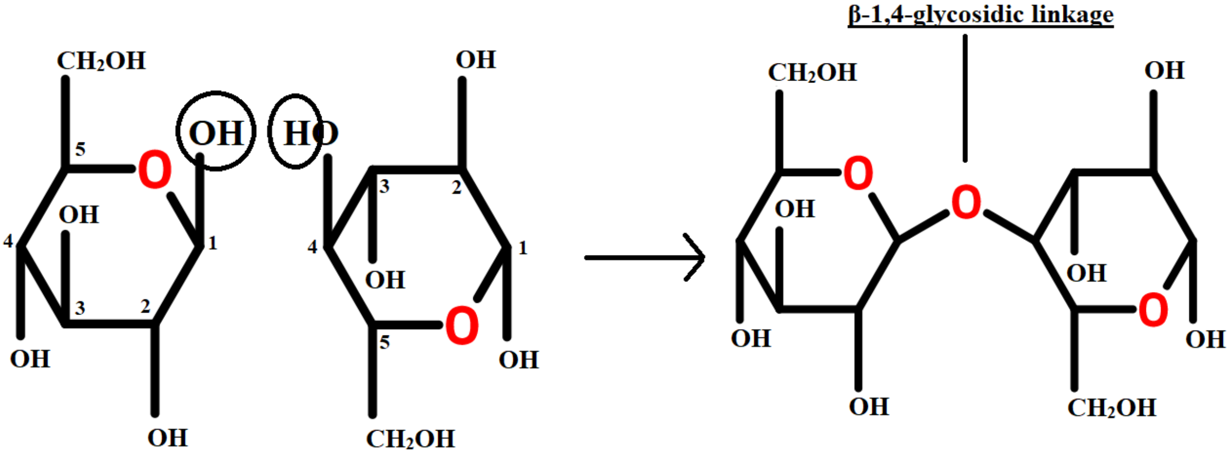
Cellulose and Chitin

Condensation polymerization of β-Glucose:



Intramolecular hydrogen bonds ➔ Long, flat, ribbon-like polymer chains.

Intermolecular hydrogen bonds ➔ Ribbon-like polymer chains are held together side by side to form sheets.

Therefore cellulose has a rigid and highly ordered structure.

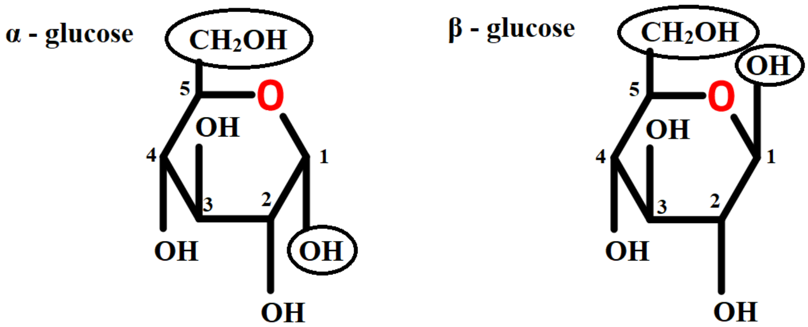
Properties of cellulose [$(C_6H_{10}O_5)_n$]:

1. High tensile strength
   - –OH groups along cellulose polymer chains can form strong hydrogen bonds with each other

2. Interactions with water
   - –OH groups in one cellulose chain can form hydrogen bonds with another cellulose chain. Less –OH groups are available for forming hydrogen bonds with water molecules. Therefore cellulose is **insoluble in water**.
   - Many polar –OH groups in the cellulose polymer chain can attract polar water molecules. Therefore cellulose **absorbs water well.**

3. Biodegradability
   - Micro-organisms can break down cellulose via hydrolysis (by breaking β-1,4-glycosidic linkages). Therefore cellulose is **biodegradable.**

Note that the -OH group at C-1 is on the same side of the ring as $-CH_2OH$ at C-5 in β-Glucose



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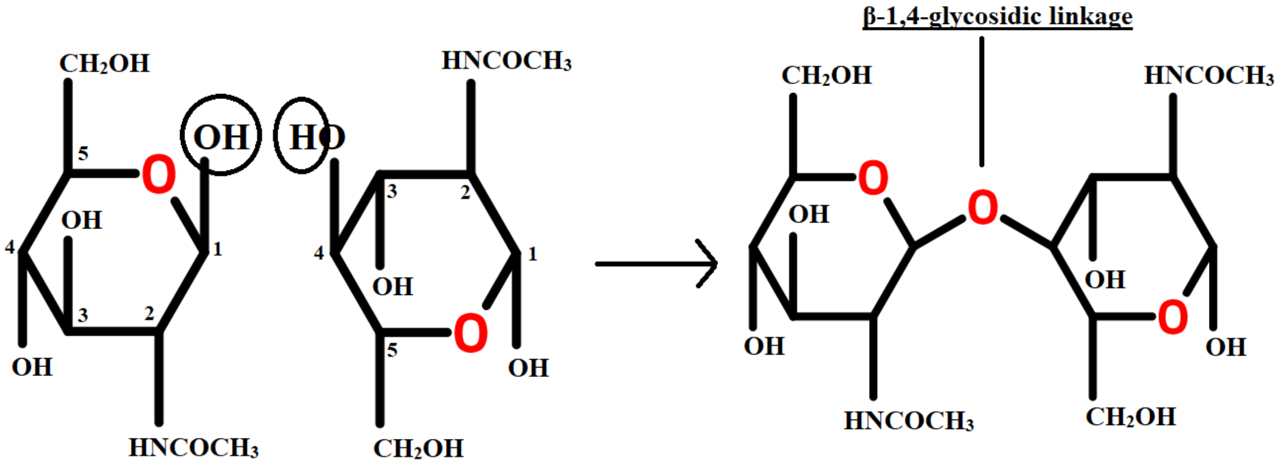
Condensation polymerization of acetylglucosamine:



The structure of chitin is similar to that of cellulose. Therefore chitin also has a rigid and highly ordered structure.

