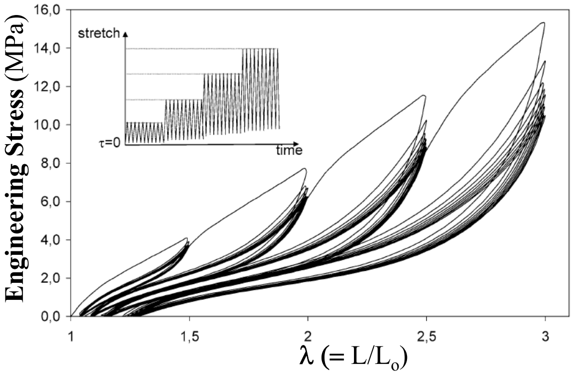
Mullins Effect and Thixotropy



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2006 NNF Summer Reading Series

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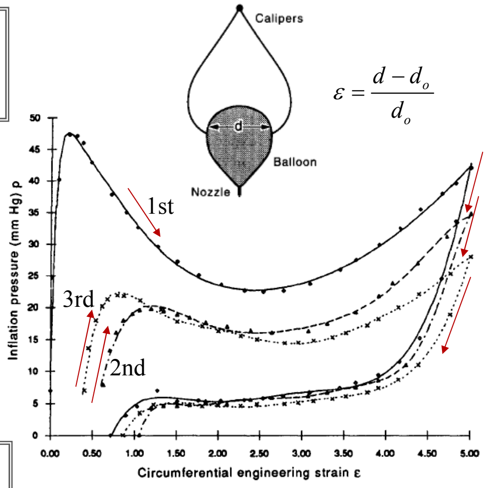
Articles

- Mullins, *J of Physical & Colloid Chem.*, 1950
- Joshi & Leonov, *Rheologica Acta*, 2001

Have you utilized the Mullins Effect?

Question
What do you do prior to inflating a toy balloon? Why?

Answer
You manually stretch the balloon prior to inflation to reduce the pressure needed to fully inflate the balloon.



$$\varepsilon = \frac{d - d_o}{d_o}$$

1 mm Hg = 133.3 Pa

Johnson & Beatty, *Int. J. of Eng. Sci.*, 1995

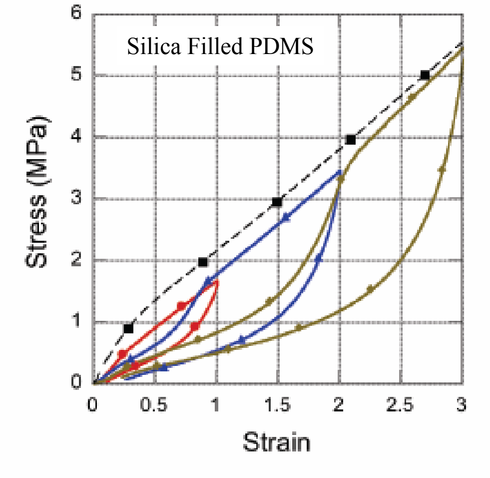
What is the Mullins Effect?

<u>Definition</u>

Phenomenon observed in elastomeric polymers where the equilibrium stress-strain response softens with the strain history.

<u>Characterized By</u>

- More compliant response at strains smaller than the previous maximum strain.
- Upon reloading the material joins the stress-strain response of the virgin material at strains greater than the previous maximum strain.
- The larger the maximum strain prior to unloading, the softer the response.



Hanson et al, *Polymer*, 2005

a.k.a Stress-Softening, Mullins Softening, Strain Softening, Stretch-Induced Softening, or Cyclic Softening

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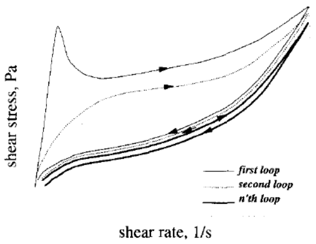
Where have we seen similar behavior?

Thixotropic/Hysteretic Loops



Barnes et al, *JNNFM*, 1997

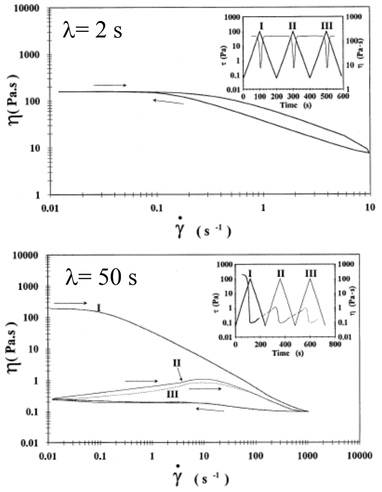
<u>Recall From Barnes & Giorgia</u>

Linear Viscoelasticity→ microstructure responds to flow but remains unchanged.

