Constitutive Equations for Polymers

References:

- FA Morrison, *Understanding Rheology*, Oxford (2001)
- RG Larson, *Constitutive Equations for Polymer Melts and Solutions*, Butterworths (1988)
- RB Bird, RC Armstrong, O Hassager, *Dynamics of Polymeric Liquids*, Vol. 1+2, Wiley (1987)
- PJ Carreau, D DeKee, and RP Chhabra, *Rheology of Polymeric Systems*, Hanser (1997)

I. Elastic $\underline{\underline{\tau}}(t) = -G\underline{\underline{C}}^{-1}(t',t)$

II. Viscous

A. Newtonian $\underline{\underline{\tau}}(t) = -\mu\dot{\underline{\underline{\gamma}}}(t)$

B. Generalized Newtonian $\underline{\underline{\tau}}(t) = -\eta(\dot{\gamma})\dot{\underline{\underline{\gamma}}}(t)$ (see Carreau et al.)

1. Power Law GNF $\eta = m\dot{\gamma}^{n-1}$
2. Bingham Plastic GNF $\eta(\dot{\gamma}) = \begin{cases} \infty & \left|\underline{\underline{\tau}}\right| \le \tau_0 \\ \mu_o + \dfrac{\tau_0}{\dot{\gamma}} & \left|\underline{\underline{\tau}}\right| > \tau_0 \end{cases}$
3. Carreau-Yasuda GNF $\eta = \eta_\infty + (\eta_0 - \eta_\infty)\left[1 + (\dot{\gamma}\lambda)^a\right]^{\frac{n-1}{a}}$
4. Ellis GNF $\eta = \dfrac{\eta_0}{1 + \left|\dfrac{\tau}{\tau_0}\right|^{\alpha-1}}$
5. DeKee GNF $\eta = \eta_1 e^{-\lambda\dot{\gamma}} + \eta_2 e^{-0.1\lambda\dot{\gamma}} + \eta_\infty$
6. Casson GNF $\sqrt{\tau} = \sqrt{\tau_0} + \sqrt{\eta_0\gamma}$
7. Herschel-Bulkley Model $\eta = \dfrac{\tau_0}{\dot{\gamma}} + m\dot{\gamma}^{n-1}$
8. DeKee-Turcotte Model $\eta = \dfrac{\tau_0}{\dot{\gamma}} + \eta_1 e^{-\lambda\dot{\gamma}}$

III. Linear Viscoelastic $\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} G(t-t')\,\dot{\underline{\underline{\gamma}}}(t')\,dt'$

A. Maxwell $G(t-t') = \left[\dfrac{\eta_0}{\lambda} e^{\frac{-(t-t')}{\lambda}}\right]$

B. Generalized Maxwell $G(t-t') = \left[\sum_{k=1}^{N} \frac{\eta_k}{\lambda_k} e^{\frac{-(t-t')}{\lambda_k}} \right]$

C. Jeffreys $G(t-t') = \left[\frac{\eta_0}{\lambda_1}\left(1-\frac{\lambda_2}{\lambda_1}\right) e^{\frac{-(t-t')}{\lambda_1}} + 2\frac{\eta_0 \lambda_2}{\lambda_1}\delta(t-t') \right]$

D. Generalized Jeffreys $G(t-t') = \sum_{k=1}^{N} \left[\frac{\eta_k}{\lambda_k}\left(1-\frac{\Lambda_k}{\lambda_k}\right) e^{\frac{-(t-t')}{\lambda_1}} + 2\frac{\eta_k \Lambda_k}{\lambda_k}\delta(t-t') \right]$

IV. Nonlinear Viscoelastic

A. Continuum Modeling (organized by type of equation)

1. Differential Models

a. Quasilinear models

i. Upper-Convected Maxwell

$$\underline{\underline{\tau}} + \lambda \overset{\nabla}{\underline{\underline{\tau}}} = -\eta \underline{\underline{\dot{\gamma}}}$$

ii. Upper-Convected Jeffreys (Oldroyd B)

$$\underline{\underline{\tau}} + \lambda \overset{\nabla}{\underline{\underline{\tau}}} = -\eta\left(\underline{\underline{\dot{\gamma}}} + \lambda_2 \overset{\nabla}{\underline{\underline{\dot{\gamma}}}}\right)$$

iii. Lower-Convected Maxwell

$$\underline{\underline{\tau}} + \lambda \overset{\Delta}{\underline{\underline{\tau}}} = -\eta \underline{\underline{\dot{\gamma}}}$$

iv. Lower-Convected Jeffreys (Oldroyd A)

$$\underline{\underline{\tau}} + \lambda \overset{\Delta}{\underline{\underline{\tau}}} = -\eta\left(\underline{\underline{\dot{\gamma}}} + \lambda_2 \overset{\Delta}{\underline{\underline{\dot{\gamma}}}}\right)$$

