Science to enable sustainable plastics

A white paper from the 8th Chemical Sciences and Society Summit (CS3)

London, UK • June 2020

Contents

About the Chemical Sciences and Society Summit (CS3) 4

Glossary of terms used in this report 5

Summary and recommendations 6

1. The impact of plastics 12

2. New sustainable plastics 20

3. Recyclability of plastics 28

4. Degradation of plastics 36

Appendix 43
- Glossary of acronyms 44
- Structures of common polymers and their recycling symbols 44
- Further reading 45

CS3 participants 46

Cite this report: **rsc.li/progressive-plastics-report**

About the Chemical Sciences and Society Summit (CS3)

The CS3 brings together leading researchers to discuss how the chemical sciences can help to tackle some of the most daunting challenges that our world faces. Previous summits have tackled topics as diverse as water resources, human health, and sustainability.

This White Paper, *Science to enable sustainable plastics*, summarizes the presentations, discussions and outcomes of the 8th CS3 meeting, held in London, UK, on 10–13 November 2019. More than 30 scientists from four participating countries gathered to discuss four major themes in sustainable plastics: their impact on the environment; new sustainable plastics; the recyclability of plastics; and the degradation of plastics.

Their goals were to assess the current status of sustainable plastics, identify the most pressing research challenges in this area, and make recommendations about how the field should progress.

The CS3 initiative is a collaboration between major international chemical societies. For this report, the collaboration involved the Chinese Chemical Society (CCS), the German Chemical Society (GDCh), the Chemical Society of Japan (CSJ), and the Royal Society of Chemistry (RSC). The meeting was supported by the National Science Foundation of China (NSFC), the German Research Foundation (DFG), the Japan Science and Technology Agency (JST), and the UK Engineering and Physical Sciences Research Council (EPSRC). CS3 summits are held every two years, and rotate among participating nations.

Glossary of terms used in this report

Additive: Most plastics contain various additives that help to maintain their long term performance. Typical additives include antioxidants, antistatic agents, colourants, curing agents, flame retardants, thermal stabilizers, UV stablizers, plasticizers and lubricants.

Bio-based or bio-derived plastic: A polymer that is produced from biological resources, including chemicals derived from plants and algae. For example, polylactide is produced from sugar, which is harvested from plants like sugar cane.

Biodegradable plastic: A plastic that undergoes accelerated degradation by organisms and biomolecules such as enzymes, forming small molecules that are metabolized by natural organisms. Biodegradable plastics should break down to natural materials that can be returned to the environment without pollution or deleterious effects.

Biopolymer: A naturally occurring polymer, such as cellulose or starch.

Chemical recycling: A process whereby the polymer is degraded into monomers and chemical raw materials that can be reused to make new polymer and basic chemicals. After chemical recycling, the end-product polymer and basic chemicals are chemically identical to that produced initially.

Circular economy: A system in which resources are kept circulating for as long as possible, through efficient material use, reuse and recycling loops. It is an alternative to the linear economy in which materials are made, used and disposed.

Closed-loop recycling: A recycling system in which plastic is repeatedly recycled and reused without compromising the quality of the material. Such recycling currently applies to the chemical recycling of polyethylene terephthalate (PET).

Compostable plastic: A sub-class of biodegradable plastics that are decomposed in compost, either at lower temperatures in home composting systems or at higher temperatures in industrial composting facilities.

Degradable polymer or plastic: A term used to refer to a polymer or plastic containing chemistries that allow the chain to be disassembled either through recycling or through biodegradation.

Disassembly: The breaking of polymer chains into shorter sub-units and monomers so as to aid recycling. Chain disassembly may also be triggered at an appropriate time in degradable polymers.

Environmentally degradable plastics: Plastics that can be completely broken down and assimilated into the natural environment over time without any negative toxicity or environmental effects.

Mechanical recycling: A recycling process in which waste plastic is reformed into new plastic products through melting and extrusion. Mechanical recycling often leads to poorer material properties and a reduction in value compared to the original plastics.

Open-loop recycling (also known as cascaded recycling): A recycling process whereby waste material is transformed into new product and waste. This process is often associated with lower-grade applications for plastics. For example, polyolefins are recycled by open-loop processes to produce additives for tarmac.

Upcycling: A recycling process to create a product of higher quality or value than the original. For example, plastic pipes could be chemically modified to improve their heat resistance, or confer antibacterial properties.

Summary and recommendations

Plastics have helped to build the modern world. They keep our food fresh and safe; they are used to build our cities, homes and even the mattresses we sleep on; they power the green revolution, producing light-weight electric vehicles and solar cells; they are essential components of mobile phones and computers; and they enable medical advances, from masks, contact lenses and heart diaphragm pumps to artificial tissues (see box: **What are plastics?**).

Plastics are essential to create a more sustainable society, and to ensure that future technologies develop rapidly and cost effectively. Plastic packaging reduces food waste by prolonging its shelf life, and has an important role to play in detecting food quality. Recent developments in plastic composites mean that plastic can form 50% of the primary structure of aeroplanes, resulting in significant greenhouse gas emissions savings.

Future technologies central to reducing our reliance on fossil fuels will also require plastics. In electric vehicles, for example, it is possible to replace even more metal components than in petrol cars, and to use light-weight plastics in energy recovery devices, cooling pipes, pumps, fans and casings. The use of plastics in electric vehicles is already growing rapidly. Wind turbine blades require plastic composites and adhesives, while batteries rely on plastics in their housing and may even apply them as electrolytes and other components. Plastics are also widely used in home insulation, reducing energy usage, and they play critical roles in the construction sector as pipes and conduits, cladding, seals, adhesives and gaskets. In future, plastic composites could replace metals in load-bearing structures and will likely be important in intelligent buildings as components of detection and monitoring systems. Plastics are essential as the active layer in water purification systems and deliver efficiencies in agriculture, such as reducing water usage and increasing productivity. Future technology sectors such as robotics, drones, electronics, personalized healthcare and diagnostics each rely on the development of better plastic materials.

Despite these benefits, the use of plastics is also causing major environmental challenges. Plastic manufacturing consumes significant quantities of petrochemicals: in Europe, for example, it accounts for roughly 4%–6% of all oil and gas use, according to industry group Plastics Europe. Since plastics are interwoven with the petrochemical industry, they are subject to its fluctuations, geo-politics and contributions to CO_2 emissions.

Discarded plastic pollutes the natural world, with microplastics and nanoplastics being detected in many ecosystems (see box: **Sizing up plastic pollution**). The majority of plastic waste is generated and emitted on land, but research on plastic pollution initially focused mainly on the marine environment, where

What are plastics?

Plastics are primarily comprised of polymers, along with various additives (such as stabilizers, flame retardants, and plasticizers) that affect the physical properties of the material.

Polymers are long-chain molecules built from smaller repeating units called monomers. Some polymers contain only one type of monomer building block; others, known as co-polymers, may contain two or more different types of monomer.

Polymer chains assemble across multiple length scales (see Figure 4.2: **Structure of plastics at different scales** p40) and detailed understanding of how the properties of plastics, including their disassembly, relate to their different structures is a key challenge in polymer science.

plastic particles are reported to occur from tropical to pristine polar areas, and from beaches to deep-sea sediments. Later, river and lake systems were examined, where plastic particles were found even in remote mountain lakes. Plastic particles have more recently been found in the atmosphere and in terrestrial ecosystems, especially in urban and agricultural soils. The ingestion of plastic particles together with food has already been investigated in a variety of organisms from aquatic and terrestrial habitats, and the resulting effects on organisms and human health are still under discussion.

Possible risks associated with plastic particles cannot be generalized because microplastics and nanoplastics comprise a very heterogeneous group of particles that vary in polymer composition, additive content, size, shape, ageing state, and consequently in their physicochemical properties. However, the ubiquitous contamination of the environment with microplastics and nanoplastics, along with the possible associated risks to ecosystems and ultimately to human health, has recently attracted a great deal of public and scientific attention.

For many members of the general public, plastics now epitomize a disposable way of life and are associated with cheap, low-quality and low-value products. The visible evidence of plastic pollution and as yet unknown impacts of these materials are driving a reconsideration of their life cycles, designs and uses. Technical solutions will be needed to ensure that in future plastics combine useful properties with better end-of-life options, and chemistry will play a central role in delivering these.

Developments in chemistry will be key to understand and mitigate the impact of plastics in the environment. Chemistry can help to develop efficient ways to recycle the plastics we use today and, in the longer term, create replacements that are made from sustainable starting materials, are more amenable to recycling at end-of-life, and have reduced environmental persistence or impact.

Sustainability across the entire plastics life cycle must be a core design feature of the polymers of the future. It is also clear that a suite of materials will be required to meet the myriad of applications, just as different plastics are applied today. This means that underpinning investment is recommended in a range of different technologies and options. It is also essential to emphasize that no single solution is suitable for all scenarios, geographies or products. Different countries already employ a wide range of waste management practices, with varying degrees of environmental impacts. As such, the most sustainable option for a particular location is not necessarily a global solution.

In some scenarios, improved sustainability will arise from deployment of polymers built entirely from renewable, biologically-derived feedstock chemicals, or from wastes like CO_2 where the raw materials used to produce the polymer are carbon neutral. For some applications, durable or longer-lasting polymers, which can be reused multiple times prior to efficient closed-loop

Sizing up plastic pollution

The size of a piece of plastic is an important factor in determining its impact on the environment. Commonly accepted size ranges are:

Macroplastics: larger than 2.5 centimetres across

Mesoplastics: 5 millimetres to 2.5 centimetres

Microplastics: 1 micrometres to 5 millimetres

Nanoplastics: smaller than 1 micrometre

---

1 centimetre = 10 millimetres
1 millimetre = 1,000 micrometres
1 micrometre = 1,000 nanometres

recycling, will be the best option. In yet other scenarios, it will be important to design polymers to incorporate special chemical and physical features to make them 'degradable on demand' – such features will reduce energy use and improve selectivity for closed-loop recycling. Fundamentally, there is a need to design polymers for efficient disassembly. Such an approach has the potential to enable closed-loop recycling over multiple cycles and to reduce, or even nullify, environmental persistence if they escape from waste systems.

We recognize that building this new future for plastics necessitates a major collaboration between sciences, engineering, technology, materials design, humanities, human behaviour, policy, regulation, economics and business. This report focuses only on the contributions and solutions that could be technically feasible, and on the research challenges specific to chemistry and the chemical sciences. It deliberately avoids making recommendations on policies or regulations for recycling, waste management systems, use of financial incentives and taxation (the **Further reading** appendix p45 includes references to recent policy briefings and reports from expert working groups that address some of these important parallel issues).

