Chem Factsheet

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Biodegradable Polymers

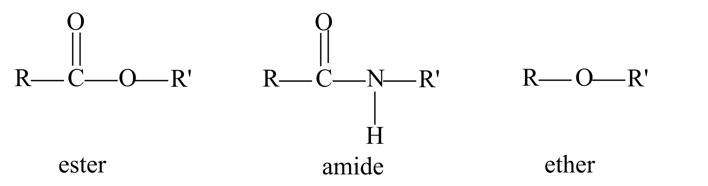
After completing this Factsheet, you will be able to:
- Recall the definition of biodegradable.
- Recognise the problems caused by non-biodegradable polymers,
- Recall the necessary properties of biodegradable polymers,
- Give examples of naturally occurring and synthetic biodegradable polymers,
- Give uses of some common biodegradable polymers.

What Are Biodegradable Polymers?

Biodegradable polymers are long molecules that can be broken down, or decomposed, after use by the action of bacteria or other living organisms. The products of this decomposition are naturally occurring compounds such as the gases carbon dioxide and nitrogen, water, and inorganic salts. This reduces the pollution caused by disposal of non-biodegradable polymers such as poly(ethene) and poly(vinyl chloride)/PVC.

Biodegradable polymers can be made by condensation reactions of monomers to form ester, amide, and ether functional groups.

Fig. 1 Common bonds linking monomers in biodegradable polymers

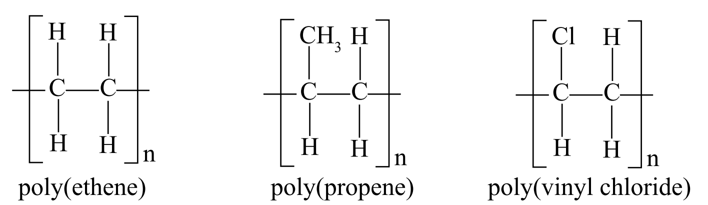


There are many examples of both natural and man-made biodegradable polymers, and their uses are wide-ranging – the particular use depends on the structure of the molecules, and therefore the properties of the polymer.

The Problem with Non-biodegradable Polymers

Many polymers made by addition reactions (including poly(ethene), poly(propene), and PVC) are not biodegradable because micro-organisms do not possess the appropriate enzymes to break down the carbon backbone of the molecules.

Fig. 2 Poly(ethene), poly(propene), and PVC



These polymers are essentially non-polar, so there is nothing on the carbon backbone that can be attacked by electrophiles or nucleophiles, and therefore the strong C-C bonds cannot be broken by usual hydrolysis reactions. As a result, once these polymers have been used, their disposal into landfill sites will mean that they remain intact for many, many years. This method of disposal obviously leads to a number of environmental concerns.

Similarly, disposal (accidental or otherwise) of such polymers into water courses such as rivers, lakes, and oceans leads to significant long term pollution. Millions of tonnes of plastic has already accumulated in the oceans and this is causing many serious problems for animals living in these habitats.

To avoid long term filling of landfill sites, non-biodegradable polymers can be incinerated. The energy released from their combustion can be harnessed to generate electricity. However, the combustion of a range of polymers can lead to the release of a number of harmful and toxic chemicals such as dioxins.

Another alternative is to recycle or reuse the polymers. This involves careful separation of plastics into different categories so that the recycled materials do not contain a mixture of different monomers which can give them unfavourable or undesirable properties.

History of Biodegradable Polymers

The study of ancient medicine has shown that one of the first uses of a biodegradable polymer was the stitching of wounds (suturing) with catgut. This technique dates back to at least 100AD and relies on the tough collagen molecules found in the intestines sheep and other ruminants. Over time, as the wound heals, protease enzymes in the patient's body naturally disintegrate the catgut and the body absorbs the products of the hydrolysis, i.e. amino acids.

In response to growing environmental concerns over non-biodegradable polymers, the idea of synthetic biodegradable materials was introduced in the 1980s. Biodegradable plastic bags are now increasingly common across the world as are biodegradable plastic bottles and cups.