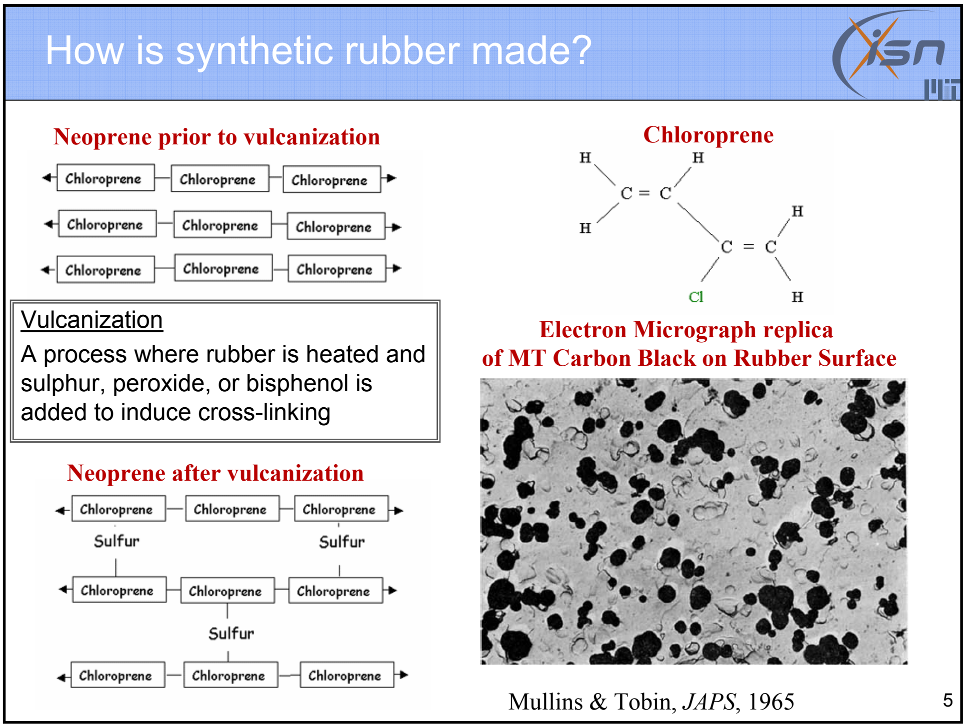
Thixotropy→ microstructure responds to flow, it breaks down with deformation, and it can be rebuilt with time.

Mullins Effect→ microstructure responds to flow and breaks down with deformation, but can not be rebuilt.

Micellar Solutions



Bautista et al, *JNNFM*, 1999



How is synthetic rubber made?

Neoprene prior to vulcanization

Vulcanization

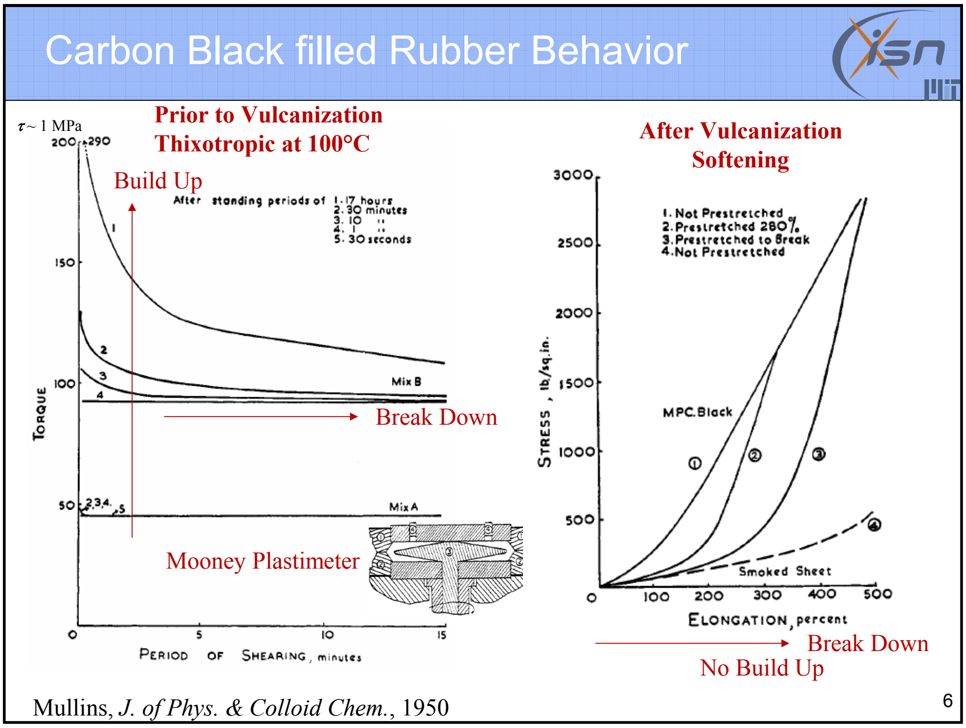
A process where rubber is heated and sulphur, peroxide, or bisphenol is added to induce cross-linking

