Polymers

Outline

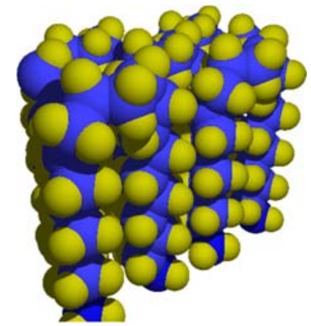
- Introduction
- Crystallinity
- Viscoelasticity
- Stress relaxation
- Advanced polymers - *applications*

Crystallinity in Polymers

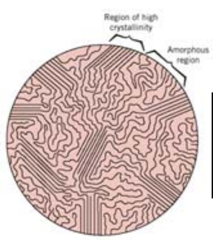
- Although it may at first seem surprising, polymers can form crystal structures (*all we need is a repeating unit, which can be based on molecular chains rather than individual atoms*)
- Some parts of structure align during cooling to form crystalline regions. (**Not** like FCC + BCC metals - *chains align alongside each other*)
- Around CRYSTALLITES the AMORPHOUS regions occur (*next slide*).

$$\%\ crystallinity = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$$

Where:
ρ_s = Density of sample
ρ_a = Density of the completely amorphous polymer
ρ_c = Density of the completely crystalline polymer



Crystallinity in Polymers



Most actual polymers contain both amorphous and crystalline regions, as shown above.

% crystallinity depends on several factors:

✓ Rate of cooling (…….. cooling – …….. crystallinity)
✓ Chain configuration (……… structures – …….. crystallinity)
(Copolymers – less crystallinity)

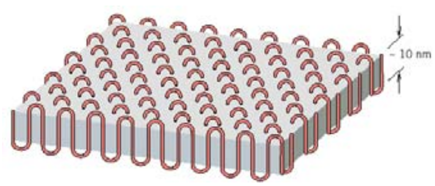
✓ Linear polymers form crystals more easily because the molecules can orient themselves readily

- Degree of Crystallinity ranges from 5 - 95%
- Higher % Crystallinity → higher strength

Polymer Crystallinity

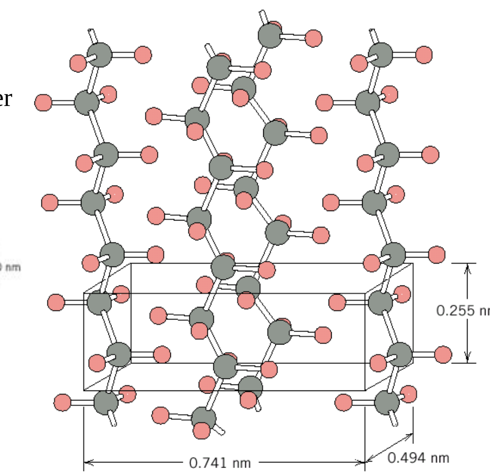
E.g.: polyethylene unit cell

- Crystals must contain the polymer chains in some way
  - Chain folded structure



Adapted from Fig. 14.12, *Callister 7e.*

Adapted from Fig. 14.10, *Callister 7e.*



Polymer Crystallinity

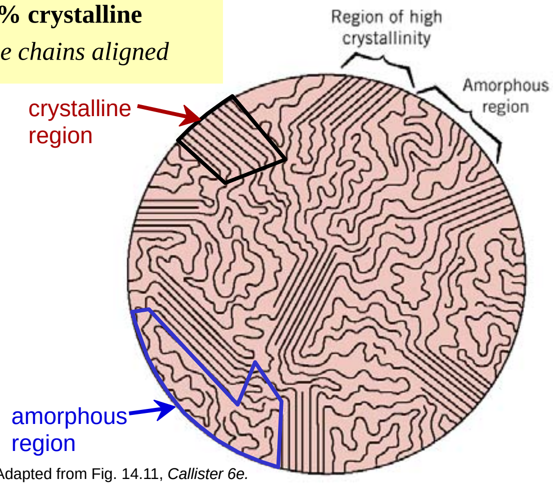
Polymers rarely exhibit 100% crystalline

- *Too difficult to get all those chains aligned*

- % Crystallinity:

  how much of the material is crystalline?

