17.Osamu_Katagiri.Individual_Infographic

Polymer Classification

Chemical Structure

- copolymer
  - graft
  - random
  - alternating
  - graft terpolymer
- Homopolymer
- graft copolymer
- Block copolymer

Structure

- Linear
- Branched
- Crosslinked

Tacticity

- Isotactic
- Syndiotactic
- Atactic

Intermolecular forces

- Elastomer
- Fiber

Thermal behavior

- Thermoplastic
- (no change)
- Thermoset

Monomer arrangement

Source

- Natural ocurring
  - Starch
  - Cellulose
  - Proteins
- Synthetic
  - Plastics

Synthesis

- Free radical
- Addition polymerization
  - Cationic/Anionic polymerization
  - Catallst
- Condensation polymerization

Polymerization

- Is a random process
- prone to mistakes in the spatial conformation

Chemical and Physical Properties

Molecular weight distribution (MWD)

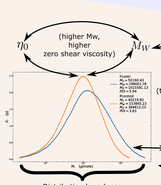
- number of individual chains
- Number average molecular weight
- Weight average molecular weight
- mass fraction
- molecules with different molecular weight
- Amount of high molecular weight chains
- Higher average molecular weight
- Polydisperity Index

$$M_n = \frac{\sum X_i}{\sum \frac{X_i}{M_i}}$$

$$M_W = \frac{\sum X_i M_i}{\sum X_i}$$

$$M_Z = \frac{\sum X_i M_i^2}{\sum X_i M_i}$$

$$PDI = \frac{M_W}{M_n}$$



- η_0 (higher Mw, higher zero shear viscosity)
- M_W
- η_∞ (thinner distribution, faster creep, slower recovery)
- M_Z
- Distribution broadness (wider distribution, higher PDI, steeper slope, lower MFI)
- PDI
- Slope of the viscosity curve

Chemical stability

- Temperature
- Strain
- Double bonds
- Free radicals
- Oxygen
- Ultraviolet exposure

- Avoid chain rupture with:
  - Thermal stabilizers
  - Additives
    - UV stabilizers
    - Antioxidant stabilizers
  - Avert high temperatures
  - Avoid frequent heating cycles

Processability

- Polymerization
- Degradation
- Molecular weight distribution
- Viscoelasticity
  - DPM
  - Additives
  - Temperature

Rheological test

- lower molecular weights maintain the Newtonian behavior at higher shear rates

$$complex\ viscosity\ \eta^*(\dot\gamma) = \frac{\sqrt{|G^*(\dot\gamma)|}}{\dot\gamma}$$

$$complex\ modulus\ G^*(\dot\gamma) = \Big[(storage/elastic\ modulus\ G'(\dot\gamma)\ [Pa])^2 + (loss/viscous\ modulus\ G''(\dot\gamma)\ [Pa])^2\Big]^{0.5}$$

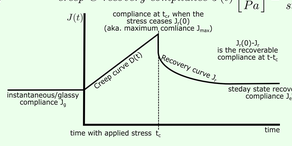
$$tan\ \delta = \frac{G''(\dot\gamma)}{G'(\dot\gamma)}$$

Oscillation test

- Compute the horizontal shift factor a_T
- Compute the vertical shift factor b_T

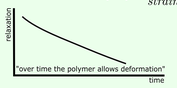
Constant stress test

$$creep\ \&\ recovery\ compliance\ J(t)\left[\frac{1}{Pa}\right] = \frac{strain}{stress}$$



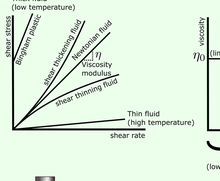
Constant strain test

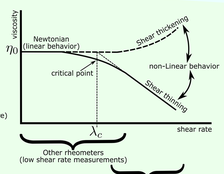
$$relaxation\ modulus\ G\ [Pa] = \frac{stress}{strain}$$



