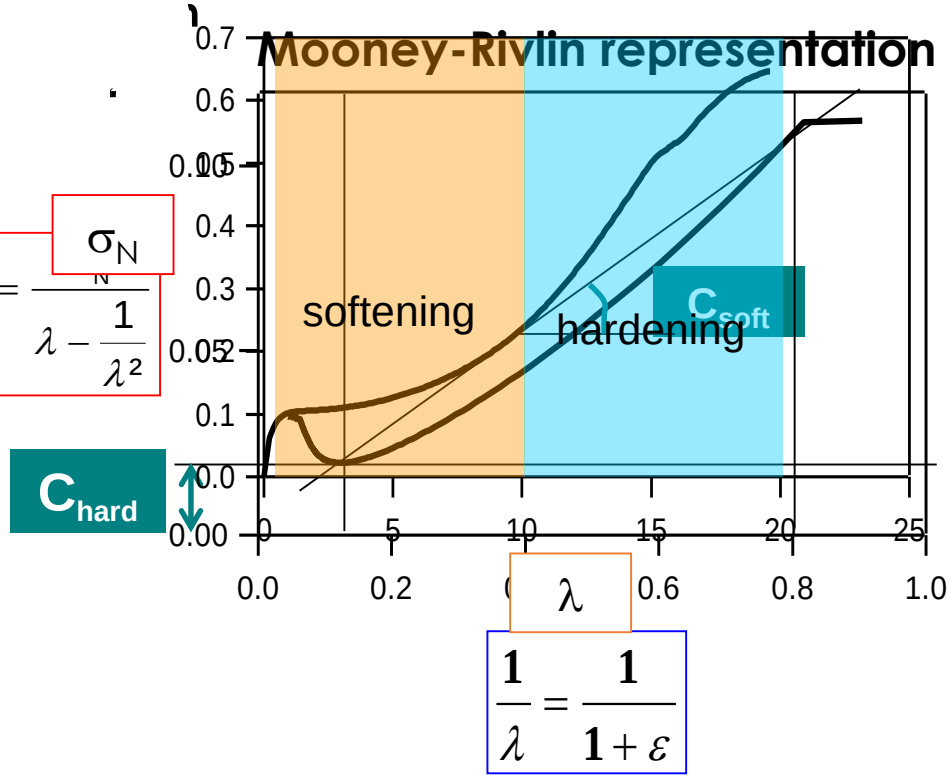
Interpretation of the tensile test for complex behavior

Room temperature

Nominal deformation rate = $1s^{-1}$



$$\sigma_R = \frac{\sigma_N}{\lambda - \frac{1}{\lambda^2}}$$



$$\frac{1}{\lambda} = \frac{1}{1+\varepsilon}$$

softening at intermediate strain ⇔ role of entanglements ➔ C_{soft} $\xrightarrow{\varepsilon \to 0}$ μ_e

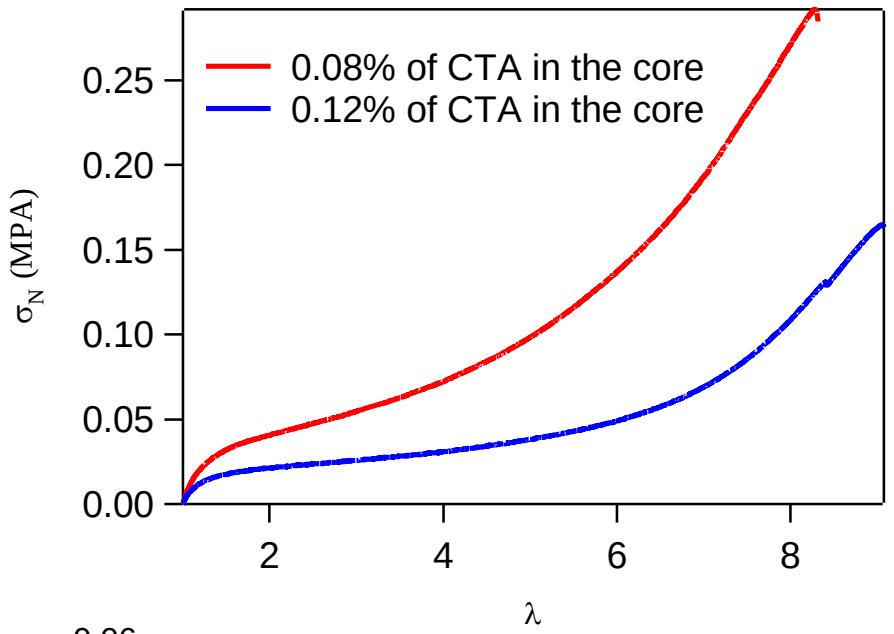
hardening at large strain ⇔ role of crosslinking points ➔ C_{hard} $\longrightarrow$ μ_x

C_{soft}/C_{hard} : viscoelastic properties at large strain

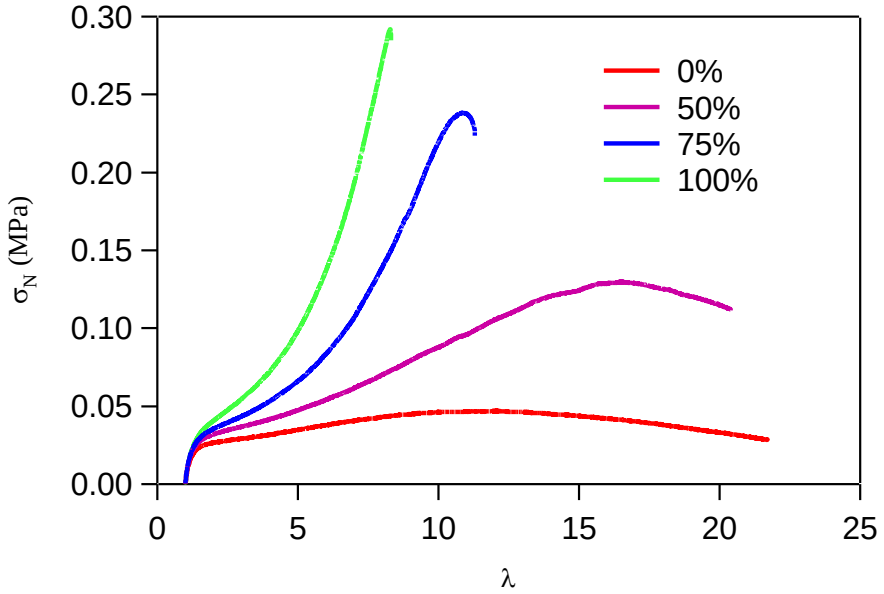
C_{soft} + C_{hard} : elastic modulus at small strain

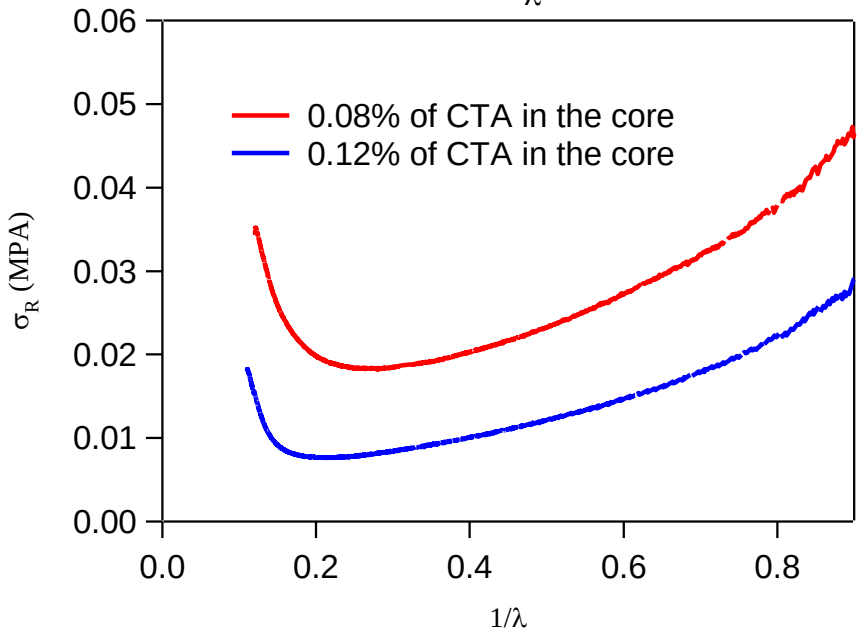
Creton, C.; Ciccotti, M.,. *Rep Prog Phys* ***2016, 79 (4), 046601.***

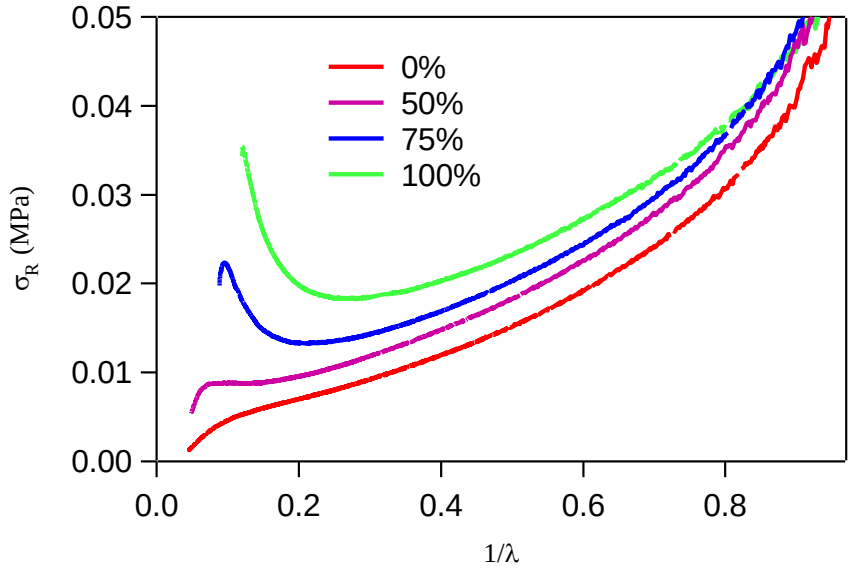
F. Deplace, C. Creton et al. J. Adh. 2009, 85, 18.



80/20 core/shell particles







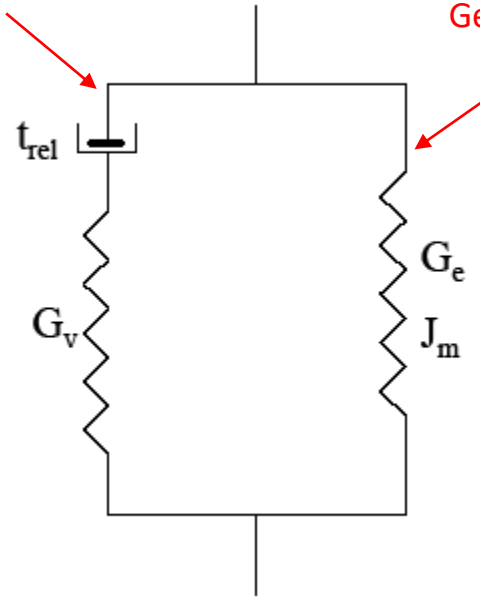
Mooney plots

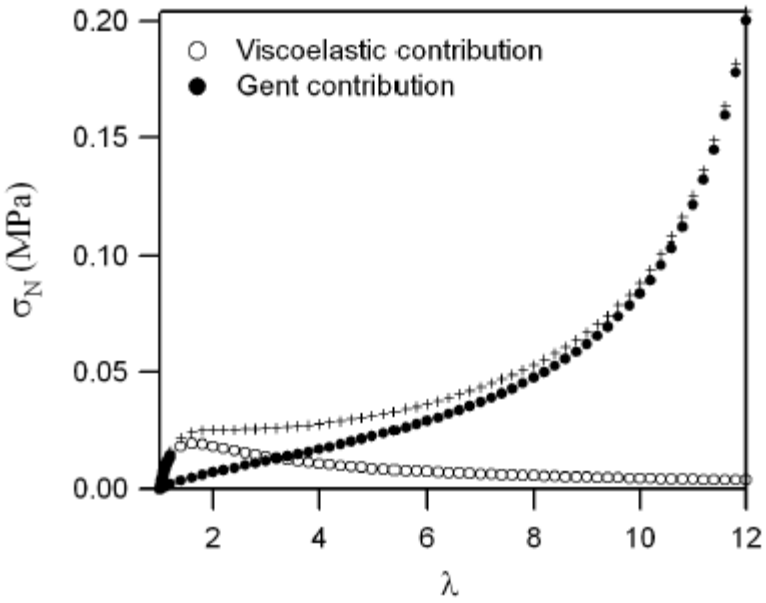
Creton, C.; Ciccotti, M.,. *Rep Prog Phys* ***2016, 79 (4), 046601.***

Some simple modeling of large strain properties combining dissipation and strain hardening

Nonlinear viscoelastic model
(UCMaxwell model)

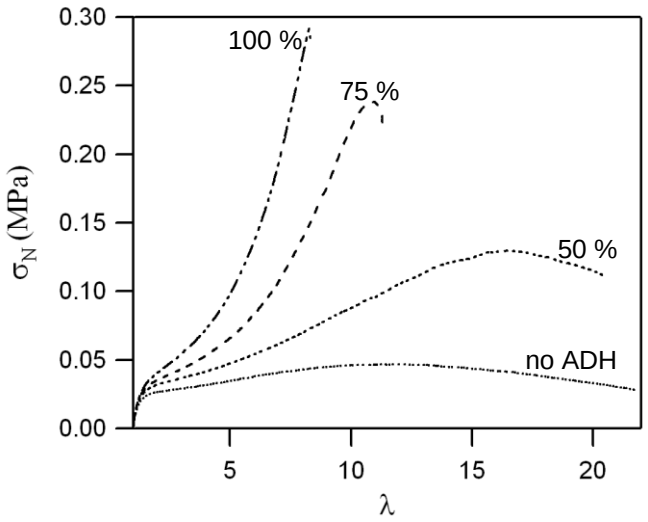
Gaussian spring
With finite extension
Gent model





Deplace, F.; Rabjohns, M. A.; Yamaguchi, T.; Foster, A. B.; Carelli, C.; Lei, C. H.; Ouzineb, K.; Keddie, J. L.; Lovell, P. A.; Creton, C. *Soft Matter* ***2009, 5, 1440-1447.***

Effect of xlinking in films made from core-shell latex particles

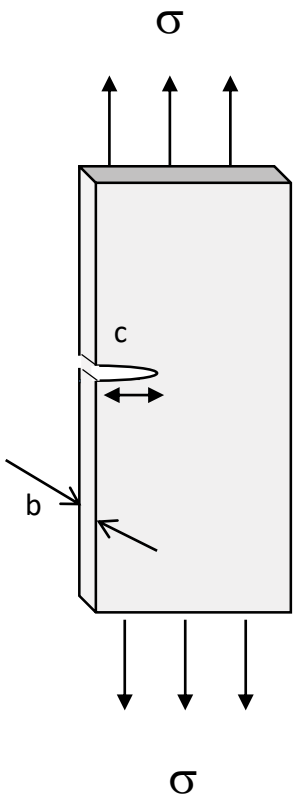


C80d0.1S20 D0.4	G_v (kPa)	G_e (kPa)	J_m	De	G_v/G_e	$3(G_e+G_v)$ (kPa)
no ADH	30.6 (± 2.11)	4.20 (± 0.398)	10^6 imposed [a]	0.382 (± 0.052)	7.30 (± 0.284)	104 (± 7.47)
50% ADH	47.4 (± 9.73)	7.76 (± 0.946)	3170 (± 748)	0.211 (± 0.068)	6.07 (± 0.581)	165 (± 31.9)
75% ADH	59.6 (± 6.96)	11.9 (± 1.01)	211 (± 21.5)	0.126 (± 0.030)	5.02 (± 0.322)	215 (± 23.5)
100% ADH	58.8 (± 4.01)	16.0 (± 0.507)	111 (± 4.60)	0.114 (± 0.021)	3.68 (± 0.204)	224 (± 13.0)

The interfacial crosslinks cause strain hardening , increased G_e and only A factor of 2 increase in initial modulus

Soft Matter ***2009, 5, 1440-1447.***

Fracture of brittle materials: a little bit of mechanics



The crack propagates when

$$\mathcal{G} = \frac{1}{b}\left(\frac{dW}{dc} - \frac{dU_{el}}{dc}\right) = \Gamma$$

Or when the local stress is higher than the bond breakage stress

$$\sigma_{loc} \approx \frac{K}{\sqrt{x}} \qquad K \approx \sqrt{\mathcal{G}E}$$

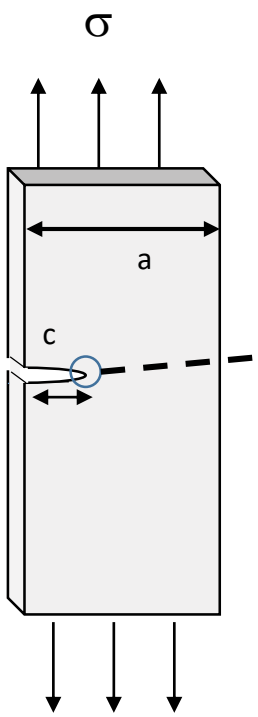
K and $\mathcal{G}$ depend on loading, elastic modulus and geometry

Γ is the dissipated energy

Separation of scales: dissipation zone size << all relevant dimensions

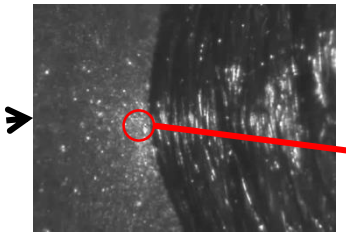
Multi-scale approach of fracture of polymer networks

Macroscopic scale (mm)