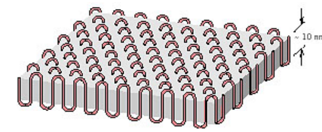
  - *TS* and *E* often ………. with % crystallinity.
  - Annealing causes crystalline regions to grow. % crystallinity …………….

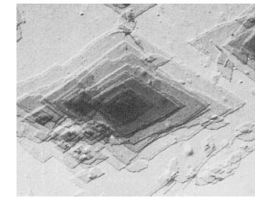


Adapted from Fig. 14.11, *Callister 6e.* (Fig. 14.11 from H.W. Hayden, W.G. Moffatt, J. Wulff, *The Structure and Properties of Materials*, Vol. III, *Mechanical Behavior*, John Wiley, Inc., 1965.)

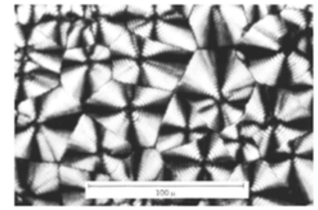
Polymer Crystal Models

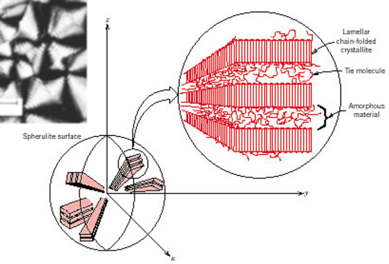
Chain folded model: crystals are actually small platelets of interwoven polymer chains





In many bulk polymers crystallized from the melt, these platelets often arrange themselves in radiating patterns to form ***spherulites****.*





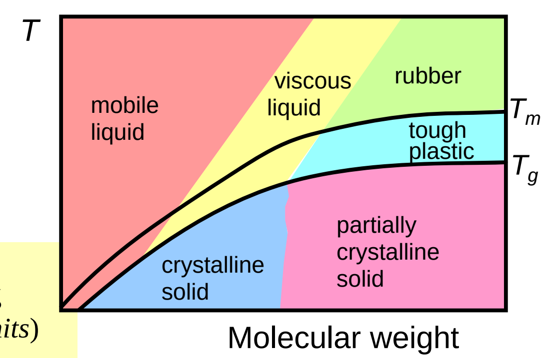
Effect of Crystallinity on Mechanical Properties

How does the % crystallinity affect the mechanical properties?

- In a semi-crystalline polymer, a higher level of crystallinity will provide:
  - Higher modulus of elasticity
  - Higher yield strength
  - Lower elongation
  - lower toughness
- The chains in the crystalline region are closely packed and cannot slide past one another.
- This does not necessarily mean that a semi-crystalline material will be always …….. than an amorphous material.
- It is more a matter of the individual material's ……………… and the ……… ……. in relation to its …..

Thermoplastics vs. Thermosets

- Thermoplastics:
  - little crosslinking
  - ductile
  - soften w/heating
  - polyethylene polypropylene polycarbonate polystyrene
- Thermosets:
  - significant crosslinking (*10 to 50% of repeat units*)
  - hard and brittle
  - do NOT soften w/heating
  - vulcanized rubber, epoxies, polyester resin, phenolic resin

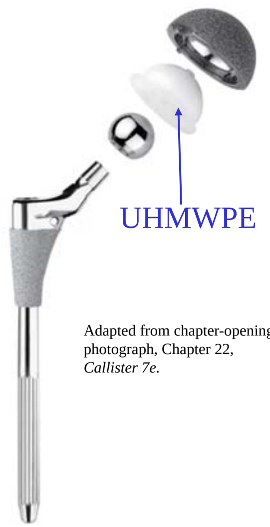


Adapted from Fig. 15.19, *Callister & Rethwisch 8e.* (Fig. 15.19 is from F.W. Billmeyer, Jr., *Textbook of Polymer Science*, 3rd ed., John Wiley and Sons, Inc., 1984.)

