Polymers

Synthetic polymers can be produced with a diverse range of properties, such as flexibility, hardness, melting point, colour, strength, or density. This means they can be designed as cheaper, better replacements for traditional materials.

Fillers are substances that are added to a polymer to lower cost of production and/or improve its properties. A filler can make it more difficult to recycle, since the filler can be hard to separate from the polymer.

There are disadvantages of synthetic polymers:

- May degrade under ultraviolet radiation (e.g. sunlight)
- May cause litter problems if not biodegradable
- May not be useful at high temperatures (particularly applies to thermoplastics)
- May be very hard to recycle
- May produce toxic products when burnt

Addition polymers form links by breaking double bonds.

 $CH_2 = CH_2$ becomes $-CH_2 - CH_2 -$

Condensation polymers form links by forming groups such as ester or amide.

$$\begin{array}{ccc} O & O \\ HO - \overset{\parallel}{C} - CH_2 - NH_2 & becomes & -\overset{\parallel}{C} - CH_2 - NH - & + H_2O \end{array} (polyamide)$$

$$\begin{array}{ccc} O & O \\ HO - \overset{"}{C} - CH_2 - OH & becomes & -\overset{"}{C} - CH_2 - O - & + H_2O & (polyester) \end{array}$$

The stronger the interaction between polymer chains, the more rigid the polymer.

- dispersion forces
- dipole-dipole interactions
- hydrogen bonding
- ion-dipole interactions
- covalent bonds (cross-links)
- lower melting point stronger interactions polymer more rigid

weaker interactions polymer more flexible

higher melting point

Polymers are often classed as either **thermoset** or **thermoplastic**, depending on properties.

Thermoset polymers

- have a high degree of cross-linking between polymer chains
- have melting points so high that the polymer will decompose rather than melt
- cannot be recycled (since they cannot be melted and remolded)

Thermoplastic polymers

- have much less cross-linking than thermoset polymers
- have lower melting points
- can be more easily recycled (since they can be melted and reshaped)

Silicates

Silicates are covalent networks containing silicon and oxygen, and aluminosilicates contain aluminium as well as silicon and oxygen. The 3D structure of silicates and aluminosilicates means they have negatively charged sites in the structure. When metal cations are found at these sites, the compound is called a silicate or aluminosilicate **mineral**.

The structure of silicates is based on the basic SiO₄ structural unit

 O_{i}^{i} (tetrahedral shape)

Oxygen atoms can shared between two silicon atoms in the silicate. When they are not, the oxygen atom has a negative charge, e.g.

In silicates and aluminosilicates, the oxidation state of silicon is always +4, oxygen -2, and aluminium +3.

This allows the charge on a silicate to be easily calculated if the ratio silicon to oxygen is known. If the ratio is $n_{\text{Si}} : n_0$, the charge on the silicate is $4 \times n_{\text{Si}} - 2 \times n_0$.

In minerals, the metal cations have predictable oxidation states (e.g. calcium +2), such that the total charge is zero on the formula for the mineral.

Soils

Silicates, and aluminosilicates are important components of rocks and soils. Their negative charge means that the metal cations in soil water form an equilibrium with metal cations adsorbed to the silicate structure, for example:

$$Na^+_{(aq)} \implies Na^+_{(soil)}$$

As metal cations dissolved in the soil water (aq) are absorbed by plant roots, the equilibrium position shifts to release cations adsorbed to the silicates (soil), meaning nutrients are continually available to plants. The total number of ions available will therefore decrease slowly over time unless replenished by an external source.

Since hydrogen ions are positively charged, they can be adsorbed to soil silicates, releasing (leaching) nutrients (metal cations) into the soil water.

 $Na^+_{(soil)} + H^+_{(aq)} \implies Na^+_{(aq)} + H^+_{(soil)}$

Flocculation

Clays contain fine silicate particles which have a negatively charged surface. If highly charged cations such as aluminium ions are mixed into water containing suspended clay particles, the particles will be flocculated into larger particles. These larger particles are too heavy to remain in suspension, and will settle forming a sediment that can be filtered off.

Water softeners

Hard water contains metal cations such as Mg^{2+} and Ca^{2+} which reduce the effectiveness of soaps, neutralising the negatively charged end of the soap molecules by forming insoluble 'scum' particles.

Hollow, porous silicate structures such as a zeolites contain many negatively charged sites where cations can be exchanged. If highly soluble ions such as Na⁺ are being held at these sites then hard water can be passed through the silicate structure and be softened. The cations causing the hardness of the water will become attached to the zeolite surface and the sodium ions will enter the water.



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Cleaning Agents

Stains

Stains can be removed if they are dissolved and washed away. The polarity of the solvent that needs to be used depends on the polarity of the stain. Non-polar solvents will be more effective at dissolving non-polar stains, and polar solvents will be more effective at dissolving polar stains.

If a stain is made up of a mixture of polar and non-polar substances, a mixture of solvents could be used.

Soaps and detergents

Soaps and detergents are cleaning agents that act to remove grease from the surface of an object. The basic structure of soaps and detergents is a long, non-polar hydrocarbon chain with a single ionic end. Within a **soap**, the ionic end is a **carboxylate** group:



Within a **detergent**, the ionic end is a **sulphonate** group.