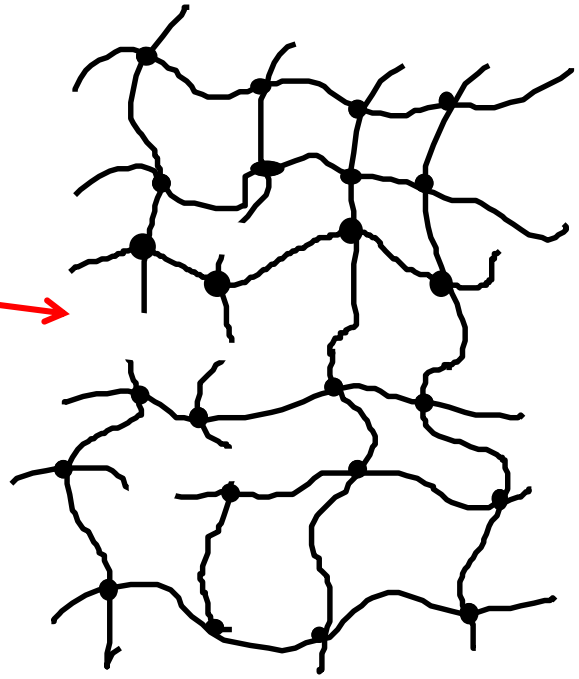
Mechanics :
fracture energy

Intermediate scale (10-100 µm)



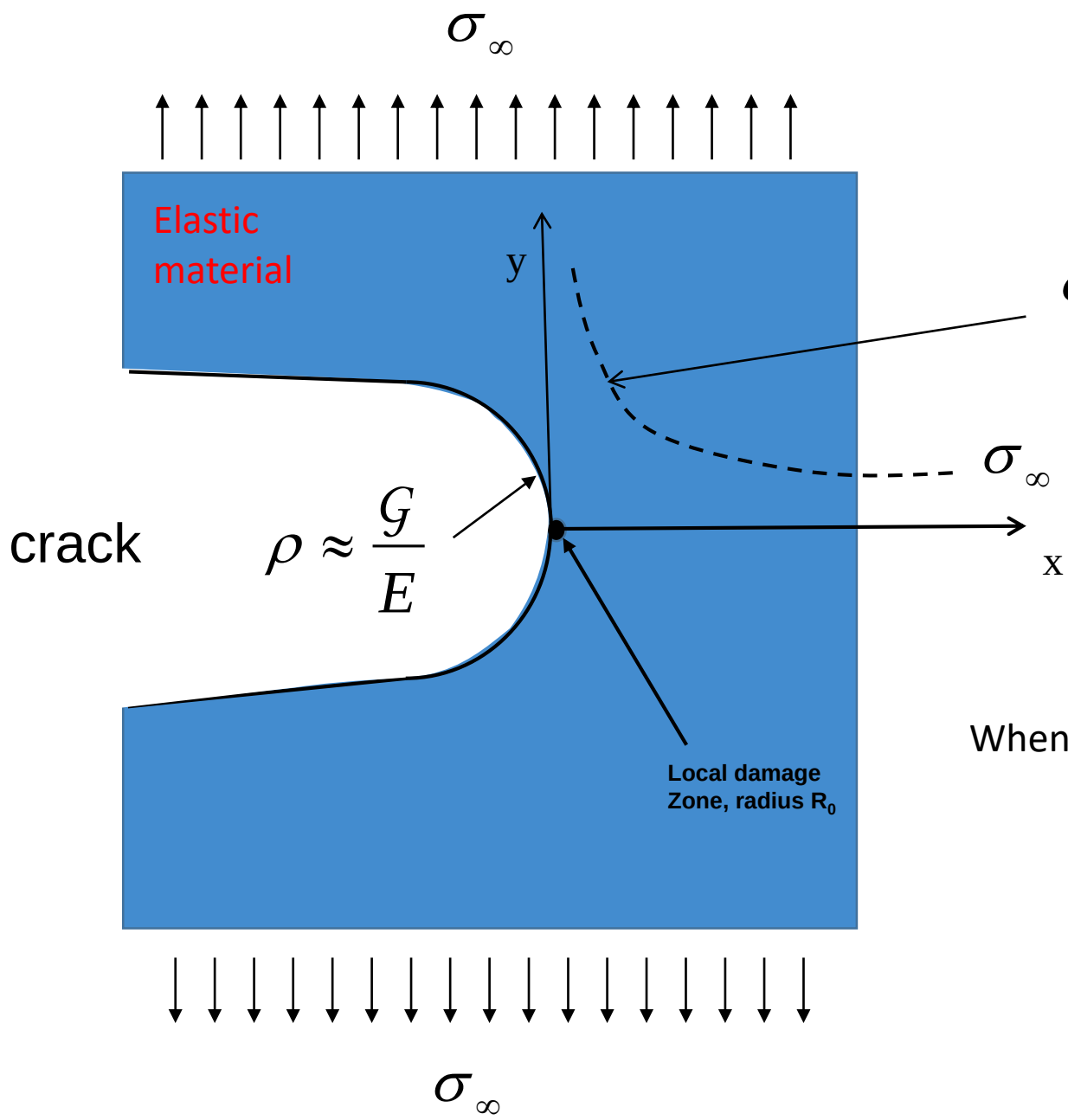
Polymer Physics:
Cavitation,
Fibril formation
molecular friction

Molecular scale (nm)



Polymer Chemistry:
Bond breaking

Experiment ⟷ Theory



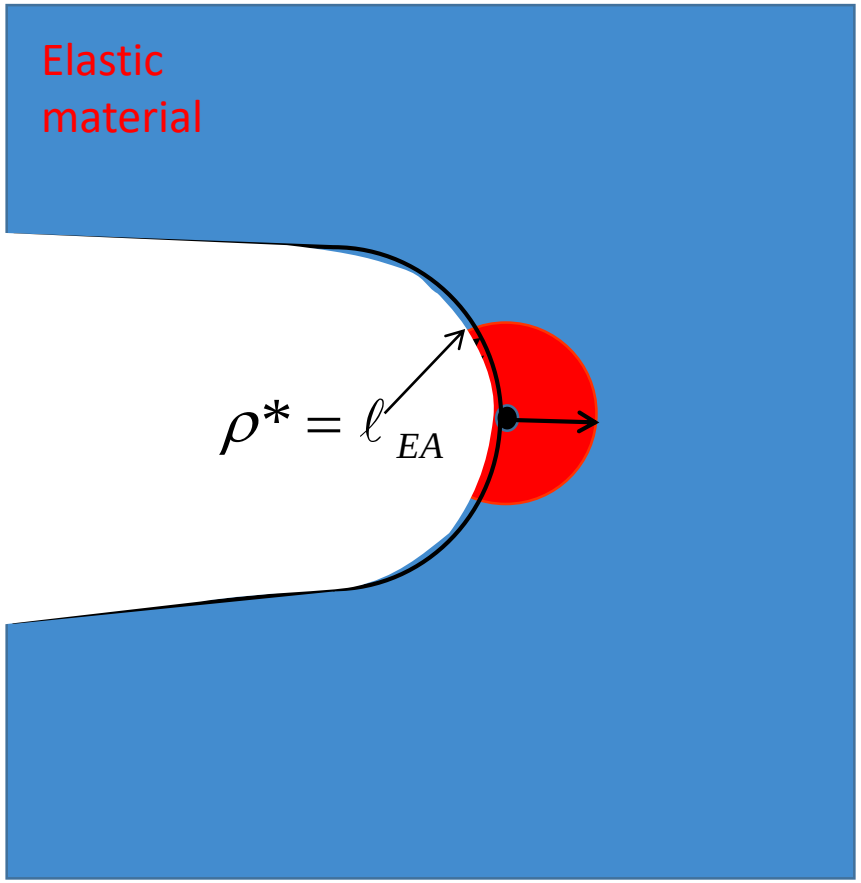
When the crack propagates

$$\frac{\mathcal{G}}{E} = \frac{\Gamma}{E} \; and \; \rho = \rho^*$$

$$\frac{\Gamma}{E} = \ell_{EA}$$

Elasto-adhesive length

Surface effects ~ bulk energy density

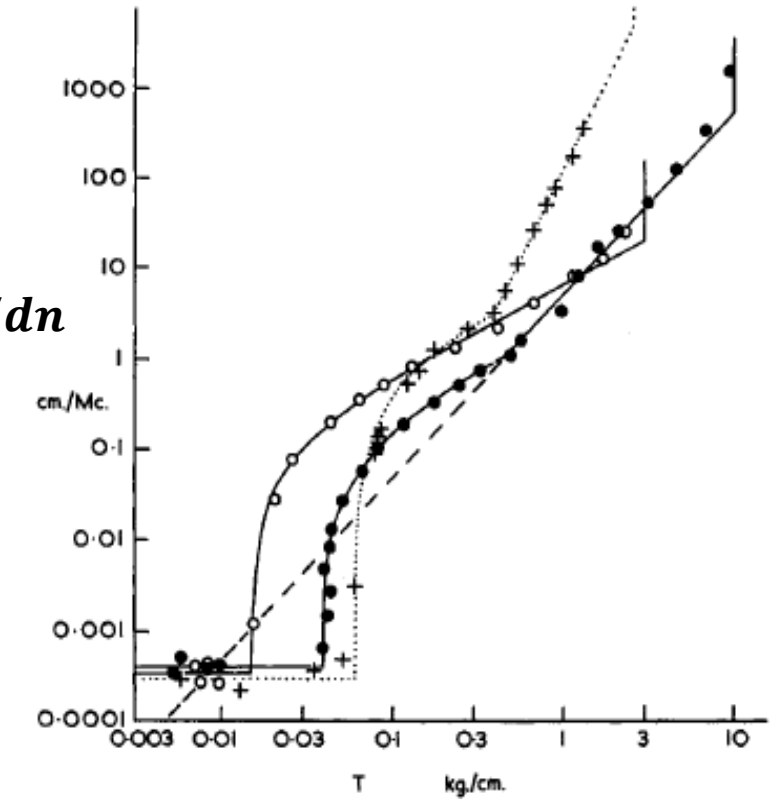


Material property if the
Dissipative zone remains
Much smaller than ℓ_{EA}

Lake, G. J.; Lindley, P. B., *Journal of Applied Polymer Science* ***1965, 9, 1233-1251.***

The Mechanical Fatigue Limit for Rubber

G. J. LAKE and P. B. LINDLEY, *The Natural Rubber Producers' Research Association, Welwyn Garden City, Herts., England*



dc/dn

$\mathcal{G}$

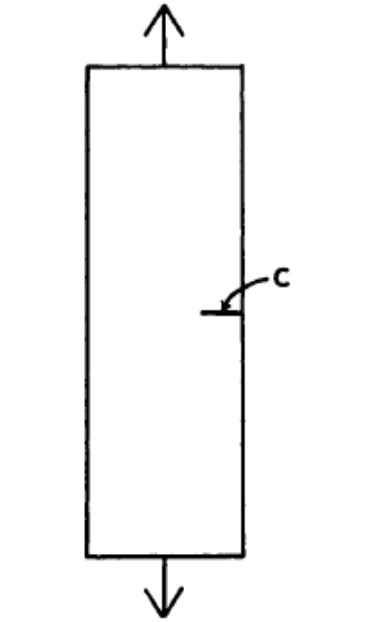
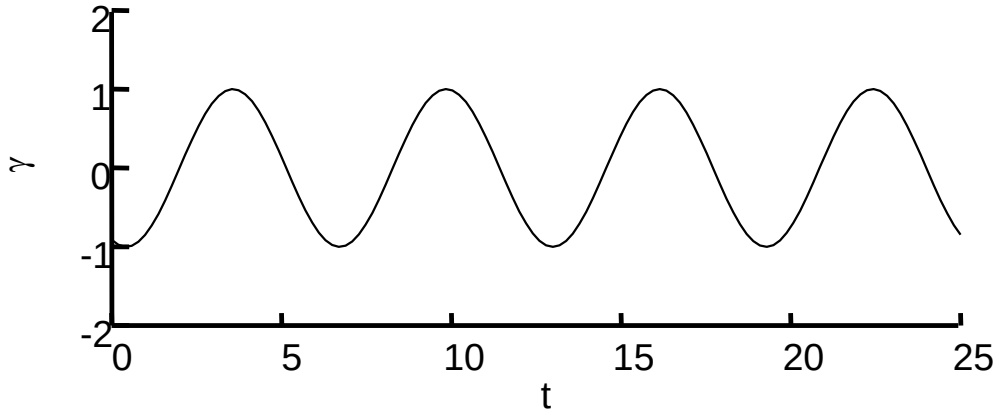


Fig. 1. Tensile cut growth test piece.



Threshold value in fatigue

Relatively independent of the elastomer

40 – 80 J/m^2

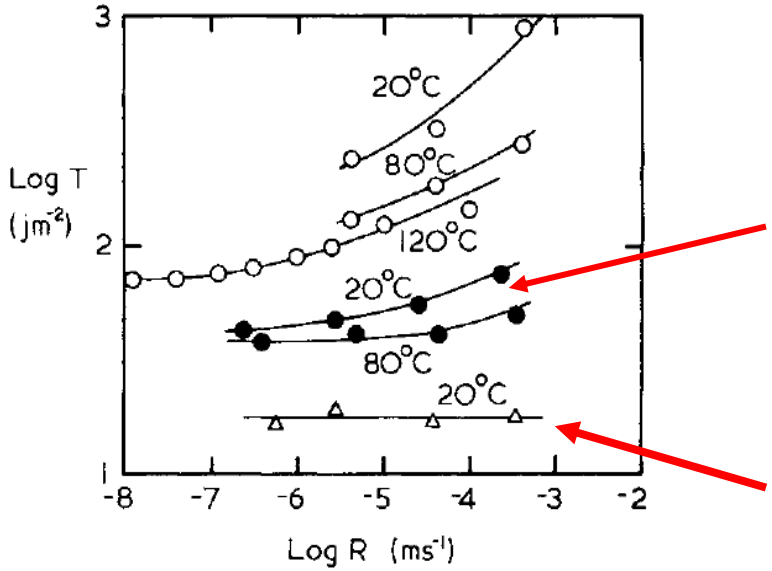
Ahagon, A.; Gent, A. N., *Journal of Polymer Science, Polymer Physics Edition* ***1975, 13, 1903-1911.***

Threshold Fracture Energies for Elastomers

A. AHAGON and A. N. GENT, *Institute of Polymer Science, The University of Akron, Akron, Ohio 44325*

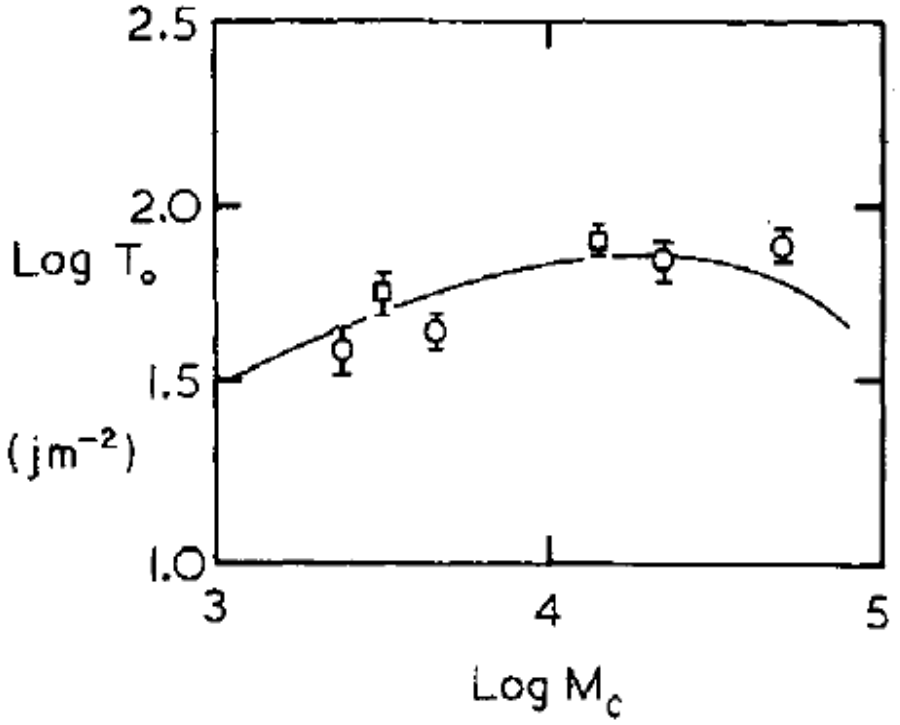
Polybutadiene (T_g = -110°C)

