



Outline

- Polymers – Introduction
- Types of polymers
- Molecular Structure and Configurations
- Mechanical Behaviour of Polymers
- Crystallinity
- Viscoelasticity
- Melting and Glass Transition Temperatures



Polymers

- You may think of polymers as being a relatively modern invention
 - however *naturally occurring* polymers have been used for thousands of years
 - wood, rubber, cotton, wool, leather, silk... etc
- Artificial polymers are, indeed, relatively recent and mostly date from after WWII
 - in many cases, the artificial material is both better and cheaper than the natural alternative

COMMERCIAL Polymers: used in large quantities for their lightweight, corrosion-resistance, and good formability.
- usually low strength and stiffness

ENGINEERING Polymers: improved strength and better elevated temperature properties.

In fact, just look around your, house, dorm or apartment room and you'll likely find plenty of examples of polymeric materials.

styrofoam cups
contact lenses
rubber tires
telephone housings
epoxies
sandwich bags
soda bottles
rubber bands
computer keyboard
cables ... etc



Types of polymers

Thermoplastics:

- *Soften on heating*, can then be formed & shaped by viscous flow. Retain shape on cooling. Process can be repeated. (Becomes plastic on heating)
- Thermoplastics generally consist of very long carbon chains with side groups of H, O, N..... etc

Thermosets

- Thermosetting plastics are formed/shaped then "Cured" or "Set" by a chemical reaction, permanently. be remelted or reshaped by application of heat.
- Other sidegroups O, N, H will be present.

ELASTOMERS (Rubbers)

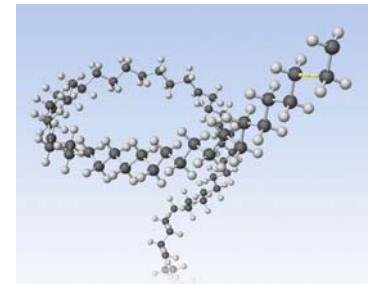
Very large elastic deformations, when loaded, (which can be recovered on unloading) up to 900% elongation possible.



Introduction to Polymers

Definition: A polymer is a molecule with a molecular weight on the order of several thousands g/mol.

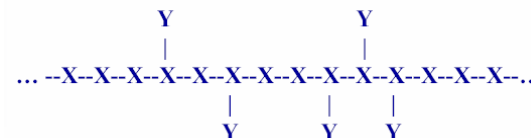
- Polymers are usually hydrocarbon-based and contain many individual repeat units.
- Sometime called *macromolecules* because of their huge size.



Suppose our repeat unit is an "X." Then, a linear polymer based on "X" would look like the following:

... --X--X--X--X--X--X--X--X--X--X--X--X--X--X--... where each "X" represents a "mer"

Sometimes, polymers contain functional side groups, called pendant groups:



We call the primary linear chain the "backbone"



Introduction to Polymers

Homopolymers vs. co-polymers: If only one type of repeat unit is present, the polymer is called a If a second monomer is also present in the chain, the resulting material is called a

Model for a **homopolymer:**



Model for an **alternating co-polymer:**



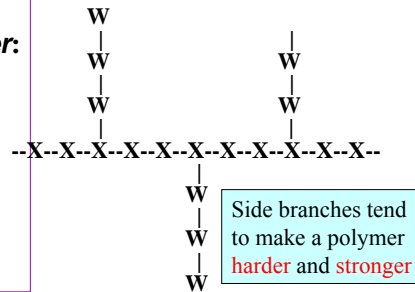
Model for a **random co-polymer:**



Model for a **block co-polymer:**



Model for a **graft co-polymer:**



Graft co-polymer: The resulting structure when chains of one type of monomer, say W, are grafted onto a backbone polymer chain of, say X.



