## Polymers on the move

## Types of polymers

Thermoplastic polymers: Polymers that soften and melt when heated. (This means that they are easy to recycle by remoulding into a new item). These polymers only have intermolecular bonds (which are much weaker than the covalent bonds in thermosets) between chains which can be broken by warming.

Thermosetting polymers: Char and burn when heated (so can't be reshaped). These have extensive cross-linking by covalent bonding. The cross-links prevent the chains moving very much relative to one another, so the polymer stays in the same shape when it is heated.

Elastomer: Polymers that are soft and springy, which can be deformed and then go back to their original shape.
A co-polymer: Is made from two different monomers. This produces a polymer with properties in between those of the two polymers you would get if you polymerised each polymer separately.

## ABS

Acrylonitrile (2-propenitrile) butadiene styrene is an example of a co-polymer and is also a thermoplastic. This material combines the strength and rigidity of the acrylonitrile and styrene polymers with the

acrylonitrile


1,3-butadiene toughness of the polybutadiene rubber. The nitrile groups from neighbouring chains, being polar, allow permanent dipole-permanent dipole forces to bind the chains together, making ABS stronger than pure polystyrene (which only experiences Van der Waals forces between chains).

styrene
Monomers in ABS polymer

| How properties of polymers are linked to uses |  |  |
| :--- | :--- | :--- |
| Polymer | Use | Reason(s) for use |
| Acrylonitrile butadiene styrene <br> (ABS) | Car facia panels | -High impact strength improves car safety <br> -Ability to be injection moulded improves <br> design flexibility. |
| Fluoroplastics (PTFE, FEB) | Engine gaskets | High maximum use temperature prevents <br> polymer from melting when engine heats up. |
| Nylons | Bearings | Exceptional anti-stick/low friction <br> characteristics |
| Poly(propene) | Carburettor parts | Durability and high chemical resistance makes it <br> long-lasting. |
| Poly(chloroethene) (PVC) | Gear wheels | Rigid, tough, hard-wearing |
|  | Car accelerator pedals | Toughness and fatigue resistance reduces wear <br> and tear from repeated use. |
| fabrics |  |  |

## Polybutadiene



Polybutadiene is a highly resilient synthetic rubber (elastomer). Due to its outstanding resilience, it can be used for the manufacturing of golf balls. Polybutadiene rubber can be used in water seals for dams due to its low water absorption properties. Rubber bullets and road binders can be also produced by polybutadiene rubber.


Polybutadiene can be formed from many buta-1,3-diene monomers undergoing free radical polymerisation to make a much longer polymer chain molecule. The propagation steps in this reaction involve free radicals at the end of growing polymer forming a covalent bond with a carbon in the next monomer.

(E)-1,4-structure

(Z)-1,4-structure

The properties of polybutadiene rely on the types of stereoisomers formed when the double bonds in buta-1,3-diene open up and a new double bond is formed. A prevalence of the E isomers will result in a crystalline plastic whereas a high percentage of Z isomer will result in a flexible elastomer.

## Polyurethane

- Polyurethane used as an adhesive to bond windscreens in place. This allows the strength of the glass to contribute to the roll-over strength of the car allowing room to reduce the body weight.
- Reducing the body weight in this way improves fuel efficiency as less fuel is needed to move a lighter vehicle.
- Polyurethane foam replaced rubberised hair in seat cushions. Chlorofluorocarbons (CFCs) were used as a blowing agent in foam production, but this was stopped when an international agreement to stop the use of CFCs was reached as they contribute significantly to ozone depletion.
- Polyurethane can be classed as an addition polymer because many monomers bond together via rearrangement of bonds without the loss of any atom or molecule.


## Formation of polyurethane repeating unit from its monomers





Two ways in which hydrogen bonding can occur between polyurethane chains

## Sticky problems

## Solvents

Vehicle paints were traditionally based on several layers of different high molecular mass polymers dissolved in solvents but have been replaced due to concerns about solvent emissions. Organic solvents are volatile organic compounds (VOCs), many of which are harmful to health. They can also undergo chemical reactions causing the formation of ground-level ozone, an air pollutant. High concentrations of ozone can be detrimental to human and animal health. They can also cause damage to building materials, forests, vegetation and crops.