Experiments at 20-120°C



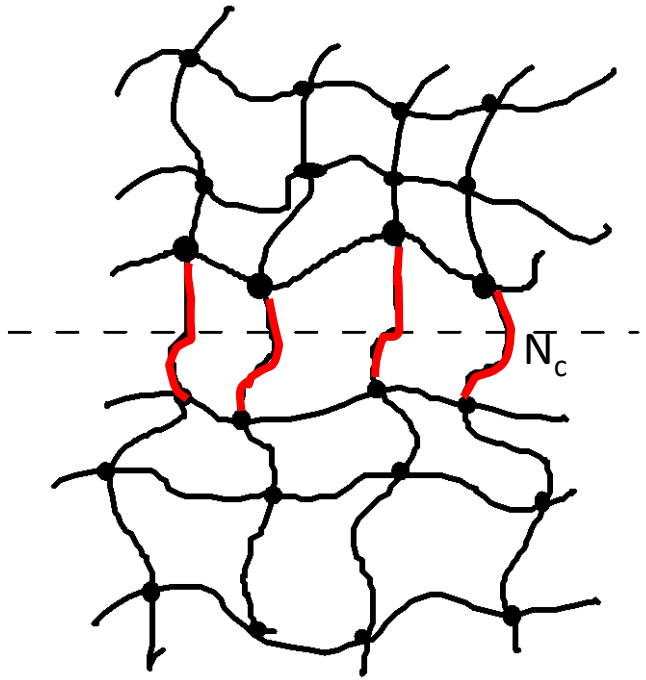
Swollen in paraffin oil

Swollen in xylene

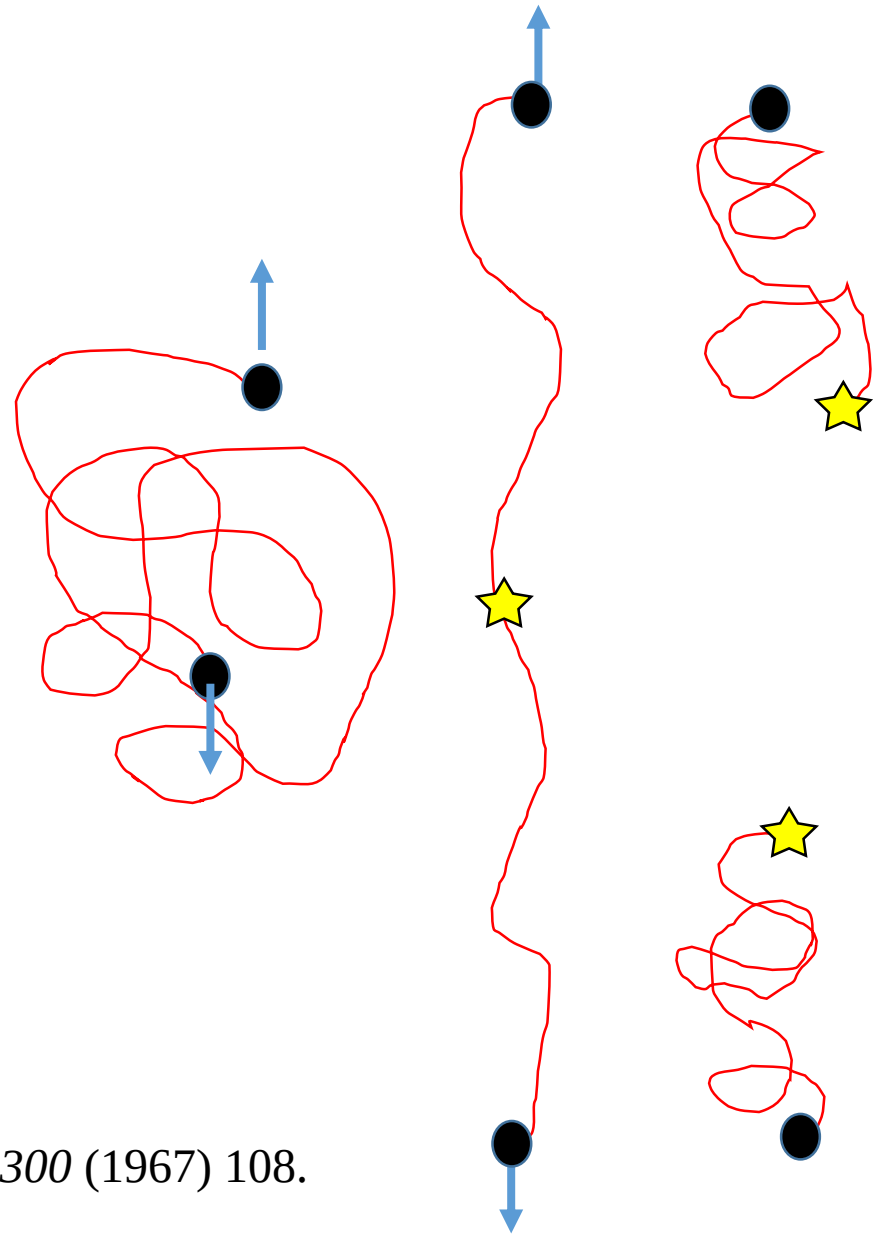


Fracture of bonds in networks: the Lake-Thomas model

$$\Gamma_o = N_c U_b \Sigma$$



N_c = number of monomers
U_b = fracture energy of a covalent bond
Σ = areal density of strands



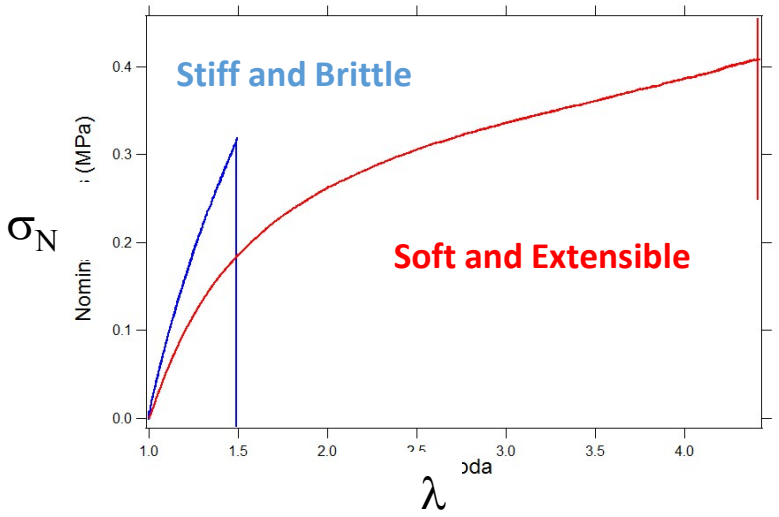
For rubbers $\Gamma_0 \sim 50\ J/m^2$

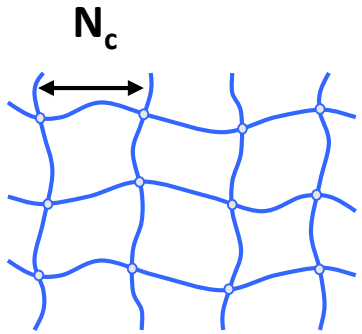
For gels $\Gamma_0 \sim 5\text{-}10\ J/m^2$

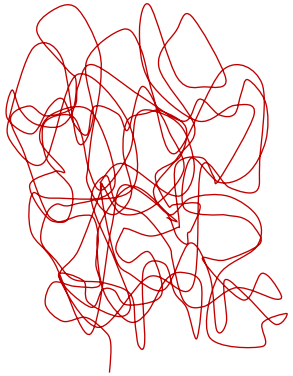
G. J. Lake, A. G. Thomas, *Proc. of the Royal Soc. A300* (1967) 108.

Trade off is found between toughness and stiffness in elastomeric networks and in simple gels

G. J. Lake, A. G. Thomas, *Proc. of the Royal Soc. A300* (1967) 108.

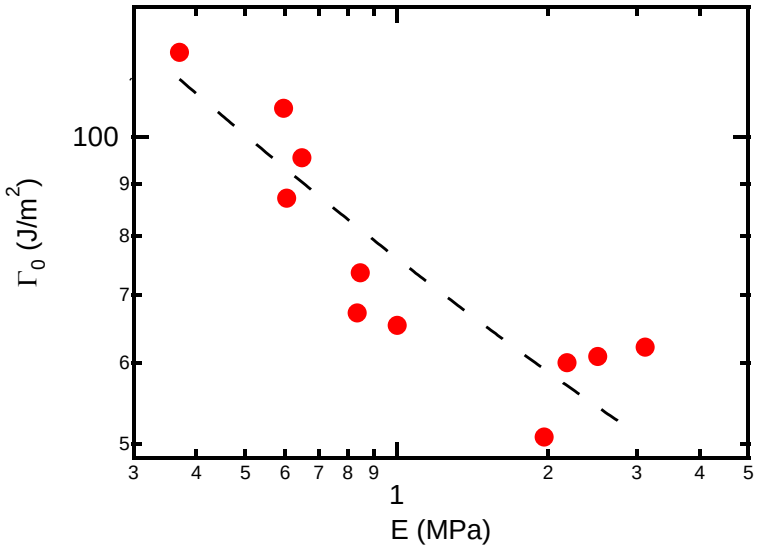






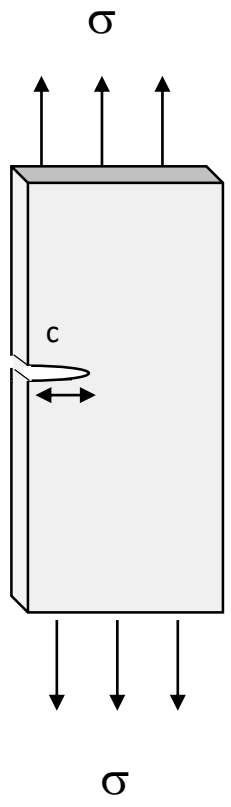
Well predicted by the Lake-Thomas theory

$$\Gamma_o \approx N_c^{1/2} U_b \approx \frac{1}{\sqrt{E}}$$



Bhowmick, A. K.; Gent, A. N.; Pulford, C. T. R., *Rubber Chemistry and Technology* ***1983, 56, 226-232.***

Consequence of Lake-Thomas Model on extensibility



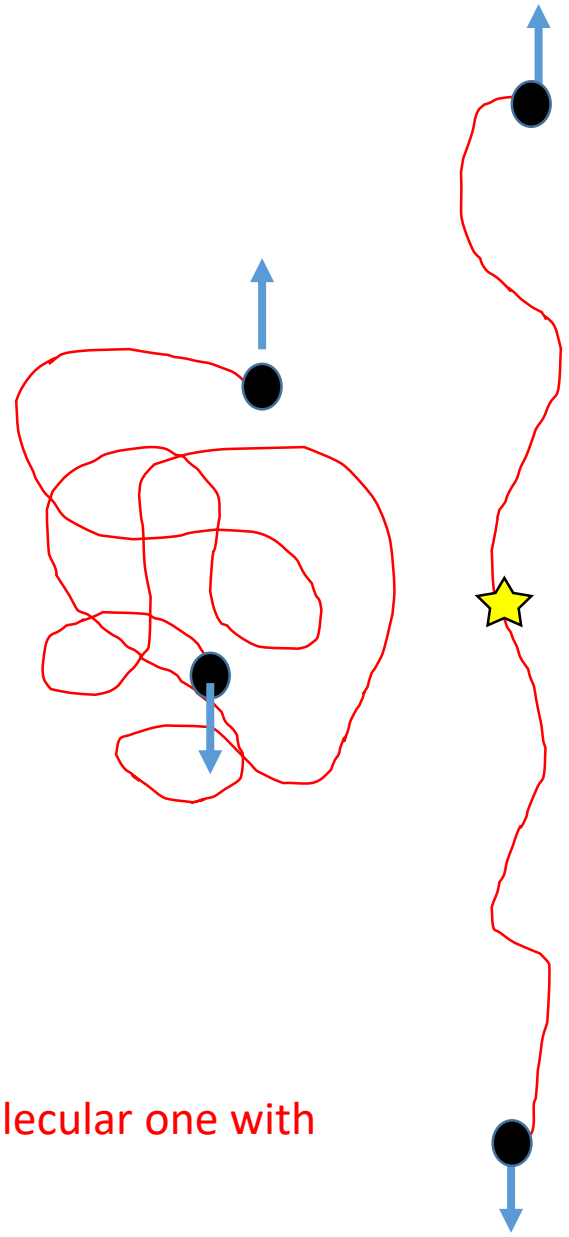
Fracture experiment

When the crack propagates

$$\mathcal{G} = \frac{6cW(\lambda_c)}{\sqrt{\lambda_c}} = \Gamma_0 \qquad W(\lambda_c) \approx E\lambda_c^2$$

with $\Gamma_0 \approx \frac{1}{\sqrt{E}}$

$$\lambda_c \approx \frac{1}{E} \approx N_c$$



Molecular extensibility

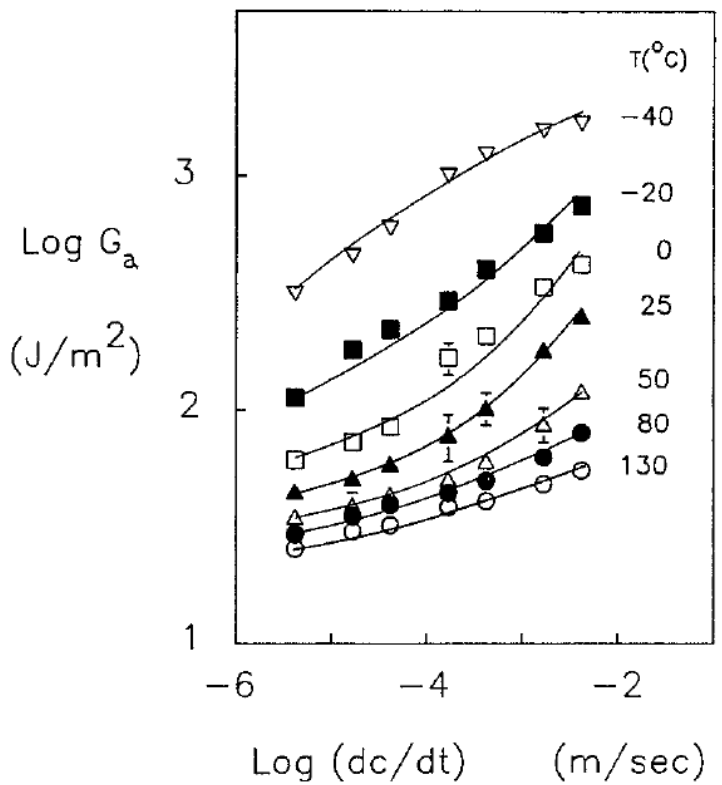
$$\lambda_c \approx \sqrt{N_c}$$

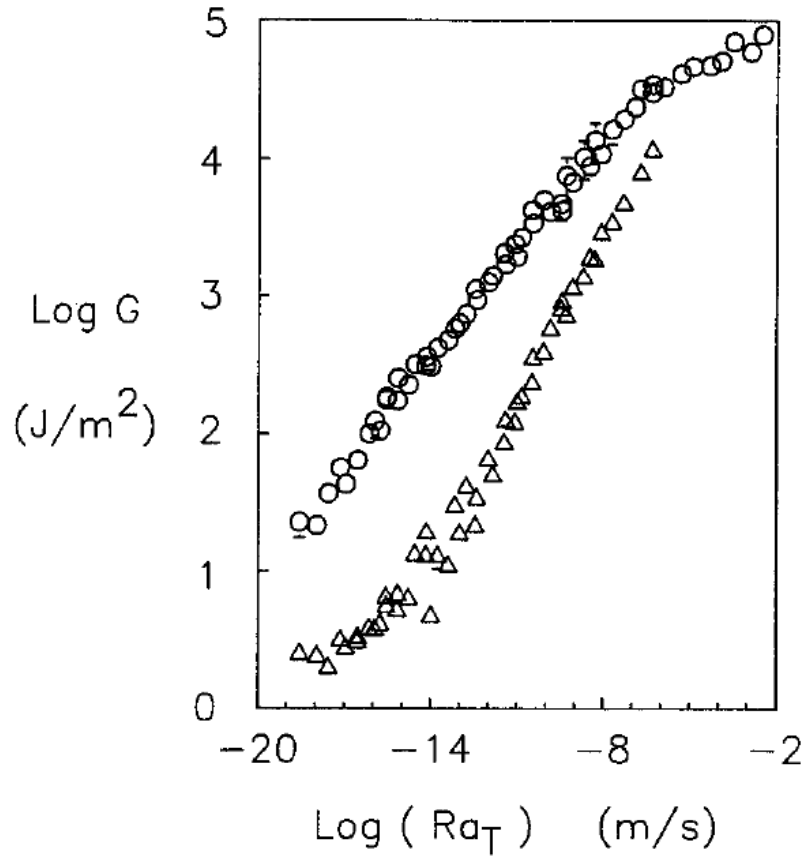
Macroscopic extensibility decreases much more than molecular one with increasing crosslinking

Toughening mechanisms

Viscoelastic Dissipation

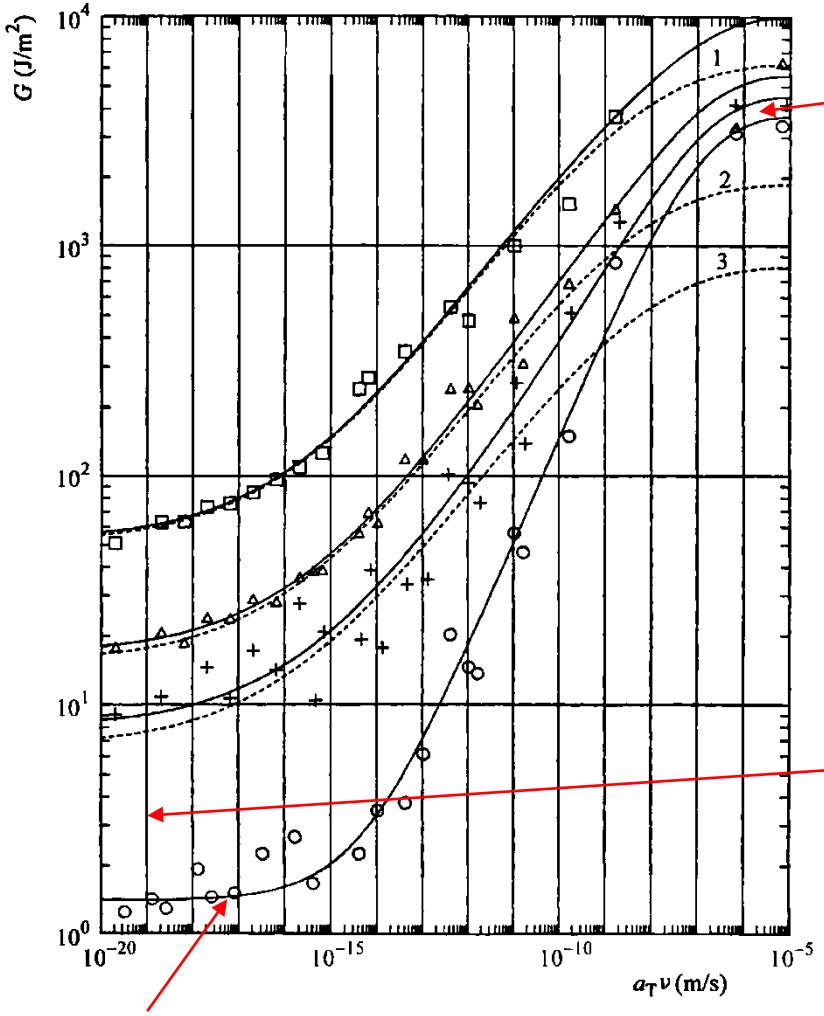
Rate dependence of fracture energy





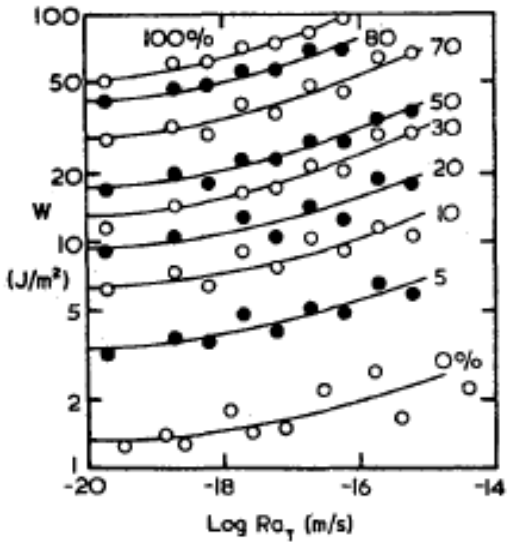
Gent, A. N. *Langmuir* ***1996, 12, 4492.***