Properties of chitin [$(C_8H_{13}O_5N)_n$]:

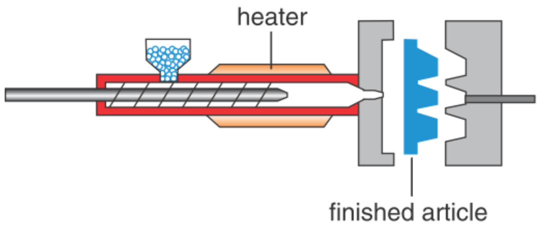
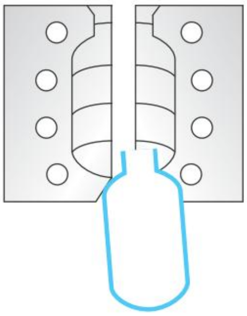
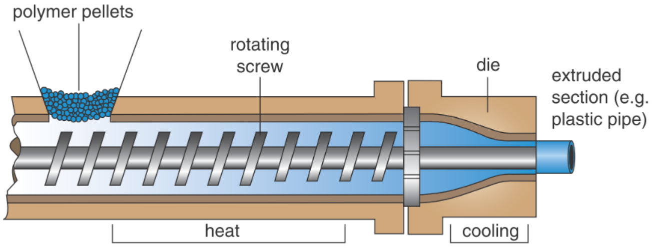
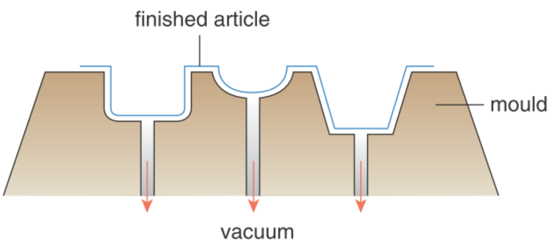
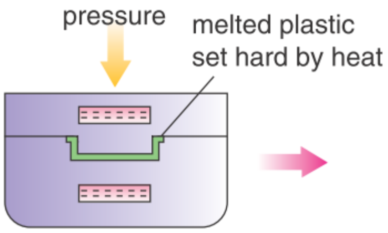
1. Hardness
   - Chitin is harder than cellulose as the acetylamino groups of chitin allow the polymer chains to interact more strongly.

2. Interactions with water
   - –OH groups and $–NH(CO)CH_3$ groups in one chitin chain can form hydrogen bonds with another chitin chain. Less –OH groups and $–NH(CO)CH_3$ groups are available for forming hydrogen bonds with water molecules. Therefore chitin is **insoluble in water**.

3. Biodegradability
   - Micro-organisms can break down chitin via hydrolysis (by breaking β-1,4-glycosidic linkages). Therefore cellulose is **biodegradable**.

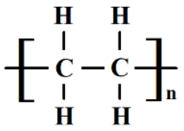
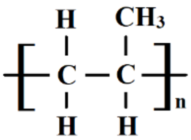
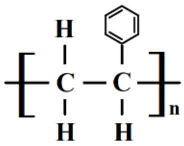
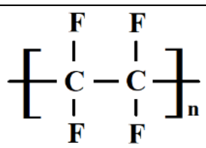
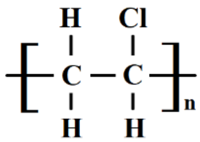
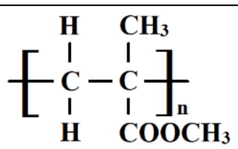
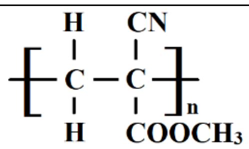
	Cellulose	Chitin
General formula	$(C_6H_{10}O_5)_n$	$(C_8H_{13}NO_5)_n$
Monomer	β-Glucose	Acetylglucosamine
Linkage	β-1,4-glycosidic linkage	
Bonding between polymer chains	Hydrogen bond (More extensive in chitin due to the presence of $-NHCOCH_3$ group)	
Structure	Rigid and highly ordered	Very rigid and highly ordered
Application	Paper, rayon, cell wall	Exoskeletons of crabs / insects

Plastic fabrication processes

Process	Diagram	Type of plastic	Example
Injection moulding		Thermoplastic	- Cups - Buckets - Bowls - Toys - Wash basins
Blow moulding		Thermoplastic	- Soft-drink bottles - Jars - Detergent bottles
Extrusion moulding		Thermoplastic	- Straws - Pipes - Ropes - Fibres - Garden hoses
Vacuum forming		Thermoplastic	- Yoghurt pots - Egg cartons - Packaging trays - Disposable cups
Compression moulding		Thermosetting plastic	- TV set casing - Electric plug casings - Electric switches - Electric sockets - Handles for cooking utensils

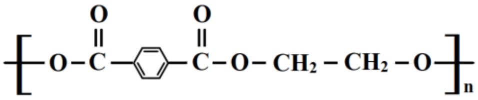
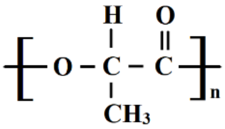
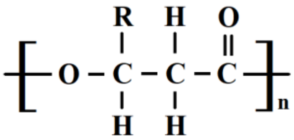
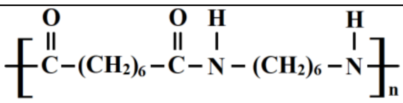
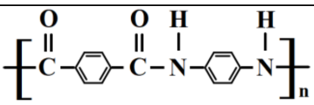
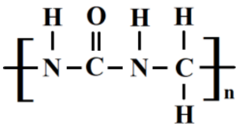
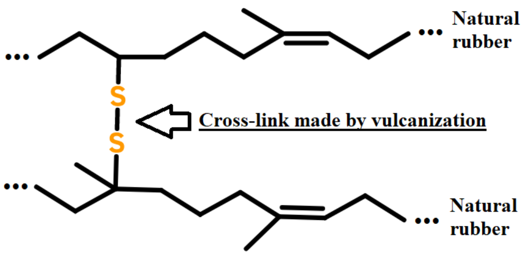
Intensive notes (Topic 14: Material Chemistry)