Advanced Polymers

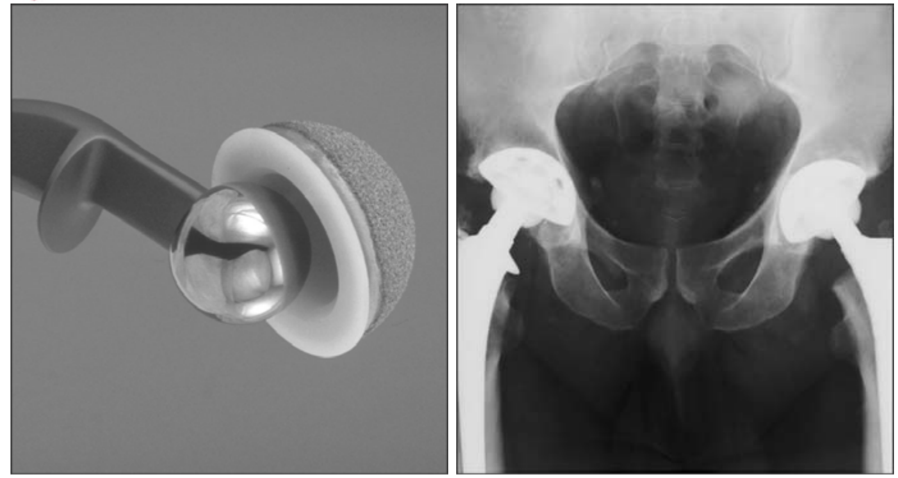
Ultrahigh Molecular Weight Polyethylene (UHMWPE)

- Molecular weight around 4×10^6 g/mol
- Outstanding properties
  - high impact strength
  - resistance to wear/abrasion
  - low coefficient of friction
  - self-lubricating surface
- Important applications
  - bullet-proof vests
  - golf ball covers
  - hip implants (acetabular cup)



Adapted from chapter-opening photograph, Chapter 22, *Callister 7e.*

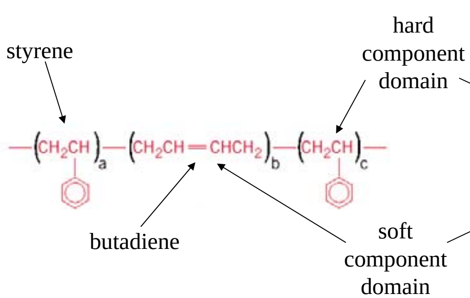
Advanced Polymers



The Stem, femoral head, and the AC socket are made from Cobalt-chrome metal alloy or ceramic, AC cup made from UMWPE

Advanced Polymers: *Thermoplastic Elastomers*

✓ Styrene-butadiene block copolymer



Crosslinked materials

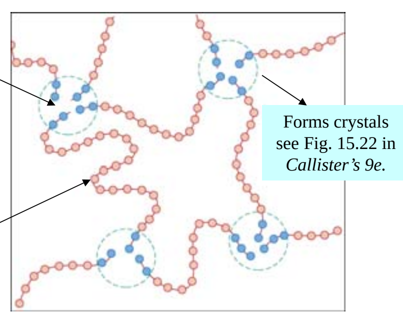
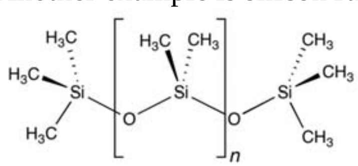


Fig. 15.22, *Callister & Rethwisch 8e.* (Fig. 15.22 adapted from *the Science and Engineering of Materials*, 5th Ed., D.R. Askeland and P.P. Phule, Thomson Learning, 2006.)

✓ Another example is silicon rubber



Viscoelasticity

- All viscous liquids deform continuously under the influence of an applied stress – *They exhibit ……… behavior*.
- Solids deform under an applied elastic stress, but soon reach a position of equilibrium, in which further deformation ceases. If the stress is removed they recover their original shape – *They exhibit ………. behavior*.
- Viscoelastic fluids can exhibit both viscosity and elasticity, depending on the conditions.

Polymers display VISCOELASTIC properties
They stretch (elastic) and they flow (viscous)

- Because of the entanglement of the molecules *thermoplastic* materials have different properties compared to other solid materials like metals.
- The polymer chains can slide past each other because in thermoplastics, chains do not share chemical bonds with the other chains around them due to the absence of significant crosslinking.

