The polymer predicament

Making plastics from plants

Synthetic polymers are fundamental to our current lifestyle: packaging, adhesives, clothes, medical devices; so much stuff is made from polymers it is impossible to list it all. But such large-scale use has brought problems. The petrochemicals that many polymers are made from are finite, so we can expect them to become increasingly expensive as we use them up, and their use is associated with greenhouse gas emissions. The long-lasting nature of many polymers also means that waste can be an issue when they are not properly disposed of. So how can we make plastics more sustainable? One alternative is renewable polymers made from plants.

Marvellous polymers

The word polymer comes from the Greek *poly*, meaning many, and *meros*, meaning part. Polymers are large molecules made by joining together smaller molecules called monomers. The same monomer can be repeated over again, such as in the polymer you are most likely to have come across, **poly(ethene)** (also known as polyethylene or polythene). Poly(ethene) is made by polymerisation of ethene:

$$nH_2C{=}CH_2 \rightarrow (CH_2{-}CH_2)n$$

where n is a large whole number.

Poly(ethene) has many uses because of its ease of manufacture and low cost. Conveniently its properties can be changed by altering the reaction conditions to give different degrees of chain length and branching. It can be thin and flexible for plastic bags or tough enough for bulletproof vests.

Alternatively, two different monomers can be used, in which case the final molecule is called a copolymer. Polyurethanes (which have the general structure [ROC(O)NHR'NHC(O)O]n) are condensation polymers produced from a monomer with isocyanate groups (–N=C=O) and a monomer with hydroxyl groups (–OH). Because a wide range of monomers can be used, polyurethanes can have different properties. They are used for such contrasting materials as motorway crash barriers and mattresses. There is such a staggering variety of useful polymers that it is easy to forget the problems they can cause.

The problems with polymers

Have you ever considered that the molecules that go into plastic bags were once part of a living organism? Today's synthetic polymers are derived from petrochemicals, the fossilised remains of plants and animals. Because this process requires millions of years of heat and pressure, petrochemicals are a finite resource that will one day run out. The production of polymers is also associated with the release of greenhouse gases like carbon dioxide (CO2). Scientists have realised that increasing levels of greenhouse gases are causing global temperatures to rise, which is predicted to have many effects on the planet, such as melting ice caps causing rising sea levels and increasing **desertification** (the production of new desert regions due to falling rainfall). Lastly, there is the waste issue. Synthetic polymers can be extremely durable and degrade very slowly, so if they are carelessly discarded they will persist in the environment for many years.

Renewable polymers

The benefit of renewable polymers is that we can still make useful things from them but they come from plants (Table 1). Because plants absorb CO2 as they grow, renewable materials remove this greenhouse gas from the atmosphere. When they are used, this CO2 is released into the environment but it will be removed from the atmosphere once again by new plants, so CO2 moves around the carbon cycle from the atmosphere to plants to renewable materials and back into the atmosphere (Figure 1). This does not cause global warming, because extra CO2 does not enter the atmosphere in the way that it does from petrochemical polymers. However, the term 'carbon neutral' shouldn't be used lightly, because CO2 (from fossil fuels) can be added to the atmosphere during the manufacture and transportation of renewable polymers.

The renewable polymer you are most likely to come across is **polylactic acid** (polylactide or PLA). PLA is made by using bacteria to ferment sugar (for example from corn grain) into lactic acid (2-hydroxypropanoic acid). The lactic acid could be polymerised directly, but the reaction produces water, which weakens the resultant polymer. In order to eliminate the water before polymerisation takes place, the lactic acid is converted into lactide:

