Plastics and Compostes Engineering

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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:

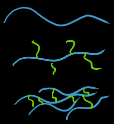
O_2

Can be aided though:

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

B Polymeric structure

- Linear
- Branched
- Crosslinked

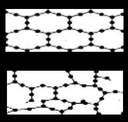


C Arrangement of monomers

- Block copolymers
- Graft copolymers

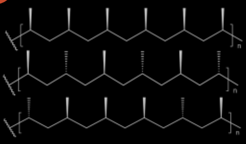
D Crystallinity

- Crystalline
- Amorphous



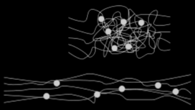
E Tacticity

- Isotactic
- Syndotactic
- Atactic



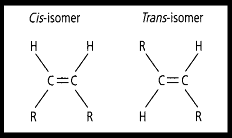
F Molecular forces

- Elastomers
- Fibers

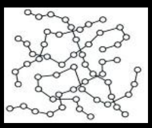


Space orientation

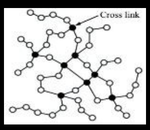
Polymeric chains are usually conformed in a zig-zag.
Trans bonds make straight chains, cis bonds cause the chain to bend.



G Thermal behavior



- Thermoplastics can be melted and reformed



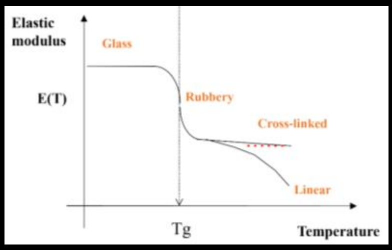
- Thermosets cannot be reformed

Glass transition temperature

Tg -> the temperature at which a material becomes softer

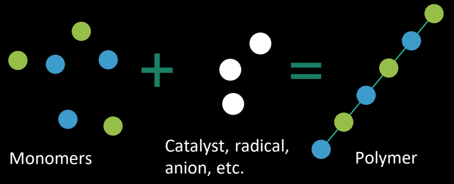
↓ branch size = ↑ Tg

↑ crosslinks = ↑ Tg



H Methods of synthesis

- Addition
  - Free radical
  - Ionic
- Condensation
- Catalysts

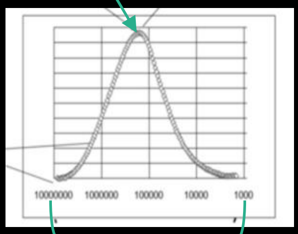


Random polymerization

- 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

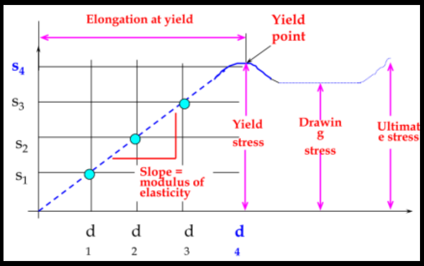
- Temperature

↑ Temperature = ↑ Viscosity

Solids

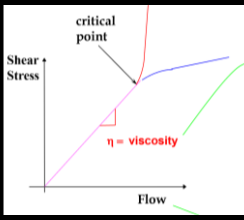
Stress (s) = F/A, a force to cause deformation
Strain (d) = (L1-L0)/L0, amount of deformation or elongation
Elastic modulus (E) = slope

↓ Velocity = ↑ Temperature = ↑ Elastic modulus

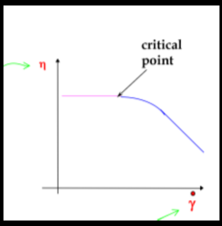


Liquids

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 η

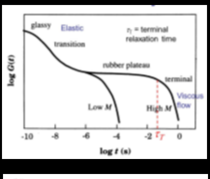
Rheometry

Creep and recovery compliance (J)

Constant stress -> strain/stress
Measures the deformation and recovery of the polymer

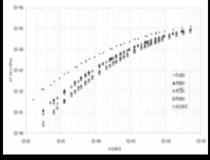
Relaxation modulus (G)

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



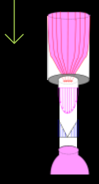
Complex modulus (G*)

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



Capillary rheometry

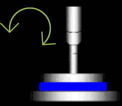
- Rabinowitch correction for shear rate
- Bagley correction for shear stress



Parallel-plate rheometry

J is the compliance
Jr(0) compliance when stress ceases
Jr compliance at any time after Jr(0)
Je^0 steady state recovery compliance
Jg instantaneous or glassy compliance

Oscillatory rheometry

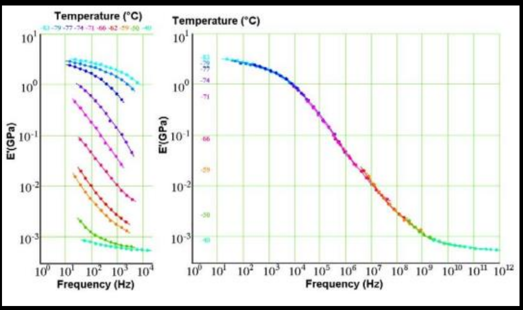


$|G^*(\omega)| = |G'(\omega)| + |G''(\omega)|$
$\tan\delta = G''(\omega)/G'(\omega)$
Complex viscosity $\eta^* = |G^*(\omega)|^{(1/2)}/\omega$