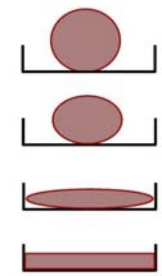
Viscoelasticity

- If you apply a load on a metal rod, it will stretch to a certain length.
- As long as the stress does not exceed the yield strength of the rod, when the force is removed, the rod will return to its original length.
- This is the elastic behavior which we studied earlier.
- However, if you apply a load on a plastic piece, it too will stretch. If you remove the load quickly the piece may return to its original length, but if you leave the load for some time, the polymer chains will slide past each other and flow to increase the length.
- The longer the load is applied, the more the plastic piece will lengthen (more flow of chains) until it breaks.
- When you remove the load from a stretched thermoplastic such as a grocery plastic bag, you can see the retraction or shrinkage with time. This is different from metals where they retract very quickly.

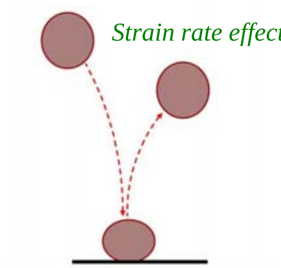
Mechanical properties of polymers are much dependent on time

Viscoelasticity

If you make a ball of a silly putty, and set it on plate, it flattens out by itself. This is a viscoelastic behavior. Gravity causes the molecules to flow to relieve the stress.



Time is relatively long; hours.



Time is short; less than 1 sec.

If you through the silly putty ball fast towards the floor it will bounce back with minimum deformation.

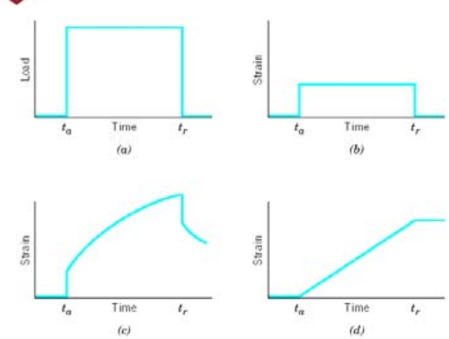
This cold flow exhibits the viscoelastic nature of thermoplastic materials.

Viscoelasticity

- As temperature increases, the polymer chains are farther apart, there is more free volume, and can slide past one another more easily.
- when strain rate is increased, the polymer chains don't have enough time to flow past one another. Therefore, they get tangled with each other and break sooner.
- Viscoelasticity is a fundamental concept that we need to understand in order to understand polymers behavior and be able to shape them.
- Most mechanical testing of plastics is actually testing of their viscoelasticity, i.e. how the plastic flows with time when different stresses are applied
- Another way to think of this as if thermoplastic materials have both *long-term* and *short-term* properties

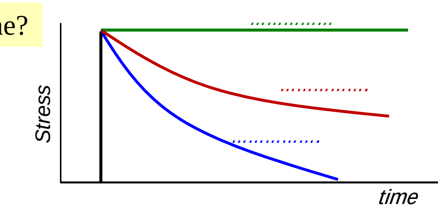
Plastics are of course very sensitive to *temperature* and *strain rate*

Viscoelasticity



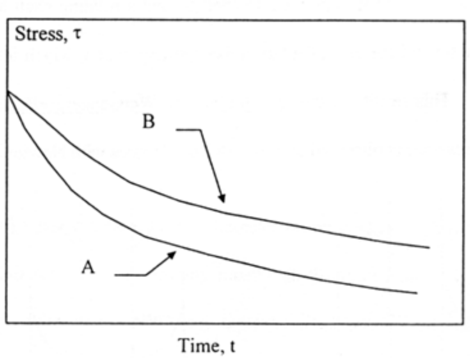
- Elastic strain is fully recoverable (b)
- *viscous strain* is not instantaneous and is time-dependant and …… …………. (d)
- intermediate behaviour is called *viscoelastic* e.g. silly putty (c)

But what happens to stress with time?



Viscoelasticity and Stress Relaxation

Stress relaxation can be measured by shearing the polymer melt in a viscometer (*for example cone-and-plate or parallel plate*). If the rotation is suddenly stopped, i.e. $\dot{\gamma} = 0$, the measured stress will not fall to zero instantaneously, but will decay in an exponential manner.