Constant shear rate test

$$viscosity\ modulus\ \eta\ [Pa \cdot s] = \frac{stress}{shear\ rate}$$



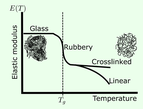


Other rheometers (low shear rate measurements)

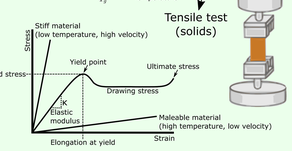
Capillary rheometers (high shear rate measurements)

- parallel plate
- high shear and low viscosities will determine the geometry
- the fluid may be "thrown" due to centrifugal forces
- cone and plate
- coaxial cylinder

Thermal behavior (Glass tansition temperature)



Tensile test (solids)

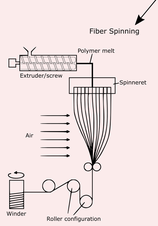


Polymer Processing

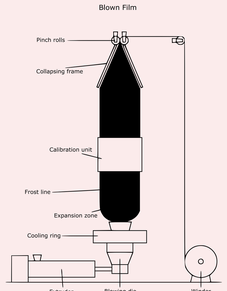
Extrusion

- Shrinkage (too much stress)
- Surging (speed variations)
- Lumpy surface (too cold)
- Bubbles (moisture)
- Pimples (resin gels)
- Shark skin (overheating)
- Extrusion defects
- Polymer rheology
- Cooling conditions
- Processing conditions
  - Die dimensions
  - Screw design
  - Relative draw speed to extrusion speed

Fiber Spinning



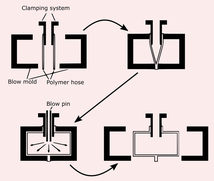
Blown Film



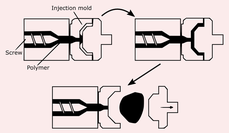
Injection

- Injection molding Defects
  - Warpage (unstructured design)
  - Jetting (high fill rate)
  - Splashes (clamp failure)
  - Charcoal-like edges (diesel effect)
  - Flash (high pressure)
  - Weld lines (uneven temperatures)
  - Ejector pin marks (early eject)
  - Silver-like surface (moisture)
  - Sink marks (thick wall sections)
  - Short Shot (low pressure)
- Processing conditions
  - Screw design
  - Injection Pressure
  - Mold layout
  - Clamping force
  - Shot size
- Injection Molding

Blow molding



Injection Molding



Empirical functions for viscosity data

$$\eta = \frac{\eta_0 - \eta_\infty}{\left[1 + (\kappa\dot\gamma)^n\right]^{\frac{(1-n)}{n}}} + \eta_\infty$$

Carreau-Yasuda

- η = Viscosity
- $\dot\gamma$ = Shear rate
- η_∞ = Infinite shear rate viscosity
- η_0 = Zero shear rate viscosity
- κ = Time constant
- n = The Power Law index
- a = The width of the transition region between the zero shear viscosity and the Power Law region

$$\eta = \frac{a - b}{\left[1 + (c\dot\gamma)^2\right]^{\frac{1-d}{2}}} + b$$

Carreau

- a = zero rate viscosity
- b = infinite rate viscosity
- c = consistency
- d = rate index

$$\eta = \frac{a}{1 + (b\dot\gamma)^c}$$

Williamson

- a = zero rate viscosity
- b = consistency
- c = rate index

$$\eta = m\dot\gamma^n$$

Power Law

- η = viscosity
- m = Consistency index
- n = Power Law index

$$\eta = \frac{a - b}{1 + (c\dot\gamma)^d} + b$$

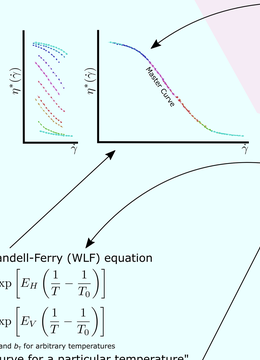
Cross

- a = zero rate viscosity
- b = infinite rate viscosity
- c = consistency
- d = rate index

$$\eta = a + b\dot\gamma^{c-1}$$

Sisko

- a = infinite rate viscosity
- b = consistency
- c = rate index



Williams-Landell-Ferry (WLF) equation

$$a_T = \exp\left[E_H\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$

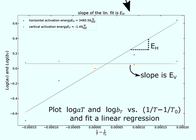
$$b_T = \exp\left[E_V\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$