In coming up with our recommendations, we emphasize that technology alone cannot provide all solutions and that parallel advances in waste management, regulation, economics and behaviour will be needed to deliver the infrastructure and ecosystems for a sustainable plastics future. We signal that experts in chemistry are well placed to provide impartial evidence for policymaking and standardization of plastics, as well as in environmental monitoring and detection.

We propose four major research challenges and their underpinning research priorities. These research challenges are interlinked and symbiotic, as such we do not recommend unbalanced selection or weighting of research in a particular direction. Our philosophy is that plastics should not be deliberately released or dumped into the environment and that efficient closed-loop waste management systems are vital to implement these technological advances and solutions. Meeting the technical challenges necessitates close integration with a range of other technical disciplines, as well as in parallel with the broader considerations outlined above.

To ensure future researchers are able to invent effectively in this space, it is important to offer multi-disciplinary training and education of chemists in areas such as polymer science, materials engineering, process design, eco-toxicology, molecular biology, environmental sciences, life cycle assessment and data science. We, as a scientific community, recognize the benefits of, and urgent need for, outreach, advocacy and public engagement activities to stimulate a public dialogue about the impacts and solutions of future plastics, and to examine material selection choices using a life cycle approach, and in the context of sustainable development goals.

Research challenge 1: To understand the impacts of plastics throughout their life cycles

a. Develop new **analytical methods** to study microplastics and nanoplastics for different types and shapes and at different size and time scales. These should include high-throughput spectroscopy and microscopy techniques that can rapidly generate reproducible data about the size distribution, structure and properties of microplastics in the environment.

b. These data should be applied in **predictive models** that simulate the transport and distribution of microplastics in the environment, which will help to understand the location, fate and persistence of plastic waste. In future, these models may also help to predict the environmental impact of new plastics before they get to market.

c. Research is needed to properly understand the factors that influence the formation of **microplastics and nanoplastics**, across a range of environments including soils, freshwater, and oceans.

d. We must understand whether there is any toxicity from plastics and their degradation products, at all size scales of waste fragments. This will require detailed knowledge of the biological pathways involved in the chemical and particle toxicity of microplastics. It should also consider both direct and indirect ecological effects, such as a reduction in food availability for other species, transportation of pollutants, and formation of biofilms.

e. The environmental impact of plastics is not limited to their end-of-life degradation. Impacts also arise across their whole life cycle. We need detailed **life cycle and sustainability assessments**, both to understand the trade-offs in environmental impacts and to identify research opportunities focused on reducing impacts.

Research challenge 2: To develop new sustainable plastics

a. **New plastics** must be designed for the circular economy and to **facilitate recycling**. Researchers should develop polymers that improve the efficiency of closed-loop recycling. This could allow for the production of materials that show outstanding properties but which are able to 'degrade on demand', with the degradation products being chemically recycled to polymer or transformed into other high value products. Central to this concept is to design polymer structures so they can be disassembled and controllably broken into smaller sub-units – oligomers and small molecules – which can be recycled and reused. New plastics capable of maintaining desirable material properties after mechanical recycling should also be targeted, for example through chain extension or self-healing processes.

b. Research is needed to produce new polymers from **non-virgin petrochemical and bio-based raw materials**. Alternative feedstocks should include recycled chemicals, for example from plastics recycling, (sustainable) biomass, industrial wastes like CO_2, and modified biopolymers like cellulose or starch. These monomers, used to create the polymers, must be scalable, abundant and truly sustainable. In the longer term, the manufacturing of plastics may need to be decoupled from the use of virgin fossil fuels and from the fuel industry.

c. New processes are needed to **manufacture, process and recycle plastics that adhere to rigorous sustainability metrics**. Central to delivery of efficient processes will be to develop catalytic systems and reactions. Even as these are being developed in the laboratory, they should demonstrate a reasonable potential for manufacturing scalability and efficiency.

d. Improving plastic sustainability in some sectors will require production of durable or longer-lasting polymers. These plastics need to maintain their properties and **performances over appropriate use time scales but be designed from the outset with managed end-of-life scenarios**. Research into alternative reinforcing interactions, especially to produce alternatives to thermoset resins and networks, is a priority. Exploration of the use of non-covalent or equilibrium interactions is recommended as a means to ensure properties are delivered while facilitating recycling and / or reprocessing. Research should also focus on how to control crystallization and loss of crystallinity in materials, as crystalline regimes confer useful properties but slow chain disassembly after use.

e. Efforts to design new plastics must consider their **properties across multiple length scales**, including monomer sequences, polymer chain interactions, as well as nanostructures and microstructures. It is important to develop new experimental methods and theories to understand the relationships between the structures and properties of polymers. In future, it may be possible to apply homoplastic composites, whereby a single polymer chemistry performs multiple functions through control across length scales. For example, ensuring that in packaging only one type of material is used for the packaging, adhesive, and barrier layer would simplify recycling.

f. Design data, analytical characterization methods and models should be developed that inform both **polymerization and depolymerization processes**. New theory and methodology is needed to accurately predict polymer performance and disassembly across multiple length and time scales.

Research challenge 3: Closed-loop plastics recycling

a. Chemical technologies are needed to improve **labelling, identification and separation of waste plastics and composites** into single-component, pure polymers. These polymers should be reprocessed into new products and / or fully recycled to pure polymer by chemical recycling.

b. **More efficient chemical recycling processes** are needed to recover valuable oligomers, monomers and / or small molecules from wastes. Chemical technologies should be developed which function effectively using polymer composites and mixtures of plastics. These technologies include new catalysts, processes and reactions allowing chemical recycling of current large scale polymers. For example, polyolefins cannot yet be chemically recycled with sufficient efficiency or chemical selectivity to monomers.

c. To deliver better plastic recyclability, reactions for **polymerization and depolymerization that are closer to equilibrium** should be investigated. This approach may bring additional property benefits, such as self-healing plastics with extended lifetimes as well as reductions in energy demand required for recycling.

d. In some scenarios, it may be appropriate to process waste plastics so as to **recover the energy** they contain – by incinerating them to generate electricity, for example. In these scenarios, any CO_2 or other greenhouse gases produced should be captured and stored in a sustainable way. It may also be possible to recycle waste CO_2 into new plastics to achieve 'carbon recycling'.

Research challenge 4: To understand and control plastic degradation

a. Research must reduce both the short term and long term environmental impact of plastics. For some applications, this involves the development of environmentally degradable polymers. These are important for applications such as disposable medical products, personal care items, and certain packaging and agricultural plastics. Such environmentally degradable polymers should be a backstop to guard against the leakage of waste plastic into the environment – they should not be seen as a substitute for recycling, or an excuse to dispose of plastics in the environment. We recommend careful examination of **standards and labelling** of polymers so as to ensure there is proper understanding of terms such as compostable, biodegradable and environmentally degradable polymers. Research is necessary to define the cause, extent, and time scale of the polymers' degradation reactions and to understand the impacts of degradation products in the natural environment.

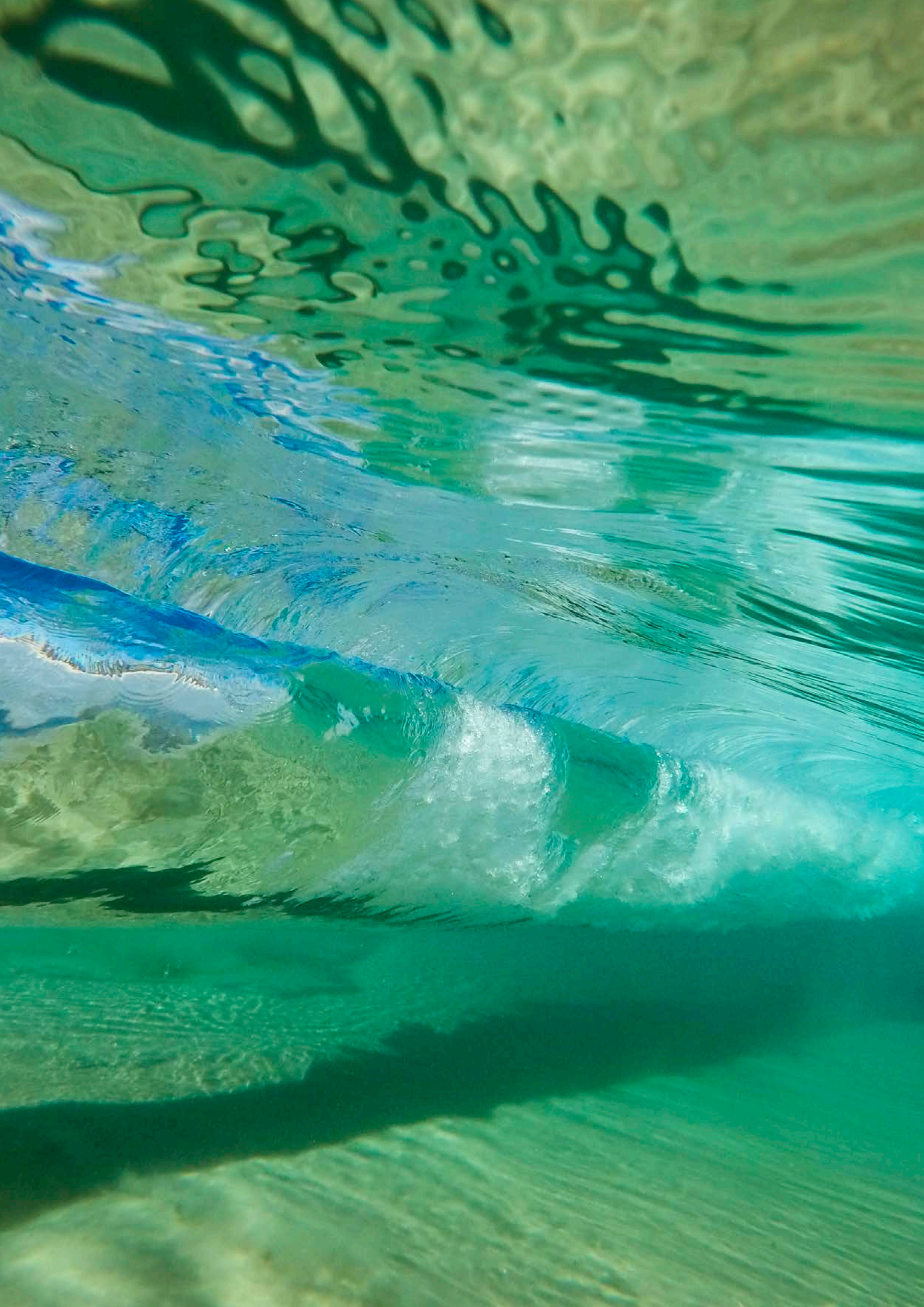
b. Research is needed to **understand the degradation of polymers in the broad range of environments** in which they are being discovered. This should include how polymer and plastic structures are influenced by humidity, pH, temperature, light, organisms and enzymes, as well as the interplay between these factors. It is recommended that such studies are conducted so as to yield better data about how the polymer chemistry, morphology and crystallinity influences degradation in a range of real environments. The fate and impact of the degradation products must also be fully considered, as should any additives included in these plastics.

c. Research is needed to develop materials that are both recyclable and **environmentally degradable**. Such materials could then be recycled multiple times, through cycles of polymerization-depolymerization, without loss of properties; but at the end of efficient recycling, they could be degraded to non-toxic products that can be metabolized by organisms in the environment. In parallel, it may also be important to develop strategies to understand and improve the environmental degradability of some of the non-degradable polymers used today.

d. Environmentally degradable polymers will need to be **competitive in performance and cost**. As such, the monomers and polymerization processes used to make these polymers must be scalable, efficient, economical, and sustainable. There is unlikely to be any single material able to deliver all properties for all applications, consequently **a range of new environmentally degradable polymers** is needed, each tailored towards specific applications and degradable over different time scales.