Neoprene after vulcanization

Chloroprene

Electron Micrograph replica of MT Carbon Black on Rubber Surface

Mullins & Tobin, *JAPS*, 1965



Carbon Black filled Rubber Behavior

Prior to Vulcanization Thixotropic at 100°C

$\tau \sim 1$ MPa

Build Up

Break Down

Mooney Plastimeter

After Vulcanization Softening

Break Down

No Build Up

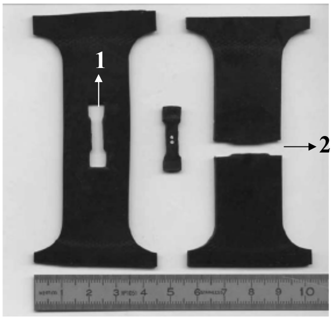
Mullins, *J. of Phys. & Colloid Chem.*, 1950

Does Mullins Effect induce anisotropy?

After Stretching

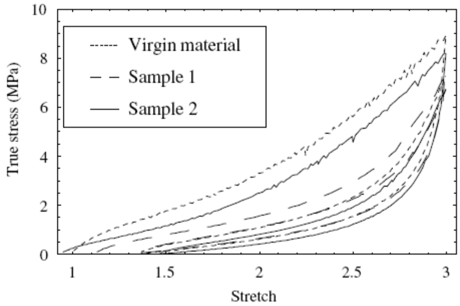
- Filled Rubber is harder than pure gum.
- Filled Rubber is more tear resistant than pure gum in direction perpendicular to stretch.
- Anisotropy cause for increased permenent set when filler is present.

Mullins, *J. of Phys. & Colloid Chem.*, 1950



Yes

Stress-softening is accompanied with a stretch induced anisotropy. Softening occurs in all directions but the greatest softening occurs in the stretch direction. The anisotropy is more pronounced in filled polymer systems.



Diani et al, *Int. J. Solid & Structures*, 2006

Mechanism(s) behind the Mullins Effect

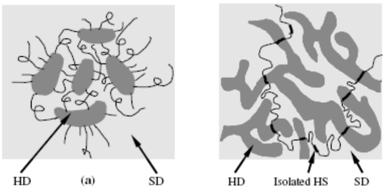
Non-filled Systems

- Structure break-up corresponds to disentanglement and orientation of the long-chain rubber molecules.

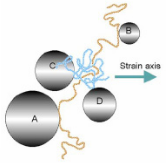
Filled Systems

- Structure break-up corresponds to particle-particle and particle-matrix interactions.

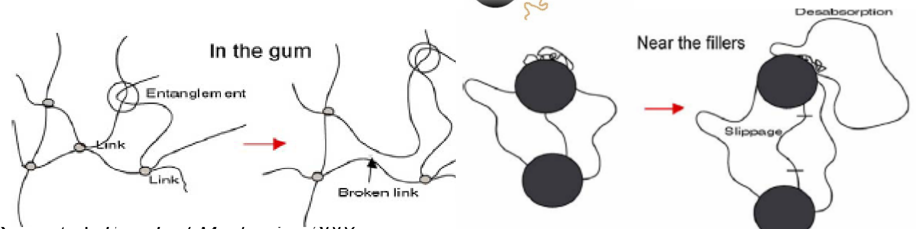
Mullins, *J. of Phys. & Colloid Chem.*, 1950



Qi & Boyce, *Mech. of Mat.*, 2005



Hanson et al, *Polymer.*, 2005



Diani et al, *Eur. J. of Mechanics*, 2006

Approaches to model Mullins Effect

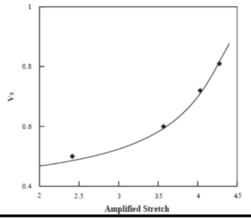
Hard & Soft Domain Decomposition

Break the microstructure into domains of hard and soft regions.