Compute a_T and b_T for arbitrary temperatures

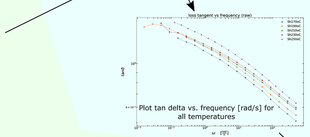
"Get the master curve for a particular temperature"

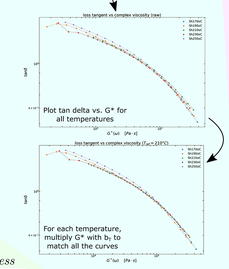
Time-Temperature Superposition TTS

- Get the activation energy E_H and E_V

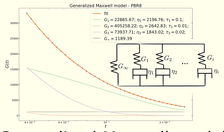


Extend the frequency range into a master curve





Generalized Maxwell model



$$G(t) = G_\infty + \sum_{i=1}^{n} G_i e^{-\frac{G_i}{\eta_i}t}$$

G_∞ is the relaxation modulus at $t = \infty$
G_i is the relaxation modulus of the ith spring
η_i is the viscosity of the dashpot for the ith series
n is the number of spring–dashpot series
τ_i is the relaxation time for a single spring–dashpot series

$$\tau_i = \frac{\eta_i}{G_i}$$

$$\lambda_i = \frac{\eta_i}{G_i}$$

Dymanic Mechanical data

$$G'(\omega) = \sum_{i=1}^{n} G_i \frac{\omega^2\lambda_i^2}{1 + \lambda_i^2\omega^2} \qquad G''(\omega) = \sum_{i=1}^{n} G_i \frac{\omega\lambda_i}{1 + \lambda_i^2\omega^2}$$

Memory function

- continuous

$$m(s) = \int \frac{H(\lambda)}{\lambda} e^{-\frac{t}{\lambda}} d\ln\lambda$$

$s = t - t'$

derivative of the relaxation modulus m(s) = G(s)/dt'

- discretized

$$\mu(t) = a_i e^{\frac{-t}{\lambda_i}}$$

Discrete relaxation spectra

$H(\lambda)\ in\ Pa$

a distribution moduli for the Generalized Maxwell model

$$G(t) = \int H(\lambda) e^{\frac{-t}{\lambda_\lambda}} d\ln\lambda_i$$

- $G_g = \int H(\lambda) d\ln\lambda$ — instantaneous modulus
- $\eta_0 = \int H(\lambda)\lambda \cdot d\ln\lambda$ — zero shear viscosity
- $J_e^0 = \frac{\int H(\lambda)\lambda^2 d\ln\lambda}{\left(\int H(\lambda)\lambda \cdot d\ln\lambda\right)^2}$ — steady state recoverable compliance

Constitutive Models

The motion and energy equations (Navier-Stokes) explain the flow of polymers and require a stress tensor in function of various kinematic tensors

- Damping function
- PTT model (PanThienTanner)
- Kinematic tensors
  - Finite Linear Viscoelasticity (Rubber-like liquid, or Lodge Network Theory)
    - Non-Linear behavior (Stress is a function of shear rate)
    - Cauchy & Finger Strain Tensors
      - Simple Shear

$$C_{ij}(t_1, t_2) = \begin{bmatrix} 1 & \gamma(t_2) - \gamma(t_1) & 0 \\ \gamma(t_2) - \gamma(t_1) & \left[1 + (\gamma(t_2) - \gamma(t_1))^2\right] & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$B_{ij}(t_1, t_2) = \begin{bmatrix} \left[1 + (\gamma(t_2) - \gamma(t_1))^2\right] & \gamma(t_2) - \gamma(t_1) & 1 \\ \gamma(t_2) - \gamma(t_1) & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