The Structure and Properties of Biodegradable Polymers

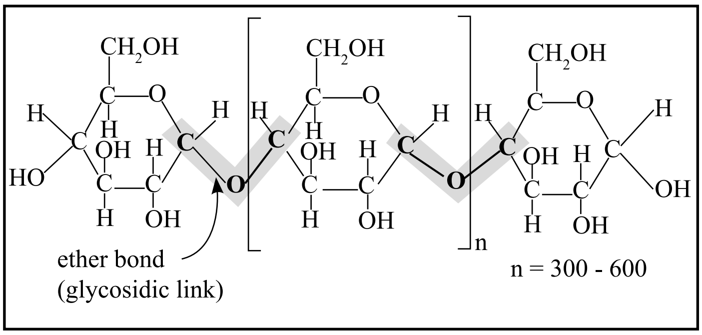
It is important that all biodegradable polymers have properties that enable them to be stable enough and durable enough for their intended use. It is not sensible to have a biodegradable plastic carrier bag that will degrade in the rain before any groceries are taken from the shop to the car! However, it is also necessary that, after their intended use, and following their disposal, they are easily broken down. Additionally, if used for medical purposes, they and their degradation products should be non-toxic, should maintain mechanical strength and durability during their life time, and should not cause an immune response in the patient.

The structure of biodegradable polymers is closely linked to their properties. They often consist of ester, amide, or ether functional groups between monomers. They can be grouped into classes based on how they are made and their structures. One class, named agro-polymers, is derived from organic matter and includes polysaccharides and proteins. Another class is called biopolyesters. These can be derived from microorganisms, or can be synthesised from natural or synthetic monomers. Additional classes are also being researched, including polyanhydrides.

Examples of Biodegradable Polymers

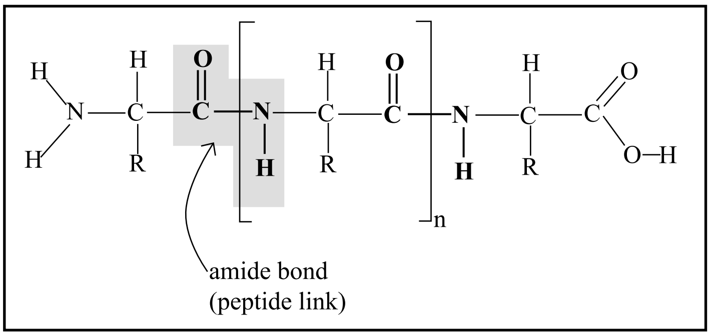
Polysaccharides - Glycosidic linkage (ether bond) between sugar monomers.
For example, starch found in potatoes.

Fig. 3 Starch



Proteins - Peptide linkage (amide bond) between amino acid monomers.
For example, plant-derived gluten or modern cutgut derived from purified collagen

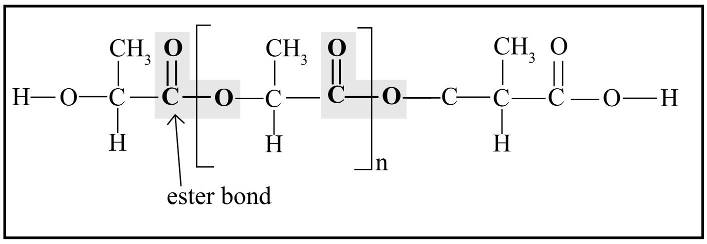
Fig. 4 Protein



Biopolyesters

Polylactic acid (PLA) is made from lactic acid molecules derived from renewable resources such as sugar cane.

Fig. 5 Polylactic acid

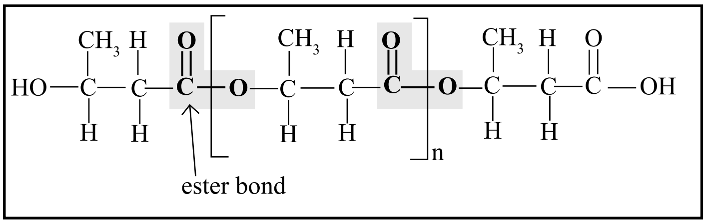


In 2010 it had the second highest consumption volume of any bioplastic in the world. It is insoluble in water and has similar properties to polyethylene terephthalate (PET or Terylene - the first polyester fabric ever produced). It can be processed into fibres or films, or can be extruded and used for processes like 3D printing and injection moulding. It can also be used as medical implants, e.g. plates, pins, and rods. Additionally it can be used as packaging material that can be decomposed after disposal. As a fibre, it has the potential to be woven into upholstery, disposable garments, and nappies. As a film, it can be made into rubbish bags that will be broken down when discarded.

PLA is degraded by the bacterium *Amycolatopsis* into harmless lactic acid that is then metabolised.

Polyhydroxybutyrate (PHB) is produced by microorganisms, including *Bacillus megaterium* when nutrients are limited.

Fig. 6 Polyhydroxybutyrate



It is formed in the cell as an energy storage molecule to be used when other respiratory substrates are unavailable. It was first isolated in 1925 and the natural biosynthesis of this molecule has been studied in depth. It starts with the condensation reaction of two molecules of acetyl-CoA, a common molecule that takes part in many biochemical processes, including the Krebs cycle of respiration. Modification of the product of the condensation reaction leads to the monomer, which is then used in the synthesis of PHB.

