Imperial College London

Materials and Manufacturing

Polymers

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Module leader

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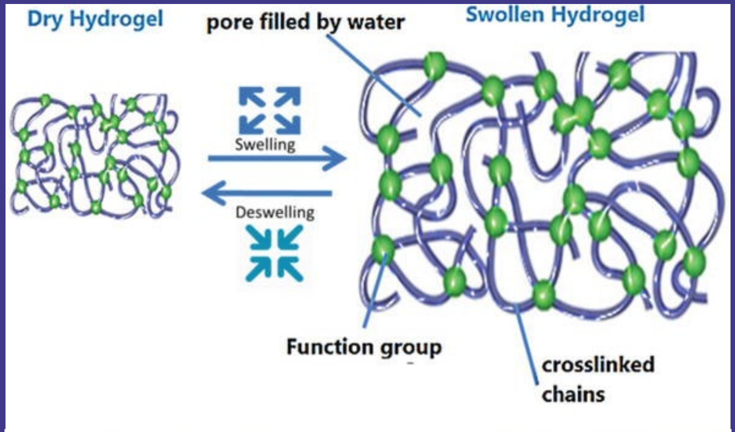


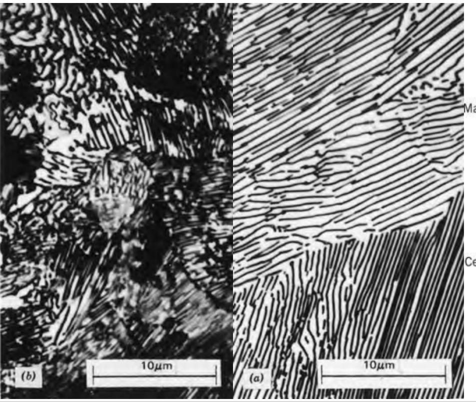
https://www.youtube.com/watch?v=VTU3JNAIOG8

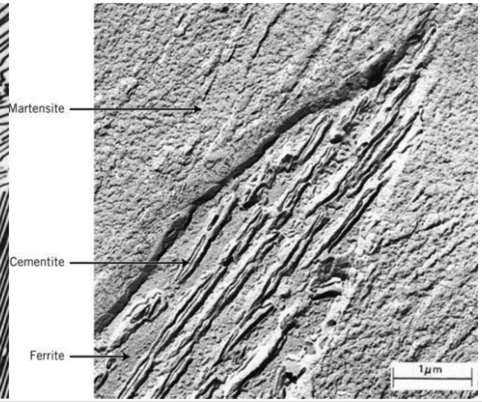
Dyson School of Design Engineering

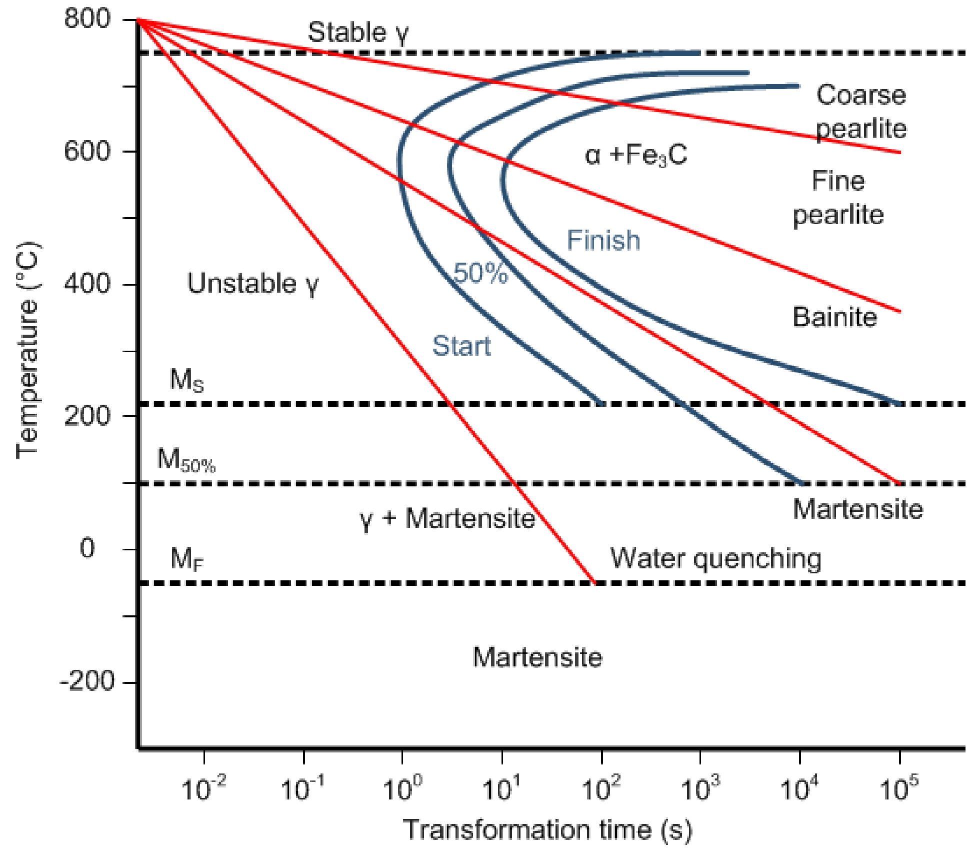
Last time on M&M…

Altering material properties

- Grain size effects – Hall-Petch equation
- Solid solution hardening
- Strain hardening (cold working)
- Precipitation hardening
- Non-equilibrium structures
- Different heat treatments
- Fine pearlite, course pealite, bainite, martensite, tempered martensite
- Time-Temperature Transformation plots







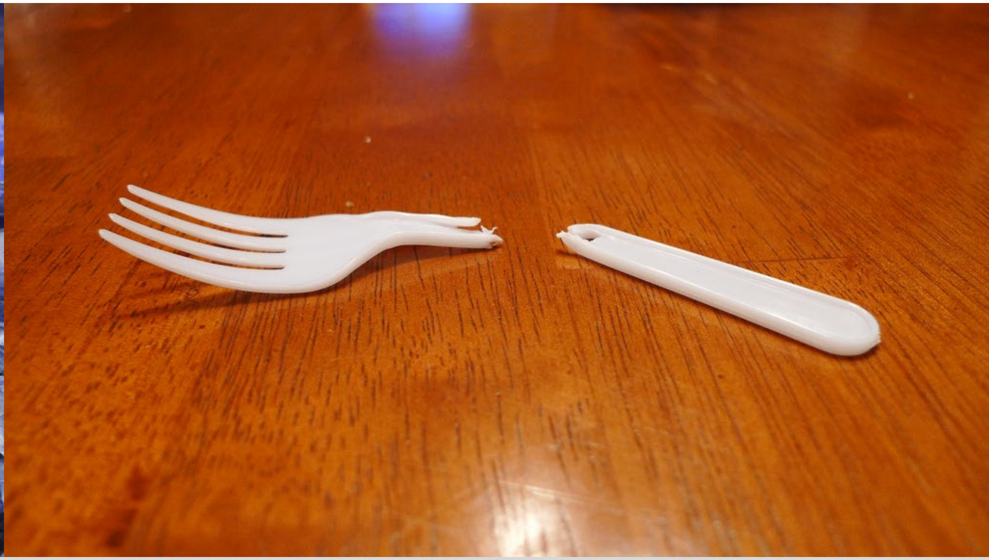
Learning objectives

- Describe the three main classes of polymer and their key characteristics
- Define the nature of interatomic and intermolecular bonding in polymers
- Explain how the strength and stiffness of a polymer relates to its chain length and side groups
- Evaluate the key mechanic properties of polymers for a given stress-strain curve
- Explain the origins of the glass transition and how it is affected by molecular structure

Why is it important?