Polymerization

Plastic	Properties		Uses
 Polyethene (PE)	**LDPE (branched PE)**	- Light, flexible - Soften in boiling water	- Bags - Wrapping film
	HDPE (unbranched PE)	- Light and rigid - Resistant to chemicals - Higher density and melting point than LDPE	- Bottles - Buckets - Boxes
 Polypropene (PP)	- Resistant to chemicals - High melting point and more rigid than PE		- Food container - Ropes - Baskets, boxes - Luggage cases
 Polystyrene (PS)	**PS**	- Transparent - Hard but brittle	- Transparent container - Sample bottles
	Expanded PS	- Heat insulator - Light	- Food boxes, foam cups - Packaging materials
 Polytetrafluoroethene (PTFE) or Teflon	- Heat and chemical resistant, high melting point - Non-sticky (a layer of partial negative charges on the surface of a PTFE chain repel other substances) - Non-toxic - Resistant to tear		- Frying pans - Cable insulation - Containers for corrosive chemicals
 Polyvinyl chloride (PVC)	- Toxic - Rigid - Soft and flexible when mixed with plasticizer - Electrical insulator - Water-resistant		- Floor tiles - Sewage pipes - Shower curtains - Insulating covering for electric wires
 Polymethyl methacrylate (PMMA) or Perspex	- Transparent (Due to presence of -$COOCH_3$ group) - Hard, tough, rigid - Not easily scratched		- Aeroplane windows - Car windows - Advertising sign boxes - Plastic optical fibre
 Polycyanoacylate	- Monomers can polymerize rapidly in the presence of water / alkaline conditions		- Instant glue - Fingerprint detection

The above polymers are usually synthesized by addition polymerization (Monomer molecules join together repeatedly to form polymer molecules <u>without the elimination of small molecules</u>)

The monomers of the above polymers should contain C=C double bond.

Plastic	Properties	Uses
 Poly(ethylene terephthalate) (PET) or Dacron	- Strong and tough - Smooth and flexible - Resistant to water and most chemicals (exceptacids alkalis) - Low density	- Fibre and clothes - Lightweight sails - Bottles for water and drinks
 Polylactide (PLA)	- Non-toxic - Biodegradable and biocompatible - Renewable monomer (Lactic acid → Lactide → PLA)	- Surgical stiches - Medical threads - Drug carriers - Plastic bags
 Polyhydroxyalkanoate (PHAs) or Biopol	- Non-toxic - Biodegradable and biocompatible	- Disposable drinking cups, utensils and razors - Drug carriers - Wound dressings, screws, bone plates
 Nylon (Nylon 6,8 above) 6-C diamine & 8-C dioic acid / dioyl dichloride	- Strong and tough - Elastic - Can be dyed to give different colors	- Ropes, Nets - Fishing lines - Badminton racket strings
 Kevlar	- Very strong and rigid - Low density - Heat resistant	- Bullet-proof vests - Protective clothing for fireman
 Urea-methanal*	- Electrical and heat insulator - Chemical resistant - Hard and rigid	- Electric plug casings, electric sockets, electric switches - Casing for electrical appliances
 Vulcanized rubber*	- Harder and more elastic than natural rubber - Elastomer - Resistant to abrasion, chemicals, and electric currents - Impermeable to gas	- Car tyres - Footwear

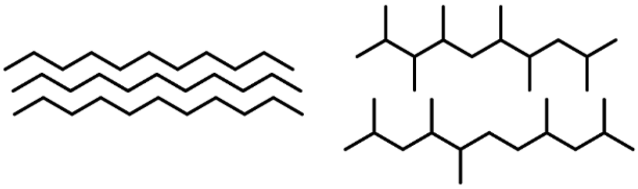
The above polymers are usually synthesized by condensation polymerization (Monomer molecules join together repeatedly to form polymer molecules with the elimination of small molecules)

The monomers of the above polymers should be bifunctional (except ring-opening polymerization).

Structures and properties of plastics

A. Density

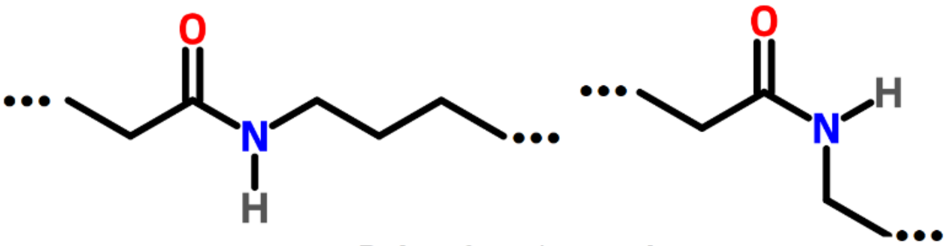
- When ethene is polymerized at high temperatures and pressures, low-density polyethene (LDPE) is produced.
  When ethene is polymerized at lower temperatures and pressures in the presence of Zigler-Natta catalyst, high-density polyethene (HDPE) is produced.
- HDPE has a lower degree of branching. HDPE molecules can pack more closely than those of LDPE. Therefore **HDPE has a higher density than LDPE.**
- Van der Waals' forces between HDPE molecules are stronger than those between LDPE molecules. Therefore **HDPE is stronger than LDPE.**