1. The impact of plastics

Plastics are an essential part of modern life, and an indispensable tool in sustainable development. Some of today's petrochemical-based plastics also have concerning environmental impacts, from the greenhouse gases involved in raw material extraction and manufacturing to waste plastic pollution in the environment. Chemistry can underpin efforts to understand and mitigate these impacts by developing sustainability tools and, where appropriate, circular economies for plastics.



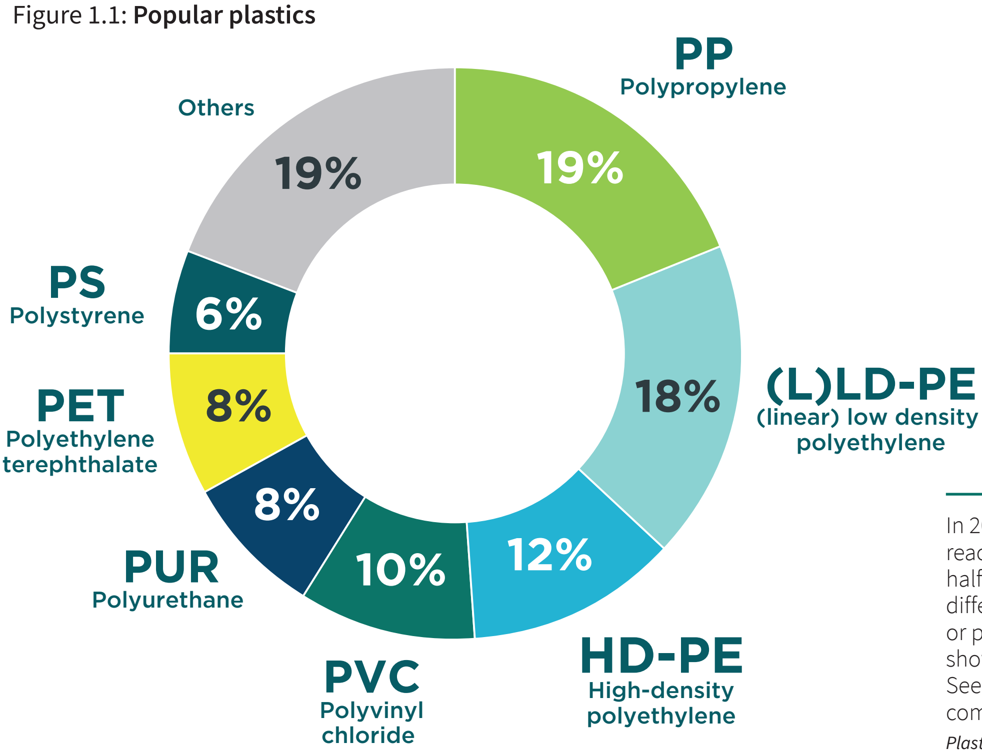
Introduction

Plastic production has grown substantially over the past few decades, and shows little sign of slowing down. The annual production of plastics currently stands at almost 360 million tonnes per year, surpassing most other human-made materials (see figure 1.1: **Popular plastics**). By 2015, humans had cumulatively made a grand total of roughly 8,300 million tonnes of plastics. About 6,300 million tonnes of that had already become waste, only 9% of which was recycled (*Sci. Adv*. 2017, DOI: 10.1126/sciadv.1700782).

In a world where one million plastic bottles are bought every minute, profligate consumption is clearly a contributing factor. But so too is the poor management of waste plastic, which too often results in discarded plastic leaking into the environment. Researchers have estimated that 31.9 million tonnes of mismanaged plastic waste enters the environment every year, with 4.8–12.7 million tonnes of that going into the oceans (*Science* 2018, DOI: 10.1126/science.aar7734) and significant quantities contaminating terrestrial ecosystems (*Environ. Sci. Technol*. 2019, DOI: 10.1021/acs.est.9b02900). This pollution poses a threat to wildlife, to our environment, and to ourselves.

Plastics manufacturing requires not only petrochemical feedstocks but also energy. Thus, their manufacture contributes to overall industrial CO_2 emissions (see figure 1.2: **The carbon footprint of plastics**). Manufacturing methods that apply non-fossil energy sources or reduce energy consumption can have a huge benefit. Today, the feedstock monomers used to make the most ubiquitous plastics are co-products of the fossil fuel industry, but in the long term we will need to reduce our reliance on fossil fuels and develop plastic technologies that are not predicated on virgin petrochemical feedstocks (see chapter 2: **New sustainable plastics**). It is worth emphasizing that plastics have a lower embedded energy than many alternative materials, such as glass or steel. Provided that efficient waste management can be developed, there are many scenarios in which using plastic is a more sustainable choice, particularly in terms of CO_2 emissions, than selecting an alternative material. Selecting a material for a particular application, such as packaging, should involve a balanced and evidence-based life cycle and sustainability assessment. We strongly caution against substituting plastics for 'alternatives' without such analysis.

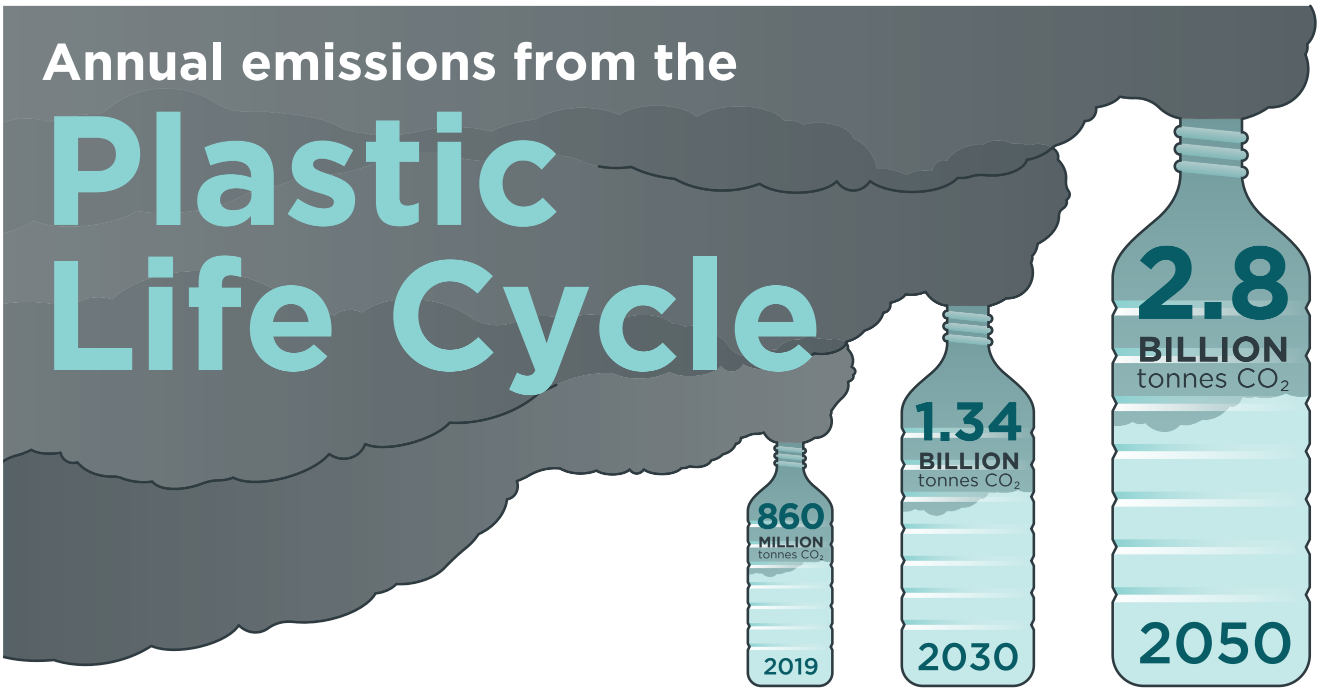
Figure 1.1: **Popular plastics**



In 2018, global plastics production reached 359 million tonnes. About half of these plastics were made from different forms of polyethylene (PE) or polypropylene (PP). (Percentages show relative demand in Europe). See **Appendix** for the structures of common polymers.

Plastics – the Facts 2019, PlasticsEurope (2019)

Figure 1.2: **The carbon footprint of plastics**



The production, management and incineration of plastics added 860 million tonnes of CO_2 (or equivalent greenhouse gases) to the atmosphere in 2019, equal to the emissions from almost 200 typical coal-fired power stations. For comparison, global CO_2 emissions exceeded 36 billion tonnes in 2019. The carbon footprint of plastics is expected to triple in size by 2050.

Plastic & Climate: The Hidden Costs of a Plastic Planet, Center for International Environmental Law (2019)

There are many strategies to replace fossil-based polymers that could improve the sustainability of plastics. One approach involves substituting existing fossil-based plastics with their bio-derived equivalents. The polymer molecules in the bio-derived plastic are identical to those in the fossil-derived version, but their monomers come from different sources. This contrasts with an alternative approach – replacing existing polymers with entirely new materials. New polymers may be very desirable when plastics are being designed to facilitate recycling or environmental degradation, but it can lead to less desirable consequences, such as incompatibility with current processing or blending technologies, or produce materials that have inferior physical and chemical properties.

Microplastics abound

The impact of plastic pollution partly depends on the size of the plastic waste (see box: **Sizing up plastic pollution** p07). Large plastic objects, such as polyethylene bags, have been found inside whales' stomachs. Seabirds have been found to eat smaller chunks of plastic, while discarded fishing lines ensnare mammals like sea lions. In 2012, the United Nations estimated that plastic waste killed roughly one million seabirds and more than 100,000 marine mammals each year.

