


1 What are polymers?

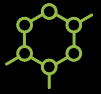


A polymer is a material composed of macromolecules consisting in a chain of repeating subunits. 

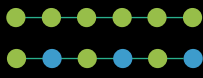
Polymers are found in everyday life as: **synthetic plastics** -> polystyrene, **natural biopolymers** -> DNA, and **proteins**.

2 Classification of polymers

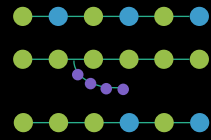
A Chemical structure



- Homopolymer
- Copolymer



- Alternating
- Graft
- Random



Chemical stability

Depends on:



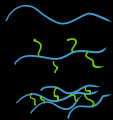
Can be aided though:

- Additives, stabilizers
- Averting high temperatures
- Avoiding frequent heating cycles

B Polymeric structure



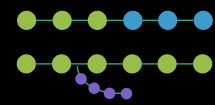
- Linear
- Branched
- Crosslinked



C Arrangement of monomers



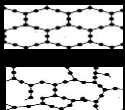
- Block copolymers
- Graft copolymers



D Crystallinity



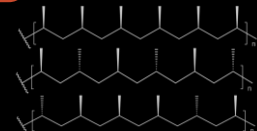
- Crystalline
- Amorphous



E Tacticity



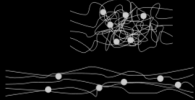
- Isotactic
- Syndotactic
- Atactic



F Molecular forces

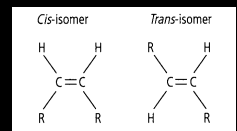


- Elastomers
- Fibers

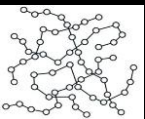


Space orientation

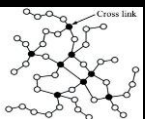
Polymeric chains are usually conformed in a zig-zag. Trans bonds make straight chains, cis bonds cause the chain to bend.



G Thermal behavior



- Thermoplastics can be melted and reformed



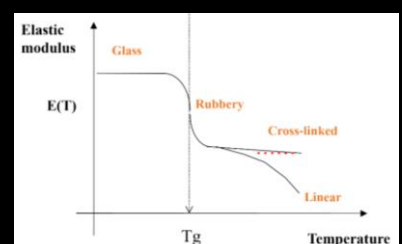
- Thermosets cannot be reformed

Glass transition temperature

Tg -> the temperature at which a material becomes softer

↓ branch size = ↑ Tg

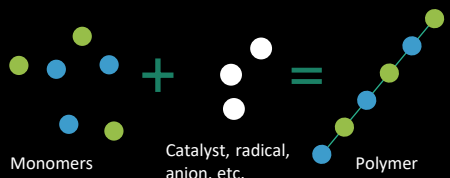
↑ crosslinks = ↑ Tg



H Methods of synthesis



- Addition
 - Free radical
 - Ionic
- Condensation
- Catalysts

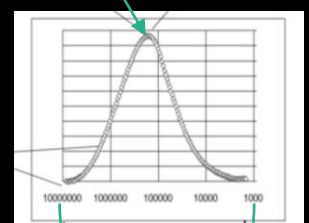


Random polymerization

- No. avg. molecular weight (Mn): number of molecules
- Weight avg. molecular weight (Mw): weight of molecules
- Polydispersity index (PDI): Mw/Mn

↑ PDI = ↑ Random = ↑ Wide of curve

Mn



PDI

3 Rheology

The study of the properties of matter which determine how it will deform/flow when subjected to an external force(s). It looks for a quantitative relation, modulus, between the force applied and the resulting deformation/flow.

3 Rheology



Internal variables that affect viscosity

- Molecular weight
 - ↑ MW = ↑ Viscosity
- Molecular weight distribution (PDI)
 - ↓ PDI = ↓ Velocity of viscosity decrease

- Molecular architecture
 - ↑ Branches = ↓ Viscosity
- Molecular shape
 - ↑ Entanglement = ↑ Viscosity
- Molecular concentration
 - ↑ Concentration = ↑ Viscosity