HDPE **LDPE**

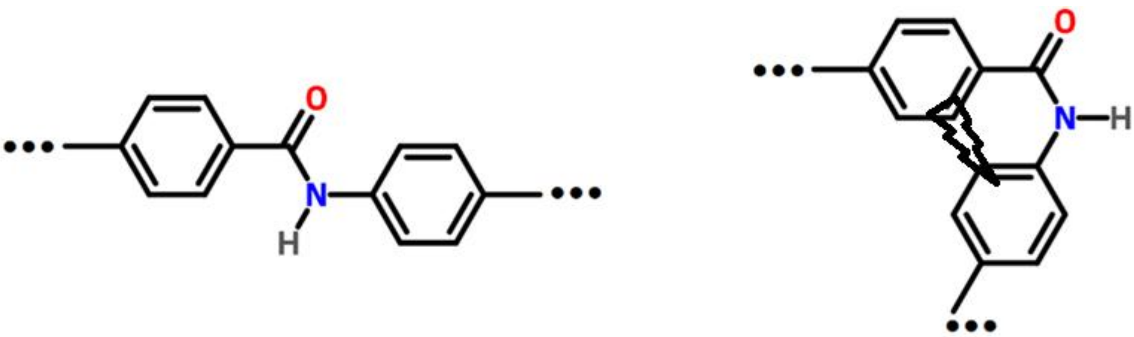
B. Strength and rigidity

- C–N bond in nylon is free to rotate. When –C=O and –N–H groups are on the same side, polymer chains will be bent. This reduces the hydrogen bonds between polymer chains



Both conformations are okay

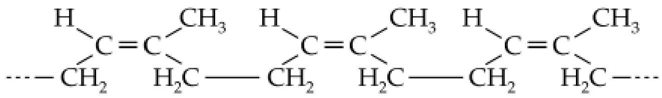
- C–N bond in Kevlar is not free to rotate. –C=O and –N–H groups in Kevlar cannot be on the same side (Large benzene rings CANNOT be on the same side). Polymer chains in Kevlar are straight. A more extensive network of hydrogen bonds forms between the Kevlar polymer chains. Kevlar polymer molecules are in a sheet-like structure and stacked together to forma a highly ordered structure. Therefore Kevlar is very strong.



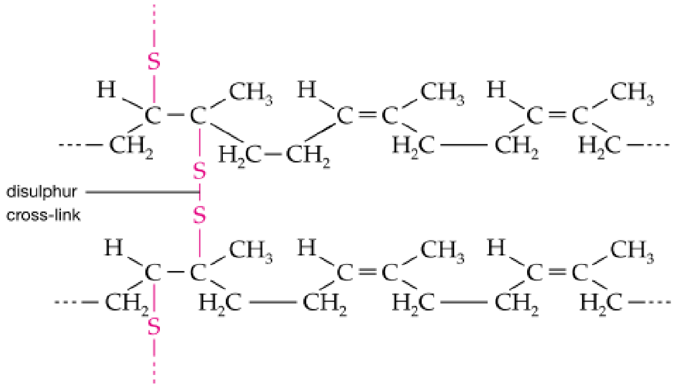
Conformation on the right is less favored as two benzene rings cannot come close to each other

C. Elasticity

- Natural rubber (poly(methylbuta-1,3-diene)) is sticky at high temperature. At low temperatures, it breaks easily.

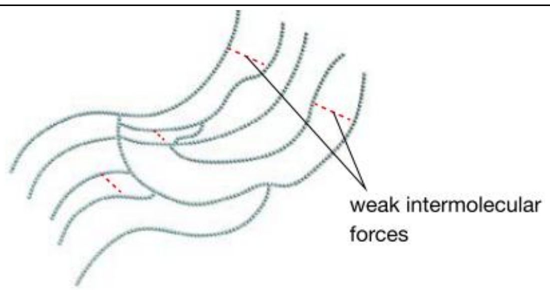
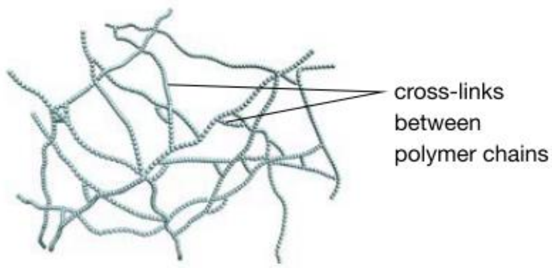


- Vulcanization is done by adding a small amount of sulphur to natural rubber. It allows polymer chains to form disulphur cross-links. Vulcanized rubber is produced.



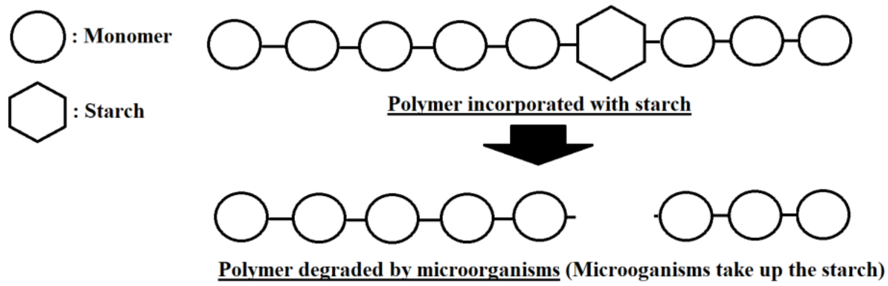
- Polymer chains in vulcanized rubber are held together by disulphur cross-links. They cannot slip easily over each other. Therefore vulcanized rubber is harder than natural rubber
- Vulcanized rubber is more elastic than natural rubber. When a vulcanized rubber is stretched, polymer chains can only move slightly without breaking the disulphur cross-links. When the stretching force is removed, polymer chains return to their original positions as polymer chains are still held together by the disulphur cross-links

D. Thermal properties

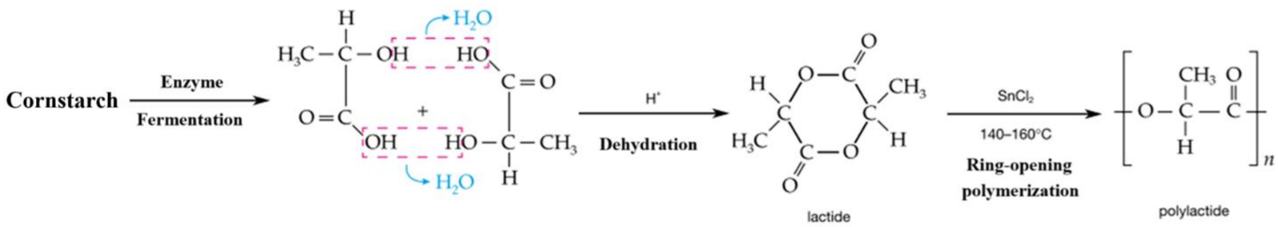
Thermoplastic is a plastic which can be repeatedly soften by heating and harden again on cooling.	**Thermosetting plastic** (thermoset) is a plastic which, once set hard, cannot be soften again by heating.
	