Transition between threshold regime and viscoelastic regime



Adherence
(viscoelastic dissipation and large strain damage mechanisms)

$V_{crack} >> 0$



High temperature
Low rate
region

Bond breakage dissipation

$V_{crack} \rightarrow 0$

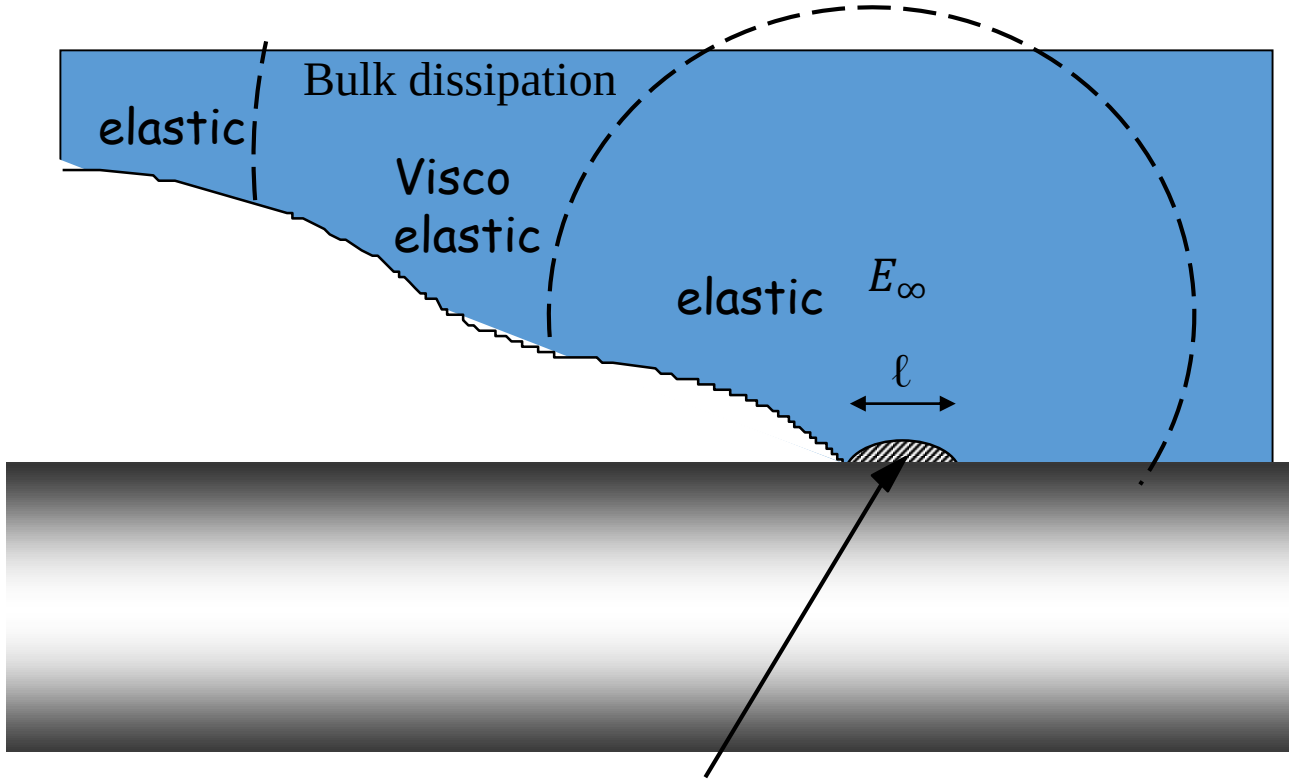
Maugis, D., *J. Adhes. Sci. Technol.* ***1995, 9 (7), 1005-1008.***

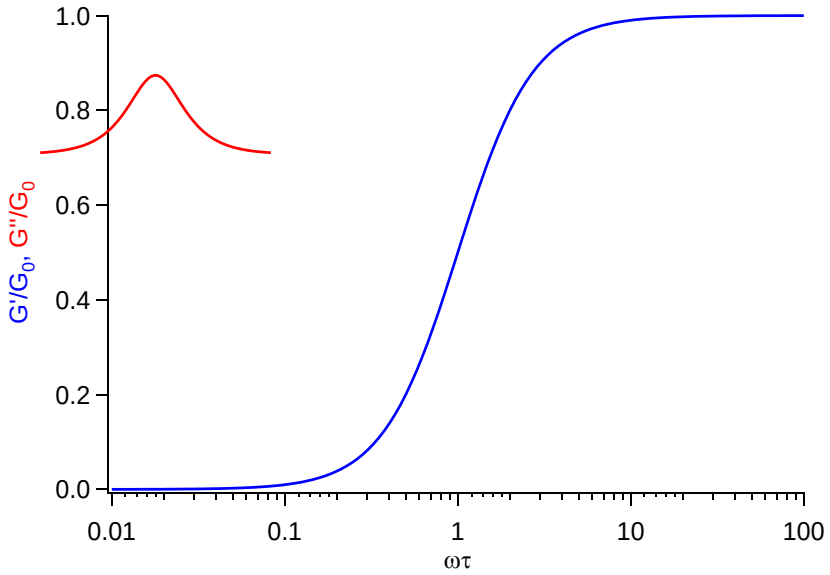
Modeling crack propagation in single relaxation time viscoelastic materials

P. G. de Gennes, *Comptes Rendus de l'Académie des Sciences de Paris, Série II 307* (1988) 1949.

C. Y. Hui, D. B. Xu, E. J. Kramer, *Journal of Applied Physics 72* (1992) 3294.
D. B. Xu, C. Y. Hui, E. J. Kramer, *Journal of Applied Physics 72* (1992) 8.

Persson, B. N. J.; *J. Phys.-Cond. Mat.* ***2005, 17, (44), R1071-R1142.***, *Phys Rev E* **2005**, 71, (3), 036123.





Local non-linear dissipation

2 important parameters: G" and the size of the dissipative zone

Quantitative result

$$\frac{\Gamma(V)}{\Gamma_0} \cong \mu_\infty \int_{\omega_1}^{\omega_2} \frac{\mu''}{\mu'^2 + \mu''^2} \frac{d\omega}{\omega}$$

Cutoff frequencies:

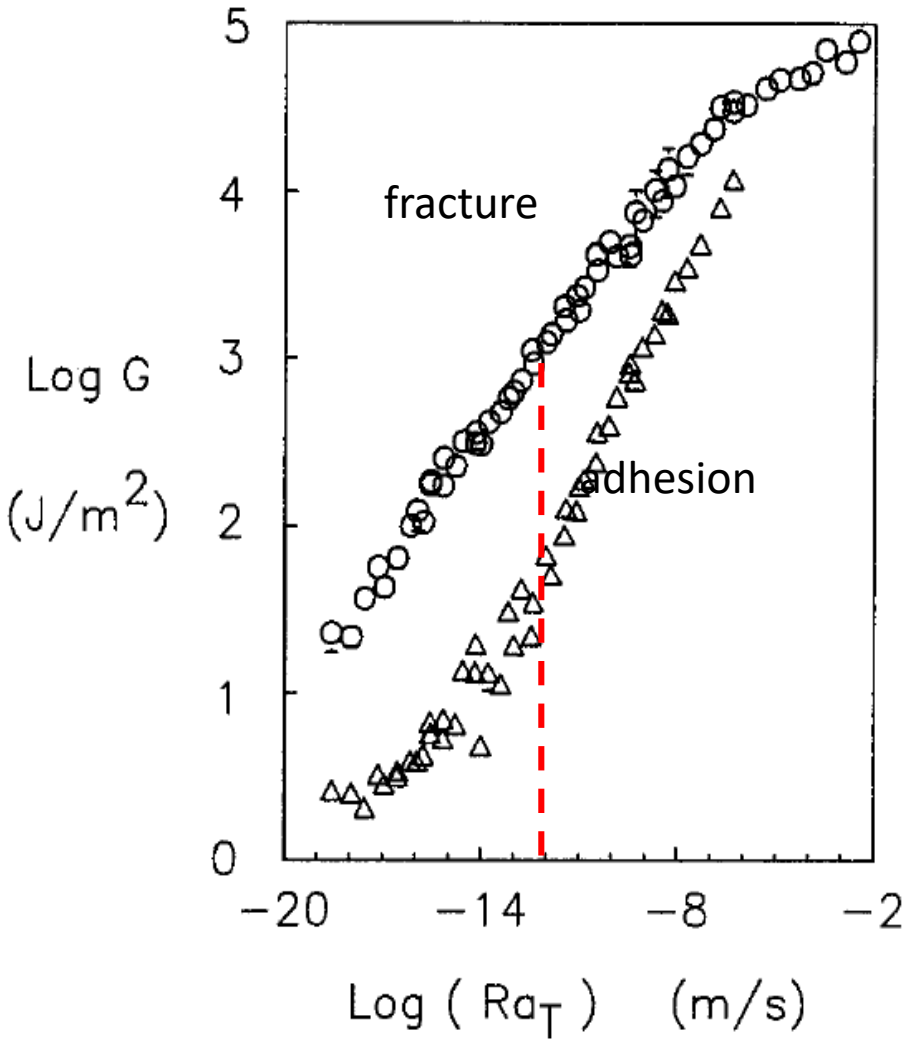
$\omega_1 = V/L$ L = size of the deformed zone

$\omega_1 = V/\ell$ ℓ = Size of the zone where nonlinear deformation is important

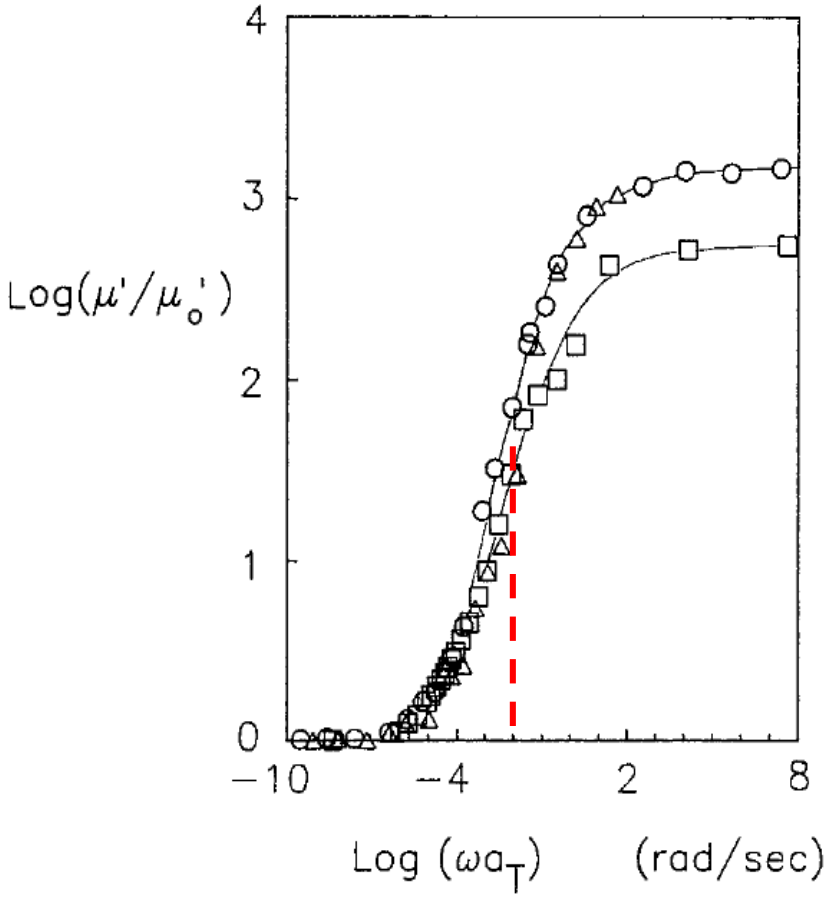
In principle: prediction of $\Gamma(V)$ as a function of the linear viscoelastic Properties of the material

Saulnier, F.; Ondarcuhu, T.; Aradian, A.; Raphael, E. Macromolecules 2004, 37, 1067-1075.

Fracture vs. Crack velocity



Elastic modulus vs frequency

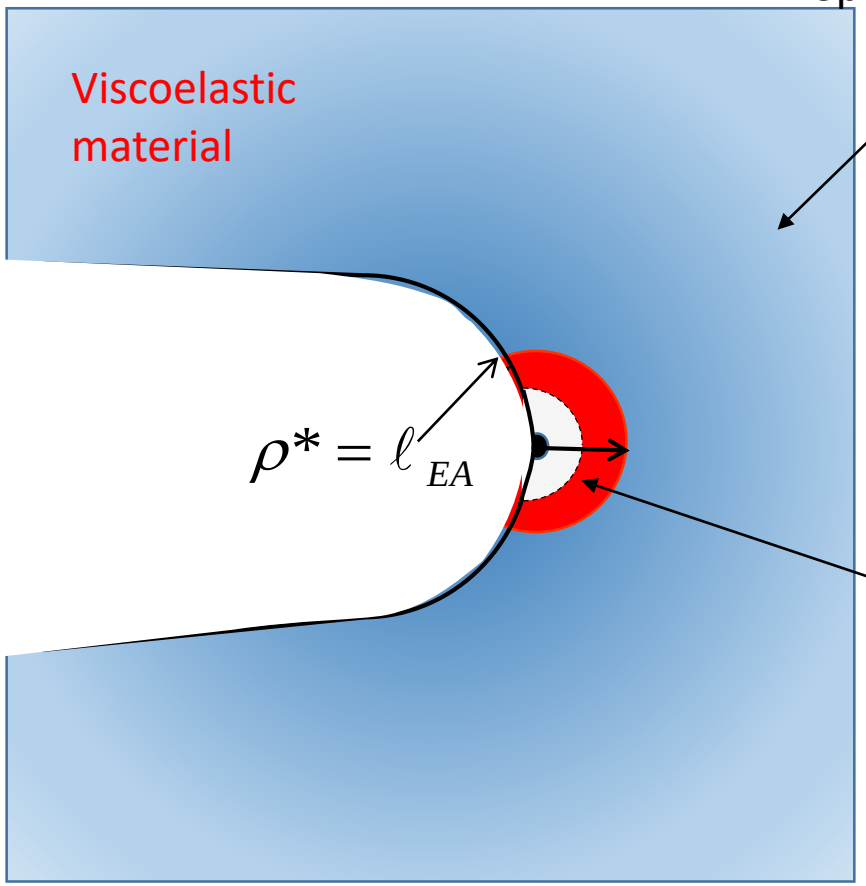


Linear theory: strain rate depends on distance and is given by

$$\dot{\varepsilon} \approx \frac{V}{d}$$

$d = 10^{-10}$ m

Dissipation depends on crack
Speed. Linear viscoelasticity holds



Persson, B. N. J.; *J. Phys.-Cond. Mat.* ***2005, 17, (44), R1071-R1142.,***
Phys Rev E **2005,** 71, (3), 036123.

Dissipation is controlled by
Large strain behavior.
Can be rate dependent

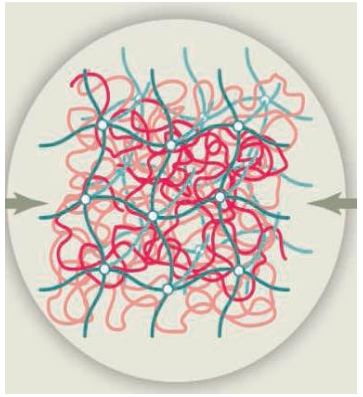
For materials that are very elastic (low tan δ), in the *linear regime* (gels), this toughening mechanism does not work !