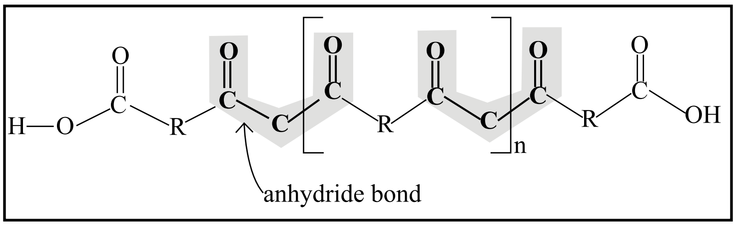
Originally, its properties were seen to be not as good as those of poly(propene). However, PHB is not derived from non-renewable resources and is biodegradable, making it a more sustainable material than poly(propene). Under the trade name Biopol, it is used for medical applications such as internal sutures as it is degraded by enzymes in the body after incisions have healed. Therefore it does not need to be removed after use.

PHB can also be injection-moulded and vacuum-formed. It has a range of uses such as disposable razors, shampoo bottles, and disposable cutlery.

A range of bacteria species can degrade PHB, including *Bacillus* and *Streptomyces* as well common microbes found in soil. This makes PHB products attractive for disposal in landfill sites as their lifetime in the ground, unlike poly(propene) based products, is short.

Polyanhydrides are characterised by anhydride bonds between repeating units.

Fig. 7 Polyanhydride structure



They are primarily used in the pharmaceutical industry and are actively being researched as drug delivery materials. Gliadel wafers are devices for giving chemotherapy for brain tumours. They are made from a gel that contains the chemotherapy drug together with a polyanhydride. After insertion at the site of the tumour in the brain, the drug is released at a controlled rate as the polymer degrades. This means that the drug is targeted directly at the tumour and does not need to be transported around the body by the circulatory system. The body breaks down the polyanhydride into non-toxic dicarboxylic acid monomers that are then metabolised by the body.

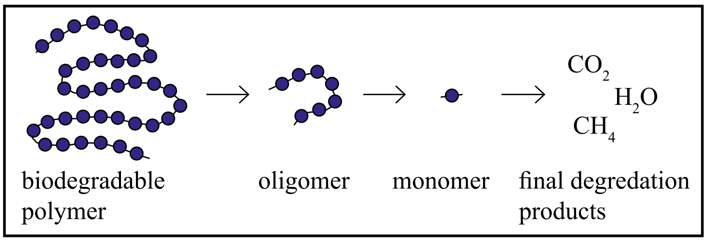
Degradable vs. Biodegradable

It is a common misconception that degradable and biodegradable mean the same thing. However, degradable plastics disintegrate into small fragments (not individual monomers) when exposed to heat or sunlight for an extended period of time. They are still made from petroleum-based monomers and, if buried in landfill sites, will not disintegrate due to the lack of heat and sunlight.

Breakdown of Biodegradable Polymers

The complete breakdown of biodegradable polymers results in even the monomers being broken down into gases such as carbon dioxide or methane. Partial breakdown is said to be when the polymers are converted back into monomers.

Fig. 8 Breakdown of biodegradable polymers



Following the initial breakdown by physical processes, the polymer is converted into short chains of monomer units still joined together. These fragments are called oligomers. They are then absorbed by microorganisms where they are metabolised by cellular enzymes and broken down through aerobic or anaerobic processes into the final end products. In the process, ATP is made. Common enzymes found in these bacteria are proteases (which break down peptide, or amide, bonds), esterases (for ester bonds), and glycosidases (for glycosidic, or ether bonds). They catalyse oxidation or hydrolysis reactions and use the polarity in the bonds between monomer units as a target for electrophilic or nucleophilic attack.

Questions

1. Outline the essential properties of a biodegradable polymer that is used for medical purposes.

2. Describe the differences between agro-polymers and biopolyesters.

3. PLA and Terylene have similar properties. Suggest why using PLA instead of Terylene is more sustainable.

Answers

1. For medical usage, biodegradable polymers should be:
   (a) stable enough for the duration of their desired use,
   (b) be non-toxic,
   (c) be degraded into non-toxic products that can be metabolised or excreted,
   (d) should not illicit an immune response in the patient.

2. Agro-polymers are derived from biomass. Biopolyesters are derived from microorganisms or made from natural or synthetic monomers.

3. Terylene is made from monomers derived from non-renewable petroleum-based monomers. PLA is derived from lactic acid from renewable sources such as sugarcane.

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