Polymers are in widespread use in our world today, their application has grown significantly over the past few decades. As engineers, we need to have a working knowledge of polymer properties and be aware of their strengths and their limitations.

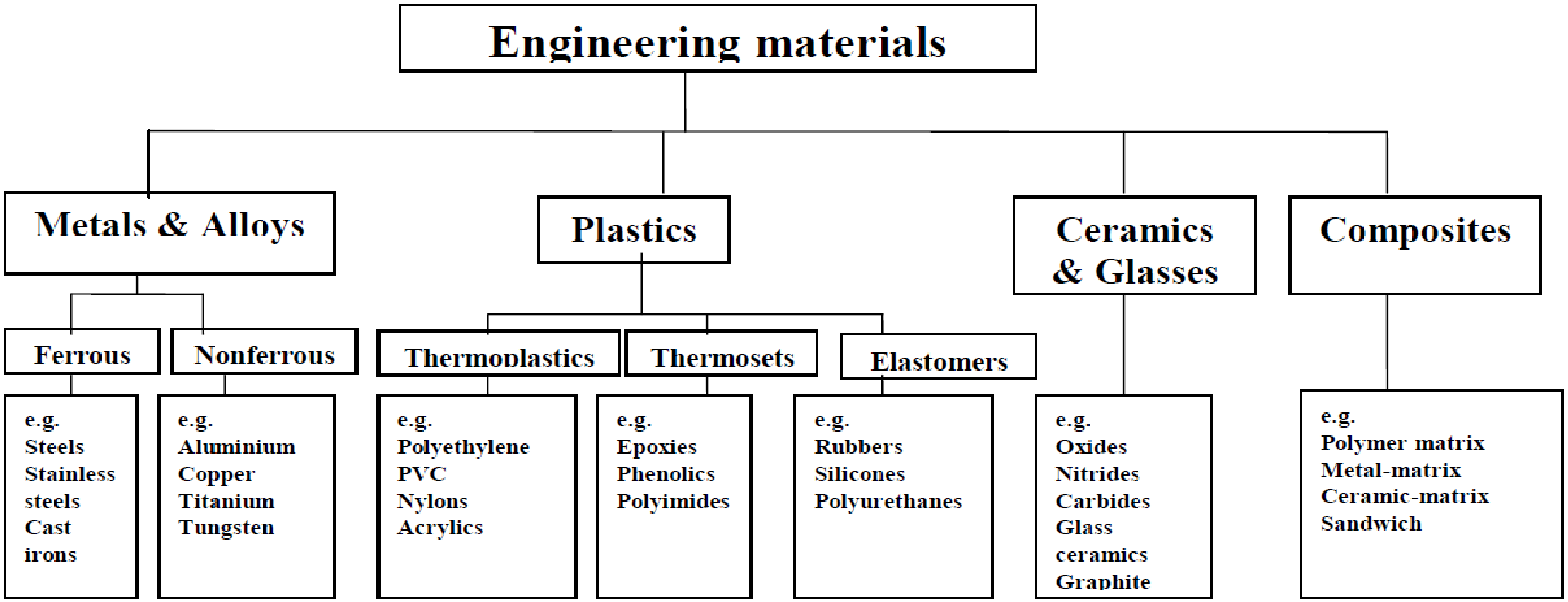
Used wisely, polymers can offer great benefit to modern design but we are all too familiar with problems caused by simply replacing metal with a polymer (with little or no change in design) plastic cutlery being an obvious example.



Shrink wrap fittings

- An interesting application of heat treatment in polymers is the shrink-wrap used in packaging
- Shrink-wrap is a polymer film, usually made of polyethylene
- It is initially plastically deformed (cold drawn) by about 20-300% to provide a prestretched (aligned) film
- The film is wrapped around an object to be packaged and sealed at the edges
- When heated this prestretched material shrinks to recover 80-90% of its initial deformation, which gives a tightly stretched, wrinkle-free, transparent polymer film
- For example, CDs and many other objects that you purchase are packaged in shrink wrap

Classification of polymers



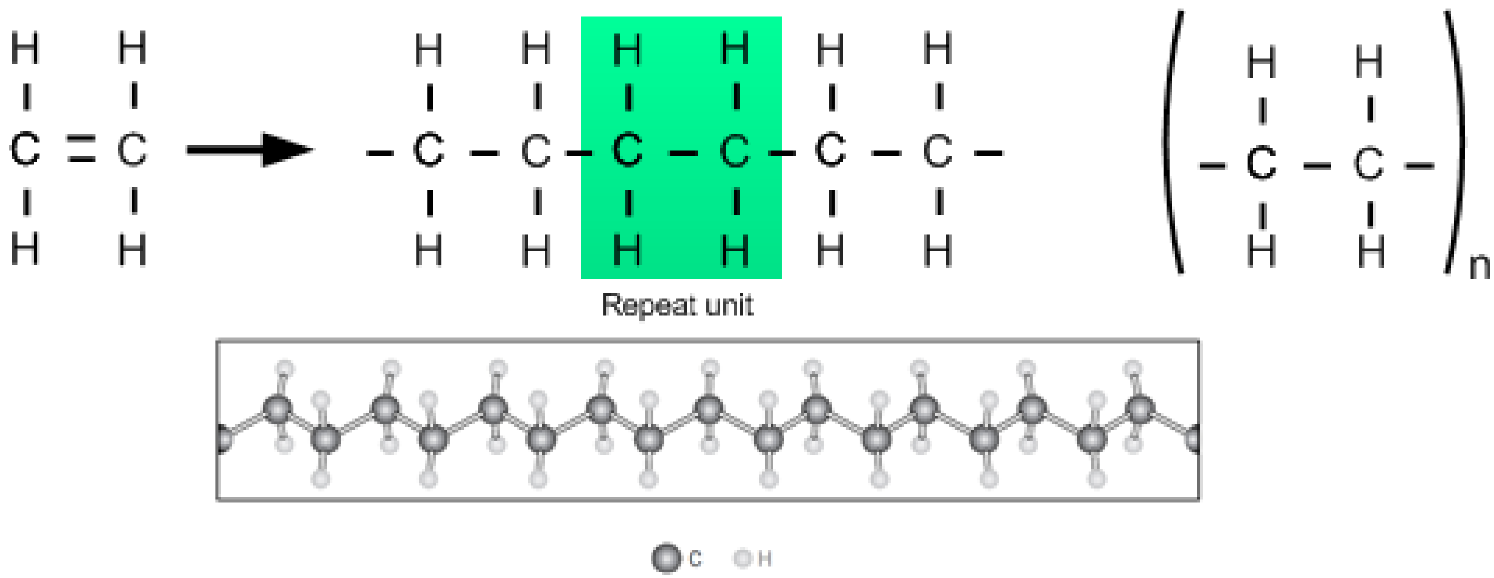
Polyethylene

Epoxy glue

Silicon rubber

Chain structure

- A polymer consists of a long chain of molecules (i.e. **macromolecules**)
- Atoms of the chain are held together by **covalent bonds**
- A polymer is made by **polymerisation** of a **monomer** base unit
- During polymerisation the double bonds between carbon atoms is broken and reforms with neighbouring monomers
- Commercial polymers have between 10^3 and 10^5 monomers per chain