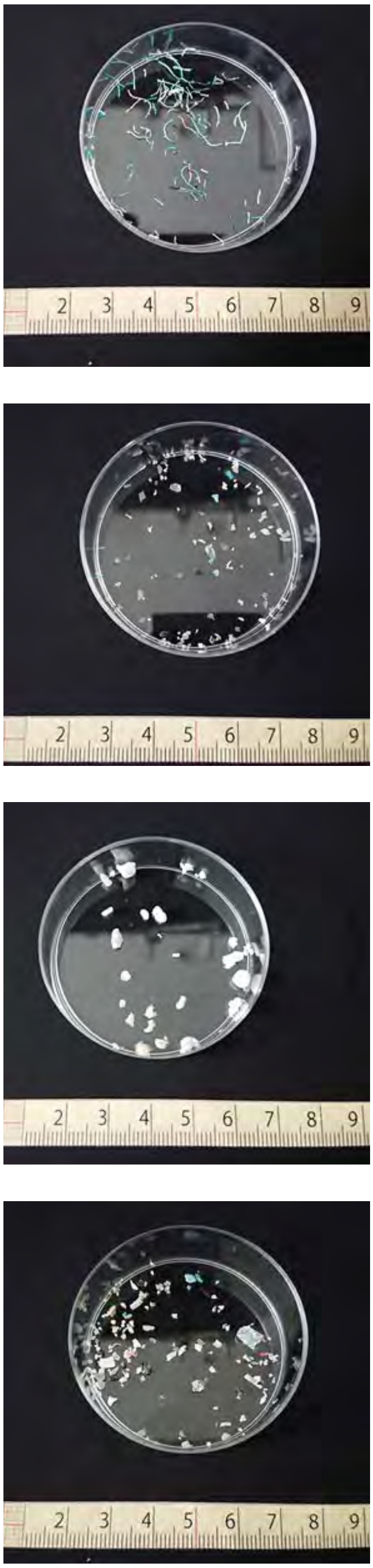
Fragments or fibres of waste plastic that are less than 5mm across are known as microplastics. These may be produced at that size or they can form when larger plastic items break down in the environment. Microplastics have probably been in the environment since plastics were first mass produced, but the first report of their detection in oceans dates from 1972 (*Science* 1972, DOI: 10.1126/science.175.4027.1240), and over the past 15 years research has shown that these particles are ubiquitous in the environment.

Microplastics are just the right size for plankton, bivalves and other filter feeders, and soil dwelling organisms at the base of the food chain to consume. Larger animals that feed on these creatures then accumulate microplastics in their own bodies. For example, a recent survey of 102 sea turtles found that every single animal had microplastics in its guts (*Global Change Biology* 2018, DOI: 10.1111/gcb.14519).

It is not yet known whether these tiny fragments harm the animals that ingest them. Microplastics have been shown to slow the digestive systems of aquatic worms, for example, so that they put on less weight as they grow. Additives to plastics, such as phthalate plasticizers, can also bioaccumulate in worms, potentially hampering their reproduction. Meanwhile, humans are exposed to microplastics, for example when they eat seafood, although the consequences of this exposure are unknown. The oral uptake of microplastics may have negative effects on the gut microbiome, which is essential for the absorption of nutrients and plays an important role in the immune system. One potential risk that has been intensively discussed but not yet sufficiently investigated and understood is the transition of microplastics via the digestive tract into cells and tissue, which can lead to inflammatory processes. A further yet unexamined risk is the inhalation of microplastic particles via the air we breathe. When microplastics break into fragments smaller than one micrometre, they form nanoplastics which, because of their smaller sizes, are much more likely to be absorbed by living creatures. As yet, relatively little is known about the biological impact of nanoplastics.

Microplastics may even hamper the natural world's ability to counteract climate change. Microscopic organisms called phytoplankton use photosynthesis to collectively capture millions of tonnes of carbon per day from the atmosphere, and some types of phytoplankton excrete this carbon in fecal pellets that sink to the bottom of the ocean, acting as a long term carbon storage mechanism. But when phytoplankton consume microplastics, it changes the composition of fecal pellets so that they are more likely to float, and release their carbon back into the atmosphere.

Microplastic fragments found in the ocean include fibres, granules and flakes.
Atsushi Takahara and Atsuhiko Isobe



Tracking microplastics

To understand more about the origins and behaviour of microplastics, research teams collect microplastic samples from water, sediments, soils, air, plants and animals. These samples are studied using a wide range of techniques, including optical and electron microscopy, X-ray analysis, and Raman and infrared spectroscopy. This analysis can reveal what the microplastics are made of, their physical forms, and how they are generated. Plastics break down into microplastics via a range of different chemical and physical mechanisms that include exposure to ultraviolet radiation, oxidation, thermal breakdown, and simply tumbling around in surf (see chapter 4: **Degradation of plastics**).

These data can feed into large scale simulations of plastic waste distribution and behaviour in the environment. Preliminary models of plastic pollution in the Pacific Ocean, for example, are already starting to predict how plastic waste moves around (*Nat. Commun*. 2019, DOI: 10.1038/s41467-019-08316-9). Complementary research in freshwater and terrestrial systems should continue in parallel.

To generate more of these data, researchers need to be able to run their analyses more quickly, perhaps using high-throughput methods that could operate for instance in river systems, sewage treatment plants or on research vessels at sea. The predictive models also depend on understanding how long certain plastics are likely to survive in the environment and how quickly they degrade, which is intrinsically linked to their chemical and material properties. Microplastics also leach additives, and may pick up persistent organic pollutants or toxic metals during their time in the environment, both of which can have additional environmental impacts. In principle, these factors can also be incorporated into microplastic models.

Microplastic samples in the marine environment should be collected not only from the sea surface, but also from a range of depths in the ocean, and in ocean-floor sediments. This approach could help to reveal the fate of microplastics of various densities, and also improve our understanding of the historical fate of microplastics that entered the oceans decades ago (*Sci. Adv*. 2019, DOI: 10.1126/sciadv.aax0587). Some researchers are already studying the plastic in preserved samples of dead animals in the International Environmental Specimen Bank. This repository contains hundreds of thousands of specimens, including fish and seabirds, and researchers are gearing up to explore this trove to look for evidence of historic microplastic pollution.

Bringing data from many different sources and combining them into useful models will require a multidisciplinary research effort, involving more collaboration between many different fields: polymer chemistry, analytical chemistry, biochemistry, environmental chemistry, physical oceanography and informatics.

Mulch films

Plastic pollution is not restricted to oceans and freshwater. In some countries, farmers are facing a growing threat from plastic pollution in soil, due in part to an agricultural practice known as mulching. Plastic mulch films, comprised of polyethylene sheets, are used to cover crop fields soon after planting. They raise soil temperatures, limit weed growth and prevent moisture loss; as a result, water usage is reduced, while earlier harvesting and higher crop yields are feasible. As the world’s population grows and food demand increases, plastic mulch film has a key role to play in agriculture. For example, in 2018, China used 1.4 million tonnes of plastic mulch film to cover approximately 20 million hectares of land used to grow crops.

But when farmers remove the film, it often leaves shreds of residual plastic, and because polyethylene is not degradable, these plastic residues accumulate in the soil. The structure of soil becomes depleted, which may limit plant growth and foul machinery. Mulching is important for efficient agriculture, and despite its problems farmers are loath to lose the benefits of the practice. Alternative plastics could reduce these environmental impacts, and one strategy could be to develop plastic films that are environmentally degradable. Such a material would obviate the need for gathering up waste plastic, while ensuring that any residues left behind would break down to benign compounds in the soil. Combining these properties in a single plastic is not trivial, but it is a challenge that chemistry is well placed to tackle (see chapter 4: **Degradation of plastics**).

Plastic mulch film is used to improve the efficiency of growing crops.

Conclusion

Plastic pollution has serious impacts on our natural environment. Microplastics and nanoplastics are of particular concern, and we need systematic research to properly understand the factors that influence their formation across a range of environments including soils, freshwater, and oceans. That will require new analytical methods that researchers can use to study microplastics and nanoplastics at different size scales.

Predictive models that simulate the distribution of microplastics in the environment will also help to understand the fate and persistence of plastic waste. These models could track the location of microplastics, the standing stock of plastic fragments in environmental reservoirs, and the fluxes between them.

Researchers need to understand the environmental toxicity of plastics and their degradation products at all size scales, as well as the biological pathways involved in the chemical and particle toxicity of microplastics and nanoplastics. Studies should also consider both direct and indirect ecological effects, such as a reduction in food availability for other species, transportation of pollutants, and formation of biofilms. These potential impacts may be caused not only by petrochemical-based plastics, but also by bio-based plastics if they are fragmented into small particles in the environment.

The environmental impacts of plastics are not limited to their end-of-life degradation. Impacts also arise during the manufacture and application of plastics, through the use of energy and other resources. We need detailed life cycle and sustainability assessments, both to understand the trade-offs in environmental impacts and to identify research opportunities focused on reducing harm.

Overall, it is clear that a ‘business as usual’ approach to plastic waste is unsustainable and that a range of current and future industries require innovation in the plastics sector to deliver more sustainable products. Chemistry can play a crucial role in ensuring that we can continue to reap the benefits of plastics, but in a much more sustainable way.