Molecular Structure

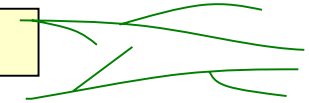
Linear polymers

- long, 'straight', flexible chains with some van der Waals or hydrogen bonding



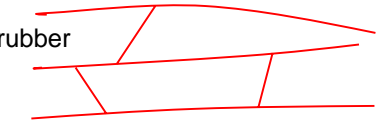
Branched polymers

Chain packing efficiency is reduced compared to linear polymers (lower density)



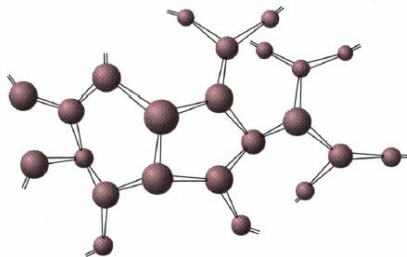
Crosslinked polymers

- cross linkage happens either during synthesis or in a separate process, typically involving addition of impurities which bond covalently
- this is termed vulcanisation in rubber



Molecular Structure

Network polymers: 3D networks made from trifunctional mers. Examples: epoxies, phenolformaldehyde



Classification of Polymers

- Linear polymer** - Any polymer in which molecules are in the form of spaghetti-like chains.
- Thermoplastics** - Linear or branched polymers in which chains of molecules are not interconnected to one another.
- Thermosetting polymers** - Polymers that are heavily cross-linked to produce a strong three dimensional network structure.
- Elastomers** - These are polymers (thermoplastics or lightly cross-linked thermosets) that have an elastic deformation > 200%.

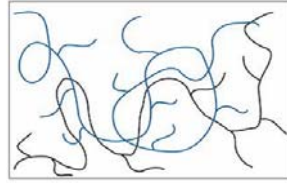
Note that branching can occur in any type of polymer (e.g., thermoplastics, thermosets, and elastomers).



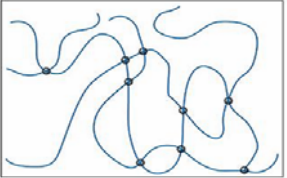
Classification of Polymers



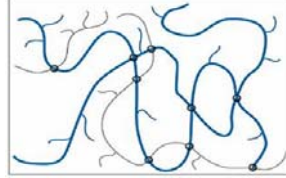
(a) Linear unbranched polymer: notice chains are not straight lines and not connected.



(b) Linear branched polymer: chains are not connected, however they have branches.



(c) Thermoset polymer without branching: chains are connected to one another by covalent bonds but they do not have branches



(d) Thermoset polymer that has branches and chains that are interconnected via covalent bonds



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** get **AMORPHOUS** regions (see next slide).

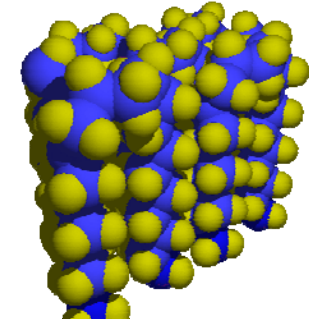
$$\% \text{ crystallinity} = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$$

Where:

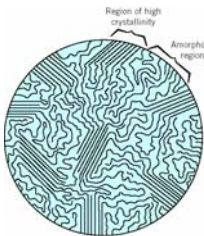
ρ_s = Density of sample

ρ_a = Density of the completely amorphous polymer

ρ_c = Density of the completely crystalline polymer



Crystallinity in Polymers



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

% **crystallinity** depends on several factors:

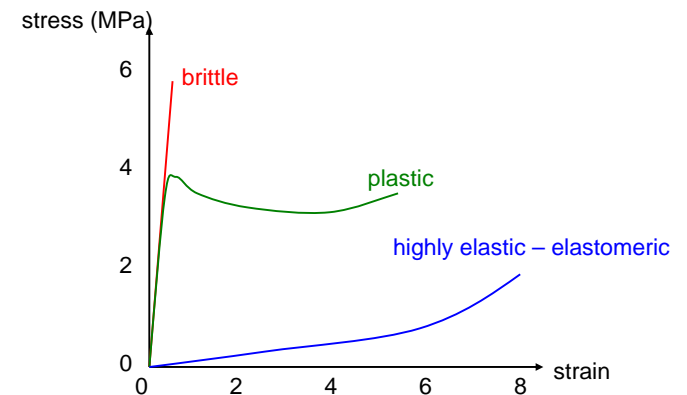
- ✓ **Cooling rate** (..... cooling – crystallinity)
- ✓ **Chain configuration** (..... structures – crystallinity)
(Copolymers – less crystallinity)
- ✓ Linear polymers form crystals **more easily** because the molecules can orient themselves readily