## Problems with paint:

- Vehicle must be heated to $>150^{\circ} \mathrm{C}$ to increase the mass of some of the layers or to melt others. This consumes large amounts of energy and there is no obvious alternative as lowering the bake temperature would lead to problems with the performance of the adhesive.
- Polymer-based paints require protection against ultraviolet light, otherwise they will degrade.
- Paints designed to adhere to metals will generally adhere much less well to polymeric substrates.


## Bonding Polyalkenes

In the following equation $\mathrm{X} \cdot$ represents a free radical (traditionally $\left.\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2} \mathrm{O} \cdot\right)$. A radical is a particle with an unpaired electron and is therefore highly reactive.
$\mathrm{X} \cdot+\mathrm{nCH}_{2}=\mathrm{CH}-\mathrm{CO}_{2} \mathrm{R} \mathrm{X}-\left(\mathrm{CH}_{2}-\mathrm{CHCO}_{2} \mathrm{R}\right) \mathrm{n} \cdot$

## reaction 1

"Acrylic adhesives bond a wide range of plastics, for instance polycarbonate or ABS, but are ineffective on poly(ethene) or poly(propene) because they can't get a chemical 'grab' on the unreactive surfaces."

The phrase 'can't get a chemical grab' refers to the fact that only weak instantaneous dipole-induced dipole bonds can form between poly(ethene) and the adhesive. Polycarbonate and ABS can form permanent dipole-permanent dipole and hydrogen bonds, respectively, with the adhesive.

Surface-H + R•Surface•+ RH
reaction 2
Reaction 2 is a more effective adhesive with $\mathrm{R} \cdot$ representing the alkyl radical $\mathrm{CH}_{3} \mathrm{CH}_{2} \bullet$ ). This radical is much more reactive than the alkoxy radical used in equation 1 . However, long-term data durability of the bonds in both methods is non-existent as the processes are relatively new.
(Both of these reactions are examples of propagation reactions as there are radicals on both sides of the equation.)

## Scrap heap challenge

Unlike steel, polymers are not easily recyclable.
Thermoplastics: As the polymer chains separate on heating, simple thermoplastics, such as nylon or polycarbonate can be melted down and reuse albeit in less stringent applications.

Thermosets: Thermosetting plastics (such as polyurethane foam) char on heating and so cannot be recycled in the same way as thermoplastics.

## What is the best way to recycle polyurethane foam?

| Approach | Advantage | Disadvantage |
| :--- | :--- | :--- |
| Digest the foam in ethylene <br> glycol (ethane-1,2-diol) to yield <br> polyols suitable for synthesising <br> rigid insulating polyurethane <br> foam. | -Can be used to make a large <br> range of products. <br> -Ethylene glycol is cheaply <br> available. | -Requires market for the product <br> -Ethylene glycol is toxic and <br> therefore needs to be handled <br> carefully. |
| Chop the foam up and compress <br> it, and use the resulting material <br> in, for instance, carpet backing. | -Cheap <br> -Easy, as it does not require any <br> chemical expertise | -Requires market for the product <br> -Limited uses. |
| Recover some of the energy used <br> to make the foam by burning it in <br> an incinerator. | The heat generated by <br> incinerating polyurethane could <br> be used to generate electricity in <br> a power station. | -Carbon dioxide, carbon <br> monoxide and nitrous oxides are <br> formed. <br> -Carbon dioxide is a greenhouse <br> gas and contributes to global <br> warming |
| -Carbon monoxide is poisonous |  |  |$|$| -Nitrous oxides lead to acid rain |
| :--- |
| (which can kill wildlife and |
| vegetation). |

## Long-term forecast

## Oil based plastics

Most plastics are oil-based. The monomers used to form oil-based polymers are extracted from crude oil by fractional distillation and/or cracking. This is a significant problem as the supply of petroleum is being depleted and it takes millions of years for crude oil to form. This will result in higher fuel costs in the future, prompting the search for alternative plastics.

## Vehicles of the future

High fuel costs will create the need to maximise fuel efficiency, by using lightweight polymers. However, these polymer themselves are made from oil so this isn't a long-term solution. The difficulty of recycling plastics is also an issue and alternatives will need to be investigated.