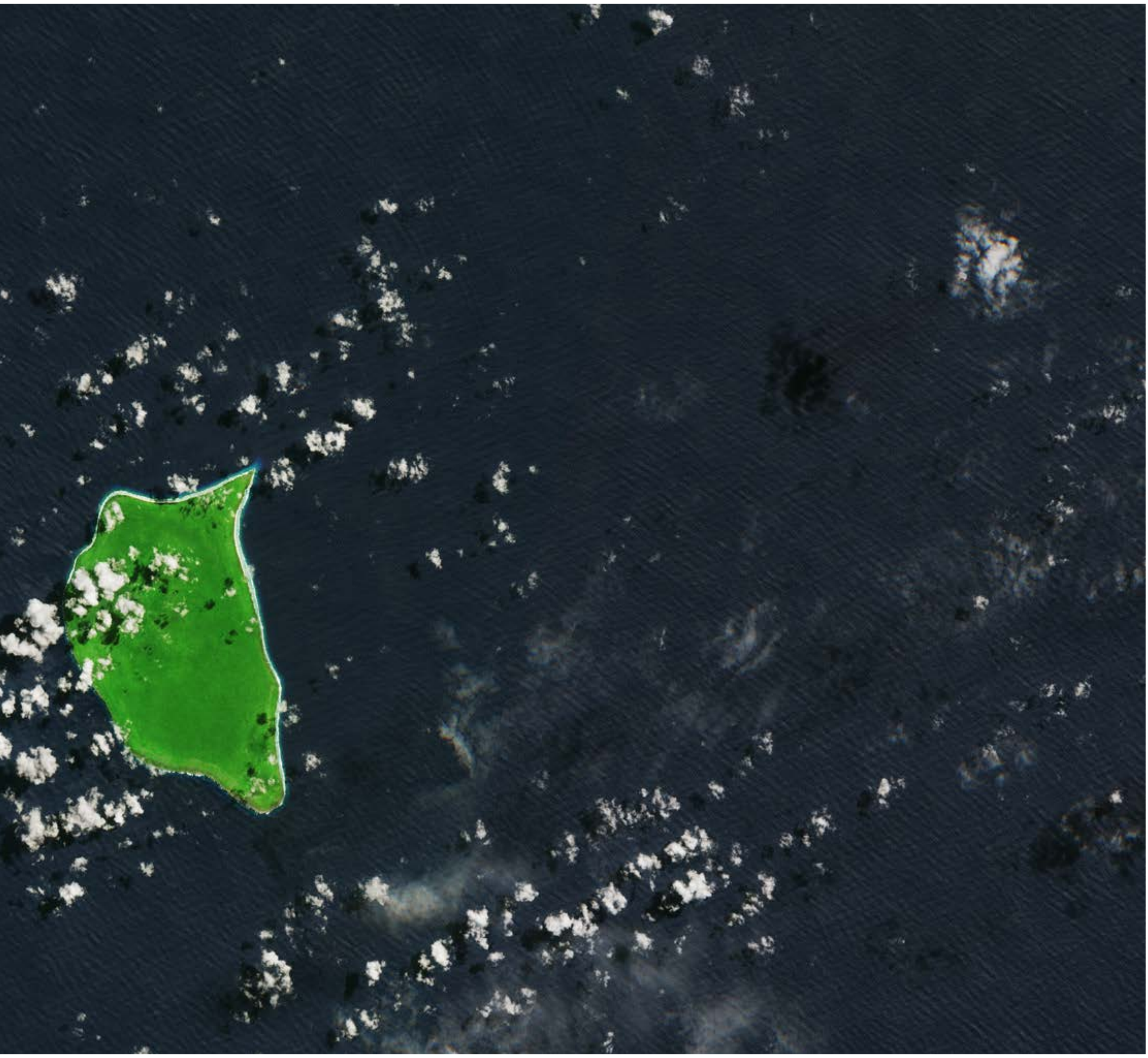
Central to this change in sustainability will be to transform our current ‘linear plastics economy’ into a ‘circular economy’. The linear economy involves producing, using and then disposing products; in contrast, the circular economy aims to turn this into a loop, so that unwanted products are reused or recycled, many times, in processes powered by renewable energy. Moving to a circular economy could dramatically reduce our use of resources, and help to meet the targets set out in the 2016 Paris Agreement on climate change. These changes will also be critical in ensuring we meet UN Sustainable Development Goals.

It is also essential to develop better ways to recycle plastic waste. To enable this, chemists can develop new technologies to disassemble and break down plastic waste into oligomers and small molecules that can be reused to make plastics and other high value products. Meanwhile, using renewable raw materials and energy-efficient manufacturing processes can help to reduce the climate impact of plastics (see chapter 2: **New sustainable plastics**). At almost every stage of the plastic life cycle, the technologies needed to enable a circular economy for plastics will depend on chemistry.

Above and overleaf: Henderson Island – a remote, uninhabited South Pacific island whose sandy beaches are World Heritage sites – was announced in 2017 to have the highest density of plastic rubbish on its shores of any place in the world.

earthsky.org/earth/henderson-island-pacific-plastic-pollution-study

Overleaf: Plastic on a beach in Lanzarote, 2018.



2. New sustainable plastics

To develop sustainable plastics, researchers are creating polymers that not only have excellent properties during their useful life, but also offer options for end-of-life management. A life cycle assessment approach should underpin these developments, which should improve the efficiency of polymer production and reduce energy inputs. In some contexts, it may be beneficial to use waste plastics, biologically-derived feedstocks or even CO_2 as raw materials to make new plastics. Ideally, renewable feedstocks should be suitable as 'drop in' substitutes in existing chemical processes.

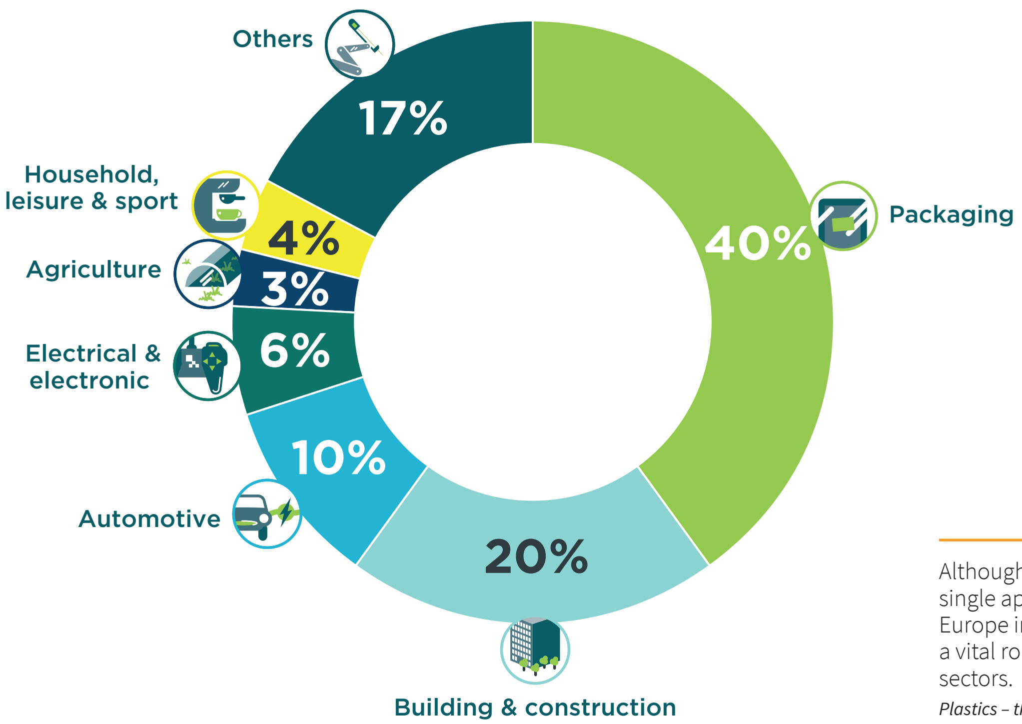
Introduction

The vast majority of plastics on the market today are made from petrochemicals, which are ultimately derived from oil and gas. Continuing to use these raw materials will require a reduction in both energy use and carbon emissions associated with these processes. These reductions need more research into improved manufacturing and processing methods. In the longer term, it seems likely the world will shift from a manufacturing system based predominantly on fossil fuels, towards one that makes products from a range of sources including recycled chemicals and renewable raw materials, using processes powered by renewable energy. Chemistry can also help to develop routes to make plastics that recycle waste CO_2 as a co-monomer and lock it into the polymer backbone.

Most common petrochemical-derived polymers such as polyethylene and polypropylene take many years to break down in the environment. These molecules are carbon chains that typically do not contain chemical groups that could act as obvious ‘break points' for chemical or biological degradation, and in many cases are water resistant. The polymer chains can assemble to form crystalline regions that confer excellent thermal and mechanical properties, making the material extremely durable in use, but also less amenable to degradation after use (see chapter 4: **Degradation of plastics**).

Only a handful of polymers have been designed to be easily degradable in the environment – for example the polyester polybutylene adipate terephthalate (PBAT), which is used as a compostable packaging material because it has similar properties to low-density polyethylene (LDPE) but reacts with water to fully degrade. There are almost no commercial polymers that have been explicitly designed to make recycling easier. Plastics need to be designed for recycling and the area of depolymerization chemistry needs fundamental exploration, theoretical understanding and exploitation. One option is to exploit the benefits conferred by biologically sourced monomers, which tend to be more oxygen rich than hydrocarbons, and to use these oxygen-bearing chemical groups to provide ‘break points' for degradation. Another option is to exploit non-permanent interactions between chains to produce polymers that can disassemble, or crystallites that can be disrupted with a lower energy cost.

Figure 2.1: **The uses of plastics**



Although packaging was the largest single application for plastics in Europe in 2018, these materials play a vital role in a wide range of other sectors.

Plastics – the Facts 2019, PlasticsEurope (2019)

Designing new plastics is important for sectors as varied as packaging and construction, and specialized plastics are also needed in many other sectors, including electronics, transportation, furnishing, leisure and agriculture (see figure 2.1: **The uses of plastics**). These areas may accelerate uptake of new sustainable plastics and help new materials secure a foot-hold in the market.

Polymers from renewable resources

Bio-based polymers currently make up a tiny proportion of the plastics market. Polylactic acid (PLA, also known as polylactide) is one of the most widely used bio-based synthetic polymers, found in products such as disposable cutlery and plastic cups. Thanks to the aliphatic ester chemical groups in the polymer chains, PLA can be completely broken down by industrial composting processes (see figure 2.2: **A sustainable cycle**). Life cycle assessments suggest that PLA has lower overall CO_2 emissions compared with conventional petrochemical plastics such as polyethylene and polypropylene (*J. Polym. Environ*. 2019, DOI: 10.1007/s10924-019-01525-9).

PLA is most commonly made by a ring-opening polymerization of lactide, a cyclic diester made from lactic acid. This starting material is produced by the fermentation of plant sugar extracted from crops such as sugar cane. Work is ongoing to utilize waste lignocellulosic feedstocks, including food and agricultural wastes, in order to make lactic acid production even more sustainable. Other lactones and cyclic monomers can be polymerized either to make variants of PLA or other aliphatic polyesters, and these approaches allow for some control over the polymers' chemical, physical, thermal and mechanical properties (*Chem. Rev*. 2018, DOI: 10.1021/acs.chemrev.7b00329).

Other bio-based polymers can be produced using monomers such as terpenes, including pinene derived from pine tree oil (*Polym. Chem*. 2014, DOI: 10.1039/C3PY01320K; *Angew. Chem., Int. Ed.* 2016, DOI: 10.1002/anie.201509379), limonene oxide derived from waste citrus fruit peel, and succinic anhydride (*Angew. Chem., Int. Ed*. 2018, DOI: 10.1002/anie.201801400).

Figure 2.2: **A sustainable cycle**

Plastics that are made from bio-based feedstocks, and which are recyclable or biologically degradable, could offer a more sustainable alternative to petrochemical-based plastics.

Plastic rulers amongst recyclable plastics. These rulers have been made from recycled materials.

Researchers have developed highly active and selective catalysts for these (co-) polymerization reactions, but further improvements are needed to translate these to sustainable industrial processes that produce plastics with more desirable characteristics such as higher mechanical strength and better barrier properties.