- Degree of Crystallinity ranges from 5 - 95%
- The % Crystallinity → strength



Mechanical Properties of Polymers

- There are three typical classes of polymer stress-strain characteristic





Mechanical Properties of Polymers

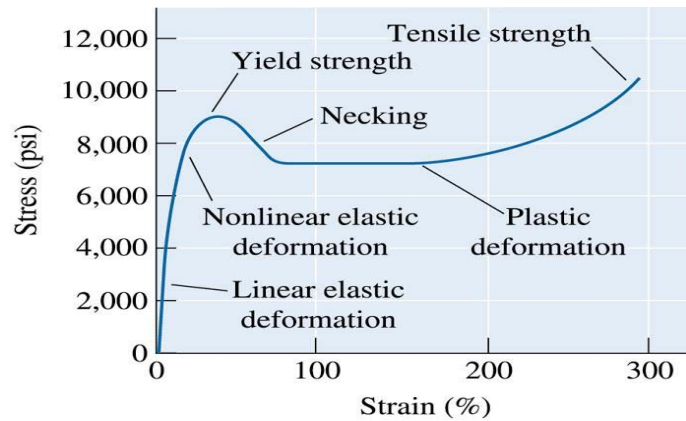
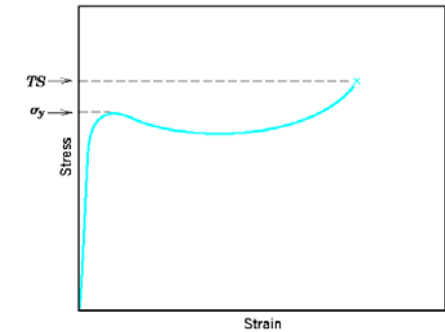


Figure 15.17 The stress-strain curve for 6,6-nylon, a typical thermoplastic polymer. (The Science and Engineering of Materials – by D.R. Askeland and P.P. Phule)



Mechanical Properties of Polymers

- Elastic modulus is very much lower than for metals or ceramics
- Beyond the yield point sample deforms plastically.
- Tensile stress (TS) is the stress at fracture
- TS may be less or greater than the yield strength.



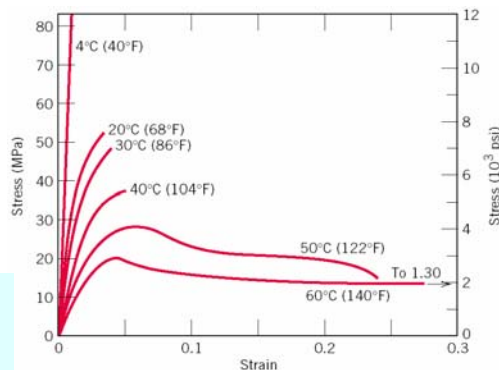
- Modulus of Elasticity
 - may be as low as 7 MPa or as high as 4×10^3 MPa (compare to 48×10^3 - 410×10^3 MPa for metals)
 - TS polymers 100 MPa (metals up to 4100 MPa)
- Elongation
 - Often elongate plastically as much as 1000% (compare to metals - rarely over 100%)



Mechanical Properties of Polymers

- Decreasing T,
- ✓ E
 - ✓ TS
 - ✓ %EL

Mechanical properties are very T dependent - even close to room T

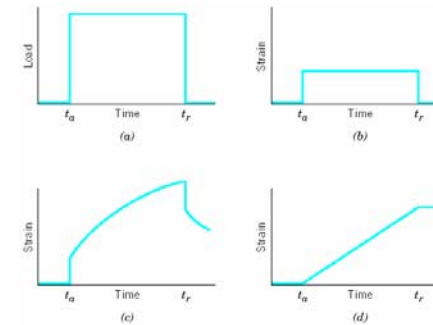


Effect of temperature on stress-strain behavior of PMMA (left).

Increasing strain rate causes the same effects as decreasing T.