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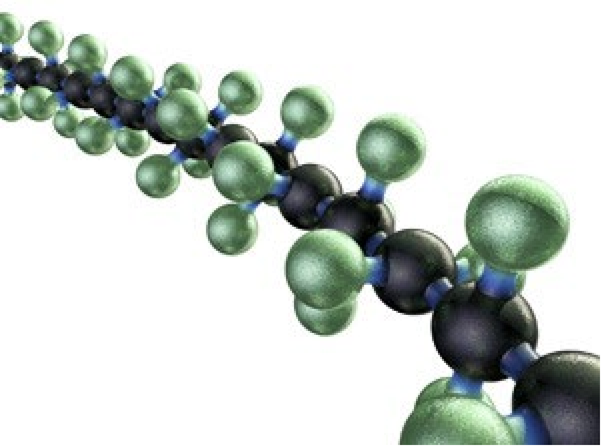
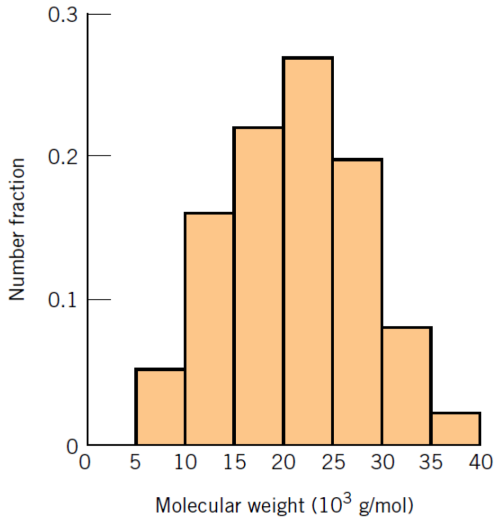
Chain length

- Both the mechanical and the flow properties (important for processing) of a polymer depend strongly on the length of the chains that form during polymerisation
- The **molecular weight** of the polymer is the typical metric by which we represent this
- The molecular weight is the molecular weight of the monomer multiplied number of monomers in the chain
  - For example the monomer of polyethene (C_2H_4) has a molecular weight of (12x2)+(4x1)=28
  - If 10^4 monomers polymerise to make a single chain the molecular weight is 28×10^4
- As not all chains are the same length the molecular weight of a polymer is often quoted by the **number average molecular weight** $\bar{M}_N$





$$\bar{M}_N = \frac{\Sigma N_i M_i}{\Sigma N_i}$$

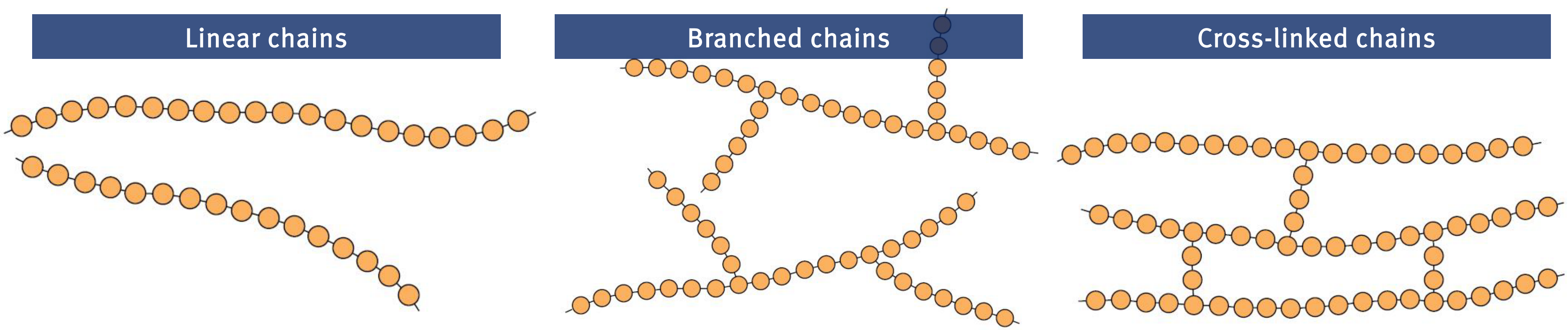
$\bar{M}_N$ = Number average molecular weight

M_i = Molecular weight of component *i*

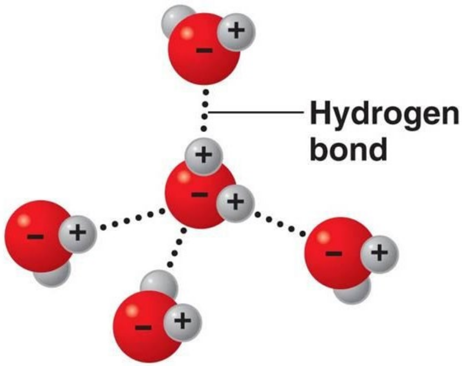
N_i = Chain length of component *i*

Chain or network formation

- A polymer may form **linear chains**, **branched chains** or **cross-linked networks** of polymer chains
- **Thermoplastics** have linear or branched chains and will melt on heating
- **Elastomers** have a few cross-links to help prevent melting but retain elasticity
  - Cross-linking help to prevents melting
- **Thermosets** have many cross-links to prevent melting and also to give additional material stiffness