It is important to note that simply because a monomer can be produced from renewable resources does not guarantee improved sustainability. For example, bio-based polyethylene terephthalate (PET) can be produced by making the ethylene glycol co-monomer from glucose, but this gives rise to impacts such as eutrophication and acidification. The other co-monomer for PET, the aromatic diacid, cannot currently be economically produced from renewables. Alternative aromatic monomers derived from sugars show promise to produce fully bio-based polymers with similar properties to PET, but there are still challenges with monomer and polymer production. Better catalysts and processes could help, for example by using high pressure CO_2 together with new catalysts to reduce polymerization temperatures and energy consumption.

It must be stressed that the material properties of a polymer are decisive for its applications. The thermal and mechanical properties of PLA, for example, define its possible applications, and exclude many others.

Using waste molecules

Better reuse of waste molecules, either from industrial, agricultural or other chemical processes, will be important in reducing the carbon emissions associated with plastics. But CO_2 can also be used, in conjunction with a co-monomer, as a building block for plastics. In many ways, it is an ideal feedstock – it is cheap, abundant, and is the waste product from many industrial processes.

For example, polycarbonates can be produced by reacting epoxides with CO_2. This process is operating at commercial scale, and life cycle assessments have quantified the reductions to overall greenhouse gas emissions (*Green Chem.* 2014, DOI: 10.1039/c4gc00513a). The CO_2 copolymerization process is critically dependent upon the catalyst, and recent inventions have uncovered the opportunity to increase performances using mixed-metal catalysts, for example of magnesium and zinc (*Chem. Sci*. 2019, DOI: 10.1039/C9SC00385A). As chemists develop a better understanding of how these metals cooperate, that should help to develop better catalysts that can make the process even more efficient, reducing manufacturing costs and prompting wider adoption of these plastics.

It is also possible to add carbon monoxide to ethene during its polymerization, which introduces carbonyl groups into the polyethylene chain. These can act as convenient break points, so that chemical reactions involving enzymes or light could degrade the polymer molecules in the environment after a few months. Such materials are already being used in some plastic packaging, but it takes extremely high pressures to drive the polymerization reaction that produces them, raising manufacturing costs and making the process very energy intensive. So chemists are developing catalysts and methods that can make such polymers under much more moderate conditions, which could offer a more convenient route to such degradable plastics (*Macromolecules* 2014, DOI: 10.1021/ma5012733 and *Polym. Chem*. 2014, DOI: 10.1039/c3py01637d).

In the longer term, chemistry has a key role to play in generating completely new and disruptive technologies for plastics, potentially replacing some carbon-based monomers with new materials based on other elements. For example, sulfur is a large scale waste from the petrochemical industry and finding ways to recycle it into polymers could be useful. Polythioesters exploit sulfur to introduce convenient break points in the polymer structure that could be targeted by future recycling processes.

Natural polymers such as cellulose, chitin and starch can serve as renewable and environmentally degradable resources, either to make monomers or as materials in their own right. Cellulose is a major component of natural plant fibres, and the world's most abundant natural polymer. It is already used to make a range of products including cellophane film, textiles and packaging.

But processing cellulose can be challenging. Cellulose molecules are held together by networks of hydrogen bonds, which means that cellulose does not melt and does not easily dissolve in common solvents. Chemists are developing a range of strategies to make cellulose processing easier, for example by exploiting ionic liquids to dissolve cheaper low-grade cellulose feedstocks such as corn husks or wheat straw. This can reduce the cost or number of steps involved in cellulose processing (*ACS Sustainable Chem. Eng*. 2017, DOI: 10.1021/acssuschemeng.7b00488). Finding new ways to fine-tune the physical properties of cellulose derivatives may help to open up applications such as low-cost packaging, or to avoid the use of additives such as plasticizers.

Rolls of cellulose-based plastic film.

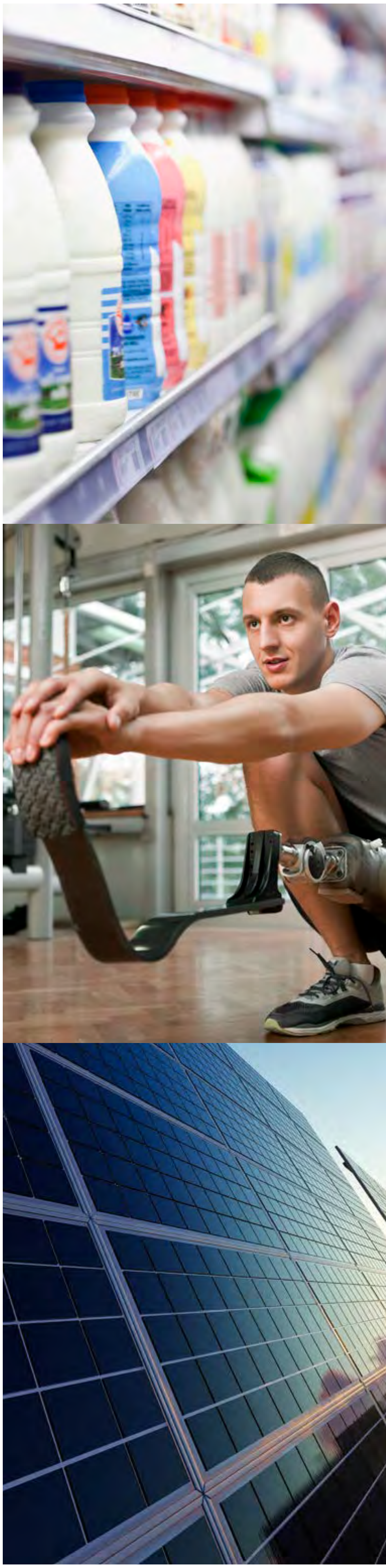
Significant research effort is devoted to the efficient transformation of lignocellulosic wastes into monomers for plastic production. This research effort benefits from expertise in heterogeneous catalysis, engineering, bio-processing and synthetic biology. It also allows for the production of polymer-natural fibre composites and for the improvement of natural materials like paper by producing polymer composites.

Conclusion

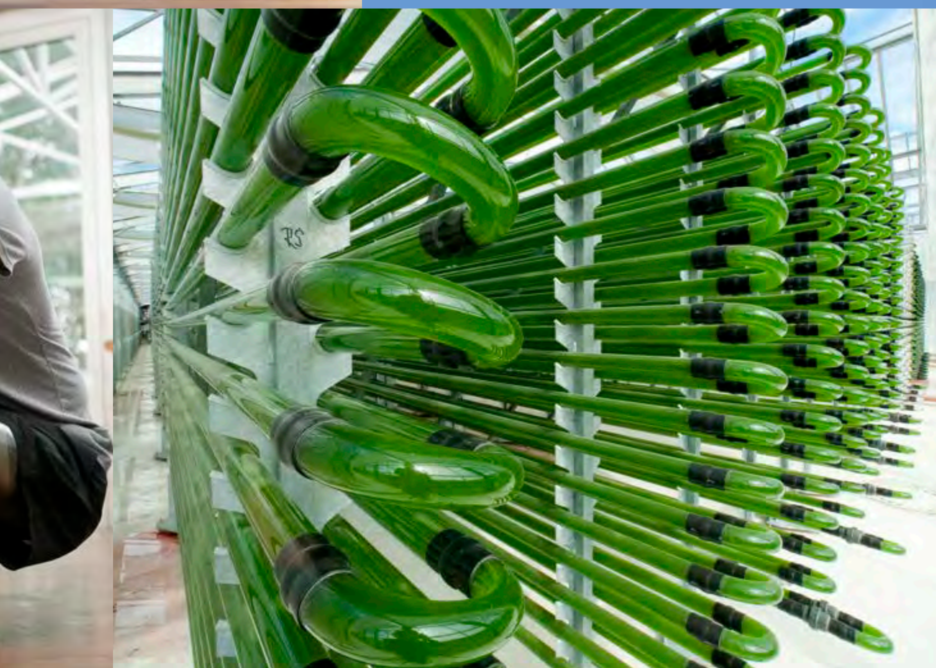
In future a range of recycled and reused chemical raw materials should be used to make polymers. These raw materials can and should include the products of chemical recycling of existing plastics. Because polymers are manufactured at large scale, the decisions about which monomers to deploy are guided to a large extent by feedstock availability and price. Techno-economic and sustainability assessment should be integrated at an appropriate stage of technology translation and ensure that fundamental research is well targeted.

The infrastructure used to make and process polymers represents a large capital investment that should not be abandoned in the short term. Thus, the development of sustainable ‘drop in’ substitutes for the highest-volume plastics (like polyethylene and polypropylene), which could use the same infrastructure, is a research priority.

When designing polymers, sustainability assessment over the entire materials life cycle is important. For example, future materials should be designed to minimize toxicity and environment impacts. As chemists find new ways to turn renewable molecules and recycled wastes into polymers it is important to design those polymers so that they can ultimately break down to environmentally non-persistent biochemicals and products. Moreover, any new plastics will need to be easier and less energy intensive to recycle. Research is needed to improve understanding of how polymer structure and microstructure affect their physical properties, recycling and degradation chemistries.



The many uses and varieties of plastic.




FACE

3. Recyclability of plastics

In the transition from a linear to a circular economy, much more of the plastic waste we produce must be recycled. Chemists can help to achieve this goal by finding more efficient ways to recycle the plastics we use today, and by developing new plastics that can be more effectively recycled in the future. This should include a greater emphasis on chemical recycling technologies that upcycle waste polymers into valuable chemicals, to be fed back into polymer manufacturing processes or used in other processes.

Introduction

Much of the plastic in use today can already be recycled in some way. For technical, economic and logistical reasons, though, far too little plastic waste actually goes through recycling processes. According to an analysis led by the Ellen MacArthur Foundation, roughly one-third of the world's plastic packaging waste is lost into the environment. In comparison, about 14% is collected for recycling, and 40% is disposed of in landfill. The remaining 14% is collected and burned, sometimes in energy-from-waste incinerators that can harness that heat to generate electricity (see figure 3.1: **The fate of plastic packaging waste**). These percentages represent a global average, however, and they vary between countries.

Some of the waste plastic that pollutes the environment has been discarded carelessly, but there are also problems with the way that waste plastic is handled after it is collected. This waste often contains a mixture of different plastics and other waste that must be separated before it can be recycled, a process that can be very labour intensive. Waste management companies often bale up this waste and ship it to countries with lower labour costs for recycling, but it is all too common for some of this plastic to be lost during transport.

Most of the plastic that is recycled goes through mechanical and thermal processing to re-make other plastic products. Thermoplastics such as polyethylene and polypropylene could, in principle, be recycled by reprocessing but in practice most mechanical recycling of these materials leads to a significant compromise in properties and lower-value applications. Thermosetting plastics and resins, such as some polyurethanes and epoxy-resins, cannot be easily chemically or mechanically recycled.