Viscoelasticity

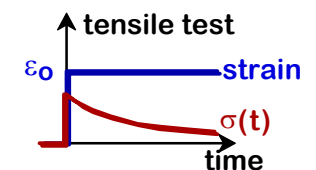


- Elastic strain is fully recoverable (b)
- viscous strain is not instantaneous and is time-dependent and not reversible (d)
- intermediate behaviour is called viscoelastic e.g. silly putty (c)

- time dependent relaxation modulus:

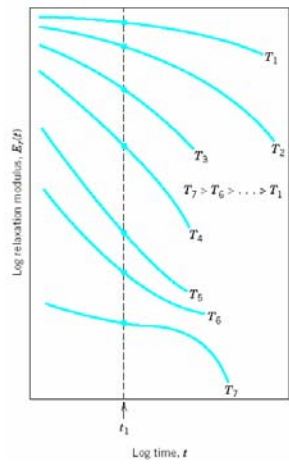
$$E_r(t) = \frac{\sigma(t)}{\epsilon_0}$$

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

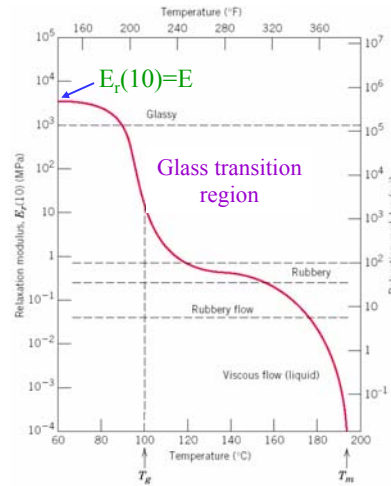




Temperature Dependence of the Relaxation Modulus



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



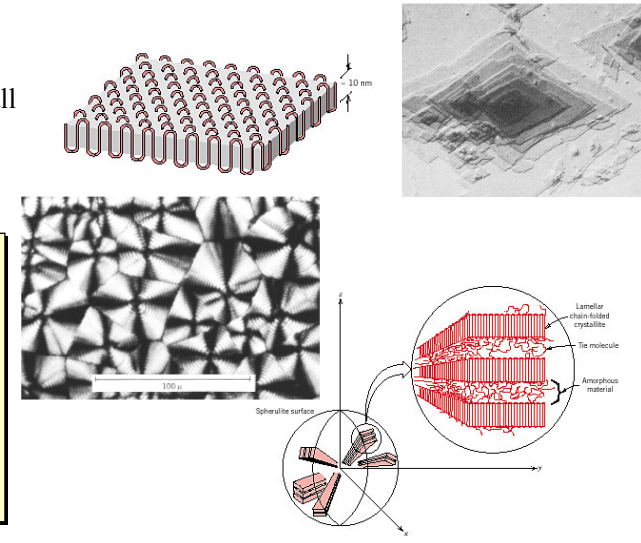
Polystyrene, $t_f = 10s$



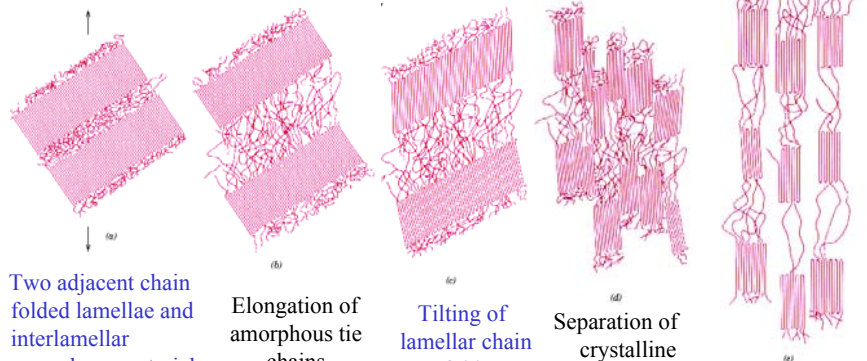
Molecular Structure: Polymer Crystal Models

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**.