Account for domain evolution→ deformation breaks up hard region and creates a greater soft volume fraction

Amplification of the strain

Qi, Bergström, & Boyce
Mullins & Tobin



Damage Evolution

N*n = constant

n = chain density

N = average number of segments in a chain

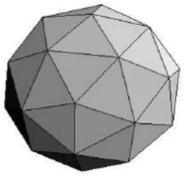
Marckmann, Simo,
Govindjee, & Lion

Direction Dependent Damage Evolution

Include directional weight

& Strain Amplification

Diani et al



Directional model

$$\Psi = \sum_i \omega_i \Psi_i\left(\underline{C}, \underline{u}_i\right)$$

Modeling of rubber from liquid to solid

Kinetics

Elastic Finger Tensor (aka Left Cauchy Green Tensor) $\mathbf{B} = \mathbf{F}\mathbf{F}^{\mathrm{T}}$

Free & Trapped Chain Finger Tensor Evolution (Incompressible)

$$2\theta \overset{\nabla}{\mathbf{B}}_{free/trap} + f_{free/trap}(I_1, I_2, \xi)\left[\mathbf{B}^2_{free/trap} + \mathbf{B}_{free/trap}\frac{(I_2 - I_1)}{3} - \boldsymbol{\delta}\right] = \mathbf{0}$$

$$f_{free} = b(I_1, I_2) = \exp\left[m\left(\frac{I_1}{3} - 1\right)\right]$$

$$f_{trap} = f(\xi) = \xi$$

$$I_1 = tr[\mathbf{B}]$$

$$I_2 = tr\left[\mathbf{B}^{-1}\right]$$

Debonding factor (ξ) evolution $\theta \frac{d\xi}{dt} + \xi = \theta \sqrt{2 \cdot tr\left[\frac{\nabla \mathbf{v} + (\nabla \mathbf{v})^T}{2}\right]^2} \frac{(1 - \xi)}{\gamma^*} \quad (0 \le \xi \le 1)$

Scalar Measure of Yield Strain

Modeling of rubber from liquid to solid

Free Energy, Stress, and Dissipation

Free Energy

$$\psi = \psi_{free} + \psi_{trap} + \psi^{(i)}{}_{trap,\xi} + \left(\psi_e\right)$$

$$\psi_{free/trap} = \frac{3G}{2\left(n+1\right)}\left\{\left(1-\beta\right)\left[\left(\frac{I_1}{3}\right)^{n+1} - 1\right] + \beta\left[\left(\frac{I_2}{3}\right)^{n+1} - 1\right]\right\}$$

Non-linear Parameters

β ($0 \le \beta \le 1$)

n ($n > 0$)

$$\psi_e = \frac{-1}{2} G_e \left(I_m^e - 3\right)\ln\left(\frac{I_m^e - I_1^e}{I_m^e - 3}\right)$$

1st Invariant at Fully Extended Limit

Stress

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_{free} + \boldsymbol{\sigma}_{trap} + \boldsymbol{\sigma}_e$$

$$\boldsymbol{\sigma}_{free} = 2\frac{\alpha+\xi}{1+\alpha}\left(\mathbf{B}_{free}\frac{\partial\psi_{free}}{\partial I_1} - \mathbf{B}_{free}^{-1}\frac{\partial\psi_{free}}{\partial I_2}\right)$$

$$\boldsymbol{\sigma}_{trap} = 2\frac{1-\xi}{1+\alpha}\left(\mathbf{B}_{trap}\frac{\partial\psi_{trap}}{\partial I_1} - \mathbf{B}_{trap}^{-1}\frac{\partial\psi_{trap}}{\partial I_2}\right)$$

$$\boldsymbol{\sigma}_e = 2\frac{\partial\psi_e}{\partial\mathbf{B}}$$

Dissipation

$$\mathbf{D} = \mathbf{D}_{free} + \mathbf{D}_{trap}$$

$$\mathbf{D}_{free/trap} = tr\left(\boldsymbol{\sigma}_{free/trap}\cdot\mathbf{e}_{free/trap}\right)$$

$$\mathbf{e}_{free} = \frac{b(I_1, I_2)}{2\theta}\left[\mathbf{B}_{free} - \mathbf{B}_{free}^{-1} + \frac{\boldsymbol{\delta}}{3}\left(I_2 - I_1\right)\right]$$

$$\mathbf{e}_{trap} = \frac{f(\xi)}{2\theta}\left[\mathbf{B}_{trap} - \mathbf{B}_{trap}^{-1} + \frac{\boldsymbol{\delta}}{3}\left(I_2 - I_1\right)\right]$$