Toughening mechanisms

Sacrificial Bonds

Recent tough and stiff networks: additional sacrificial bonds to dissipate energy

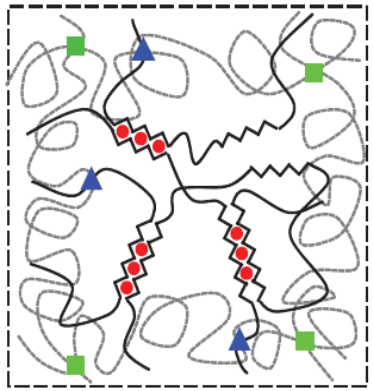
Double covalent networks



Breakable covalent bonds

Gong, J. P. et al. (2003) Adv. Mat. **15(14): 1155-1158.**

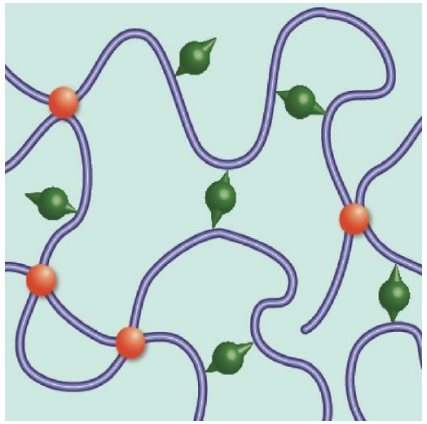
Covalent + Slow bonds



Partially healable and
Breakable ionic bonds

Sun, J.-Y., et al. (2012). Nature **489(7414): 133-136.**

Covalent + fast bonds



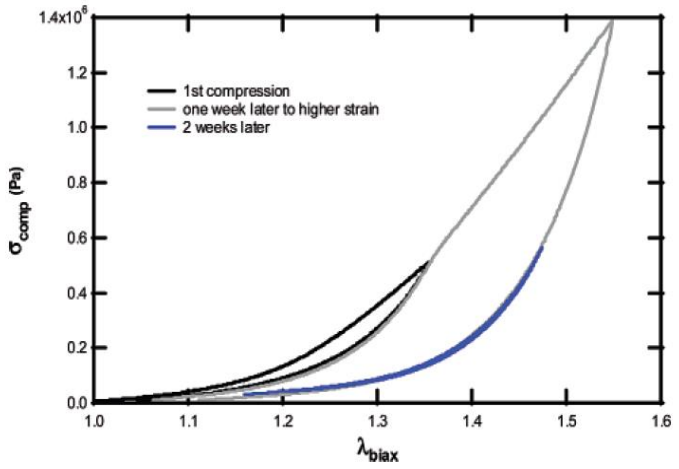
Fast healing bonds

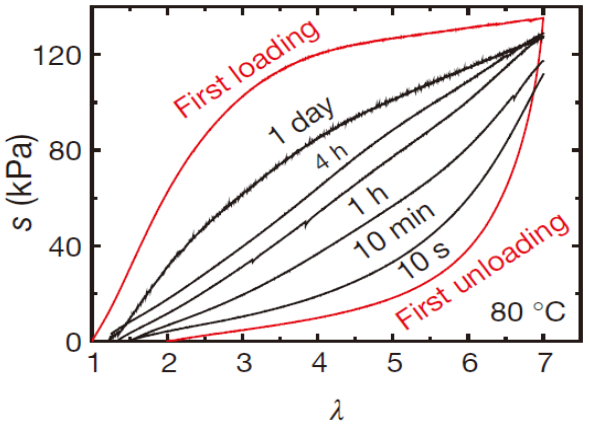
Mayumi, K.; et al.
Extreme Mechanics Letters
2016, 6, 52-59

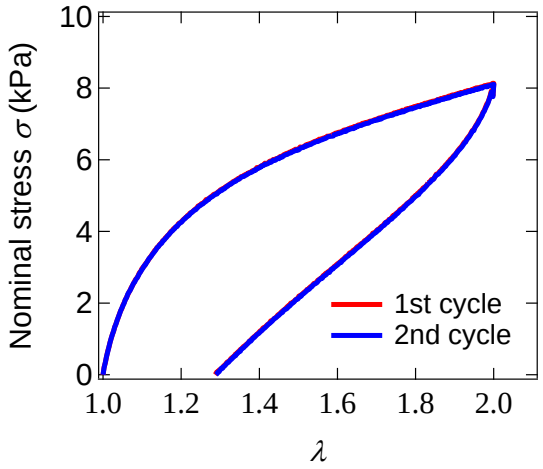
Non-healing sacrificial bonds

Slow and partial recovery

Fast and complete recovery







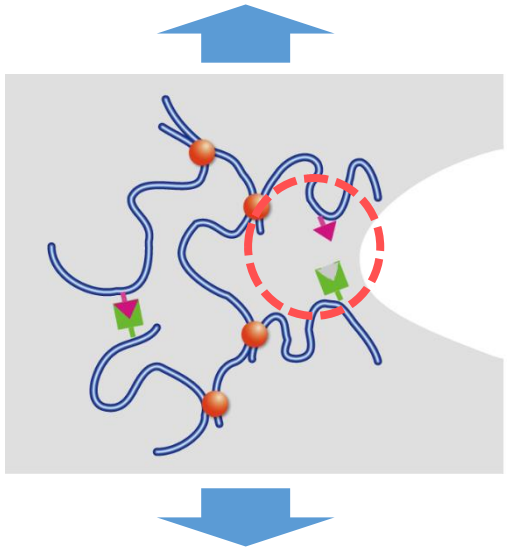
No viscoelatic dissipation

Large viscoelastic dissipation

Viscoelastic dissipation depends on strain rate

How do we characterize fracture toughness (Γ) of a soft hydrogel with sacrificial bonds by using the energy release rate $\mathcal{G}$?

The material is not linear elastic, has a strain rate dependent behavior, but no internal friction



How does bond breaking/healing dynamics can improve fracture toughness for a soft material with no internal friction ?

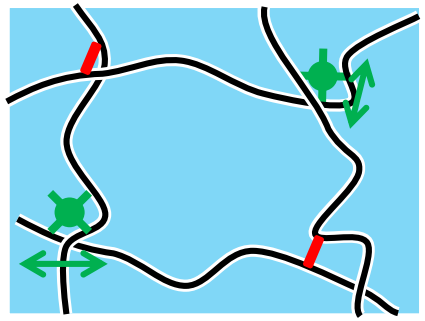
Hydrogel Model system

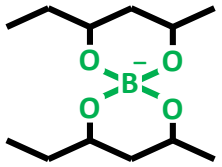
Model dual crosslink gel

Simple chemical structure

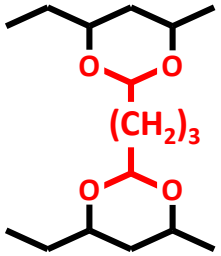
Well defined life time of transient crosslinks

Poly vinyl alcohol (PVA)



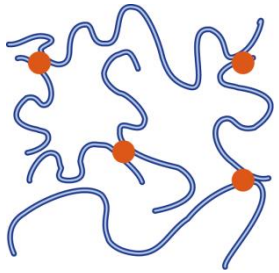


transient (physical) bond



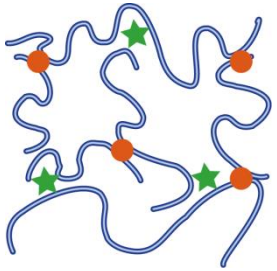
permanent (chemical) bond

PVA solution → Xlinked by glutaraldehyde (GA)



swollen in water

deswollen in Borax/NaCl Solution

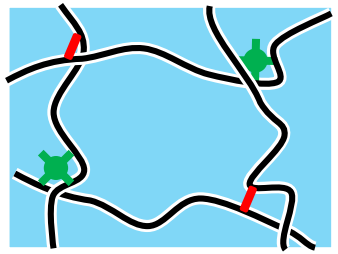


12,5 wt% polymer in water

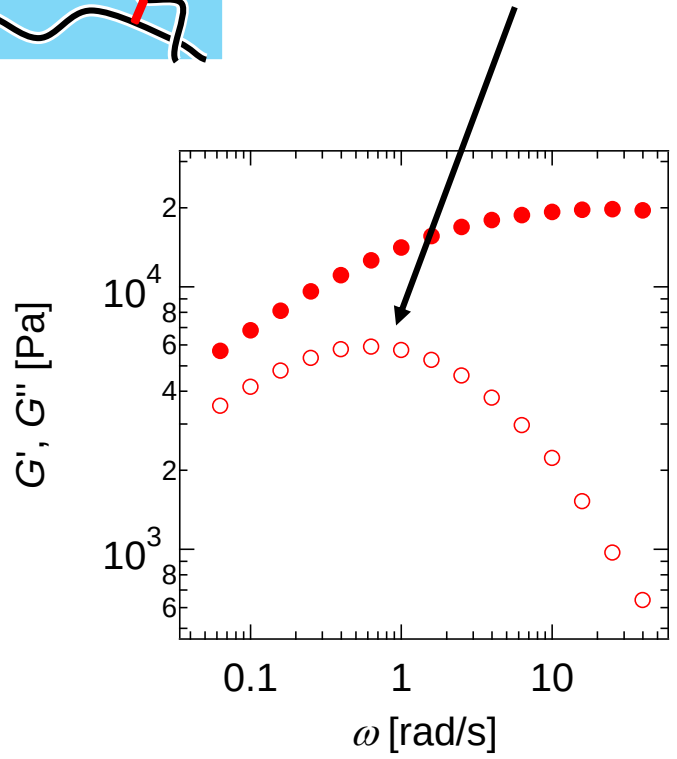
K. Mayumi, A. Marcellan, G. Ducouret, C. Creton and T. Narita, ACS Macroletters, 2013, 2, 1065

Linear viscoelasticity

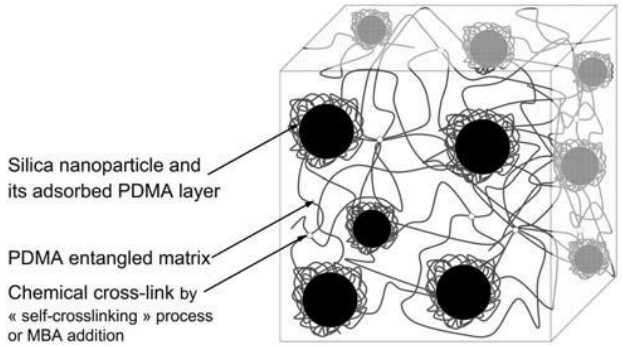
Single Relaxation

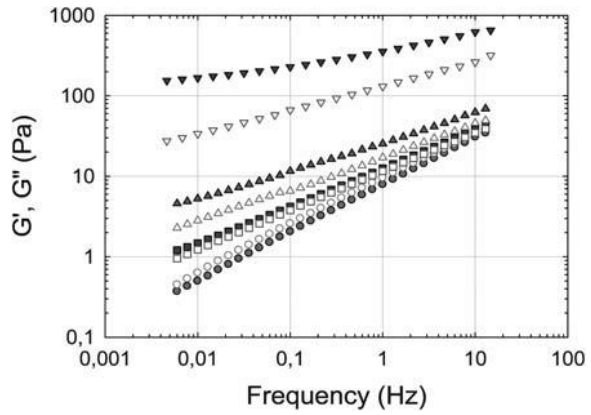


Single relaxation time



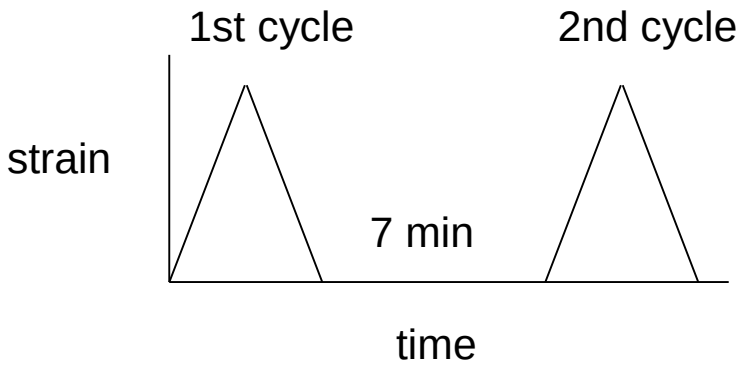
T. Narita, et al., *Macromolecules*, 46, 4174 (2013).

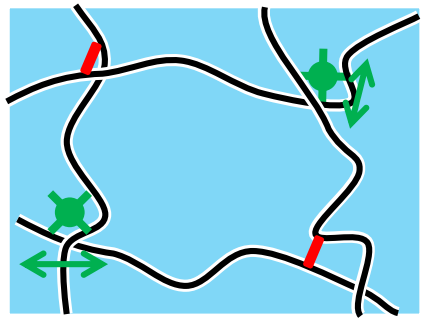


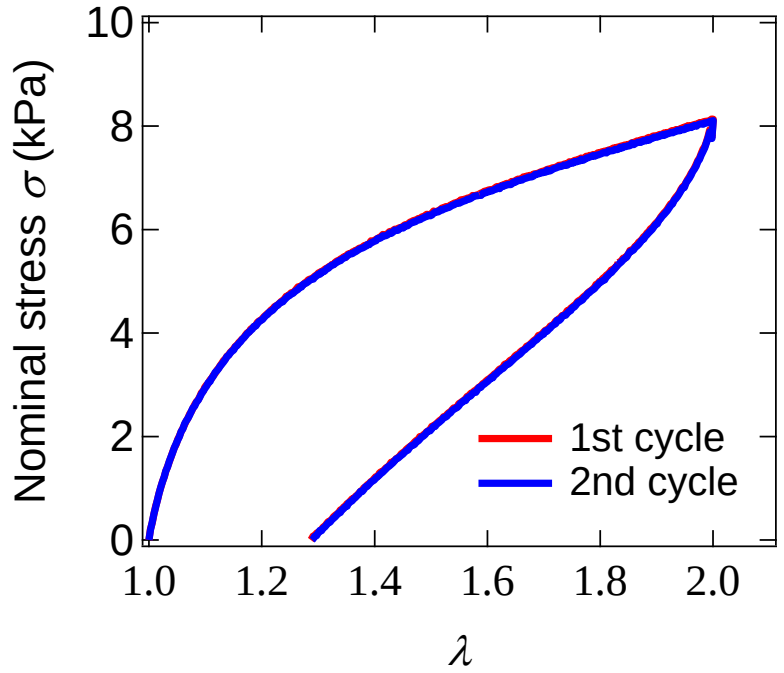


wide distribution of relaxation times

L. Carlsson, Soft Matter, 6, 3619 (2010).







Large hysteresis

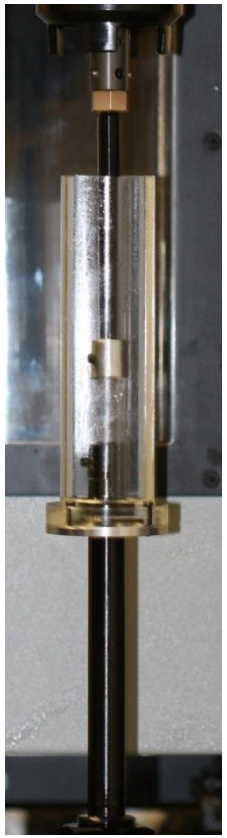
Perfect recovery

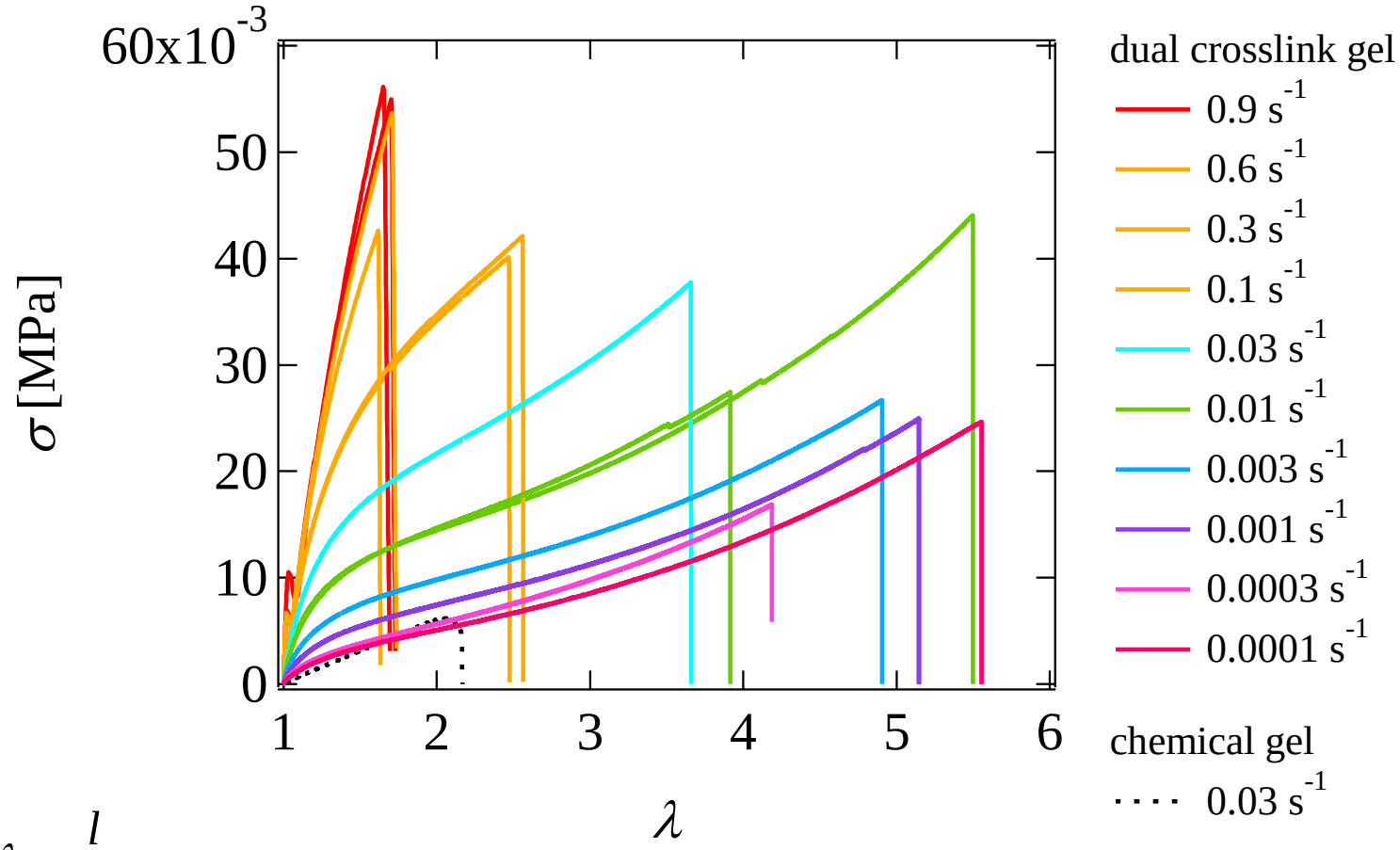
Reversible crosslinks are broken and healed

Loading/unloading curves of hybrid gels. The interval time between cycles was 7 min.

Uniaxial Stretching in oil: strain rate dependence

oil bath ➡ wide range of stretch rates dλ/dt





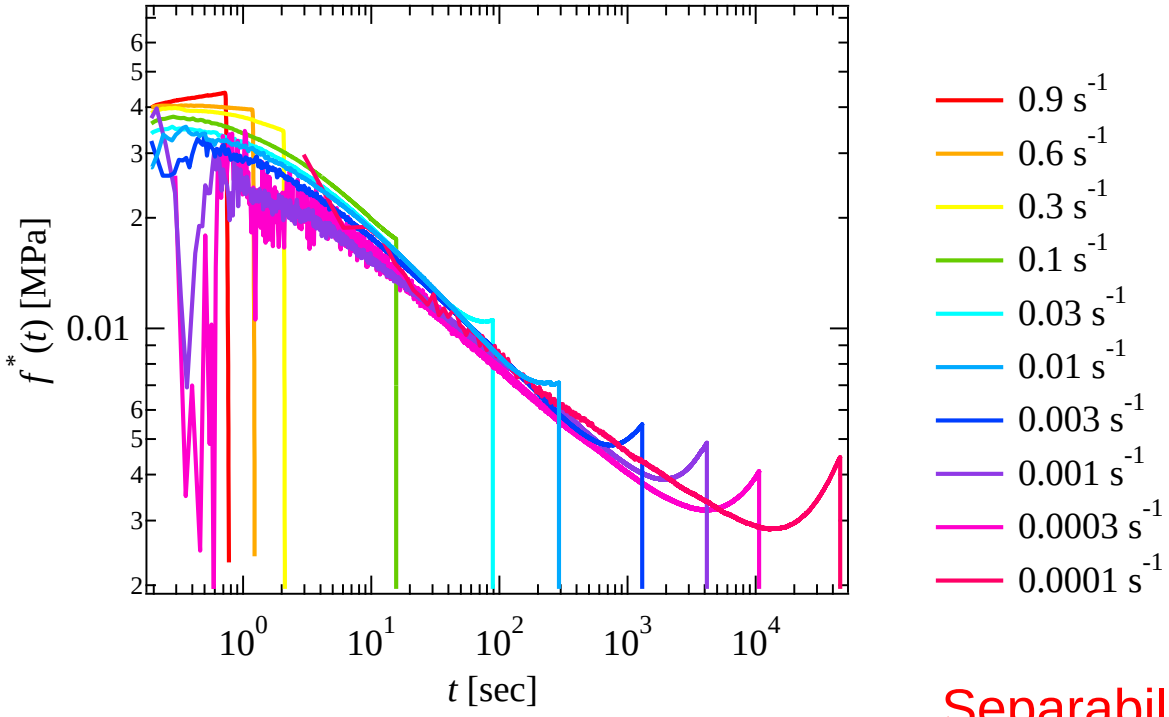
$$\lambda = \frac{l}{l_0}$$

Physical crosslinks improve extensibility !