- At higher temperatures, intermolecular forces between thermoplastic polymer chains are overcome. Polymer chains can slide over one another. Therefore thermoplastics softens and melts upon heating. - At lower temperatures, thermoplastic polymer molecules come closer and the intermolecular forces get stronger. Therefore thermoplastics hardens again upon cooling.	- In thermosetting plastic, cross-links are present between polymer chains. Therefore the polymer chains in thermosetting plastics have little motion. Thermosetting plastics do not soften upon heating. - Under very strong heating, thermosetting plastics decompose instead of melting. This produces carbon, causing the plastics to turn black (charring)

E. Biodegradability

- Some plastics can be degraded by other chemicals
  (e.g. Ester linkage in polyesters and amide linkage in polyamides can be hydrolyzed by acids / alkalis)
- Biodegradable plastics are polymeric materials that can be broken down within a relatively short time through the action of micro-organisms. There are two ways to synthesize biodegradable plastics:
  1. Incorporation of biodegradable substances into polymer
     - Starch / cellulose molecules can be incorporated into PE.
     - Micro-organisms can take up the starch, breaking the polymer chains apart. The small pieces of plastics can degrade much faster as they have larger surface area.



  2. Synthesizing plastics using renewable resources
     e.g. PHA and PLA (Can be broken down by enzymes in microorganisms easily)

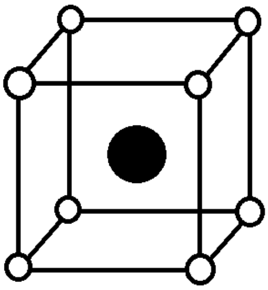
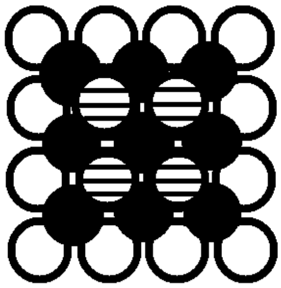
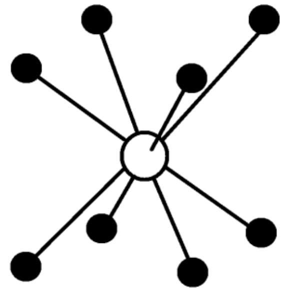
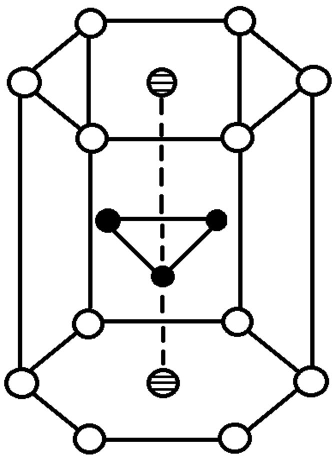
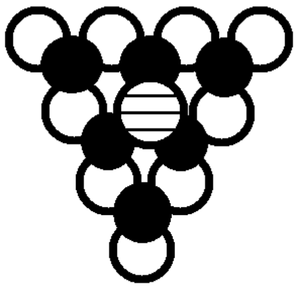
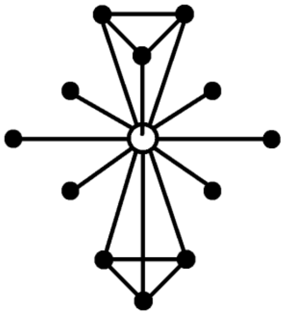
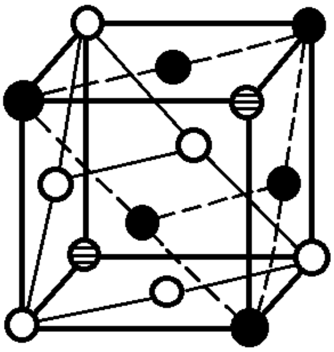
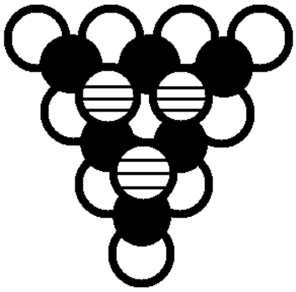
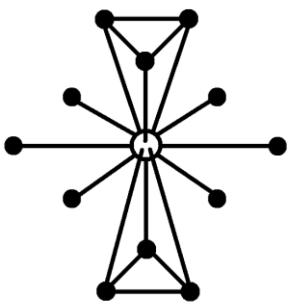


Recycling plastics

- Non-biodegradable plastic waste buried in landfill sites. However, it takes a long time for plastics wastes to be degraded. This leads to a waste of land resources. In addition, it may also pollute underground water.
- Incinerating plastic waste produces poisonous gases (HCl, Cl_2, dioxins, SO_2). This causes serious air pollution.
- Recycling plastics are preferred. It is because:
  1. Saving non-renewable plastic raw materials (From petroleum)
  2. Reducing volume of solid waste
  3. Causing less air pollution
  4. Converts some plastic wastes to useful products
- Problems associated with recycling plastics:
  1. Hard to sort out plastic from other waste
  2. Hard to identify the type of plastic (Code on plastic articles indicates the type of plastic)
  3. Hard to remove additives (pigments, plasticizers)
  4. High land cost (expanded PS) and labor cost