Modeling of rubber from liquid to solid

Chemorheological Evolution

Relaxation Time

$$\theta_i\left(T, X\right) = \theta_{i0} f_1(T)\varphi_1(X)$$

$$\theta_i\left(X\right) = \theta_{i0} \qquad (i\text{=}1,2,\ldots,5) \quad (0 \le X \le 1)$$

$$\theta_6(X) = \theta^0{}_{long}(X) \quad (0 \le X \le X_c)$$

$$\theta_6(X) = \theta_{long}(X_c) \quad (X_c \le X \le 1)$$

$$\theta_i\left(X\right) = \text{prescribed} \qquad (i\text{=}7,\ 8,9)$$

Parameters found using small strain steady creep

$\alpha = 21.1$

$\gamma^* = 0.385$

Parameters found using intense steady shear flows

$m = 3$

$\beta = 0.4$

Relaxation Modulus

$G_i(\theta, T = T_0) = \text{use asymptotic fit to data} \quad (i\text{=}1,2,\ldots,5) \quad (0 \le X \le 1)$

$G_6(X) = G^0{}_{long} + k_1 X \quad (0 \le X \le X_c)$

$G_6(X) = G_{long}(X_c) + k_2(X - X_c) \quad (X_c \le X \le 1)$

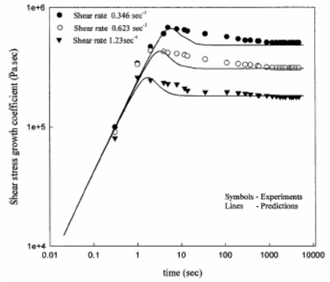
$G_i\left(X\right) = \text{prescribed} \quad (i\text{=}7,\ 8,9)$

$G_e = 0 \quad (0 \le X \le X_c)$

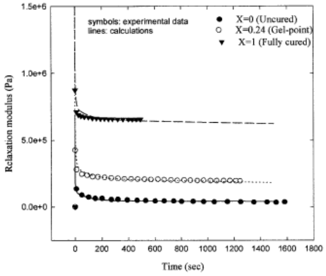
$G_e = k_s(X - X_c) \quad (X_c \le X \le 1)$

Joshi & Leonov Model Predictions

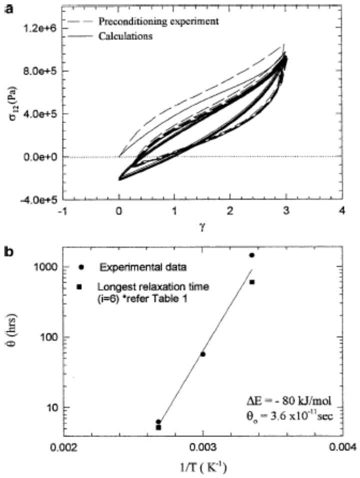
Yield Stress Behavior in Shear Start-Up



Stress Relaxation



Stress Softening



Question

Is stress-softening reversible?

Conclusions

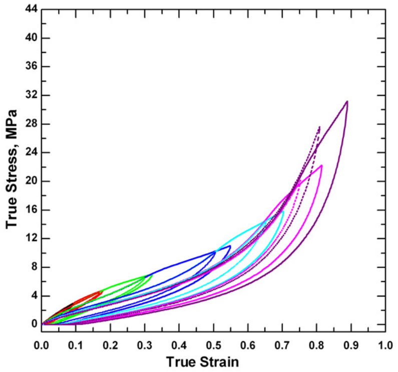
- Mullins Effect is a phenomenon observed in polymers where the material softens with strain history.
- Softening induces anisotropy.
- Softening is more prominent in filled-polymer systems.
- It is possible to utilize thixotropic kinetics to model the behavior of a rubber from solution, through vulcanization, to a solid.

Outstanding Question

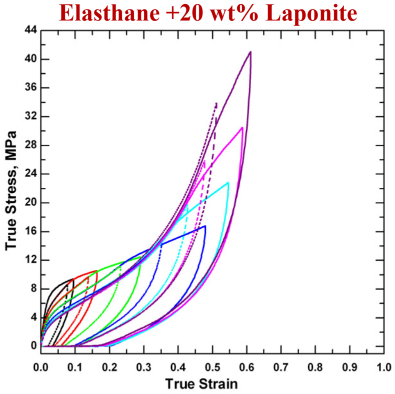
Is Mullins Softening Reversible?

Elasthane/Laponite Nanocomposites

Pure Elasthane



Elasthane +20 wt% Laponite



<u>Observations</u>

- Filled Elasthane is stiffer than pure Elasthane even after softening.
- The Mullins Effect is more pronounced in filled Elasthane.
- Anisotropy cause for increased permanent set in filled Elasthane.
- Yield at large deformations indicates particle-matrix interactions & at small deformations particle-particle interactions. What interactions dominate here?