      - Simple Extension

$$C_{ij}(t_1, t_2) = \begin{bmatrix} e^{2\gamma(t_2)-\gamma(t_1)} & 0 & 0 \\ 0 & e^{-\gamma(t_2)-\gamma(t_1)} & 0 \\ 0 & 0 & e^{-\gamma(t_2)-\gamma(t_1)} \end{bmatrix}$$

$$B_{ij}(t_1, t_2) = \begin{bmatrix} e^{2\gamma(t_2)-\gamma(t_1)} & 0 & 0 \\ 0 & e^{-\gamma(t_2)-\gamma(t_1)} & 0 \\ 0 & 0 & e^{-\gamma(t_2)-\gamma(t_1)} \end{bmatrix}$$

  - Linear Infinitesimal Viscoelasticity (LIVE) "non-zero normal stress with increasing shear rate"
    - Simple Shear

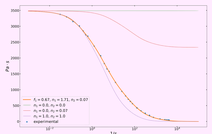
$$\gamma_{ij}(t \geq 0) = \begin{bmatrix} 0 & \gamma & 0 \\ \gamma & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

    - Simple Extension

$$\gamma_{ij}(t \geq 0) = \begin{bmatrix} 2\gamma_0 & 0 & 0 \\ 0 & -\gamma_0 & 0 \\ 0 & 0 & -\gamma_0 \end{bmatrix}$$

- Oscillatory data in the widest range (with high shear rate viscosity data)

Wagner model



Fit the Wagner model at several shear rates with $t = \infty$

$$\eta(t = \infty, \dot\gamma_0) = f_1 \sum_{i=1}^{n} \frac{a_i}{\alpha_i^2} + f_2 \sum_{i=1}^{n} \frac{a_i}{\beta_i^2}$$

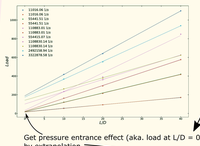
$$\alpha_i = \frac{1 + n_1\lambda_i\dot\gamma_0}{\lambda_i} \qquad \beta_i = \frac{1 + n_2\lambda_i\dot\gamma_0}{\lambda_i} \qquad f_2 = 1 - f_1$$

$\eta(t, \dot\gamma_0)$ = shear viscosity
t = time
$\dot\gamma_0$ = shear rate
a_i = the ith elastic value of the Maxwell element
λ_i = the ith characteristic time of the Maxwell element
f_1, f_2, n_1, n_2 are fitting parameters

with the fitted parameters, estimate:

- Recovery compliance
- Elongational viscosity
- Stress growth
- Creep compliance
- First normal stress difference
  - at constant shear rate
  - at constant shear stress

Bagley correction



Get pressure entrance effect (aka. load at L/D = 0) by extrapolation

$$corrected\ Load = apparent\ Load - Load_{at\ L/D\ =\ 0}$$

$$corrected\ Shear\ Stress = \tau_w = \frac{corrected\ Load}{2\pi \frac{Diameter_{capillary}}{2} Length_{die}}$$

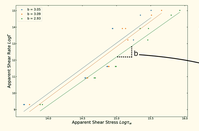
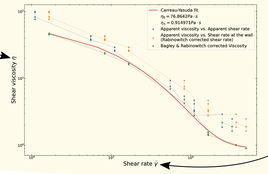
$$viscosity\ \eta = \frac{\tau_w}{\dot\gamma}$$

Rabinowitch correction

- Force applied
- applied pressure
- apparent shear stress
- corrected shear stress
- Capillary
- deformation/flow
- apparent shear rate
- corrected shear rate

$$Flow\ rate\ Q = Velocity\ \pi \frac{Diameter_{barrel}}{2}^2$$

$$apparent\ Shear\ Rate\ \Gamma = \frac{4Q}{\pi Radius_{capillary}}^3$$



$$corrected\ Shear\ Rate\ \dot\gamma = \frac{3 + b}{4}\Gamma$$