External variables that affect viscosity

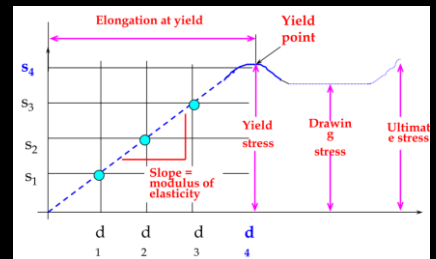
- Time
 - Rheopectic: ↑ Time = ↓ Viscosity
 - Newtonian: linear
 - Thixotropic: ↑ Time = ↑ Viscosity
- Pressure
 - ↑ Pressure = ↑ Viscosity
- Temperature
 - ↑ Temperature = ↑ Viscosity



Solids

Stress (s) = F/A , a force to cause deformation
 Strain (d) = $(L1-L0)/L0$, amount of deformation or elongation
 Elastic modulus (E) = slope

↓ Velocity = ↑ Temperature = ↑ Elastic modulus

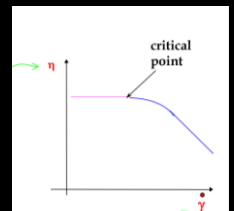


Liquids

Shear stress (τ_{yx}) = F/A
 Flow (Q) = A/v
 Viscosity (η) = slope



Q is translated to shear rate ($\dot{\gamma}$), how fast the velocity changes due to F
 $\eta = \tau_{yx} / \dot{\gamma}$



Zero shear viscosity: Newtonian viscosity (constant)
 Critical point: intersection of Newtonian and non-Newtonian behavior

Brookfield viscometer

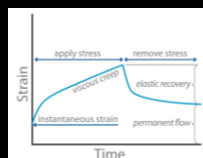
Measures viscosity



Rheometry

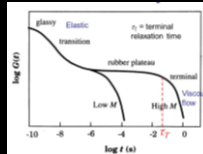
Creep and recovery compliance (J)

Constant stress → strain/stress
 Measures the deformation and recovery of the polymer



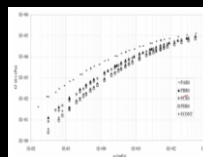
Relaxation modulus (G)

Constant strain → stress/strain
 Measures the response in time of the polymer against the plate



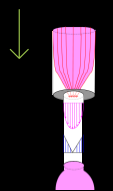
Complex modulus (G*)

Constant strain → stress/strain
 Measures the response in angular velocity (Oscillatory rheometry)



Capillary rheometry

- Rabinowitch correction for shear rate
- Bagley correction for shear stress



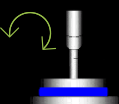
Parallel-plate rheometry

J is the compliance
 $J_r(0)$ compliance when stress ceases
 J_r compliance at any time after $J_r(0)$
 J_e^0 steady state recovery compliance
 J_g instantaneous or glassy compliance



Oscillatory rheometry

$|G^*(\omega)| = |G'(\omega)| + |G''(\omega)|$
 $\tan \delta = G''(\omega)/G'(\omega)$
 Complex viscosity $\eta^* = |G^*(\omega)|^{1/2} / \omega$

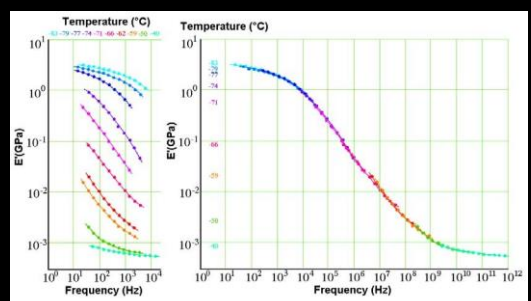


Time-Temperature superposition

- Obtain information at different temperatures G' , G'' , and get $\tan \delta$
- Shift data to superpose curves and get shift factors aT and, in the given case, bT
- Obtain the curve aT vs $\log(1/t - 1/t_0)$ and from slope obtain activation energy over the glass T_g
- With the Arrhenius equation obtain the aT and bT for the objective time
- Plot the master curve at the objective time

$$a_T = \exp \left[\frac{E_H}{R} \left(\frac{1}{T + 273} - \frac{1}{T_0 + 273} \right) \right]$$

$$b_T = \exp \left[\frac{E_V}{R} \left(\frac{1}{T + 273} - \frac{1}{T_0 + 273} \right) \right]$$