Time-Temperature superposition

1. Obtain information at different temperatures G', G'', and get tan δ
2. Shift data to superpose curves and get shift factors aT and, in the given case, bT
3. Obtain the curve aT vs log(1/t-1/t0) and from slope obtain activation energy over the gas cst
4. With the Arrhenius equation obtain the aT and bT for the objective time
5. Plot the master curve at the objective time

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



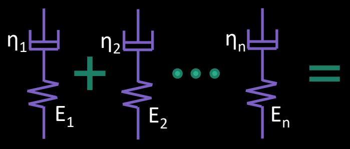
4 Viscoelastic Models

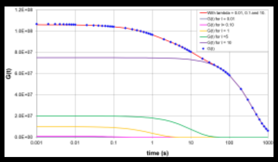
Linear

Maxwell elements

dashpot -> viscosity
spring -> elasticity

Obtain λ and G
Calculate H(λ)

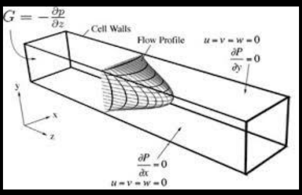




Non-Linear

Navier-Stokes

Describes the flow of incompressible fluids



Mass equation

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

+

Momentum equation

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

$$where \;\; \bar{\nabla} \equiv \frac{\partial \hat{\imath}}{\partial x} + \frac{\partial \hat{\jmath}}{\partial y} + \frac{\partial \hat{k}}{\partial z}$$

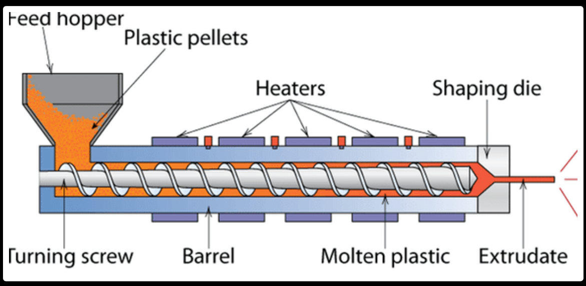
Constitutive equations

- Wagner model -> get n1 and n2 and then estimate normal stresses N1 and N2, Je, Jr, elongational viscosity η_e
- PTT model
- Rubber-like liquid model
  - Memory function
  - Damping function

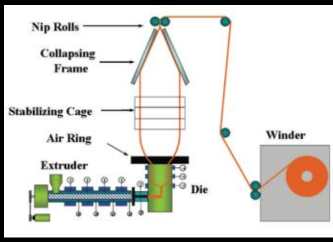
Tensors (to use Maxwell as non-linear)
- Cauchy
- Finger Strain

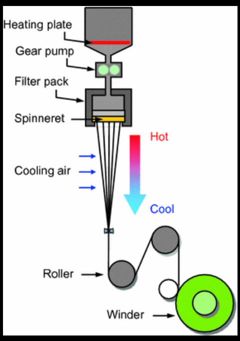
5 Polymer processing

A Extrusion



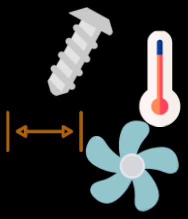
Some types of extrusion:
- Fiber-spinning (right)
- Blown film (below)





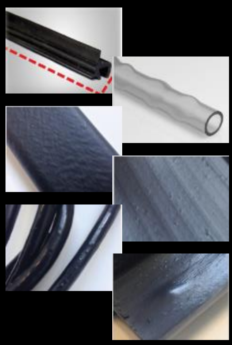
Important parameters:

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

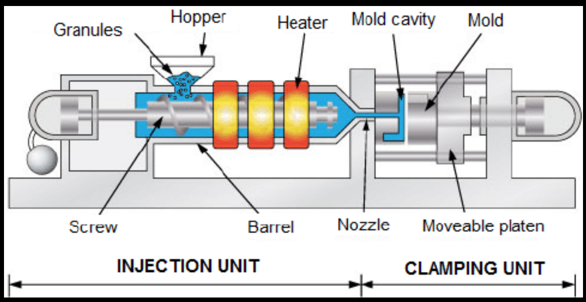


Defects:

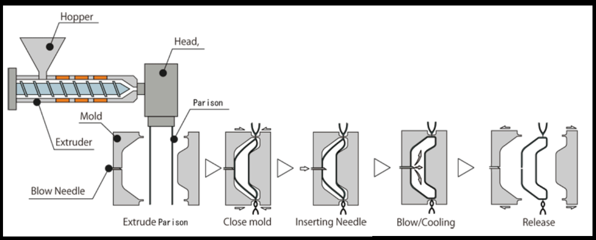
- Excessive shrinkage
- Surging
- Sharkskin / orange peel
- Pimples
- Lumpy surface
- Bubbles



B Injection Molding

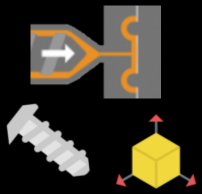


Blown Molding



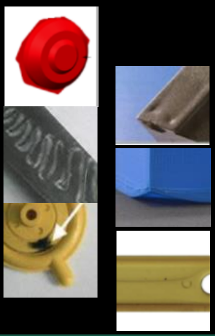
Important parameters:

- 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!!!