v. Corotational Maxwell

$$\underline{\underline{\tau}} + \lambda \overset{\circ}{\underline{\underline{\tau}}} = -\eta \underline{\underline{\dot{\gamma}}}$$

vi. Corotational Jeffreys

$$\underline{\underline{\tau}} + \lambda \overset{\circ}{\underline{\underline{\tau}}} = -\eta\left(\underline{\underline{\dot{\gamma}}} + \lambda_2 \overset{\circ}{\underline{\underline{\dot{\gamma}}}}\right)$$

b. Models (quasi)linear in stress, at most quadratic in rate of deformation

i. Reiner-Rivlin

$$\underline{\underline{\tau}} = -\left(\phi_1(II_{\underline{\underline{\dot{\gamma}}}}, III_{\underline{\underline{\dot{\gamma}}}})\underline{\underline{\dot{\gamma}}} + \phi_2(II_{\underline{\underline{\dot{\gamma}}}}, III_{\underline{\underline{\dot{\gamma}}}})\underline{\underline{\dot{\gamma}}}^2\right)$$

ii. Second-Order Fluid

$$\underline{\underline{\tau}} = -\left(\eta_0 \underline{\underline{\dot{\gamma}}} - \frac{\Psi_1^0}{2}\overset{\nabla}{\underline{\underline{\dot{\gamma}}}} + \Psi_2^0 \underline{\underline{\dot{\gamma}}} \cdot \underline{\underline{\dot{\gamma}}}\right)$$

iii. Oldroyd 8-constant (frame-invariance considerations) (see Bird, et al. Vol. 1)

iv. Oldroyd 4-constant(frame-invariance considerations)) (see Bird, et al. Vol. 1)
v. Johnson-Segalman (nonaffine internal slip; see Larson)
vi. Phan-Thien Tanner (nonaffine internal slip; see Larson)

c. Models quadratic in stress

i. Giesekus model (anisotropic drag)

$$\underline{\underline{\tau}} + \lambda \overset{\nabla}{\underline{\underline{\tau}}} - \frac{\alpha\lambda}{\eta_0} \underline{\underline{\tau}} \cdot \underline{\underline{\tau}} = -\eta_0 \dot{\underline{\underline{\gamma}}}$$

ii. Leonov model (leakage of elastic strain; see Larson)

2. Integral Models

a. Based on quasilinear models

i. Lodge model

$$\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} \frac{\eta_0}{\lambda^2} e^{\frac{-(t-t')}{\lambda}} \underline{\underline{C}}^{-1}(t',t)\, dt'$$

ii. Lodge rubberlike liquid

$$\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} \frac{\partial G(t-t')}{\partial t'} \underline{\underline{C}}^{-1}(t',t)\, dt'$$

iii. Integral UC Jeffreys (Oldroyd B) model (same as Lodge Rubberlike Liquid with $G(t-t')$ given above under IIIC)

iv. Cauchy-Maxwell Model

$$\underline{\underline{\tau}}(t) = +\int_{-\infty}^{t} \frac{\eta_0}{\lambda^2} e^{\frac{-(t-t')}{\lambda}} \underline{\underline{C}}(t,t')\, dt'$$

v. Integral LC Jeffreys (Oldroyd A) model (given below, with $G(t-t')$ given above under IIIC)

$$\underline{\underline{\tau}}(t) = +\int_{-\infty}^{t} \frac{\partial G(t-t')}{\partial t'} \underline{\underline{C}}(t,t')\, dt'$$

b. General nonaffine motion models

i. K-BKZ models (rubber elasticity theory; no molecular assumptions)

$$\underline{\underline{\tau}}(t) = +\int_{-\infty}^{t} M(t-t') \left(2\frac{\partial U}{\partial I_2} \underline{\underline{C}} - 2\frac{\partial U}{\partial I_1} \underline{\underline{C}}^{-1} \right) dt'$$

ii. Rivlin-Sawyers models

$$\underline{\underline{\tau}}(t) = +\int_{-\infty}^{t} M(t-t') \left(\Phi_2(I_1,I_2)\underline{\underline{C}} - \Phi_1(I_1,I_2)\underline{\underline{C}}^{-1} \right) dt'$$

B. Molecular Modeling (organized by type of model)
   1. Temporary Networks (see Larson)
      a. Green-Tobolsky (UCM)
      b. Yamamoto (breakage probability depends on chain extension
      c. Phan-Thien Tanner (Yamamoto with different closure)
   2. Bead Spring (see Bird, et al. Vol. 2)
      a. Dumbbell (UCM)
      b. Rouse (Generalized UCM)
      c. Zimm
   3. Reptation (see Larson, current literature)
      a. Doi-Edwards (RS or K-BKZ)
      b. Refinements on DE (tube-length fluctuations, constraint release, chain stretching)
      c. Pom-pom (branched polymers)