When a surface covered in grease is soaked in water containing soap or detergent, the non-polar hydrophobic (water-fearing) end of the soap or detergent dissolves in the grease while the hydrophilic (water-loving) end forms ion-dipole bonds with water molecules. Agitation such as scrubbing causes **micelles**, small particles of grease surrounded by soap or detergent molecules. These have a negative surface charge, so they repel each other and stay in suspension, which allows them to be washed away.



Saponification

Soaps can be produced in a process called **saponification**. Triglycerides (fats and oils) are hydrolysed (reacted with water) under alkaline conditions by boiling in a concentrated solution of sodium hydroxide. This breaks the fats or oils down into soluble sodium carboxylate salts (soaps).



Hard water

Hard water contains calcium and magnesium ions in solution. When soaps are used in hard water, they will react with the metal cations to form an insoluble precipitate:



The effectiveness of soap will be significantly reduced in hard water, since the insoluble precipitate (scum) cannot perform the cleaning action.

Detergents will not form an insoluble substance with the metal cations, and therefore are still effective in hard water.

Materials

Phosphates and tripolyphosphates



Tripolyphosphate ions are often added to detergent formulations to improve their effectiveness. **Advantages** are that tripolyphosphates:

- keep calcium and magnesium ions in solution by forming water-soluble complex ions
- this prevents scum formation so that the detergent is less affected by water hardness
- keep clay particles in suspension (deflocculation) by attracting the highly charged cations
 - this prevents larger clay particles forming which would settle onto fabrics being washed
- keep the pH mildly alkaline by attracting the hydrogen ions and forming covalent bonds
 - this ensures that detergent anions remain in ionic form so cleaning action can occur
 - also causes a small amount of alkaline hydrolysis of the grease into water-soluble products

Phosphates fertilisers provide phosphorus in a soluble form, so that plants can easily absorb it through their roots.

Disadvantages to using phosphates and tripolyphosphates include that it washes into natural bodies of water and acts as a fertiliser for algae.

The increase in nutrient concentration in bodies of water is called **eutrophication**. Eutrophication and algal blooms reduce the ability to use bodies of water for commercial and recreational use.

- Some algae produce toxins which make the water unsafe for drinking.
- Excessive and rapid growth of algae (algal blooms) on the surface prevents sunlight reaching below the water surface.
- Underwater plants are unable to photosynthesise which prevents oxygen in the water being replenished.
- Anaerobic conditions are created, and aquatic animals die due to lack of oxygen.

Enzymes in detergents

Enzymes are often added to detergent formulations to assist the breakdown of stains that would otherwise require higher temperatures and more mechanical energy to remove. Examples of such stains include proteins, oils, blood, grass, milk and sweat.

Since enzymes are proteins, they are sensitive to changes in pH and temperature (this sensitivity can be explained in terms of their 3D structure).

Enzymes added to detergent formulation must be able to tolerate the presence of any surfactants and bleaches found in the formulation, must not be too sensitive to alkaline conditions, and must be able to handle the range of temperatures used by washing machines.

Bleaches

Coloured stains can often be oxidised to colourless substances. This process is called bleaching.

Chlorine bleaches

In order from strongest to weakest, hypochlorous acid (HOCl), hypochlorite (OCl⁻), and chlorine (Cl₂) are all oxidising agents. In aqueous solution they are in equilibrium which can be shown using the equations below.

$H^+ + OCl^- \longrightarrow HOCl$	(equilibrium between hypochlorite and hypochlorous acid)
$2e^{-} + 4H^{+} + 2OCl^{-} \xrightarrow{\longrightarrow} Cl_{2} + 2H_{2}O$ $2Cl^{-} \xrightarrow{\longrightarrow} Cl_{2} + 2e^{-}$	(half-equation for relationship between hypochlorites and Cl_2) (the other half-equation to complete the above half-reaction)

The equations above can be combined to produce full-equations describing the relationship between pH and the three oxidising agents in chlorine bleaches. Two examples are shown below. $H_2O + OCl^- \implies HOCl + OH^ Cl_2 + H_2O \implies HOCl + H^+ + Cl^-$

Chlorine bleaches are most stable at a pH above 7. Below this, the equilibrium position shifts towards the chlorine side of the equilibrium (hypochlorites decompose to chlorine). Since chlorine is a weaker oxidising agent, the bleach becomes less effective.

Oxygen bleaches

Solid oxygen bleaches release hydrogen peroxide which acts as an oxidising agent:

 $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ (oxygen's oxidation number decreases from -1 to -2)

Hydrogen peroxide decomposes to release oxygen.

 $2H_2O_2 \rightarrow 2H_2O + O_2$

Oxygen is also an oxidising agent but is much weaker than hydrogen peroxide.

 $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (oxygen's oxidation number decreases from 0 to or $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ -2)

Changing the temperature will change the rates of all reactions involved:

- solid bleach releasing hydrogen peroxide
- hydrogen peroxide oxidising stains
- hydrogen peroxide decomposing to produce oxygen
- oxygen oxidising stains

Increasing the rate of these reactions increases the effectiveness of the bleach, with the exception of the decomposition to oxygen (since hydrogen peroxide is a stronger oxidising agent). It is desirable to have the H_2O_2 produced and oxidising at high rates, but not decomposing too fast to O_2 .