How can we model the mechanics of the gel ?

Reduced stress $f^* = \frac{\sigma}{\lambda - \lambda^{-2}}$

$f^*(\lambda, \dot{\varepsilon}) \rightarrow f^*(t)$



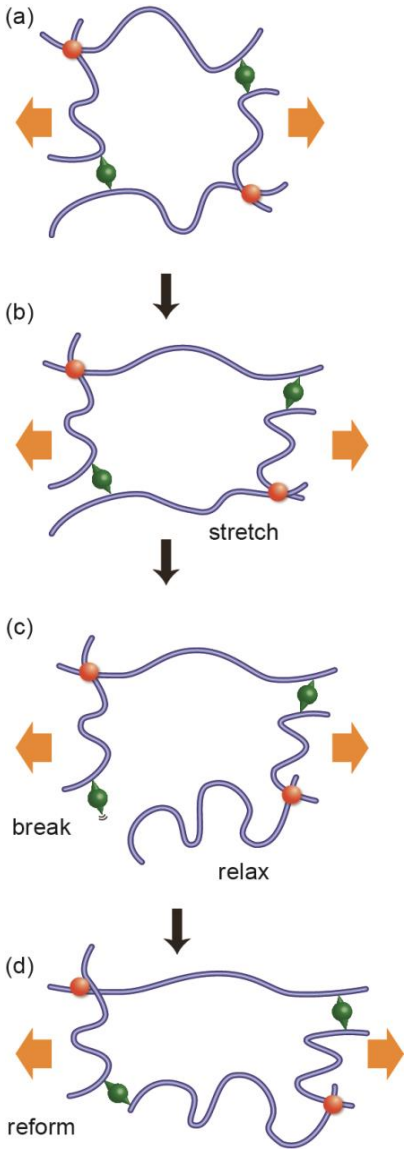
$$\sigma = \left(\lambda - \lambda^{-2}\right) f^*$$

strain time

Strain does not affect dissociation time of physical bonds

Separability of stress into strain and time terms

K. Mayumi, A. Marcellan, G. Ducouret, C. Creton and T. Narita, ACS Macroletters, 2013, 2, 1065



Ingredients of a physically based model

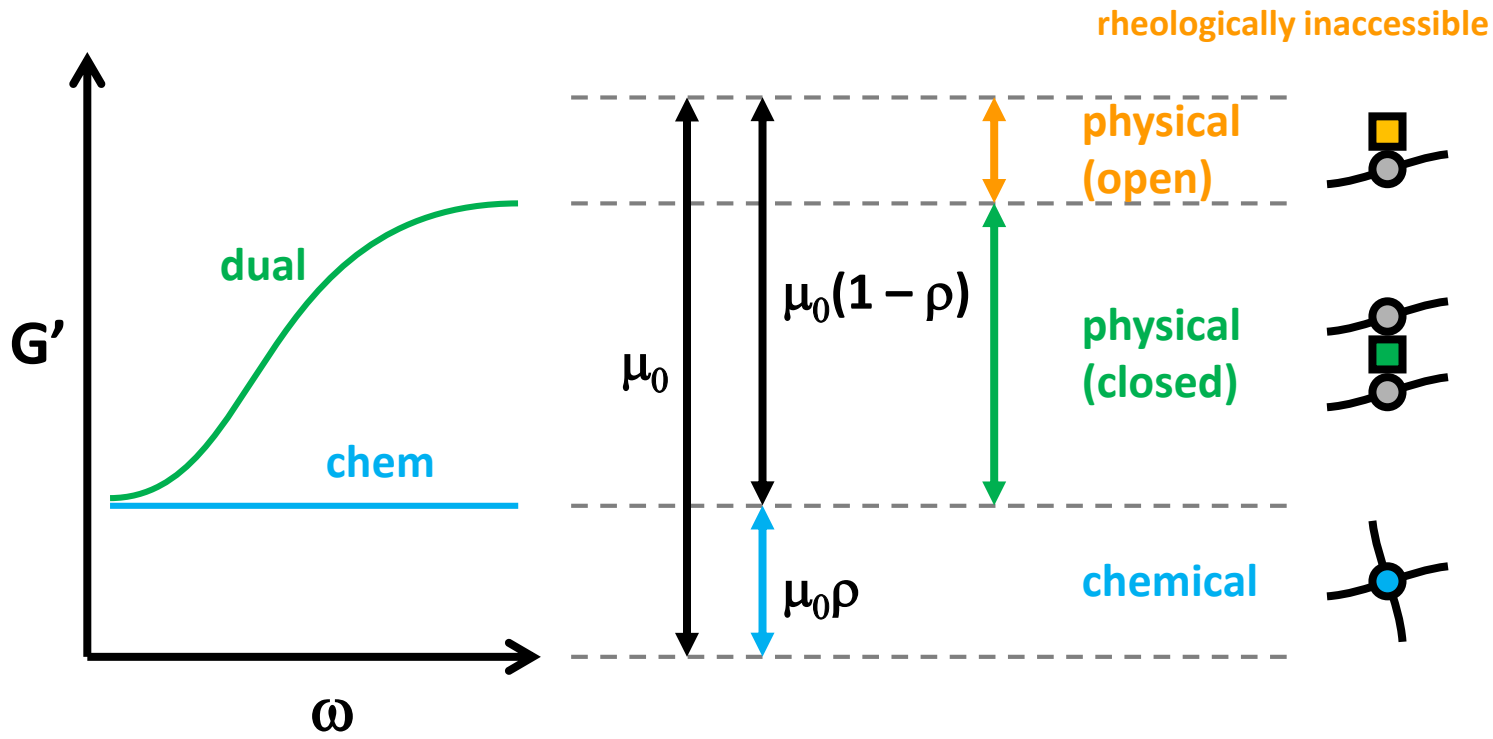
The stress is carried by the stretched chains between bonds

At t = 0, all chains are unstretched and $\sigma = 0$

During deformation,

1) bonds break and release the stress in the chain.
2) Bonds reform (healing) at a different spot and the New chain is unstretched

Physical and Chemical bonds at steady state



R. Long, K. Mayumi, C. Creton, T. Narita and C. Y. Hui, *Macromolecules*, 2014, 47, 7243–7250
Long, R.; Mayumi, K.; Creton, C.; Narita, T.; Hui, C.-Y. *J. Rheology* 2015, 59, 643.
Guo, J.; Long, R.; Mayumi, K.; Hui, C.-Y., *Macromolecules* 2016, 49 (9), 3497-3507.

3-D large strain Model: Rong Long and Herbert Hui

In uniaxial tension

$$\frac{\sigma}{\mu} = [\rho + n(t)]\left[\lambda(t) - \frac{1}{\lambda^2(t)}\right] + \bar{\gamma}_\infty \int_0^t \phi_B\left(\frac{t-\tau}{t_B}\right)\left[\frac{\lambda(t)}{\lambda^2(t)} - \frac{\lambda(\tau)}{\lambda^2(\tau)}\right] \mathrm{d}\tau$$

Governing equation

Steady state reformation rate of physical bonds

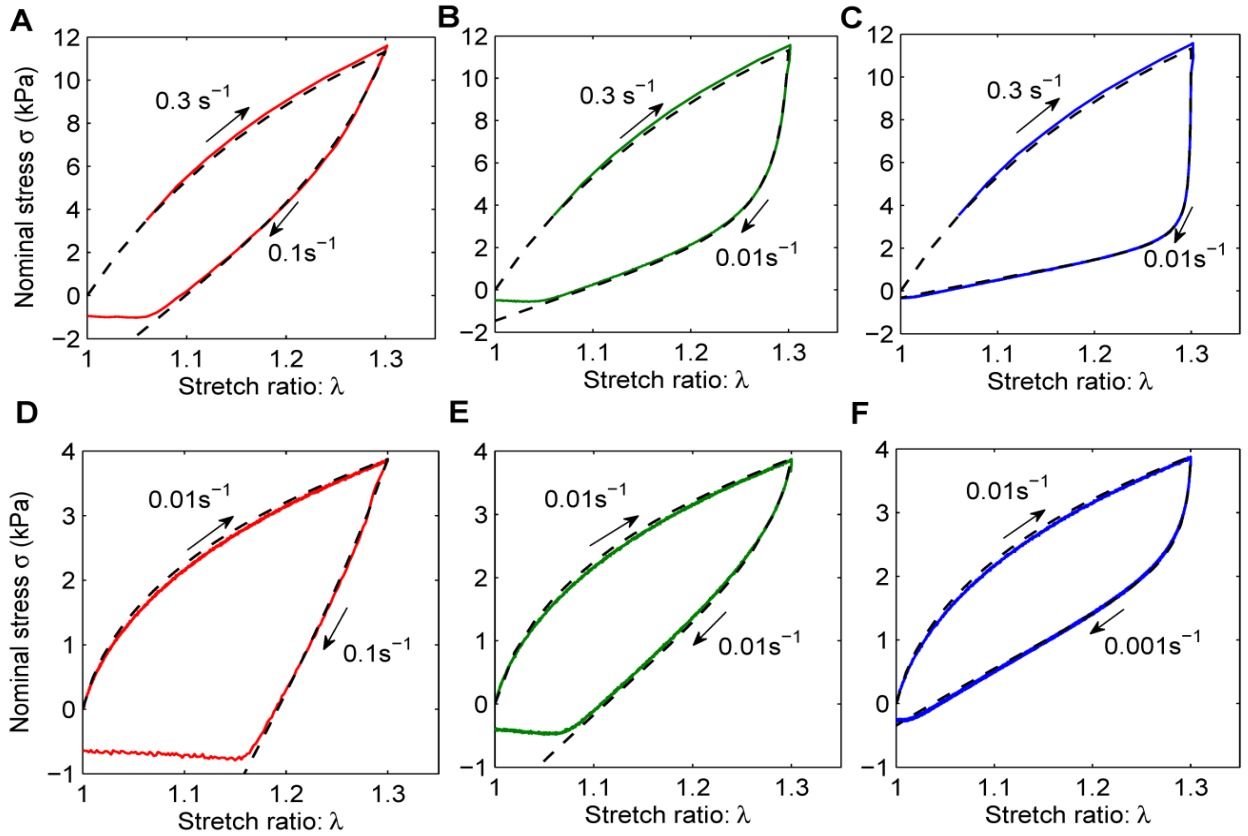
$$\bar{\gamma}_\infty = \frac{1-\rho}{t_H + \frac{t_B}{2-\alpha_B}}$$

Fraction of closed physical bonds at t = 0 and still closed at t

$$n(t) = \bar{\gamma}_\infty \frac{t_B}{2-\alpha_B}\left(1 + (\alpha_B - 1)\frac{t}{t_B}\right)^{\frac{2-\alpha_B}{1-\alpha_B}}$$

4 fittable parameters $\mu\rho$ $\mu\bar{\gamma}_\infty$ t_B α_B

R. Long, K. Mayumi, C. Creton, T. Narita and C. Y. Hui, *Macromolecules*, 2014, 47, 7243–7250
Long, R.; Mayumi, K.; Creton, C.; Narita, T.; Hui, C.-Y. J. Rheology 2015, 59, 643.

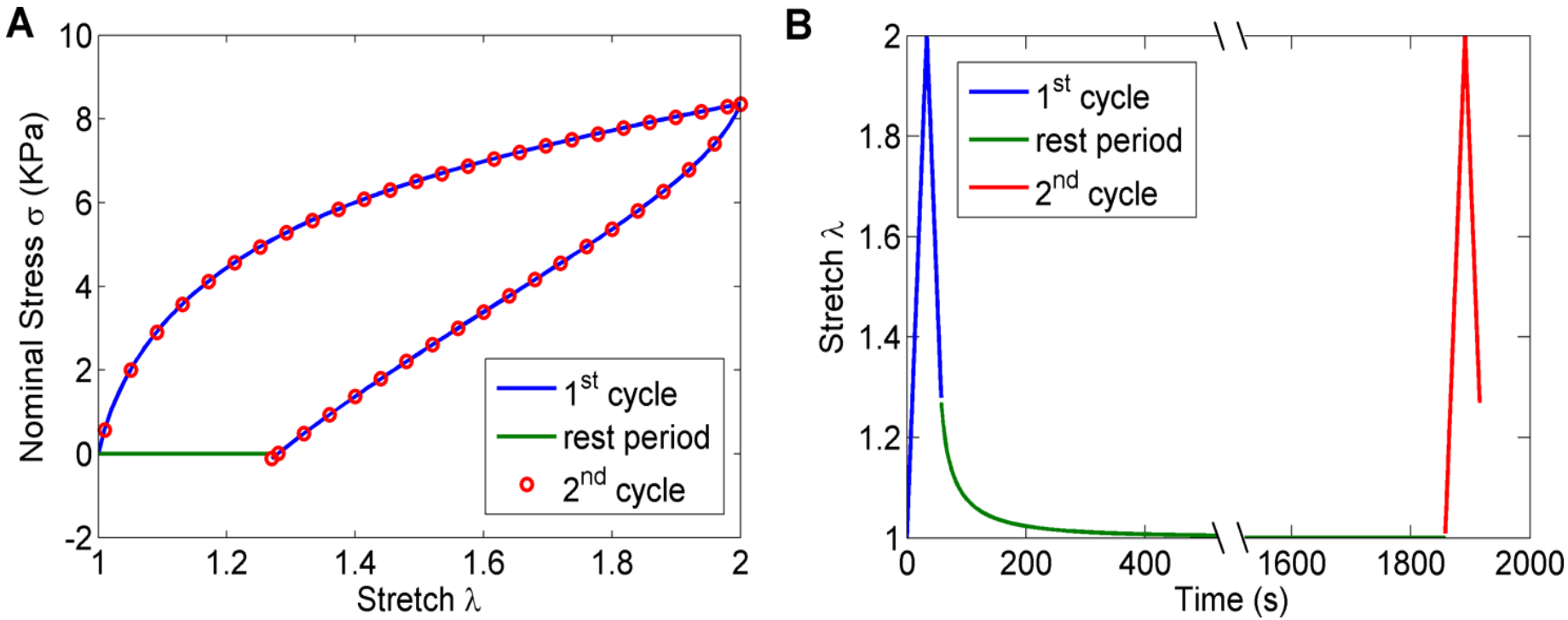


$\mu\rho = 2.6\ kPa$ $\mu\bar{\gamma}_\infty = 34\ kPa$ $t_B = 0.24\ s$ $\alpha_B = 1.6$

t_H = healing time $\bar{\gamma}_\infty = \dfrac{1-\rho}{t_H + \dfrac{t_B}{2-\alpha_B}}$ $t_H = 0.02\ s$

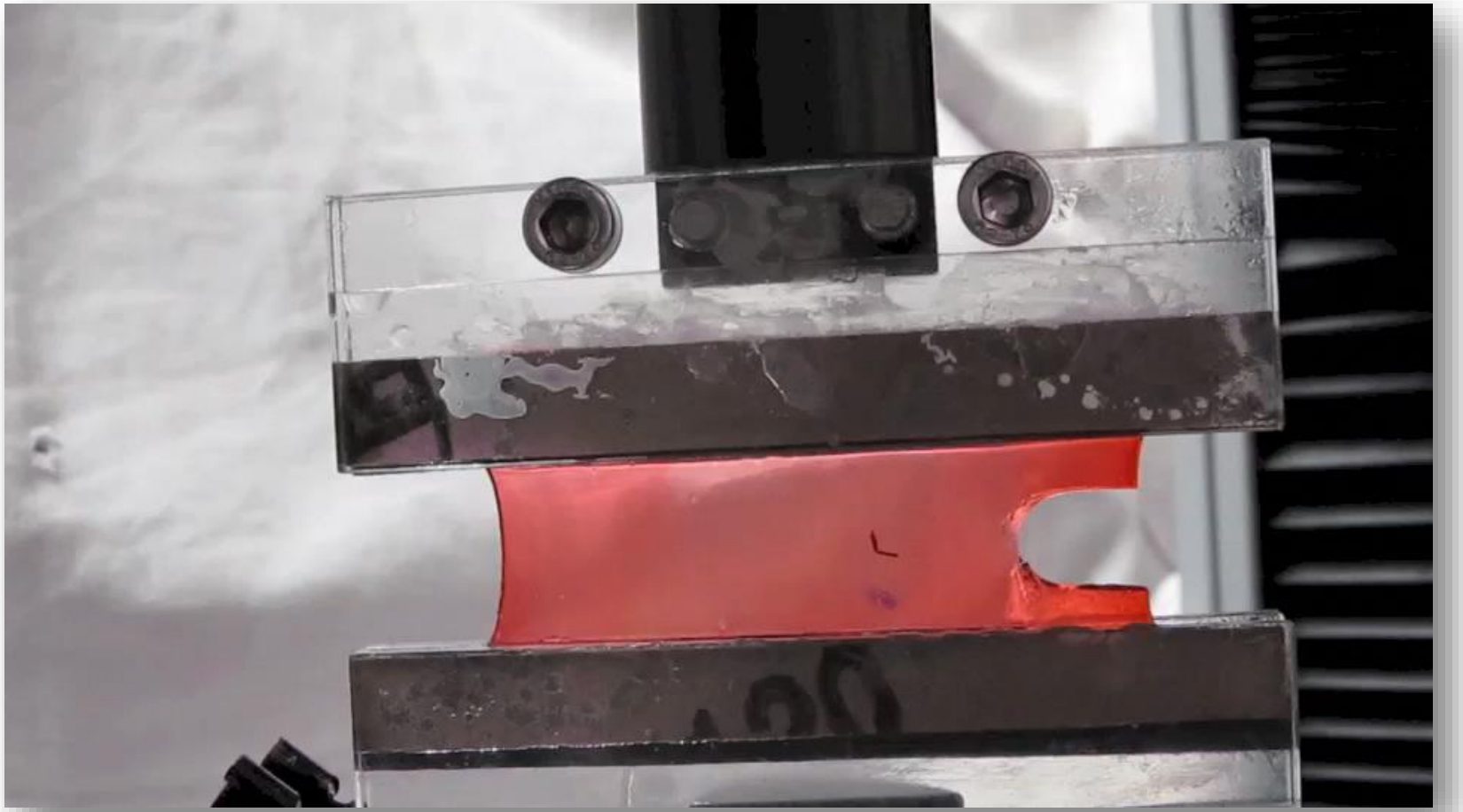
The model needs to keep track of the stress carried by each chain