Crystal structure

Unit cell is the simplest arrangement of atoms (or ions) which when repeatedly will produce the whole structure.
Coordination number is the number of atoms (or ions) immediately surrounding an atom (or ions) in a crystal lattice

Unit cell (Name of structure)	**Packing efficiency**	**Number of atoms in one unit cell**	**Coordination number**
 Body-centered cubic (Open structure)	 68%	○ $= \frac{1}{8}$ ● $= 1$ Number of atoms: $= 1 + 8\left(\frac{1}{8}\right)$ $= 2$	 8
 Hexagonal close-packed	 aba pattern 74%	○ $= \frac{1}{6}$ ● $= 1$  $= \frac{1}{2}$ Number of atoms: $= 3 + 2\left(\frac{1}{2}\right) + 12\left(\frac{1}{6}\right)$ $= 6$	a b a  12
 Cubic close-packed	 abc pattern 74%	○ $= \frac{1}{8}$ & $\frac{1}{2}$ ● $= \frac{1}{8}$ & $\frac{1}{2}$  $= \frac{1}{8}$ Number of atoms: $= 6\left(\frac{1}{2}\right) + 8\left(\frac{1}{8}\right)$ $= 4$	a b c  12

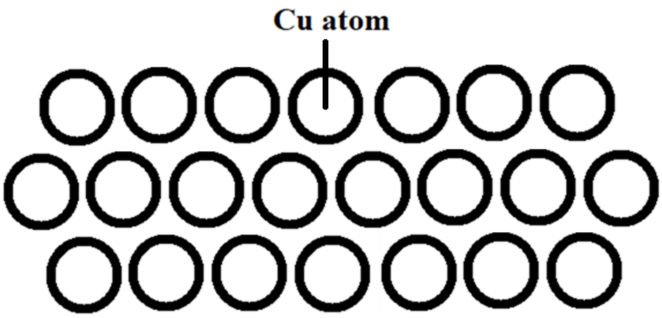
Alloy

Alloy is a homogeneous mixture with metallic properties. It is composed of two or more elements, of which at least one is a metal.

- Alloys are usually made by mixing a metal in the molten state together with one or more other elements. The mixture is cooled to solidify
- Alloys generally have the following properties:

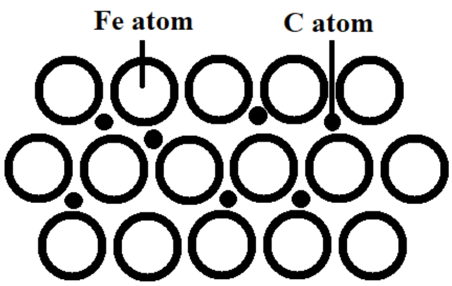
1. **Stronger and harder, less malleable and less ductile**

   In pure metals, all atoms are of the same size and are regularly arranged. Layers of atoms can slip over one another when force is applied. Non-directional metallic bonds continue to hold the metal ions and delocalized electrons. The shape of metal changes but the metal will not break. Therefore pure metals are malleable and ductile.

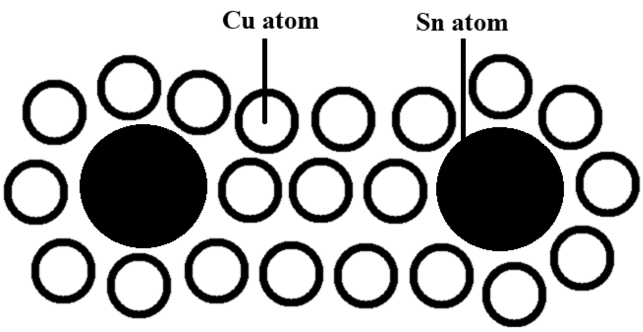


Crystal structure in pure copper metal

   In alloys, atoms of another elements are introduced into the structure of a pure metal. The structure of the metal in alloys is distorted. Layers of atoms cannot slide over each other easily.



Crystal structure of steel



Crystal structure of bronze

2. **Lower melting point**

   The sizes of atoms in alloy are different. This makes the arrangement of atoms less regular. The metallic bonds between atoms in alloy are weaker than that of pure metal. Therefore alloys generally have lower melting point. The

3. **Lower electrical and thermal conductivity**

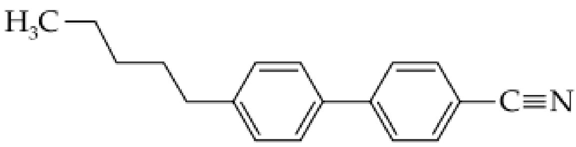
   The movement of delocalized electrons in the alloy is hindered as the arrangement of atoms in alloy is less regular than that of pure metals. Therefore alloys generally have lower electrical and thermal conductivity.

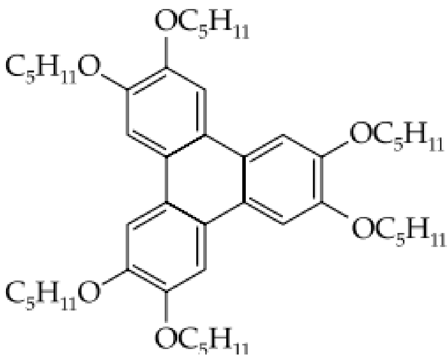
Alloy	Composition	Properties	Uses
Brass	Cu (70%) Zn (30%)	- Harder than pure Cu - More corrosion resistant than pure Cu - Golden appearance - Malleable	- Musical instrument - Ornaments - Electrical fittings - Door knobs and bolts
Nickel-brass (Coinage metal)	Cu (70%) Zn (24.5%) Ni (5.5%)	- Harder than pure Cu - More corrosion resistant than pure Cu - Shiny appearance - More wear resistant than pure Cu	- Coins (HKD 50¢, 20¢, 10¢)
Bronze	Cu (95%) Sn (5%)	- Stronger than pure Cu - More corrosion resistant than pure Cu - Yellowish-brown appearance - Malleable	- Ornaments - Statues - Church bells - Ship propellers
Mild steel	Fe (99.8%) C (0.2%)	- Stronger than pure Fe - Malleable	- Bridges - Car bodies
Stainless steel	Fe (73%) Cr (18%) Ni (8%) C (1%)	- More corrosion resistant than pure Fe - Hard and strong	- Cutlery - Surgical instruments - Cooking utensils - Car exhaust pipes - Kitchen sinks
Duralumin	Al (95%) Cu (3%) Mg (1%) Mn (1%)	- Stronger than pure Al - More corrosion resistant than pure Al - Low density	- Aircraft bodies - Spacecraft bodies
Solder	Sn (63%) Pb (37%)	- Lower melting point than pure Sn / Pb	- Joining metal wires and pipes - As connections in electric circuits
18-carat gold	Au (75%) Cu / Ag (25%)	- Stronger and harder than pure Au - Golden appearance	- Jewellery - Gold coins

