Lecture 12

October 7, 2003
Mechanical behavior of polymers

- Temperature dependent ($T_G$ or $T_M$)
- Time dependent (viscoelastic)
- Time-temperature equivalence
Creep compliance

- Apply a constant stress $\sigma$ and measure the strain as a function of time $\varepsilon(t)$.

$$D_c = \frac{\varepsilon(t)}{\sigma}$$
Relaxation modulus

- Apply a constant strain $\varepsilon$ and measure the stress as a function of time $\sigma(t)$.

$$E_r = \frac{\sigma(t)}{\varepsilon}$$
Time-temperature equivalence

\[ \log E_r \] vs. \( \log t \)

Fix T

\[ \log E_r \] vs. \( T \)

Fix t
Time-temperature superposition

\[ \log E_r \]

\[ \log t \]

- Shift factor:

\[ \log a_T = \frac{C_1(T - T_0)}{C_2 + T - T_0} \]

\( C_1 \) and \( C_2 \) are roughly constants for polymers: \( C_1 = 17.5 \), \( C_2 = 52K \).
Linear viscoelasticity

- Mechanical analogs: represent viscoelastic behavior by combinations of elastic springs and viscous dashpots.

Maxwell model

Kelvin model
Maxwell model

\[ \varepsilon_T = \varepsilon_S + \varepsilon_D \quad \sigma_T = \sigma_S = \sigma_D \]

\[ \sigma_S = E \varepsilon_S \quad \sigma_D = \eta \frac{d\varepsilon_D}{dt} \]

• Differential stress-strain relation:

\[ \frac{d\varepsilon_T}{dt} = \frac{d\varepsilon_S}{dt} + \frac{d\varepsilon_D}{dt} = \frac{1}{E} \frac{d\sigma}{dt} + \frac{\sigma}{\eta} \]
Stress relaxation by Maxwell model

\[ \frac{d \varepsilon_T}{dt} = 0 \quad \rightarrow \quad \frac{d \sigma}{dt} = -\frac{E}{\eta} \sigma \]

\[ \sigma = \sigma_0 \exp \left( -\frac{E}{\eta} t \right) \]

Relaxation time: \[ \tau = \frac{\eta}{E} \]
Linear creep by Kelvin model

\[ \varepsilon_T = \varepsilon_S = \varepsilon_D \]
\[ \sigma_T = \sigma_S + \sigma_D \]

- Differential stress-strain relation:
\[ \sigma = E \varepsilon + \eta \frac{d\varepsilon}{dt} \]

\[ \varepsilon(t) = \frac{\sigma}{E} \left[ 1 - \exp \left( -\frac{E}{\eta} t \right) \right] \]
Combined model

\[ \begin{align*}
\dot{\sigma}_1 &= E_1 \left( \dot{\varepsilon}_1 - \frac{\dot{\sigma}_1}{\eta_1} \right) \\
\sigma_2 &= E_\infty \varepsilon_2 \\
\varepsilon_1 &= \varepsilon_2 = \varepsilon \\
\sigma_1 + \sigma_2 &= \sigma
\end{align*} \]

- Differential stress-strain relation:

\[ \dot{\sigma} - (E_1 + E_\infty) \dot{\varepsilon} = -\frac{E_1}{\eta_1} (\sigma - E_\infty \varepsilon) \]

Reduce to Maxwell model \((E_\infty = 0)\) or Kelvin model \((E_1 = \infty)\).
Creep compliance