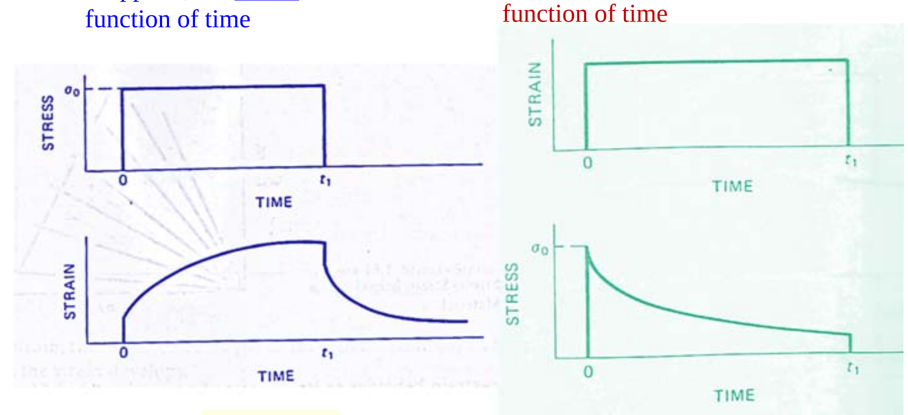


- ✓ *Relaxation is ……… for Polymer B than for Polymer A, as a result of greater elasticity.*
- ✓ *These differences may arise from polymer microstructure (…………………, ……………).*

Creep vs Stress Relaxation

When constant stress (or load) is applied, the **strain** relaxes as function of time

When constant strain is applied, the **stress** relaxes as function of time



……..

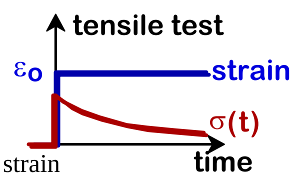
…… ……………

Physical Meaning of the Relaxation Time

Time dependent **relaxation** modulus:

$$E_r(t) = \frac{\sigma(t)}{\varepsilon_o}$$

E(t) is defined for extension flow.



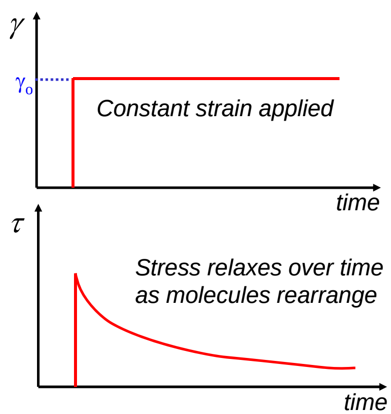
where $\sigma(t)$ is time dependent stress at a constant strain

But what if we apply shear stress?

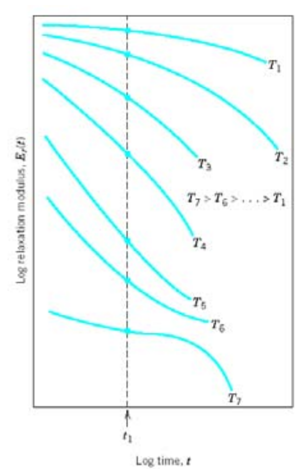
Stress relaxation after a step strain γ_o is the fundamental way in which shear *relaxation modulus* is defined.

$$G(t) = \frac{\tau(t)}{\gamma_o}$$

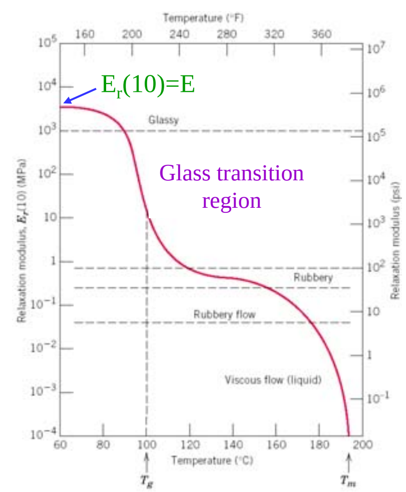
G(t) is defined for shear flow.