Liquid crystal

- Liquid crystal is a phase between solid and liquid. It flows like liquids. However, the molecules are packed orderly like solid.
- In general, liquid crystal is common among organic compounds:

1. **With long and rod-like or disc-like molecular structure**

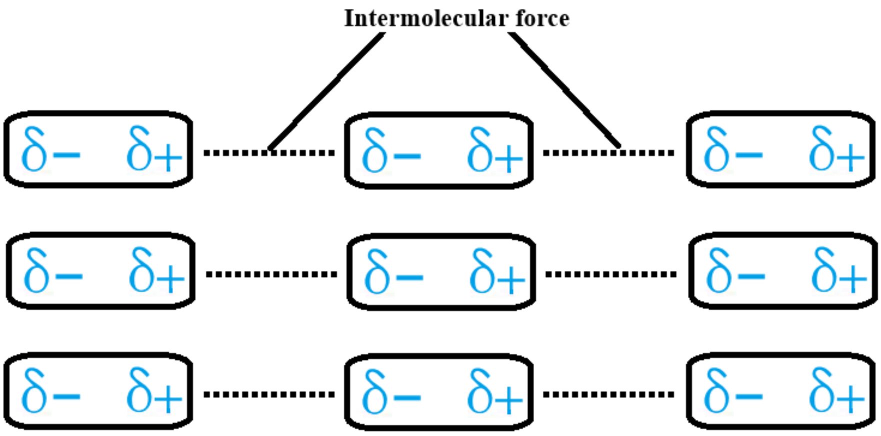




Long and rod-like **Disc-like**

These long chains cause the molecules to pack closely less readily.

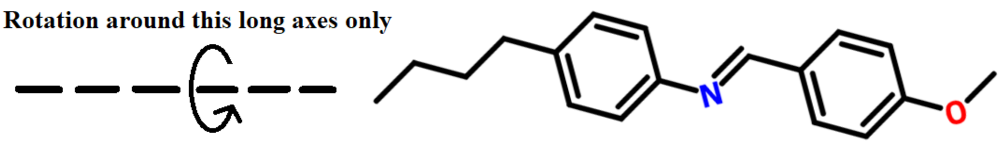
2. **Polar**



Molecules of liquid crystals are arranged along the same direction and parallel to each other

The intermolecular forces are strong. Molecules are arranged along the same direction and parallel to each other. However, the intermolecular forces are not too strong. Otherwise the molecules will be held firmly in positions.

3. **With benzene ring, cyclic structures or C=N / N=N bonds**



Methoxybenzylidene butylaniline (MBBA)

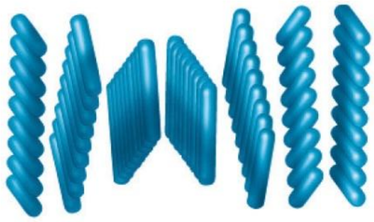
These structures add extra rigidity to the molecules. The molecules therefore can only rotate around their long axes only, but not end over end.

Different phases of organic liquid crystals

1. **Nematic phase**
   - Molecules are oriented along the same direction
   - Molecules are parallel to one another
   - No positional order

2. **Smectic phase**
   - Molecules are oriented along the same direction
   - Molecules are parallel to one another
   - Arranged in planes orderly

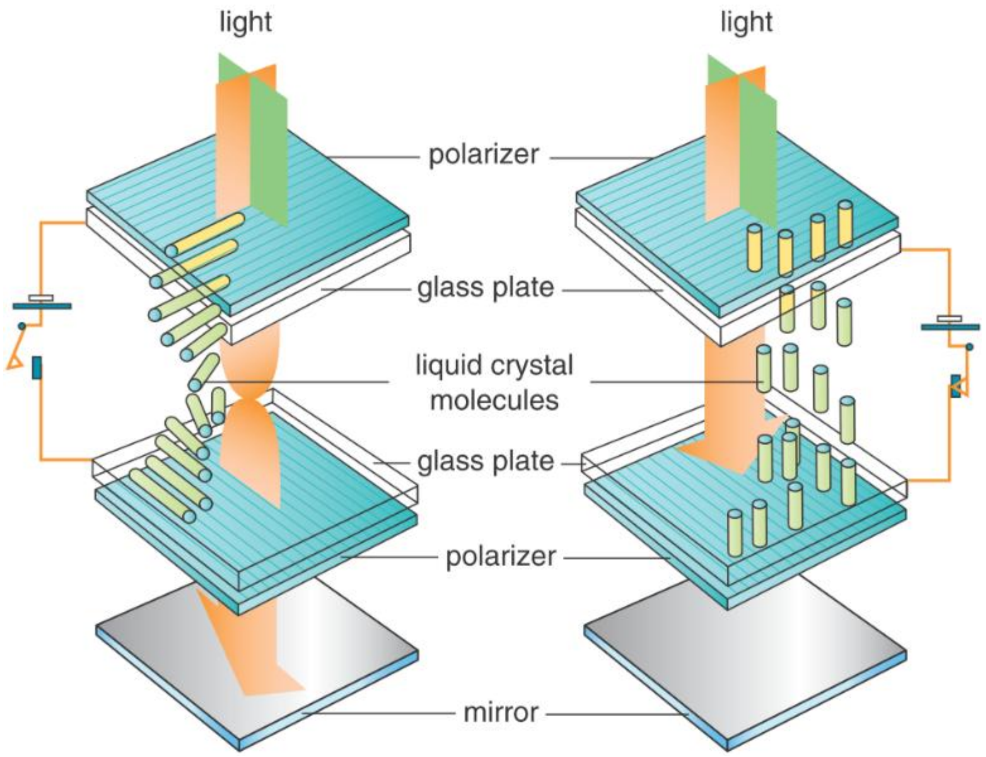
3. **Cholesteric phase**
   - Arises when the molecules are chiral
   - Arranged similarly to nematic phase
   - Molecules of adjacent layers are pointing at different angles
     - ➔ Slightly twisted planes
     - ➔ Helical arrangement