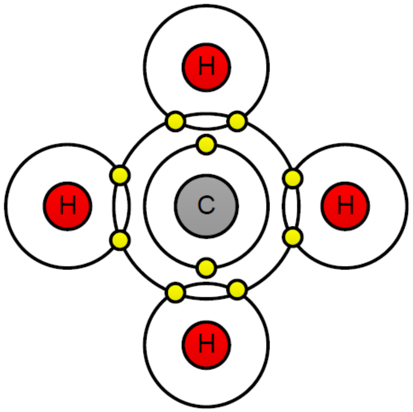


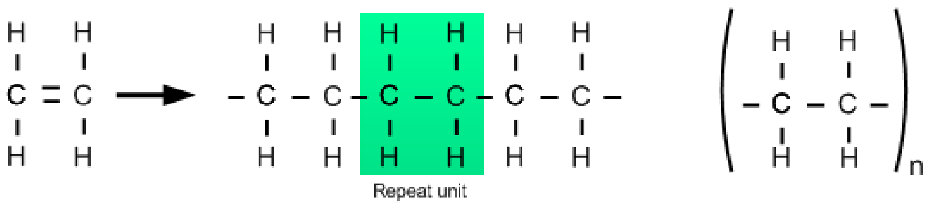
Bonding types

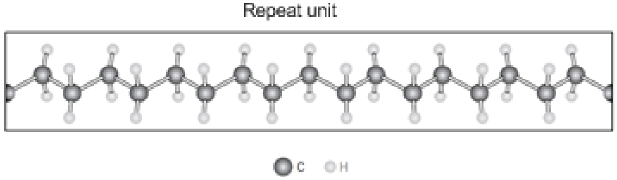


Covalent bonds

- Sharing of electrons from 2 atoms
- Strong

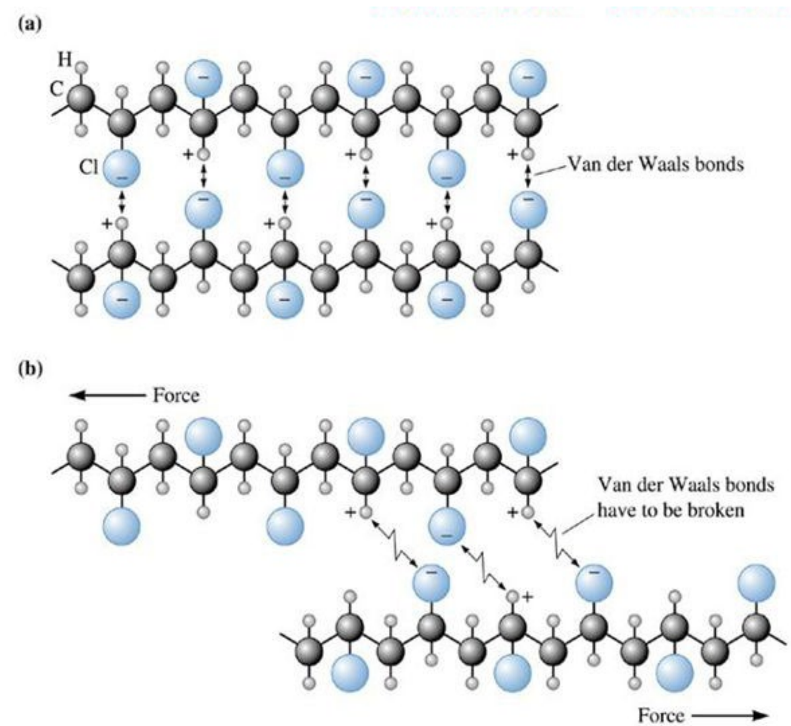






Van der Waals

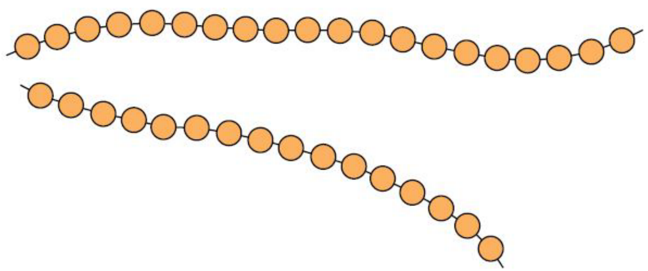
- Coulombic attraction between the positive end of one dipole and negative end of the adjacent dipole



Linear chains

- Linear polymers are those in which the repeat units are joined together in a single chain
- The long chains are very flexible and are analogous to spaghetti
- There may be extensive **van der Waals** or **hydrogen bonding** between chains
- Common polymers include:
  polyethylene (PE), polyvinyl chloride (PVC), polystyrene (PS), polymethylmethacrylate (PMMA), nylon etc

Linear chains



PVC pipes for plumbing

Spaghetti

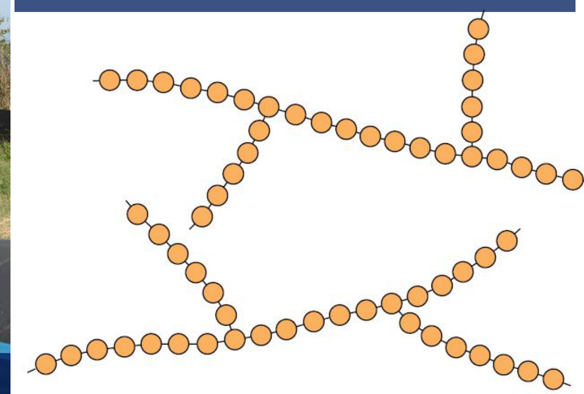
Branched chains

- Polymers may be synthesized in which side-branch chains are connected to the main ones
- The branches, considered to be part of the main-chain molecule, may result from side reactions that occur during the synthesis of the polymer
- The chain packing efficiency is reduced with the formation of side branches, which results in a lowering of the polymer density
- Those polymers that form linear structures may also be branched
- For example high density polyethylene (HDPE) is a linear polymer, but low density polyethylene (LDPE) contains short chain branches

LDPE bottles

HDPE water pipe

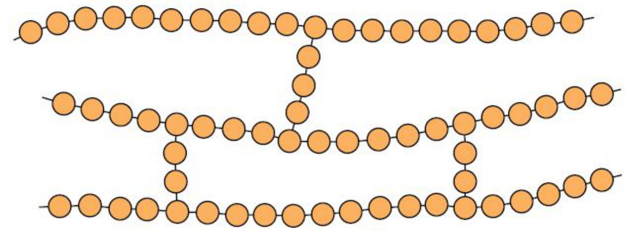
Branched chains

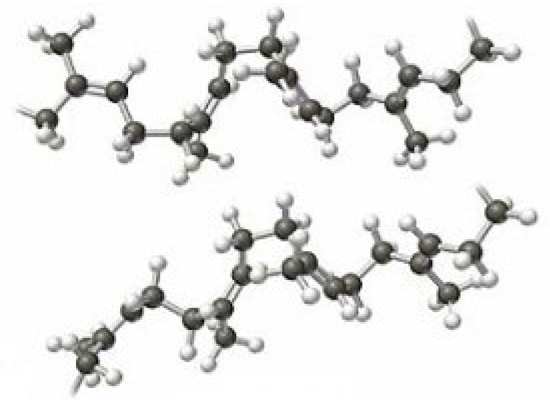


Cross-linked networks

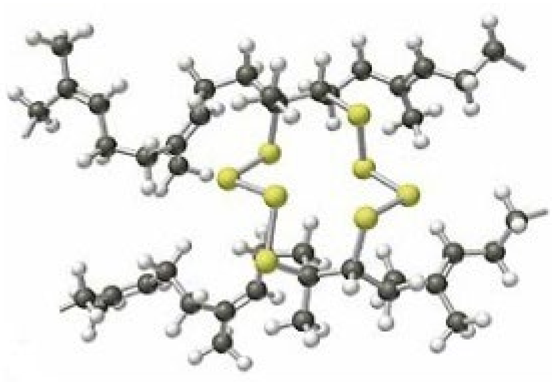
- In cross-linked polymers, adjacent linear chains are joined one to another at various positions by covalent bonds
- The process of cross-linking is achieved either during synthesis or by a non-reversible chemical reaction
- Often, this cross-linking is accomplished by additive atoms or molecules that are covalently bonded to the chains
- Many of the rubber elastic materials are crosslinked
- In rubbers, this is called vulcanization

Cross-linked chains





Before vulcanization

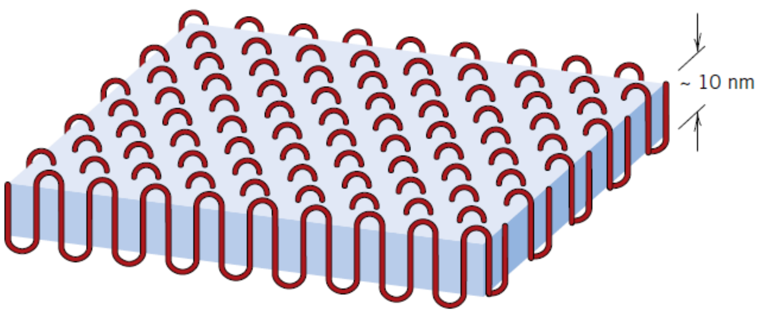


After vulcanization

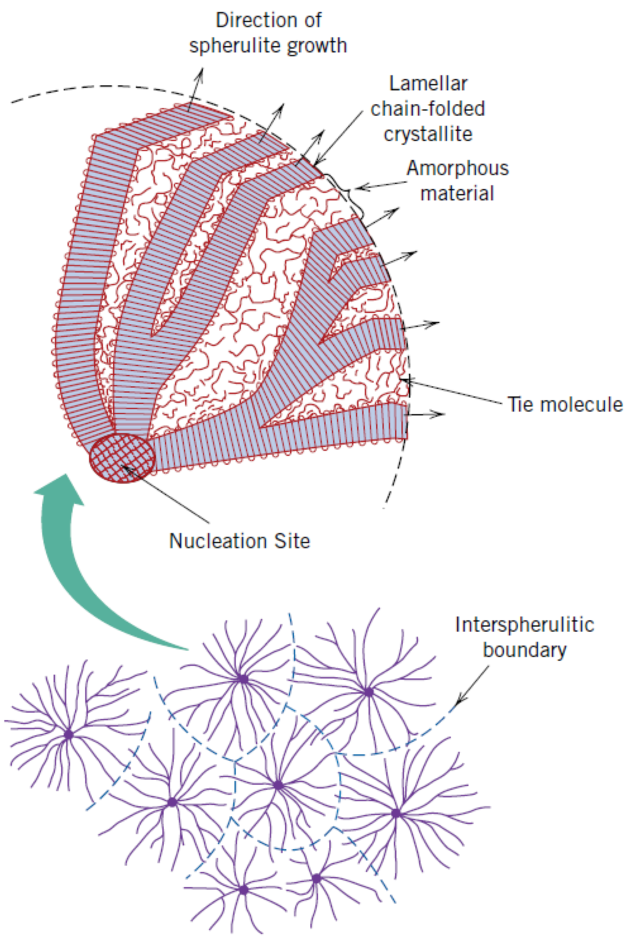
Vulcanized rubber tyres

Packing

- If polymer chains are well ordered with regular packing we call them **crystalline**
- Long branched chains and networks prevent crystalline regions from forming, so these polymers are **amorphous**
- Most polymers exhibit combinations of crystalline and amorphous regions which are known as **semi-crystalline**