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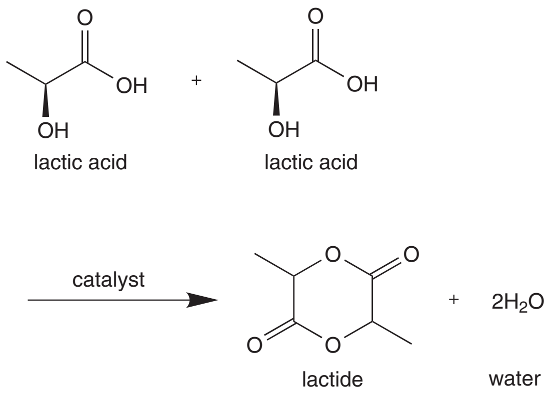
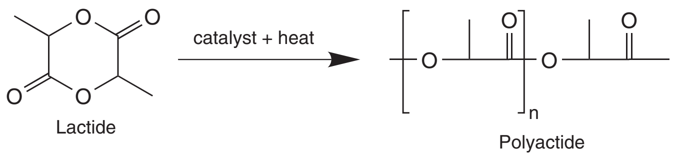


The lactide is polymerised to form the plastic PLA:



PLA is technically a polyester, so it can be used in many of the places you find traditional polyester, like food packaging, sweet wrappers and clothes (Figure 2). PLA can't do everything that other polyesters can, because it is not very resistant to heat or UV light.

However, lactic acid is chiral (see Chemistry Review Vol. 10, No. 3, pp. 6–7), meaning it has isomers with the same molecular formula but a different spatial arrangement of atoms, leading to two mirror image versions of the same molecule (Figure 3). The latest generation of PLA will have better properties, because chemists have developed ways to manipulate the amount of each isomer in the final polymer, giving it better resistance to heat. This steady improvement in functionality is just what all polymers have had to go through — when they were first invented they often didn't work very well. An early plastic called celluloid was used to make snooker balls, but the material had an alarming tendency to burst into flames, making the game of snooker in the 1870s highly unpredictable.

A load of rubbish

Synthetic polymers are robust and resilient, but this resilience means that plastics can be a waste problem, taking up space in landfill, persisting as litter on land and in the oceans. You may have heard of the 'plastic soup' in part of the Pacific Ocean, where millions of pieces of waste are swirling together in the currents.

It makes sense to recycle some types of plastics, but not every material can be recycled economically without excessive use of water or energy. A distinct advantage for renewable polymers is that they can not only be recycled, but they can be biodegradable, meaning micro-organisms can break them down into CO2, water and other simple compounds. Renewable polymers can also be suitable for composting, so they can eventually be put back into the soil. They can be exposed to the process of anaerobic digestion, which uses anaerobic microorganisms to produce renewable energy and fertiliser (Figure 4). This makes renewable polymers particularly good for food packaging because the food and its packaging could go in the same recycling bin (Figure 5).

However, not all renewable polymers are biodegradable and biodegradability isn't necessarily what you want from a polymer — nobody would be interested in biodegradable car bumpers. It is now possible to make renewable poly(ethene) from sugar cane by fermenting the sugar into ethanol, then converting this to ethene (Figure 6). Renewable poly(ethene) is very resilient, in fact it is no different to the synthetic poly(ethene) used to wrap your lunch (see Box 2 for how you can tell the difference). So bio-based doesn't have to mean biodegradable.

Conclusions

Synthetic polymers are so familiar to us that we often barely notice them. But with the twin threats of dwindling fossil fuel supplies and climate change we must consider the effects of surrounding ourselves with petrochemical products. Renewable polymers are not a magic bullet for our environmental problems, but using renewable polymers can be part of becoming more sustainable.

Further reading

'Can biomass save the planet?' (Chemistry Review Vol. 17, No. 4, pp. 17–20)
'Let chemists do the washing up' (Chemistry Review Vol. 17, No. 3, pp. 17–19)
'Waste not want not' (Chemistry Review Vol. 17, No. 1, pp. 2–5)
'Polyesters, plastics of the future' (Chemistry Review Vol. 17, No. 1, pp. 17–20)
'Detecting CO2: the hunt for greenhouse-gas emissions' (Chemistry Review Vol. 15, No. 3, pp. 27–31)
'Watch your language!' (Chemistry Review Vol. 15, No. 2, pp. 30–31)
'Global impact of fuels' (Chemistry Review Vol. 14, No. 4, pp. 28–30)
Various polymer articles in Chemistry Review Vol. 11, No. 4
'Calculating carbon dioxide (CO2)' (Chemistry Review Vol. 11, No. 2, pp. 27–29)

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Table 1 Some examples of renewable polymers and what can be made from them.