• Creep test: fix $\sigma$ and measure $\varepsilon(t)$

\[-(E_1 + E_\infty) \dot{\varepsilon} = -\frac{E_1}{\eta_1} (\sigma - E_\infty \varepsilon)\]

$$\varepsilon(t) = \frac{\sigma}{E_\infty} - \frac{E_1 \sigma}{(E_1 + E_\infty)E_\infty} \exp\left(-\frac{E_1 E_\infty}{\eta_1 (E_1 + E_\infty)} t\right)$$

$$D_c(t) = \frac{\varepsilon(t)}{\sigma} = \frac{1}{E_\infty} - \frac{E_1}{(E_1 + E_\infty)E_\infty} \exp\left(-\frac{E_1 E_\infty}{\eta_1 (E_1 + E_\infty)} t\right)$$
Creep compliance

\[ D_c(\infty) \rightarrow \infty \]

\[ D_c(\infty) = \frac{1}{E_\infty} \]

\[ D_c(0) = \frac{1}{E_1 + E_\infty} \]
Relaxation modulus

• Relaxation test: fix $\varepsilon$ and measure $\sigma(t)$

$$\dot{\sigma} = -\frac{E_1}{\eta_1} (\sigma - E_\infty \varepsilon)$$

$$\sigma(t) = E_\infty \varepsilon + E_1 \varepsilon \exp\left(-\frac{E_1}{\eta_1} t\right)$$

$$E_r(t) = \frac{\sigma(t)}{\varepsilon} = E_\infty + E_1 \exp\left(-\frac{E_1}{\eta_1} t\right)$$

Note that: $E_r(t) \neq \frac{1}{D_c(t)}$
Relaxation modulus

\[ E_r(0) = E_\infty + E_1 \]

\[ E_r(\infty) = E_\infty \]

\[ E_r(\infty) \rightarrow 0 \]
Cross-linked polymers

\[ E_r(t) = E_\infty + \sum_{i=1}^{N} E_i \exp\left(-\frac{E_i}{\eta_i} t\right) \]

\[ E_r(0) = E_\infty + \sum_{i=1}^{N} E_i \]

\[ E_r(\infty) = E_\infty \]
Integral stress-strain relation

- Commonly used in general stress/strain analyses.
- The state of stress or strain depends on the history of the applied strain or stress, respectively.

\[
\sigma(t) = \int_{-\infty}^{t} E_r(t - \tau) \frac{d\varepsilon(\tau)}{d\tau} d\tau
\]

\[
\varepsilon(t) = \int_{-\infty}^{t} D_c(t - \tau) \frac{d\sigma(\tau)}{d\tau} d\tau
\]
Histories for creep/relaxation tests

Creep: \[
\frac{d\sigma}{dt} = \sigma_0 \delta(t)
\]

\[
\varepsilon(t) = \int_{-\infty}^{t} D_c(t-\tau) \frac{d\sigma(\tau)}{d\tau} d\tau = D_c(t)\sigma_0
\]

Relaxation: \[
\frac{d\varepsilon}{dt} = \varepsilon_0 \delta(t)
\]

\[
\sigma(t) = \int_{-\infty}^{t} E_r(t-\tau) \frac{d\varepsilon(\tau)}{d\tau} d\tau = E_r(t)\varepsilon_0
\]
Lab 6

- Tensile tests
  - Cyclic loading: hysteresis loop
  - Necking

- Relaxation tests
  - Temperature control
  - 10-second relaxation modulus, $E_r(t = 10s)$
  - Extract viscosity $\eta$ based on Maxwell model
Load-displacement hysteresis

- Energy dissipated as heat due to viscous damping
Necking

- Polyethylene forms a stable neck when it is drawn out: chains unfold, straighten, and align.
- The material becomes very strong when fully drawn: steep rising of the stress-strain curve.

*Fig. 23.10.* Cold-drawing of a linear polymer: the molecules are drawn out and aligned giving, after a draw ratio of about 4, a material which is much stronger in the draw direction than it was before.
Making nylon

• Melt spinning: molten polymer (polyamide) is spun and squeezed through small holes, which solidifies to form fibers.

• Drawing: the fibers are pulled until fully drawn.
Summary

- Creep compliance and relaxation modulus
- Temperature-time equivalence
- Linear viscoelasticity models
- Integral stress-strain relations
- Plastic deformation: necking/cold drawing