Crystalline polymer



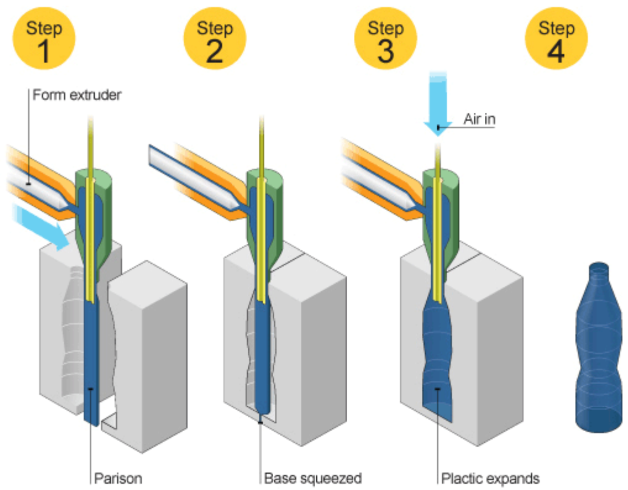
Semi-crystalline polymer

Thermoplastics

- Thermoplastics are either linear or branched chain polymers
- **Covalent bonds** exist along these chains but between the chains only secondary, **van der Waals** bonding exists
- These weaker bonds break at a lower temperature than the covalent bonds, hence thermoplastics soften upon heating and can be readily melted to a viscous liquid
- Thermoplastics are usually mass produced as pellets which are then moulded into components by end users
- Thermoplastics can be broken down into **semi-crystalline** and **amorphous**

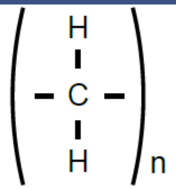
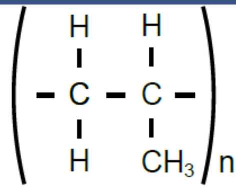
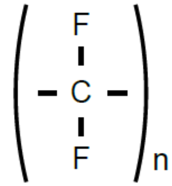
Vacuum forming

Blow molding

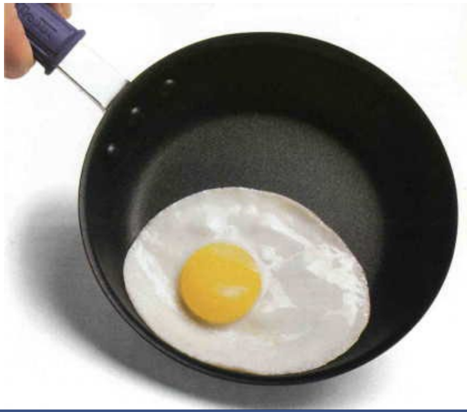


Thermoplastics

Semi-crystalline thermoplastics

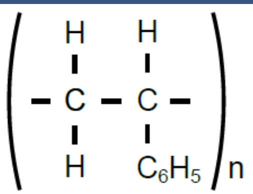
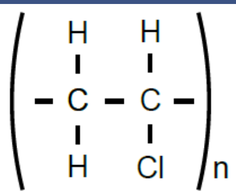
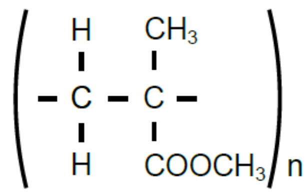
		

Polyethylene (PE)	**Polypropylene (PP)**	**Polytetrafluoroethylene (PTFE)**
Cheap, easily moulded, tough	As for PE, but has higher stiffness and UV resistance. Fatigue resistance	Excellent high temperature and chemical resistance and non-stick properties.
Tubing, film, bottles, packaging, gas/water pipes	Household products, fibres, rope, toys, stadium seats.	Non-stick pans, lubricants, chemical containers, pipes, bearings.



PTFE or Telfon can be used as a non-stick polymer coating on pans

Amorphous thermoplastics

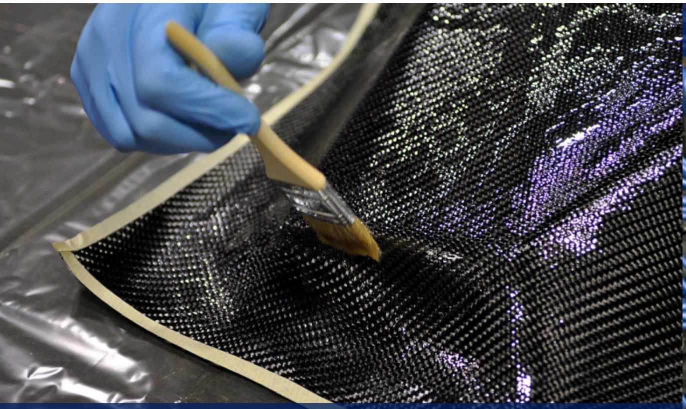
		

Polystyrene (PS)	**Polyvinylchloride (PVC)**	**Polymethylmethacrylate (PMMA)**
Optically clear, cheap, easily moulded, but brittle. Expanded to form foam.	Cheap, stiff but brittle. Can be foamed and plasticised.	Excellent optical properties (transparent), water resistant.
BIC biros, food containers. Packaging (expanded form), electrical insulation.	Window frames, and sheeting. Artificial leather (plasticised), pipes, fibres.	Transparent sheet and mouldings, aircraft domes, windows, laminates, surgical instruments.

Polystyrene packaging for delicate items

Thermosets

- **Thermosets** are highly crosslinked polymers formed by the reaction between two chemicals
- The reaction sometimes requires the application of **heat**
- Thermosets are rigid polymers (due to the strong cross-links between network chains) and as a consequence of these, they do not soften upon heating
- The cross-linking prevents any ordered packing of the chains and so thermosets are **amorphous polymers**


Resin used in carbon fibre composites

Phenolic cable insulation



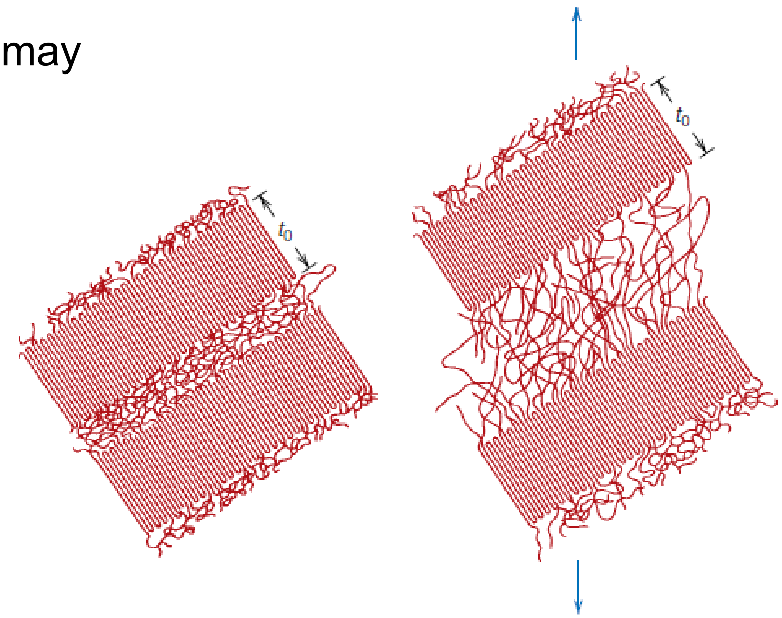
Polyester used in insulation

Elastomers

- Elastomers contain just a few cross-links between chains which imparts high elasticity
- As the number of cross-links increase, the stiffer and more brittle the elastomer becomes
- They do not soften on heating and are in bulk usage
- Polyisoprene (natural rubber) is harvested from the sap of the Hevea tree but can be produced synthetically via polymerisation
- Also produced synthetically are Polybutabiene (automotive tyres) and Polychloroprene (oil resistant seals.)