Polymer	Crop or Raw Material	Common uses
Starch-based Polymers	Wheat, Potatoes, Corn	Compost caddy bags
Polylactic acid (PLA)	Wheat, Potatoes, Corn	Food packaging
Cellulose	Farmed wood	Cereal bar wrapper
Polyhydroxyalkanoates	Plant-derived sugars or lipids	Medical devices like orthopaedic pins
Polyesters	Corn	Textiles
Polyurethane	Soy or castor oil	Car seats
Poly(ethene)	Sugar cane	Resins

Box 1 Polymers from biomass

Currently many renewable polymers are made from the edible parts of plants and cellulose from wood. As our demand for renewable polymers increases, there is increased competition for agricultural resources, running the risk of potential food shortages. In the future, we should be able to make polymers from a much wider range of biomass. Biomass is any living or recently dead plant or animal material. This includes crops and trees, but also straw, food waste, sewage, chip fat, in fact anything biological that will reduce the reliance on agricultural crops.

Box 2 Measuring renewable carbon content

It can be difficult to tell if a polymer has been made from biomass just by looking at it. Renewable poly(ethene) , for example, is identical in appearance to synthetic poly(ethene). How do we test the 'green' claims made by manufacturers?

To understand how, we have to go to the atmosphere. Cosmic rays colliding with the atmosphere can turn nitrogen into the radioactive carbon isotope ^{14}C (see Figure 1). Most of the carbon in the atmosphere is ^{12}C. Only 1 in 1 trillion carbon atoms will be ^{14}C, but this is still enough to measure. Plants use CO_2 from the atmosphere for photosynthesis, so new plant material will contain both ^{14}C and ^{12}C, as will animals that have eaten plant material. However, by the time living material has turned into fossil fuels, the ^{14}C will have undergone radioactive decay back to nitrogen, leaving only ^{12}C. So a polymer made from biomass will have detectable levels of ^{14}C, while a polymer made from petrochemicals will have none. We can test whether a polymer is biomass-based or not with an accelerator mass spectrometer — basically a sophisticated way of distinguishing the isotopes by their mass.

glossary

Anaerobic in the absence of oxygen.

Biodegradable a substance that can be degraded into carbon dioxide, water and other simple compounds when exposed to microbial, enzymatic or other biological action.

Carbon cycle the processes by which carbon from the atmosphere is incorporated into living organisms and returned to the atmosphere again.

Carbon neutral refers to achieving the overall effect of no emissions of carbon dioxide for a particular process, as any CO_2 emissions are offset by an equivalent uptake of carbon dioxide, for example by living plants.

Cellulose a structural polymer in plant cell walls. It is the most abundant organic compound found in nature. It is a polymer of glucose (a sugar) and has the formula $(C_6H_{10}O_5)n$.

Condensation polymers polymers formed by the addition of monomers with the elimination of a simple molecule such as water.

Enantiomers isomers of a molecule that are mirror images of each other. The molecules will differ in their arrangement of functional groups at a chiral centre (usually a carbon atom with 4 different groups attached).

Fossil fuel fuels (natural gas, oil and coal) formed from the remains of ancient living organisms.

Greenhouse gas a gas that absorbs infrared radiation in the atmosphere and may contribute to global warming.

Isotope isotopes of an element are atoms that have the same number of protons as each other (i.e. they have the same atomic number, meaning they are the same element) but have different numbers of neutrons in their nucleus (and hence different relative atomic masses).

Mass spectrometer an analytical technique that can be used to determine the chemical composition of a sample (see CHEMISTRY REVIEW Vol. 12, No. 4, pp. 19–22).

Petrochemical a substance derived from petroleum (oil) or natural gas.