Quantitative predictions of recovery with time with same parameters

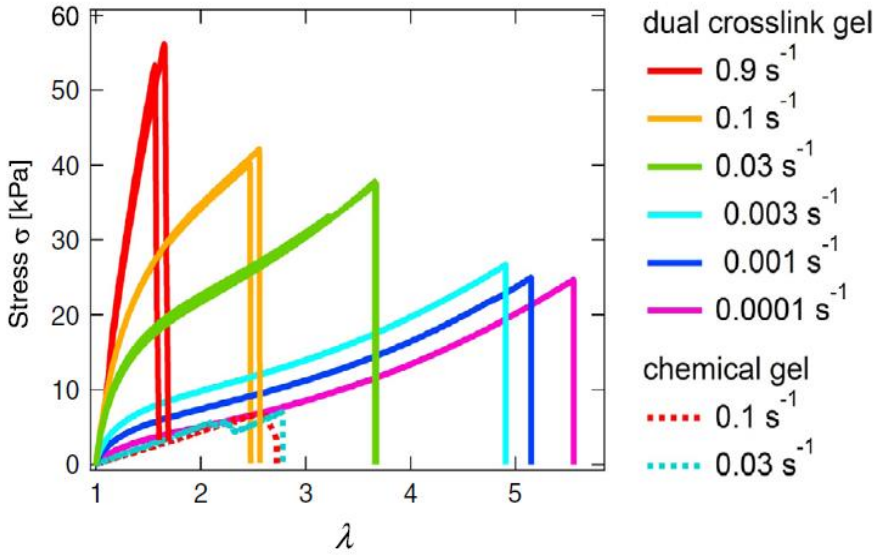


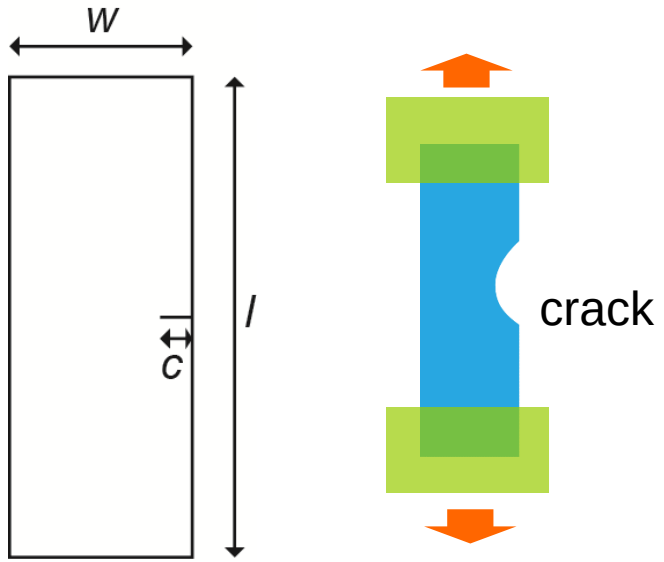
Macromolecules, **2016**, *49*, 3497-3507

How can we we use this model to understand fracture ?



Fracture experiment of the gels

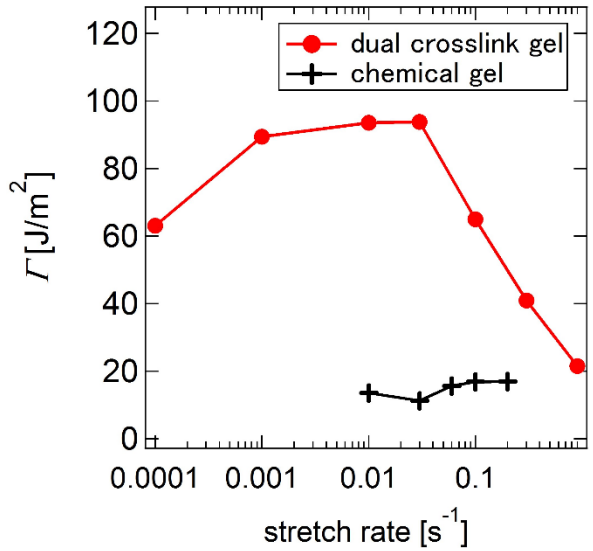




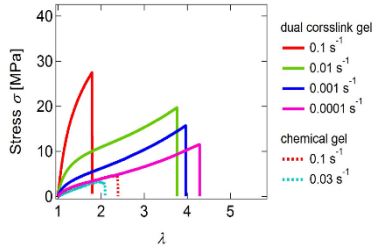
Fracture of notched samples

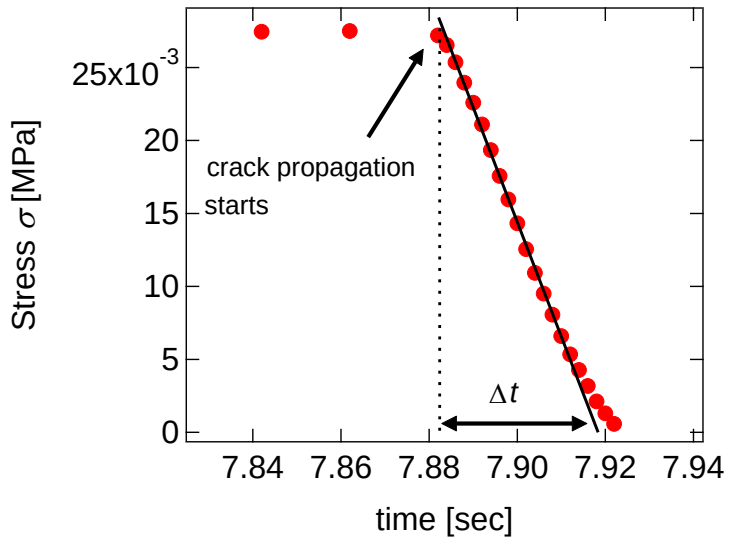
$$\Gamma = \frac{6}{\sqrt{\lambda_c}} cW(\lambda_c)$$

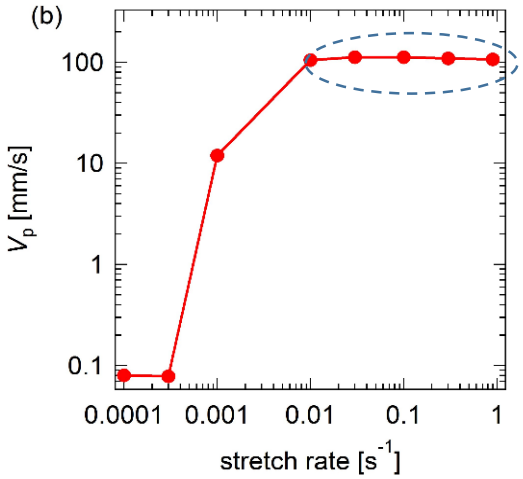
Classical way to calculate Γ



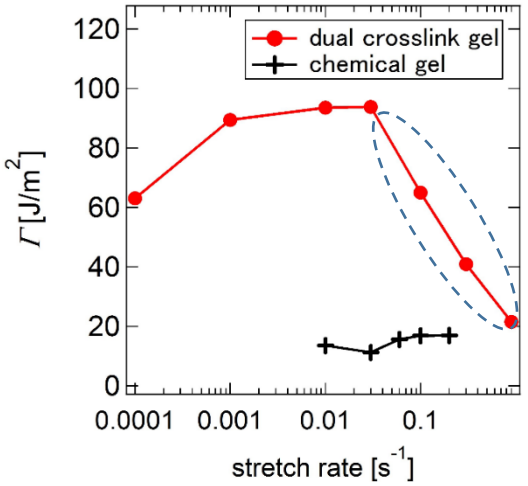
Crack propagation velocity during fracture

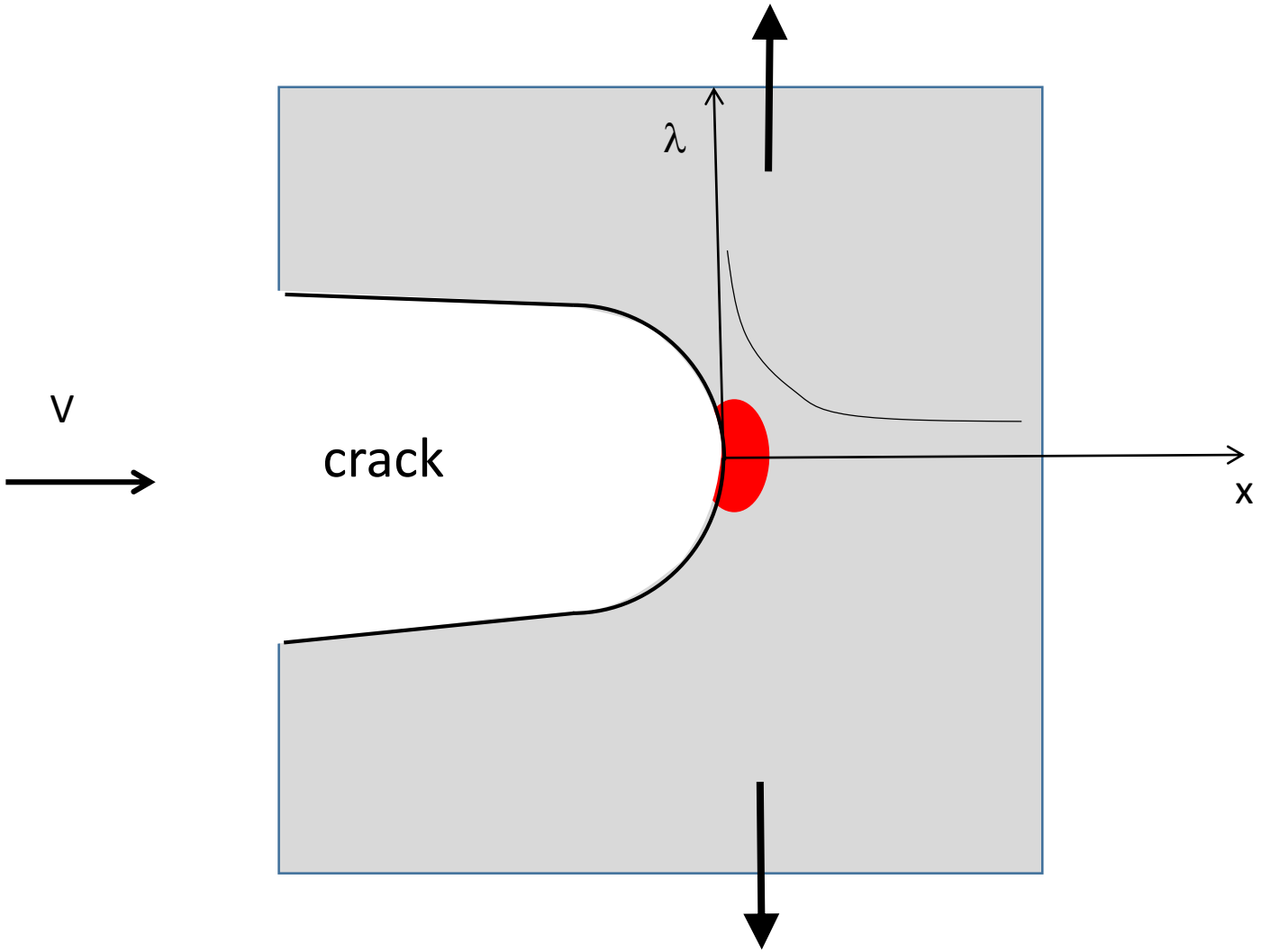






No unique $\Gamma(v)$
Relation ?



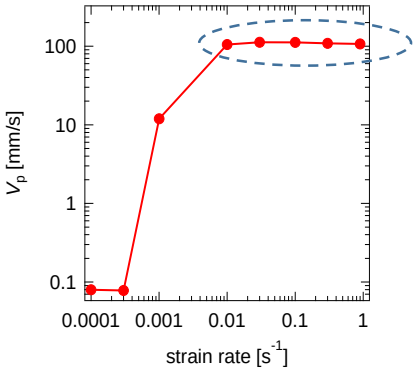


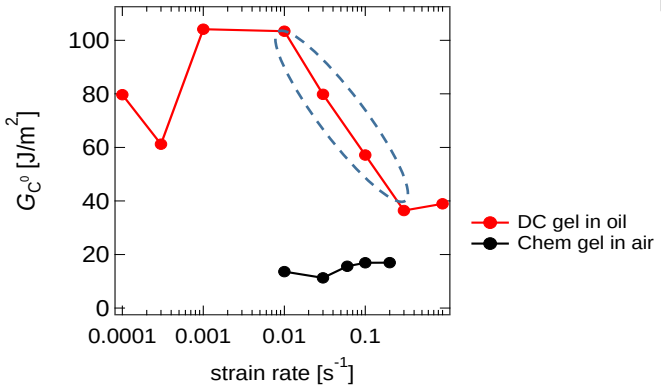
What controls crack propagation ?

Loading rate is controlled by the operator

Unloading rate is controlled by the crack speed

fast regime

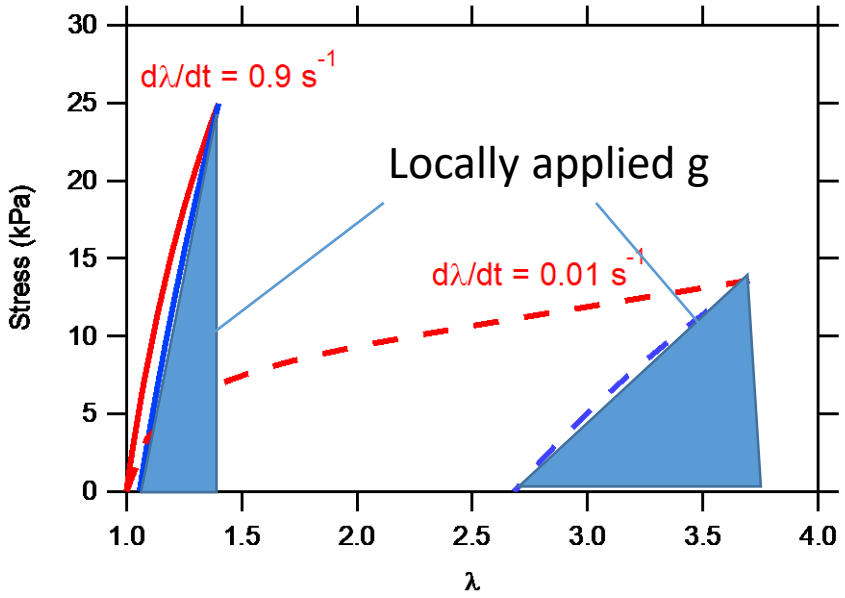




Loading rate is variable

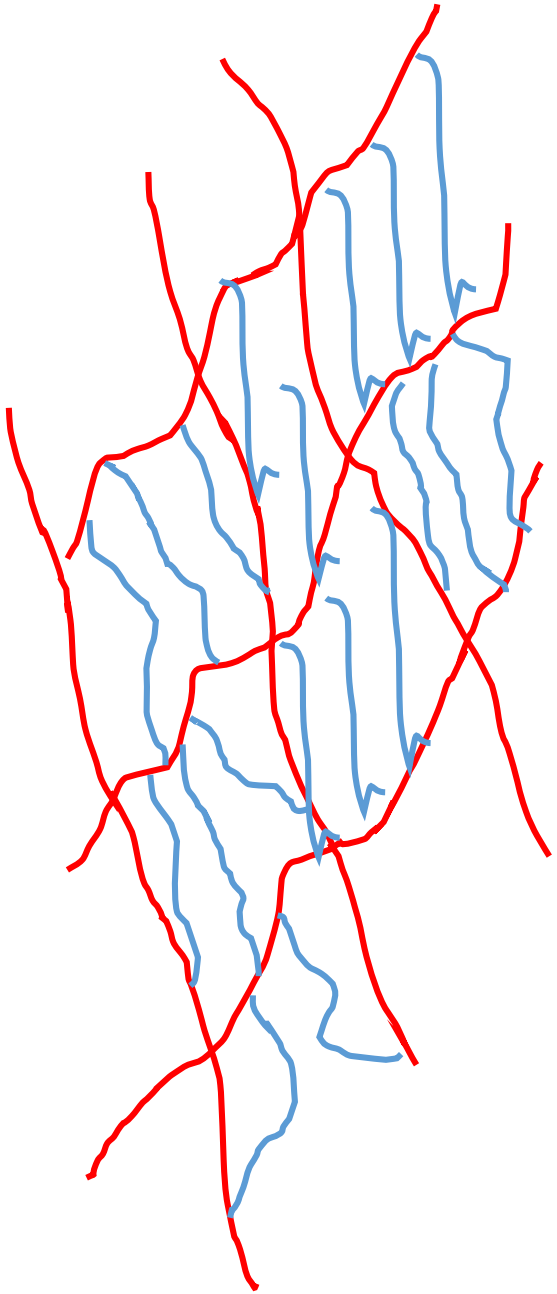
Unloading rate is constant and fast

Use the model to approximately simulate the fracture process:
Controlled loading-fast unloading