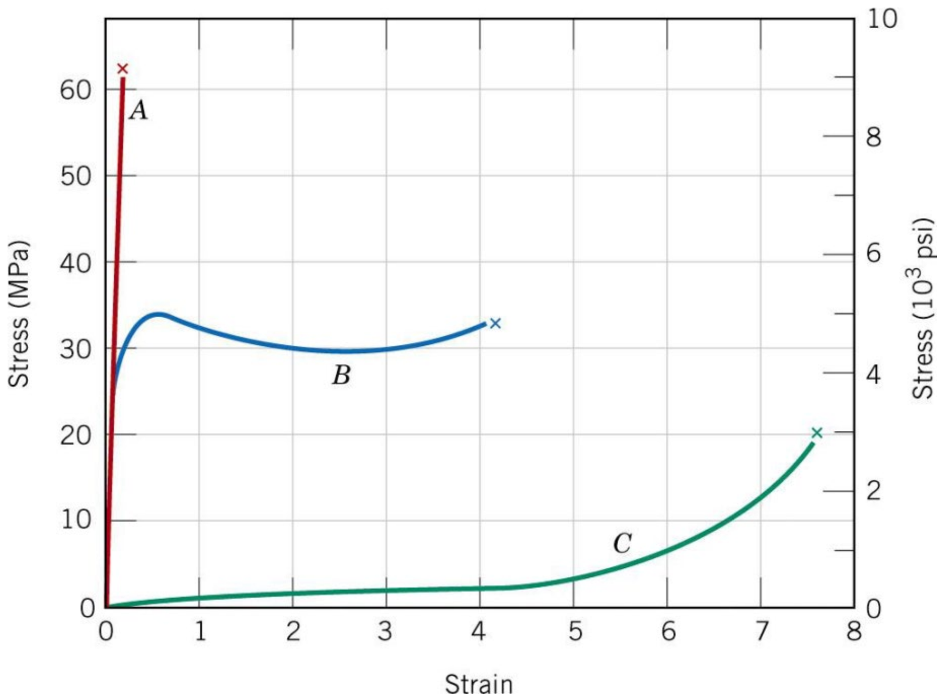
Tensile properties of polymers

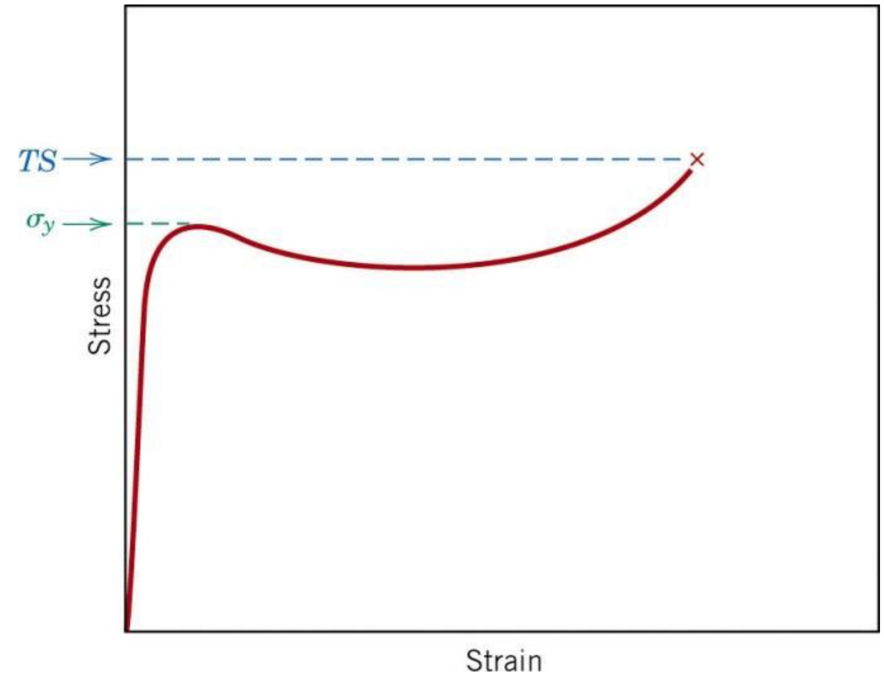
- In metals, we related their strength to their ability to resist plastic deformation and thus to their ability to obstruct the movement of dislocations. Also, stiffness was related to the stiffness of the metallic bond. In polymers the origins of strength and stiffness are different
- **Chain entanglement** occurs in the melt which becomes "frozen in" on solidification
- The longer the chains and the more bulky the side groups on these chains, then the more chain entanglement that occurs
- As a force is applied to the polymer, the chains will tend to disentangle (as spaghetti straightens) and chain slippage occurs
- As more force is applied, the chains themselves may straighten and eventually stretch
- If the chains become highly aligned, then the strength and stiffness of the polymer is controlled more by the strength and stiffness of the C-C bond



Tensile properties of polymers

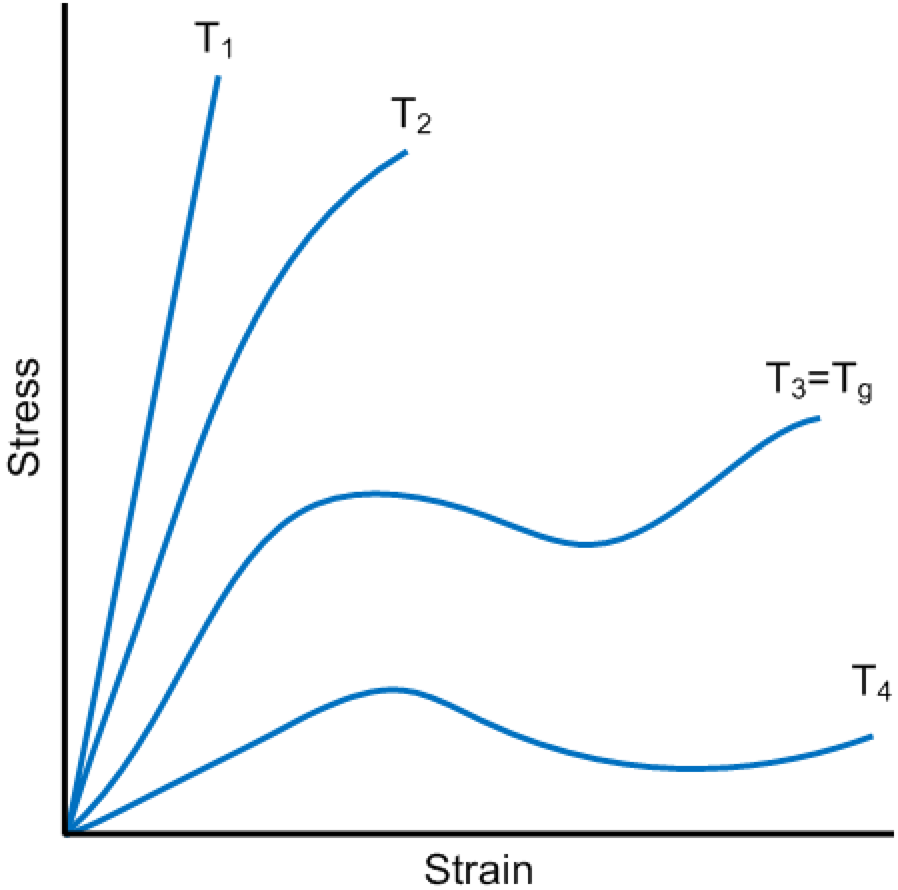
- Polymer A is brittle – Young's modulus ~ 3 GPa
- Polymer B is plastic – Young's modulus ~0.5 GPa
- Polymer C has non-linear elastic behaviour – Young's modulus ~ 0.002 Gpa
- Young's modulus for polymers can be difficult to define – Sometimes **secant lines** are drawn at 0.2% or 1% strain