Polyester esters are formed by condensation reactions between an alcohol and an acid ($ROH + HOOCR' \rightarrow ROOCR' + H_2O$). Polyesters are polymers of polyhydric alcohols (i.e. they have more than one hydroxyl group (–OH)) and polybasic acids (i.e. they have two or more replaceable hydrogen atoms, e.g. the H in –COOH).

key concepts

- Chirality
- Climate change
- Esters
- Renewable polymers
- Sustainability

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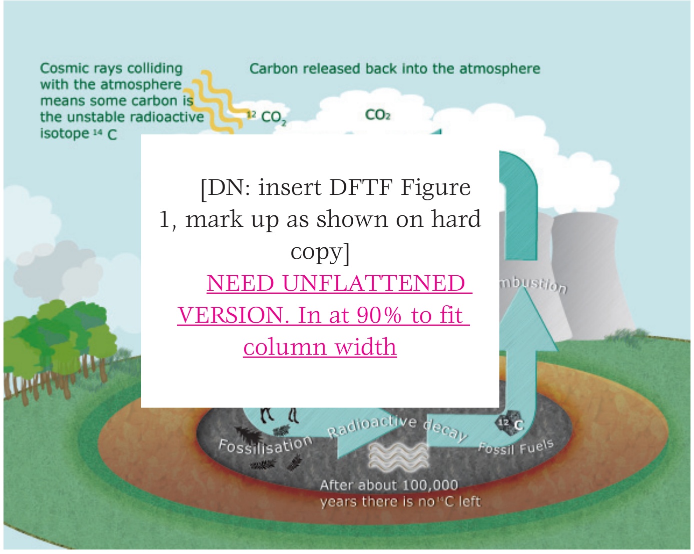

Figure 1 The carbon cycle and the generation of ^{14}C.

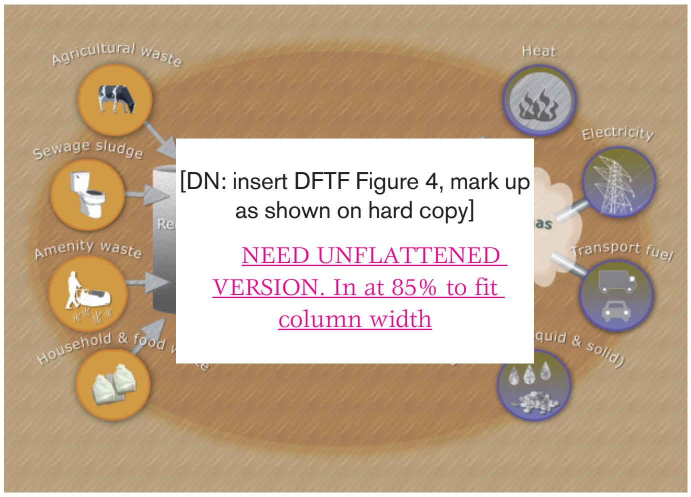

Figure 4 The process of anaerobic digestion (AD). AD could be used to get energy and fertiliser from waste, including renewable polymers.

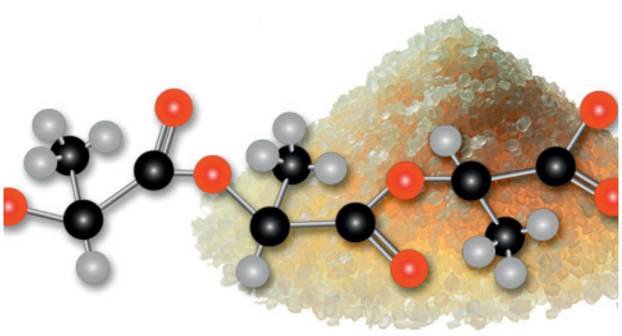

Figure 2 Grains of polylactic acid with the structure of PLA (carbon atoms are shown in black, oxygen in red and hydrogen in grey).

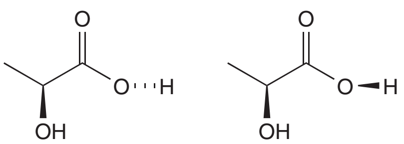

Figure 3 The two mirror image forms (enantiomers) of lactic acid.

Figure 5 Renewable polymers used in packaging.

Figure 6 Sugar cane — a raw material for poly(ethene).

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