Temperature Dependence of the Relaxation Modulus



$E_r(t)$ decreases with time and with increasing temperature



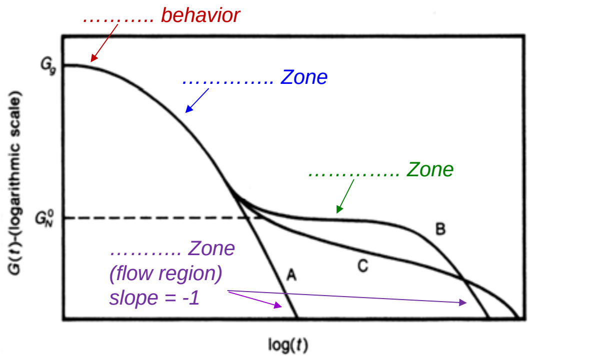
Polystyrene, t_1=10s

Stress relaxation of an uncrosslinked melt

G_o (or G_N^o) is the "*plateau modulus*"

$$G_N^o = \frac{\rho RT}{M_e}$$

where M_e is the average mol. weight between entanglements

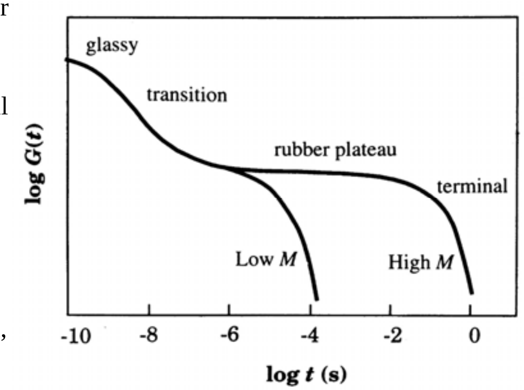


2-3. Relaxation modulus for three samples of a typical linear polymer. A is monodisperse with $M < M_C$; B is monodisperse with $M \gg M_C$, and C is polydisperse with $M_w \gg M_C$.
M_c: critical molecular weight above which entanglements exist

Stress relaxation of an uncrosslinked melt

But how would a higher molecular weight affect the tensile properties?

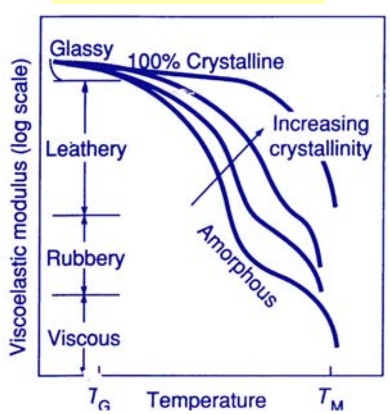
- A higher molecular weight will affect some of the properties, but typically the modulus does not change much.
- A higher molecular weight ………….. the entanglement of the polymer chains, which will …………. the elongation, toughness, and yield strength (slightly).



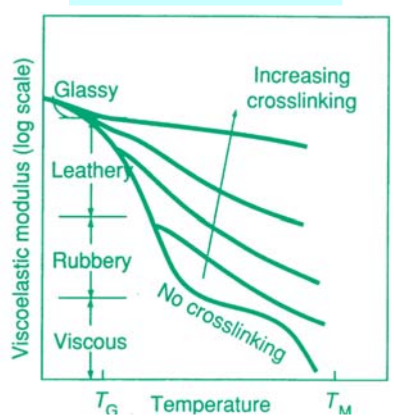
The modulus is **more dependent** on the ……….. of the molecule and **less** on …………………, so it is relatively unaffected by longer chain lengths.

Temperature Dependence of the Relaxation Modulus

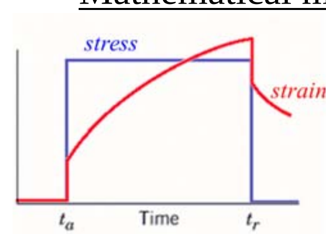
Effect of Crystallinity

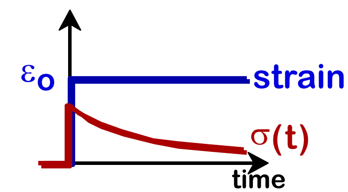


Effect of Crosslinking



Mathematical models: Hooke and Newton





- It is difficult to predict the creep and stress relaxation of polymers.
- It is easier to predict the behaviour of polymers with the assumption that they behave as **linear** viscoelastic materials.
- Deformation of polymeric materials can be divided to two components:
  - ✓ Elastic component: *Hooke's law* ($\sigma = E\varepsilon$)
  - ✓ Viscous component: *Newton's law* $(\sigma = \eta \frac{d\varepsilon}{dt})$
- Deformation of polymeric materials can be approximated by ……………. of Hooke's law and Newton's law. But these equations are only applicable at low strain.

Next time:

Electrical Properties