4 Viscoelastic Models

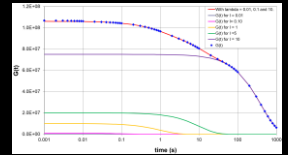
Linear

Maxwell elements

dashpot -> viscosity
spring -> elasticity

Obtain λ and G
Calculate $H(\lambda)$

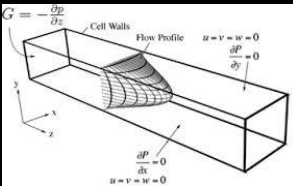
$$\eta_1 + \eta_2 + \dots + \eta_n =$$



Non-Linear

Navier-Stokes

Describes the flow of incompressible fluids



Mass equation

$$-(\vec{\nabla} \cdot \rho \vec{v}) = \frac{\partial \rho}{\partial t}$$

Momentum equation

$$\rho \left(\frac{\partial \vec{v}}{\partial t} + (\vec{v} \cdot \nabla) \vec{v} \right) = -\nabla p - \nabla \cdot \tau + \rho \vec{g}$$

$$\text{where } \vec{\nabla} \equiv \frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}$$

Constitutive equations

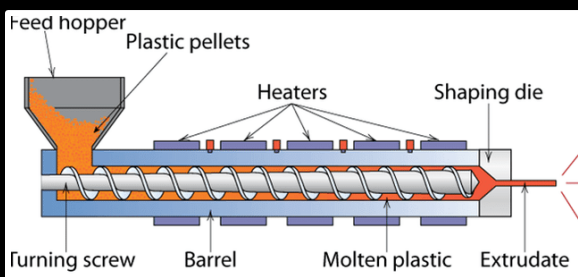
- Wagner model -> get n_1 and n_2 and then estimate normal stresses N_1 and N_2 , J_e , J_r , elongational viscosity η_e
- PTT model
- Rubber-like liquid model
 - Memory function
 - Damping function

Tensors (to use Maxwell as non-linear)

- Cauchy
- Finger Strain

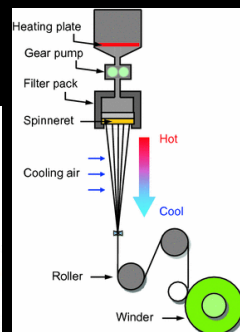
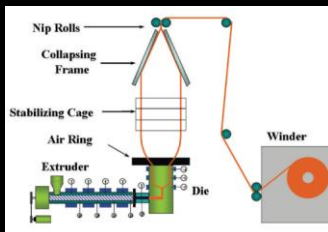
5 Polymer processing

A Extrusion



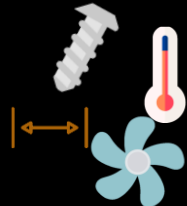
Some types of extrusion:

- Fiber-spinning (right)
- Blown film (below)



Important parameters:

- Screw rotating frequency
- Screw design
- Barrel temperature
- Cooling conditions
- Die dimensions
- Polymer characteristics

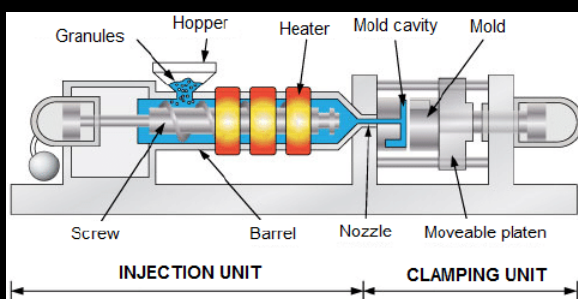


Defects:

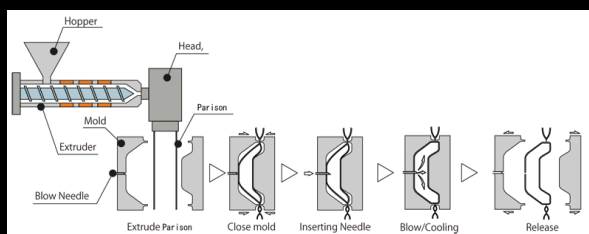
- Excessive shrinkage
- Surging
- Sharkskin / orange peel
- Pimples
- Lumpy surface
- Bubbles



B Injection Molding

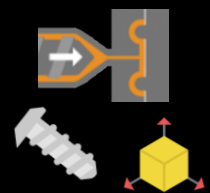


Blown Molding



Important parameters:

- Clamping force
- Shot size
- Injection pressure
- Screw design
- Mold design
- Polymer characteristics



Defects:

- Flash
- Sink marks
- Jetting
- Warpage
- Burn marks
- Weld lines



6 Final product performance!!!