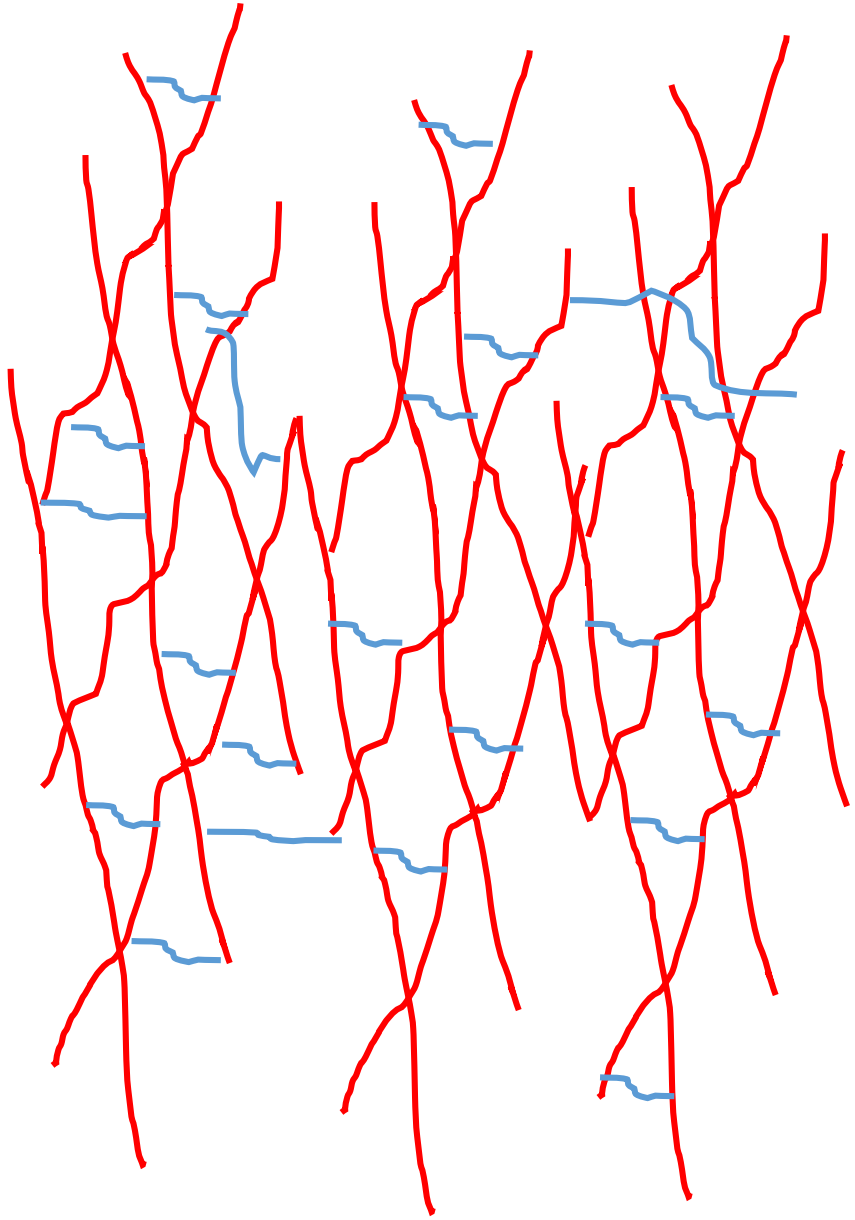


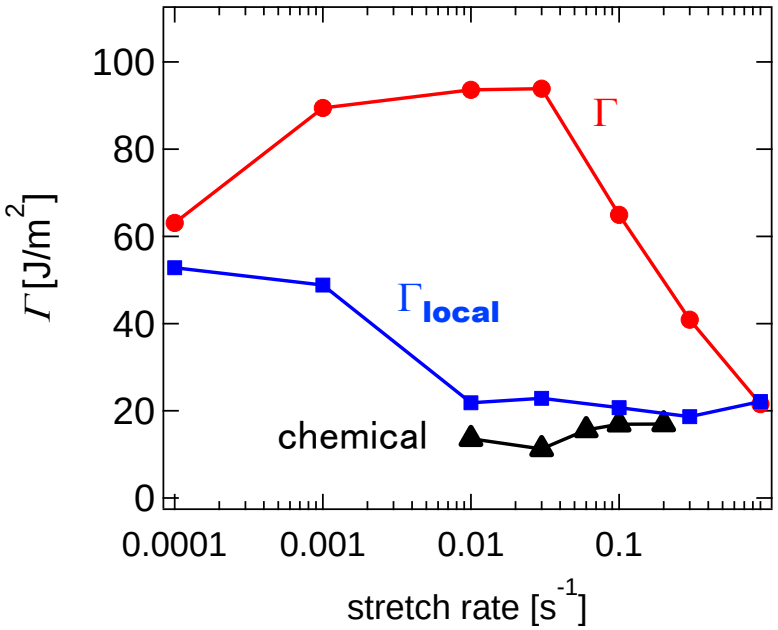
$$\Gamma_{local} = \frac{6}{\sqrt{\lambda_c}} cW_{unloading}(\lambda_c)$$

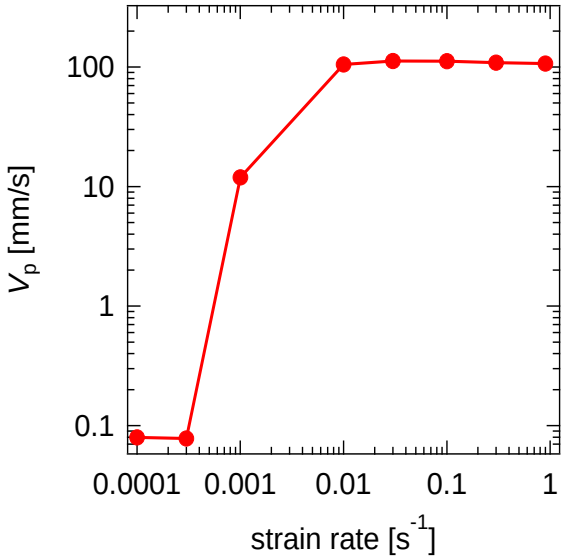
All strands are stretched and carry load



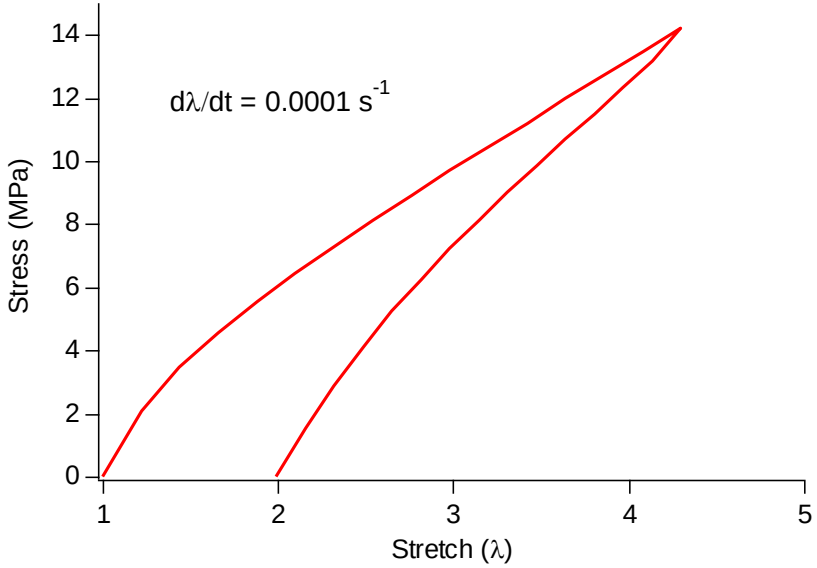
Only red strands carry load







Very slow regime



In this regime physical bonds are not dissipating energy during loading

However they need to be broken !

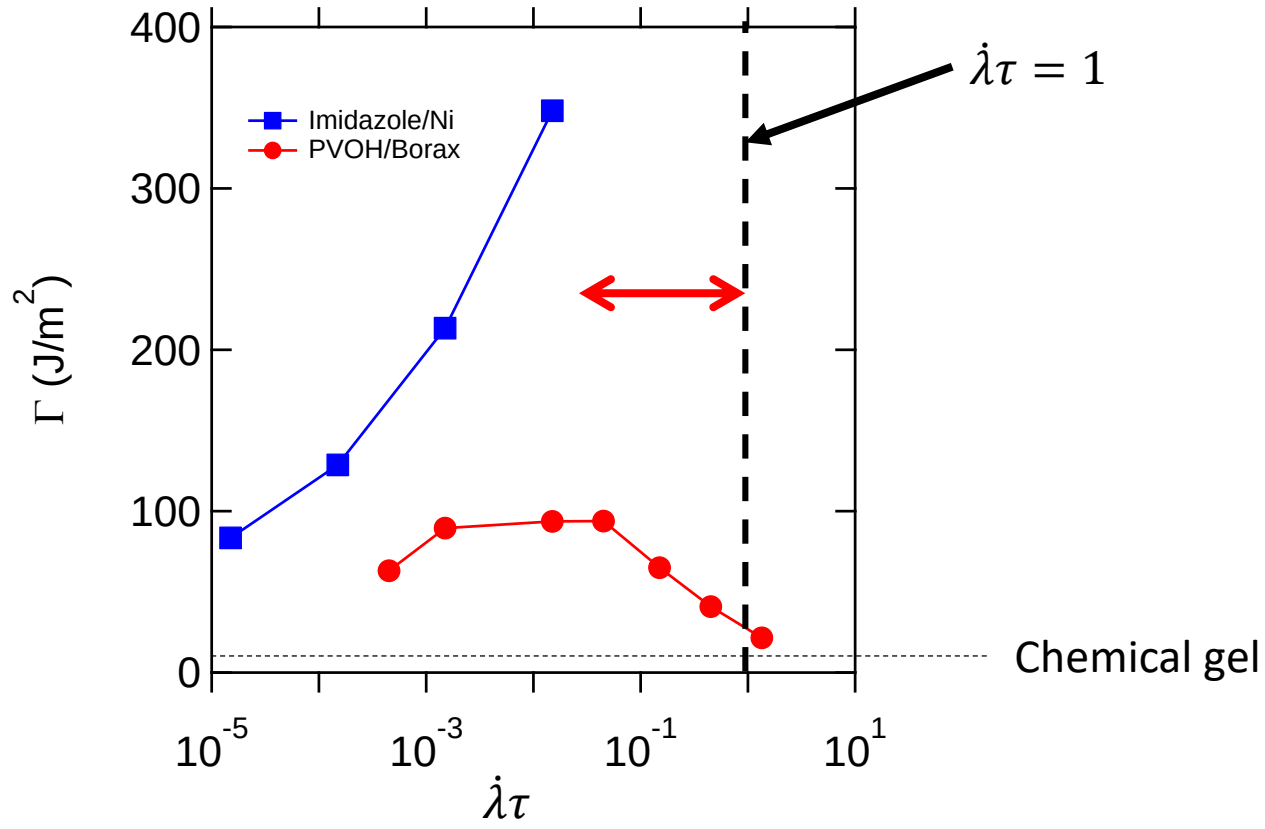
Relation between linear rheology and fracture

Normalized stretch rate

Define relaxation time τ as peak of G'' (ω)

Imidazole/ Ni^{++} : τ = 0.05 s

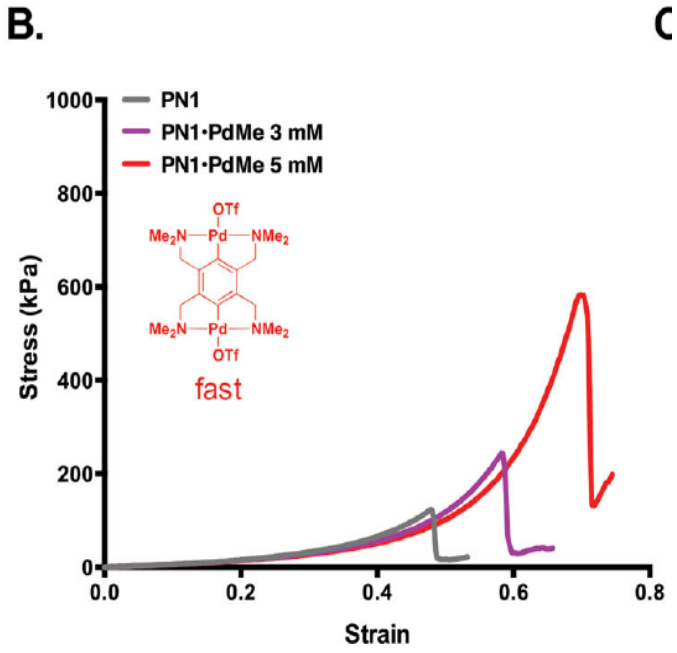
PVOH : τ = 1.5 s



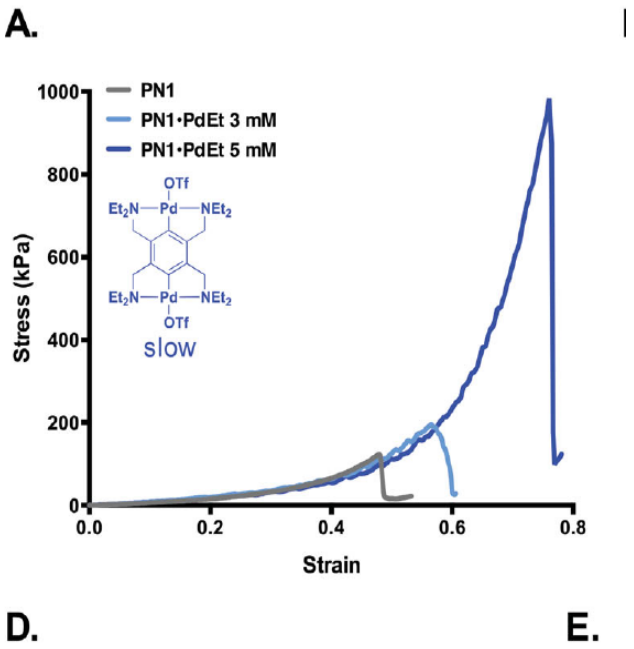
Bonds need to be dynamic to have an effect

Organogels with physical and chemical crosslinks

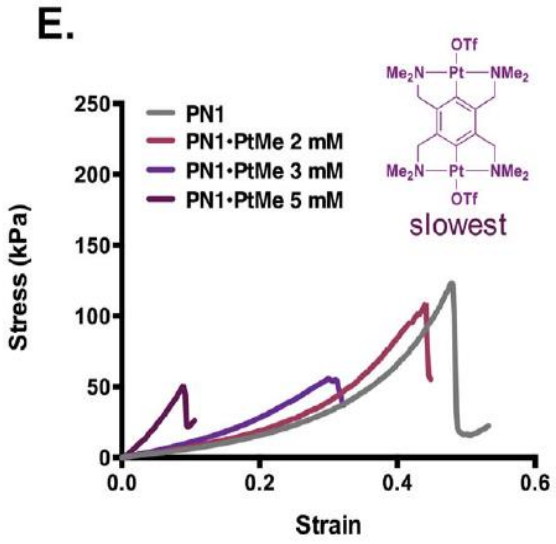
Uniaxial compression



$\dot{\lambda}\tau = 2x10^{-5}$



$\dot{\lambda}\tau = 10^{-3}$



$\dot{\lambda}\tau = 1$

Invisible crosslink increase strain and Stress at break

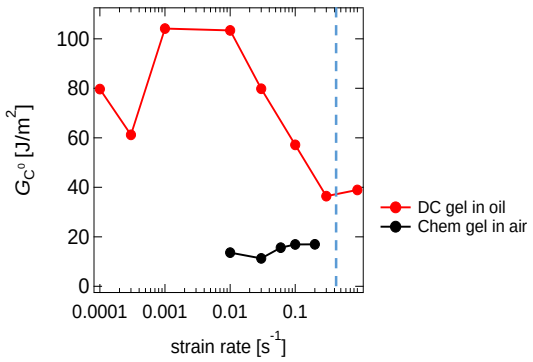
Kean, Z. S.; et al. *Adv Mater* ***2014, 26, 6013-6018***

Take-home messages: fast exchanging bonds

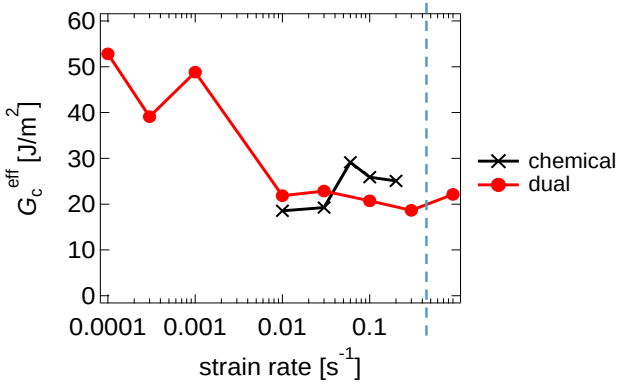
t_B ~ 0.5 s

τ ~ 1-2 s

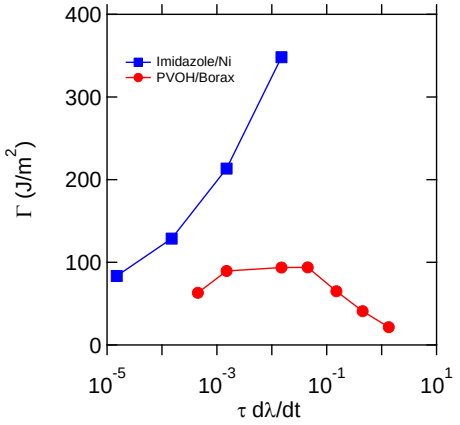
Initiation Γ



Propagation Γ



Molecular mechanisms that change local structure at the crack tip at fast rates can have important effects on fracture while being invisible during loading at usual loading rates



Optimum for $\dot{\lambda}\tau$ ~ 10^{-2}

Optimized for crack tip strain rates ?