Some niche plastic recycling processes operate efficiently – in Europe, for example, about half of the mass of a plastic milk bottle is made from recycled high-density polyethylene, material that partly comes from old milk bottles.

Only 14% of plastic packaging materials were recycled in 2013. Just 2% of plastic packaging waste was used to remake similar-quality products (closed-loop recycling), while 8% was turned into lower-value products (cascaded recycling).
The New Plastics Economy: Rethinking the future of plastics, Ellen MacArthur Foundation (2016)

Figure 3.1: **The fate of plastic packaging waste**

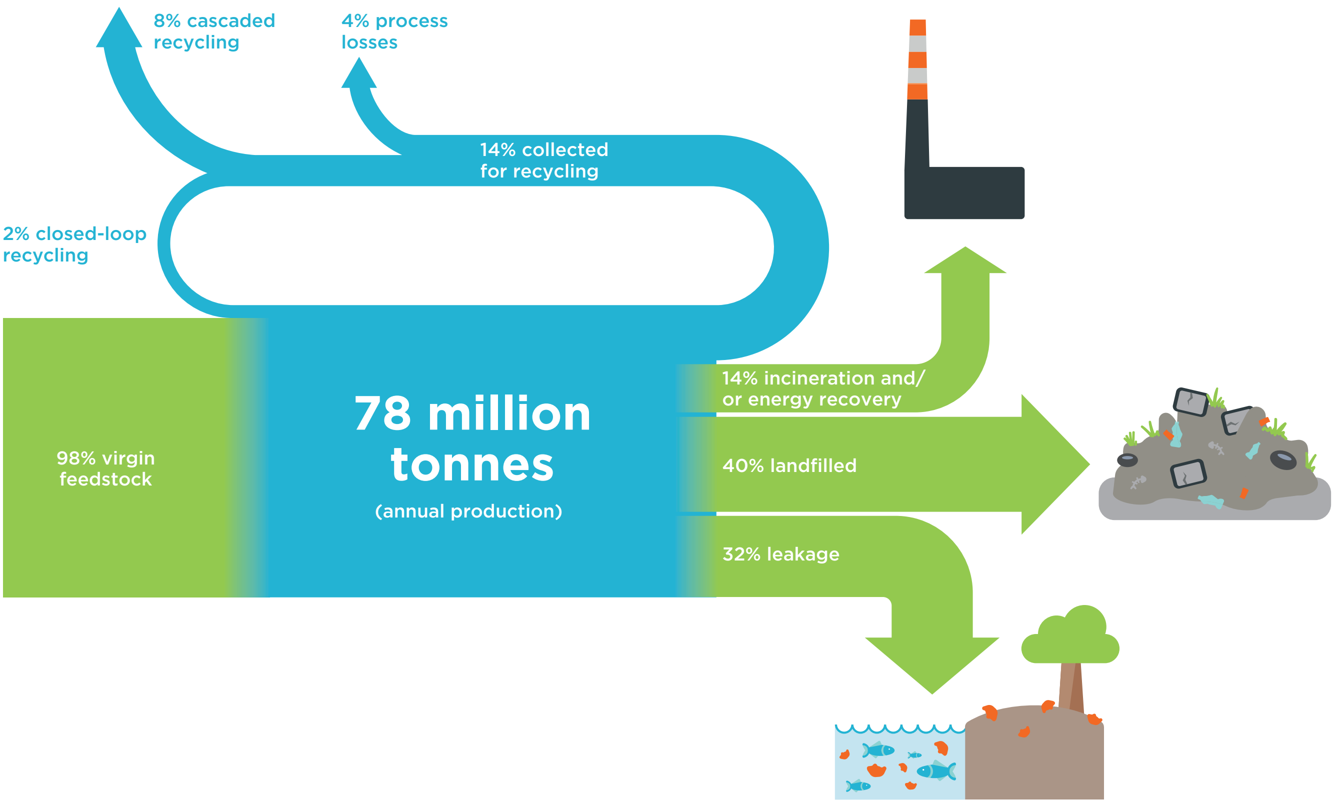
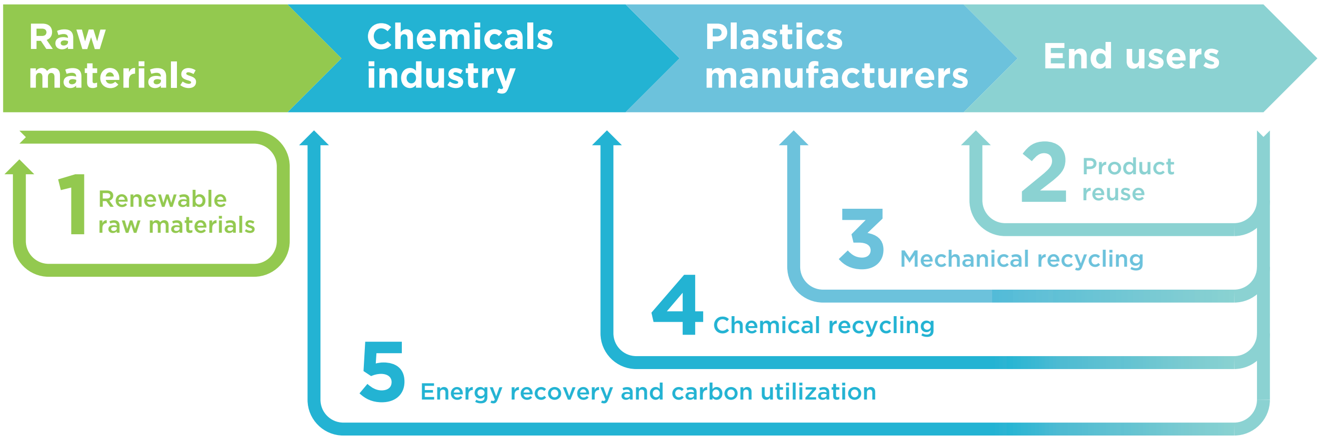


Figure 3.2: **A circular economy for plastics**



Sustainable plastics should rely on renewable raw materials (1), and be reused as much as possible (2). Once reuse is no longer possible, they should go through mechanical recycling (3) to create new plastic products, or chemical recycling (4) to afford new feedstock chemicals. Once these options are exhausted, waste plastic can be incinerated to generate energy, with CO_2 captured for use as a feedstock chemical (5).

Adapted from: *Taking the European Chemical Industry into the Circular Economy*, Accenture (2017).

Turning an unwanted product into a new version of the same product in this way is called closed-loop recycling. But other kinds of plastic are much more difficult to recycle, or are turned into products with a much lower value than the original plastic, a strategy known as open-loop or cascaded recycling.

Companies involved in plastic manufacturing and waste handling would have a greater incentive to collect and reprocess plastic waste if more value could be extracted from it. One option is known as chemical recycling, where polymer molecules are broken down into monomers or other smaller building blocks that can contribute to the virgin feedstocks used to make new plastics.

Chemical technologies have the potential to improve the efficiency of both mechanical and chemical recycling processes. They can tackle the plastic problem in two ways: by finding better ways to deal with the plastics we use today, and by developing new plastics that can be more effectively recycled in the future.

Researchers can expand the range of plastics that can be chemically recycled, for example, and help to extract more value from these materials. New chemical technologies could also help to directly and selectively recycle mixtures of plastics, avoiding expensive and labour-intensive sorting processes.

Chemical recycling will play a crucial role in extracting more value from waste plastic, and is essential to creating a circular economy for plastics (see figure 3.2: **A circular economy for plastics**).

Limited options

Plastic recycling strategies vary between countries, but these systems rely on some common basic elements. Waste plastic is collected from homes, businesses and other collection points, and transported to a waste management facility where plastics are sorted into different polymer types. This helps to ensure that each waste stream offers a relatively pure source of one particular polymer molecule, making them suitable for reprocessing into new products. In the processing facility, plastic is shredded and some impurities removed.

In mechanical recycling approaches, the plastic is melted and extruded so that the material can be re-formed into new plastic products, including bottles, clothing fibres, carpets and furniture. However, the properties of plastics that are produced by mechanical recycling are often inferior to those produced from virgin feedstocks. They may not be as strong, or may be discoloured, for example. As such, this form of recycling is sometimes called ‘downcycling’, because its products tend to have a lower value than the original plastics.

Shredded plastic waste at a recycling facility.

In cases where plastic waste is not suitable for mechanical recycling, incinerating the waste and using the heat to generate electricity can be applied, particularly if the CO_2 this generates can be captured sustainably rather than released to the atmosphere. But even this solution cannot handle all types of plastic – for example, polyvinyl chloride (PVC) causes problems in energy recovery systems because it release acids when burned that corrode pipes in the incinerator.

Chemical recycling could be an excellent and broad-ranging alternative recycling method, but currently there are relatively few commercially viable processes. This relates in part to the complex composition of some waste items, and to the use of additives and improvers which complicate recycling. Fundamentally, the chemistry of disassembly is not so well understood. Over many decades, chemists have devoted a great deal of effort to developing the 'forward' reactions that turn monomers into polymers, but comparatively little research has gone into the 'back' reactions that break down these long chains into shorter molecules. This is an important new field for future development of methodologies, theories and processes.

Chemical recycling

Perhaps the most common form of chemical recycling currently available involves a process called pyrolysis, which is a controlled thermal decomposition of hydrocarbon polymers. This process typically takes place at high temperatures of 450–700°C, under an inert atmosphere, so that the plastic does not burn. The current limitation of the process is that in most cases it creates a mixture of waxes, oligomers, unsaturates, aromatics and alkanes – in other words, it shows poor selectivity in terms of monomer production and is best suited to production of fuels from waste plastics. Another option is hydrothermal cracking, which breaks down plastic using catalyzed thermal processes and steam. The temperature of the process is somewhat lower, at 350–550°C, but it also creates a mixture of products, with only a proportion being feasible for recycling into plastic. Recycling mixed plastic waste in this way may require additional technologies that can cope with additives.

Both of these processes require a lot of energy and show limited selectivity, features that prevent wider commercial use. Better catalysts and chemical processes could help to accelerate these degradation or depolymerization reactions and so lower their operating temperatures. It is also important to explore selective production of valuable chemicals and recycling to monomers for future polymer production.