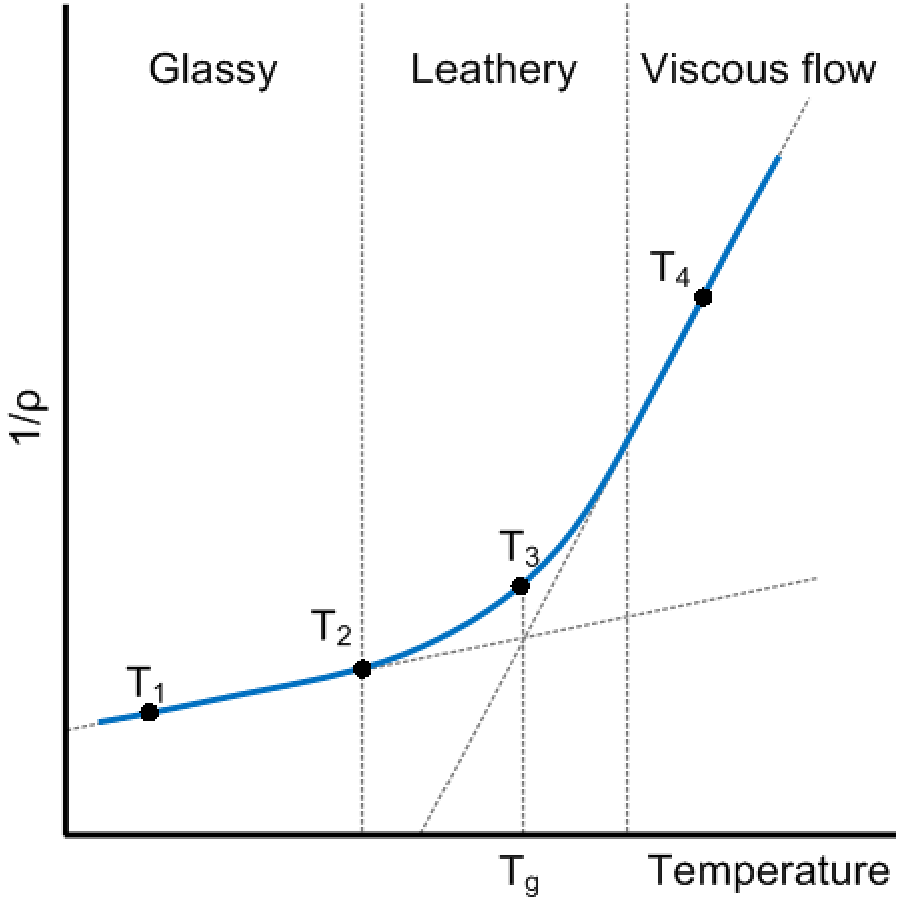




Temperature effects

- Many polymers are highly temperature sensitive. At higher temperatures they are flexible but at lower temperature they become increasingly brittle
- The temperature that this happens at is called the glass transition temperature





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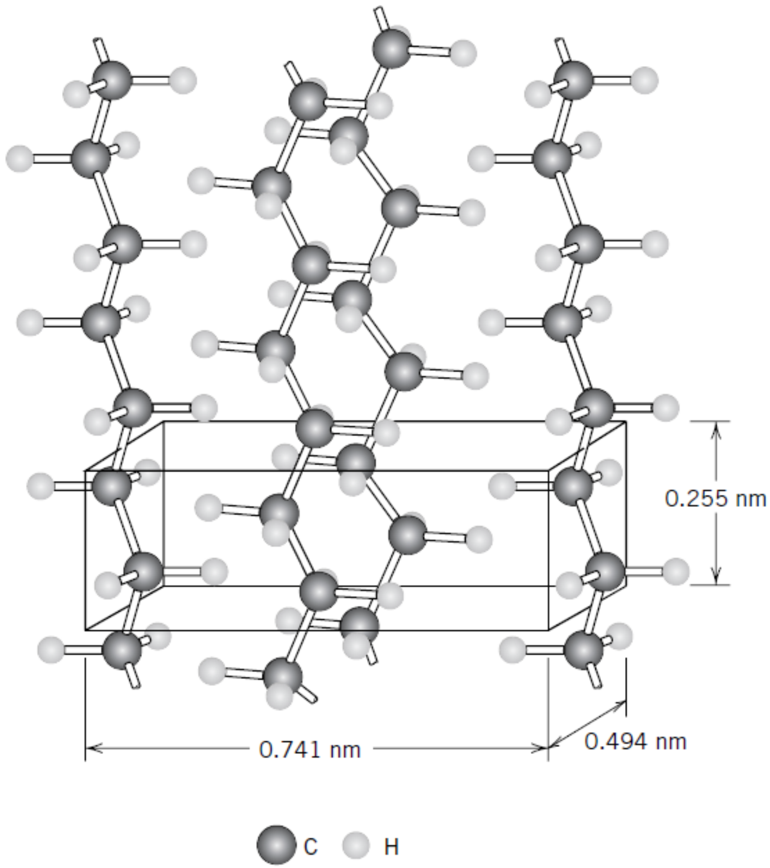
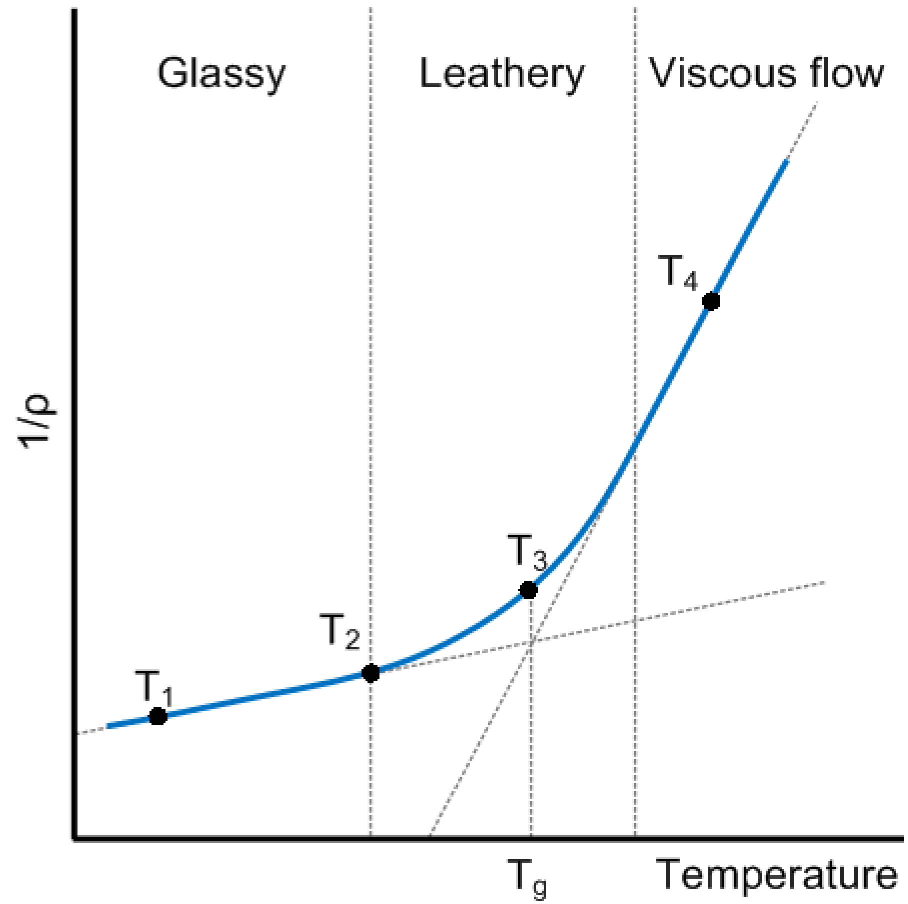
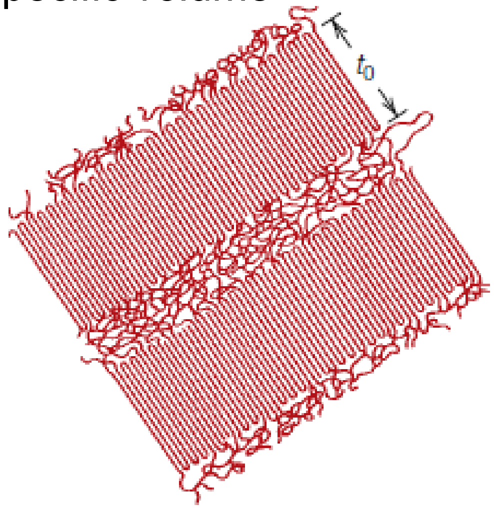
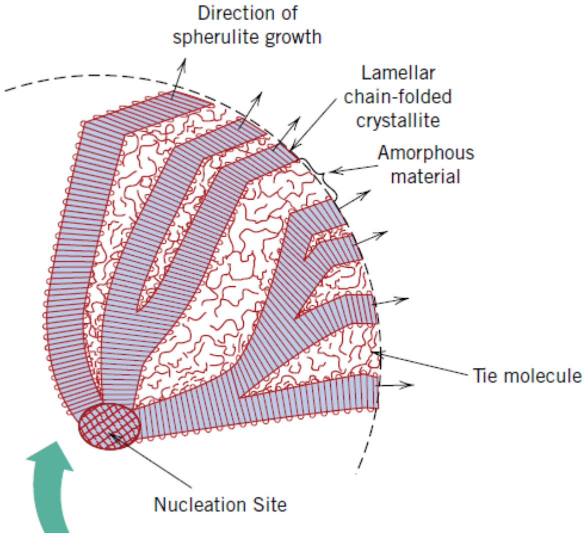