Mechanisms of Plastic Deformation - Semicrystalline Polymers



Two adjacent chain folded lamellae and interlamellar amorphous material before deformation

Elongation of amorphous tie chains

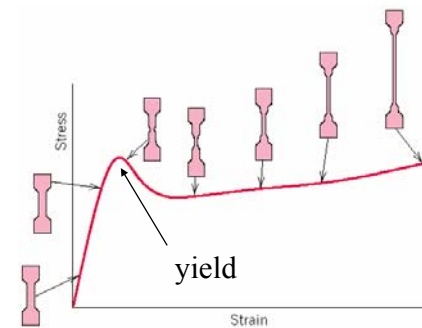
Tilting of lamellar chain folds

Separation of crystalline block segments

Orientation of block segments and tie chains with tensile axis



Plastic Deformation - Semicrystalline Polymers



Unlike metals, TS is not where neck forms, because deformation continues **outside** of neck. Neck region is actually strengthened

Mechanism - chains slip past each other (bonds rotate to allow this), some inter-molecular bond breaking.
- Result is a highly oriented structure in the neck region of our tensile specimen



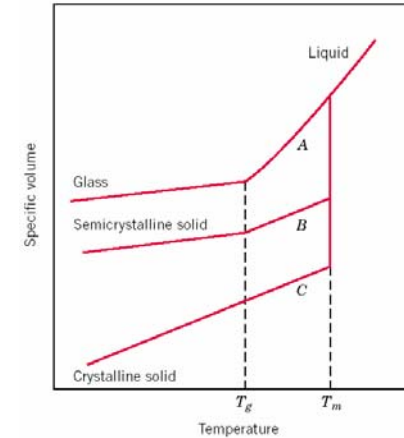
Strength in Polymers

- Major factors affect strength are **temperature** and **strain rate**:
 - In general, the strain rate has the effect similar to the temperature.*
- Other factors that influence strength
 - Tensile strength **increases** with **molecular weight** → more entangled (short strings vs long)
 - $TS = TS_{\infty} - A/M_n$
 - Strength can be increased by **increasing** the **degree of cross-linking** (*inhibits chain motion - makes it more brittle*)
 - Crystallinity** **increases** strength by increasing *intermolecular bonding*
 - Deforming** a polymer can **increase** its strength - so that chains become oriented



Melting and Glass Transition Temperature

For amorphous and semicrystalline polymers, this is a critical aspect of designing with polymers.



- Crystalline polymers:** there is a discontinuous change in specific volume at T_m
- Amorphous polymer:** continuous, no T_m - but there is an increase in slope at T_g , the glass transition temperature,
- Semicrystalline polymer:** intermediate to crystalline and amorphous, show both transitions.



Melting and Glass Transition Temperature

- Melting of a crystalline polymer
 - transforming solid with an ordered structure to a viscous liquid with a highly random structure*
- Amorphous glass transitions
 - transformation from a rigid material to one that has rubber-like characteristics*
 - temperature has large effect on chain flexibility*
- Below glass transition temperature, T_g , polymers are usually **brittle** and **glass-like** in mechanical behavior.
- Above glass transition, T_g , polymers are usually **more elastic**.

Why is That?

Bond rotations are “freezing” which means chains can’t slip past each other so polymer becomes brittle, (no plastic deformation)



Polymers and Spaghetti

- Amorphous polymers** ↔ hot, fresh spaghetti with no “clumps”
- Semicrystalline polymers** ↔ hot fresh spaghetti with some “clumps”
- Crystalline polymers** ↔ spaghetti the way my friend made it, mostly “clumps” with some free strands
- Polymer **below T_g** ↔ three day old spaghetti- left in the sun!

T_g is for simple linear polymers

T_g and T_m increase with mer complexity

Material	Glass Transition Temperature [°C (°F)]	Melting Temperature [°C (°F)]
Polyethylene (low density)	-110 (-165)	115 (240)
Polytetrafluoroethylene	-97 (-140)	327 (620)
Polyethylene (high density)	-90 (-130)	137 (279)
Polypropylene	-18 (0)	175 (347)
Nylon 6,6	57 (135)	265 (510)
Polyester (PET)	69 (155)	265 (510)
Polyvinyl chloride	87 (190)	212 (415)
Polystyrene	100 (212)	240 (465)
Polycarbonate	150 (300)	265 (510)



Next time:

Mechanical Shaping of Polymers