Uses of liquid crystals

1. Liquid crystal displays (LCDs)

Each pixel on the LCD of a TV screen contains a layer of liquid crystal molecules in the **cholesteric phase** sandwiched between two polarizers. These two polarizers are arranged perpendicular to each other.



When voltage is off (left), the polarized light is rotated by liquid crystal molecules. The polarized light is rotated to the correct orientation and is able to pass through the second polarizer ➔ Display area appear bright	When voltage is on (right), the liquid crystals reorient and line up parallel to the electric field. Polarized light is NOT rotated by liquid crystal molecules. The polarized light cannot pass through the second polarizer ➔ Display area appear dark

Molecules to be used as LCD should possess the following properties:

- Chemically stable
- Remains in liquid crystalline phase over a suitable range of temperatures.
- Rapid change in the orientation of molecules when a voltage is applied.

2. Liquid crystal thermometers

- The helical arrangement of liquid crystal molecules in cholesteric phase twists slightly as temperature changes. This twist can reflect light of different colours. The colour of cholesteric phase liquid crystal molecules changes with temperature.
- Liquid crystal thermometers can be used to measure body temperatures and detecting tumors (as temperature in the affected tissues are generally higher)

Nanomaterials

Nanomaterial is an organic or inorganic material that has a particle size up to 100 nm.

- The atoms on the surface tend to be more reactive than those in the interior. In nanomaterials, the ratio of surface area to volume is much higher than that of bulk materials. More atoms are located on the surface of the nanomaterials. Therefore nanomaterials are generally more reactive and have different properties.

Uses of nanomaterials

1. **Antiseptics**
   - Silver nanomaterials can reduce the bacteria's ability to take up oxygen. This can kill the bacteria.

2. **Sunscreens**
   - ZnO and TiO_2 can absorb UV radiation. This can reduce the damage caused by the absorption of UV light by our skin.
   - Bulk ZnO and TiO_2 are white in color while ZnO and TiO_2 nanomaterials are transparent.

3. **Drug delivery**
   - Nano-sized pills are usually made from biocompatible polymers. They can deliver anti-cancer drugs to targeted tumors.

4. **Making composite materials**
   - Carbon nano-tubes is made by rolling up a graphene (a single layer of carbon atoms in graphite) sheet. It is very strong, flexible and lightweight.
   - They are widely used in making composite materials which can be used in making aircraft bodies, bullet-proof vests and sporting equipment.

5. **Self-cleaning coatings**
   - When sunlight shines on a surface of TiO_2 nanoparticles, it trigger a reaction which can break down dirt and bacteria adsorbed on the surface. In addition, the surface becomes hydrophilic. This allows water spreads over the surface and washes away the substances on it during cleaning.
   - TiO_2 nanomaterial coating can be incorporated into construction materials to give them self-cleaning abilities.

Intensive notes (Topic 14: Material Chemistry)

Green chemistry

1. **Waste prevention**
2. **Maximizing atom economy**

$$\text{Atom economy} = \frac{\text{total mass of atoms in the desired product}}{\text{total mass of atoms in the reactants used}} \times 100\%$$

Example: By using NaOCl, this chemical plant can produce hydrazine (H_2NNH_2) a propellant used in space vehicles:

$$NaOCl + 2NH_3 \rightarrow H_2NNH_2 + NaCl + H_2O$$

(a) Calculate the atom economy. (Relative atomic masses: H = 1.0, N = 14.0, O = 16.0, Na = 23.0, Cl = 35.5)

Answer: Atom economy = (1x2 + 14 + 14 + 1x2) / [(23 + 16 + 35.5) + 2(14 + 1x3)] x 100% = 29.5%

(b) Explain why a reaction with high atom economy does not necessarily have a high yield.

Answer: Calculation of atom economy is based on 100% yield. In fact, most reactions do NOT go to completion.

3. **Using less hazardous chemical synthesis**

Corrosive chemicals: H_2SO_4, HCl, NaOH, KOH

Toxic chemicals: CO, CH_3OH, halogens, KCN, HCN, Benzene, SO_2, H_2S, 2,4-DNPH, compounds of Pb and Hg.

4. **Producing safer chemical products**
5. **Using safer solvents and auxiliaries**
   - When solvent is needed, safer solvents (H_2O) is preferred
   - Solvent-free processes are greener than processes that require solvent
6. **Designing for energy efficiency**
   - Processes with lower operating temperatures and pressures are preferred
7. **Using renewable raw materials**

Renewable raw materials: Glucose, sugars, fats, biomass, lactic acid

8. **Reducing derivatives**
   - Processes that involve fewer steps are preferred. Generally, the more steps in an industrial process:
     1. The more chemicals are needed and eventually, more wastes are produced.
     2 The lower will be the overall yield.
9. **Using catalysts**
   - Catalyst can speed up the rate (and itself remains chemically unchanged at the end). Processes using catalyst can operate under moderate conditions.
10. **Designing degradable chemical products**
11. **Developing real-time analysis for pollution prevention**
12. **Minimizing the potential for chemical accidents**