Thermal transition in polymers

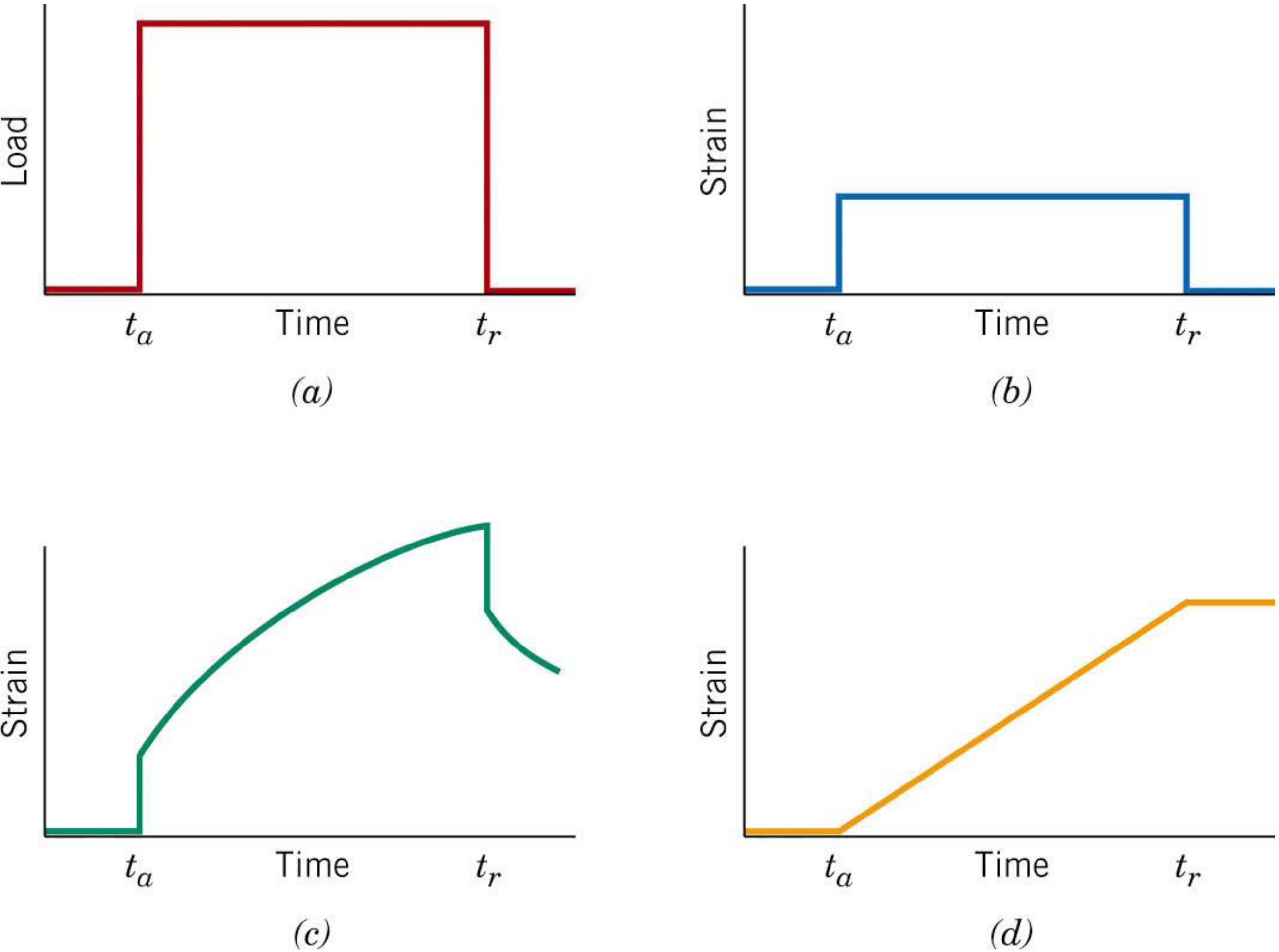
- This ductile-brittle transition is observed in **amorphous** and to a lesser extent in **semi-crystalline polymers**
- The transition in mechanical properties can be explained with reference to the specific volume (1/ρ)
- **Crystalline solids** - atoms or molecules are packed tightly together and their structure breaks down into an amorphous liquid at the melting temperature (TM). There is thus a gradual increase in specific volume up to T_m, and then a step increase at T_m
- **Amorphous solids** - atoms or molecules are randomly arranged and as such there is more free volume (empty space) within their structure. As the solid is heated, a temperature is reached at which there is an increase in the rate of change of specific volume





Time dependent behaviour

Polymers are visco-elastic materials



Summary

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