Early stage academic research is exploring different means to catalyze polyethylene recycling. This builds on a long history of research into the thermal or catalytic decomposition of many types of plastics (*J. Jpn. Petro. Int*. 2016, DOI: 10.1627/jpi.59.243). Using tandem catalysis, which applies two different catalyzed processes at once, it is feasible to explore dehydrogenation of polyethylene to introduce alkene groups. These alkenes can be subjected to cross-metathesis chemistry that allows for production of a range of shorter-chain alkenes and oligomers. These processes have been optimized to occur at around 175°C, and the reaction has been performed with real plastic waste, including plastic bottles, food packaging and shopping bags (*Sci. Adv*. 2016, DOI: 10.1126/sciadv.1501591). But much more research would be necessary to develop a large scale process using this approach, including significant improvements to reaction selectivity and to catalyst loading, tolerance and cost. The process only works for polyethylene waste, so other plastics like polypropylene and polystyrene must be completely removed before chemical processing. And the catalyst relies on expensive precious metals, so alternative metal catalysts should be explored.

Below top: A handful of pelletised recycled plastic. This is PET (polyethylene terephthalate), a plastic commonly used in liquid containers. It is relatively easily recycled and may be reused. Below bottom left: PET recycling symbol on a plastic bottle. Below bottom right: Half of the mass of a plastic milk bottle can be made from recycled high-density polyethylene, material that partly comes from old milk bottles.

It may also be possible to develop chemical recycling technologies that break down waste plastic into molecules suitable for making more valuable products than the original plastic, a strategy known as 'upcycling'. For example, plastics could be broken down into valuable chemical feedstocks, or old PVC pipes could be chemically modified to improve their heat resistance, or confer antibacterial properties (*RSC Adv*. 2019, DOI:10.1039/c9ra05081g).

Chemical analysis plays an important role in identifying, tracing and sorting different polymers from plastic waste. Techniques such as X-ray spectroscopy and infrared spectroscopy can differentiate between different polymers, but these methods struggle with certain plastics. To meet increasingly stringent requirements for the traceability of wastes, there will need to be more research into chemical and spectroscopic markers to improve recycling and ensuring accountability.

Even with improved sorting technologies, there is also a need for technologies to process and recycle mixed plastic wastes. Catalytic processes could help to selectively depolymerize certain plastics in mixed waste, making separation easier. For example, PET and polycarbonates react with ethylene glycol at different rates in the presence of a catalyst. The reaction depolymerizes polycarbonate at around 130°C, but only goes to work on PET once the temperature is raised to 180°C. This means the monomers for each polymer can be extracted separately, providing a purer source of potential feedstock chemicals with a much higher value than a mixture could offer (*Polym. Chem*. 2019, DOI: 10.1039/C8PY01284A). Alternatively, compatibilizers and block polymers may improve the properties of mixed plastic waste products and allow higher-value recycling.

Paper-plastic composites

The use of paper-plastic composites in disposable items such as coffee cups and cartons has seen significant growth over the past decade, but some of these materials pose serious recycling challenges. Paper itself is readily recycled, although this requires significant input of energy and water. In the European Union, more than 70% of new paper products are made from recycled paper. Overall, the world produces about 400 million tonnes of paper per year, and packaging accounts for roughly half of paper use.

But paper is increasingly teamed with plastics like polyethylene, along with adhesives, to make it stronger, oil resistant and waterproof. To recycle these mixed paper-plastic composites, paper fibres must be separated from the other components – but current processes are still not very efficient in this regard, producing a lot of reject material and fouling machinery in the process. Meanwhile, the European Union's Single-Use Plastics directive will ban many single-use plastic products (where alternatives are available) by 2021, which may inadvertently increase the use of paper-plastic composites.

Chemists and materials scientists should focus on ways to improve the recyclability of these paper-plastic composites. For example, bio-derived hydrophobic cellulose esters and ethers could be used to make paper water repellent and may facilitate recovery of paper fibres from these composites compared to conventional composites. In principle, these next-generation paper composites could also replace some of the polyethylene used in food packaging. But they will need to match the performance of conventional plastics – flexible but strong, oxygen impermeable, resistant to both liquid water and water vapour. If they are not recyclable, these new composites could be engineered to be compostable. Solving these challenges necessitates more collaboration between the plastics and paper industries and also for scientific understanding of how to design composites for improved performances.

Conclusion

There is a widespread perception that recycling is costly and difficult for plastics. In terms of the fundamental energy requirements of recycling, plastics have many advantages compared to materials like glass or steel, not least because typical depolymerization temperatures (ceiling temperatures) range from 100°C–600°C for most polymers. Nonetheless, the science of plastic recycling and disassembly needs urgent development and the technologies necessary to allow for efficient recycling should be developed. Polymer science can help to unlock the value in waste plastics and to improve recycling processes. Chemistry can develop technologies that make it possible to recycle a broader range of plastics, with lower energy demands and lower CO_2 emissions. One of the key targets is to develop better catalysts and processes for recycling that are highly selective in producing monomers for further polymerization. Chemistry is also essential to quantify and qualify the recyclability of plastics in general, to help guide decisions by manufacturers, consumers and policymakers.

Companies are eager for more sustainable approaches to manufacturing and recycling of plastics. We recommend the investigation of chemical recycling technologies as they have the potential to deliver multiple recycling loops, without compromising the quality of the product. But the additives to plastics need careful consideration as they may foul chemical recycling processes, and future developments need to work in parallel with material property demands to ensure that a greater proportion of plastics are recycled.

Nevertheless, it is almost inevitable that some plastic will find its way into the environment. Developing new plastics that are more amenable to environmental degradation could mitigate the impact of this pollution (see chapter 4: **Degradation of plastics**). This research effort would rely on many of the same chemical strategies used to develop plastics that are more recyclable, such as introducing chemical groups that act as convenient break points for polymer molecules. As such, environmentally degradable polymers may also facilitate recycling.

Degradable plastics can be one tool to mitigate the impacts of plastic pollution.

4. Degradation of plastics

Although some biodegradable and compostable plastics are available, there remains some confusion among the public and in industry regarding what these terms mean, and around the conditions and time scales necessary for these degradation processes. Research is needed to understand exactly how all plastics degrade in different circumstances, and the fate of their degradation products. This knowledge will help chemists to design polymers that are durable in life yet degradable on demand, and to ensure that there are not unintended environmental consequences resulting from the degradation products of plastics.

Introduction

Most plastics are designed to be durable, so that they maintain their structure and performance during their useful life. But in application sectors such as packaging this durability can give rise to pollution, because discarded waste plastic can persist in the environment for years or even decades. It is also important to emphasize that for some applications, designing plastics to be more durable and longer-lived would be a more sustainable option and should be explored. In some scenarios allowing for plastic articles to be reused multiple times, for example in refillable packaging, will represent a more sustainable option than providing multiple disposable packaged articles. Nonetheless, there is a fundamental problem with having materials that are not degradable in applications where they can make their way into the environment.

Designing a plastic to be durable in life, and degradable at the end of its life, is a major challenge. Biodegradable plastics are available today and have been developed for a number of sectors and contexts. For example, some materials were initially developed for use in medical implants that slowly break down in a patient's body. Some plastics are best suited to degradation within industrial composting facilities, which require the same sort of collection and processing infrastructure as conventional recyclable polymers. Other polymers are designed to break down in home composting bins. For such degradable polymers it is vital to understand what conditions are required, how long it takes, and what breakdown products it leaves behind. It is recognized that that current standards and test methods cannot predict breakdown in the range of complex natural environments (*R. Soc. Open Sci*. 2018, DOI: 10.1098/rsos.171792).

As we use increasing amounts of degradable plastics, their breakdown products will potentially have a greater impact on our world. Research is needed to understand the impacts of these degradation products and to ensure they do not change the environment in unexpected ways, by encouraging different microbes to thrive in soil as they feed on the plastic, or by altering the pH of soil. It is vital to anticipate and understand these impacts.

Developing new degradable polymers offers an opportunity to reduce the environmental impact of plastic pollution. But that research must be informed by a deeper understanding of the underlying chemistry of their degradation processes, and the long term consequences of this strategy. This research can also help to set standards for degradable plastics that take better account of their behaviour in real-world situations.

Breaking down plastics

It is important to recognize that bio-derived polymers – those made from molecules extracted from biological material such as plants – are not necessarily biologically degradable. Conversely, many biologically degradable polymers areactually prepared from petrochemical feedstocks. In terms of the preparation of environmentally degradable polymers, there is no need to focus only on petrochemical or biologically-derived raw materials, since either could be used effectively.

Bio-derived polymers may offer the opportunity to use more sustainable feedstocks to make plastics with a lower carbon footprint. Biologically degradable polymers can help to tackle a different problem, by reducing the persistence of plastics in the environment. With those two goals in mind, polymers that are both bio-derived and biologically degradable look particularly attractive.

The leading biologically degradable polymers by production volume are polylactic acid (PLA) and polybutylene adipic terephthalate (PBAT), with PLA being produced from biomass and PBAT being predominantly petrochemical.

Other common bio-based and biodegradable plastics include polybutylene succinate (PBS) and polyhydroxyalkanonates (PHAs) (see figure 4.1: **Global production of biodegradable and bio-based plastics**). In total, about 2.1 million tonnes of these bio-based or biologically degradable polymers were produced in 2019, making up a very small proportion of the overall polymer market.

Compared with conventional plastics used in packaging, current biodegradable alternatives need improvements to both their properties and degradation conditions. Chemistry can help to develop improved mechanical, thermal and rheological properties for these biodegradable plastics, and find ways to mass produce them more cheaply. Biologically degradable polymers will get cheaper as their scale of production increases.

Another challenge is that different materials require different conditions for complete degradation, including different temperatures, microbes and humidities. Some plastics may be degradable in the wider environment, but the rate of breakdown may vary significantly between soils, rivers, or oceans. The sheer variety of environmental conditions means that it is difficult to design polymers that are universally degradable in any circumstances.

Aside from the polymer chain chemistry, the interaction between polymer chains (or hierarchical structure) is a key factor that determines whether a plastic is degradable. PHAs, for example, form lamellar crystalline regions, roughly 10 nanometres in diameter. These crystalline sheets are separated by amorphous regions and together they build up crystalline grains called spherulites, which can be 100 micrometres across and form the building blocks of the larger structure of a plastic (see Fig 4.2: **The structure of plastics** p40). Consequently, the bulk plastic material does not behave like isolated polymer molecules – instead, plastics behave differently at various physical scales, being more or less resistant to degradation.

Plastic degradation generally happens in different stages. Larger pieces of plastic erode into smaller pieces, and then longer polymer chains in those pieces break down to shorter molecules with a lower molecular weight.

Roughly half of the plastics made from bio-based materials are not biologically degradable. Two prominent biodegradable plastics (PBAT and PBS) are largely made from petrochemical precursors. Just over one-third of so called 'bioplastics' are both bio-based and biologically degradable.
Bioplastics market data 2019, European Bioplastics (2019)

Figure 4.1: **Global production of biodegradable and bio-based plastics**

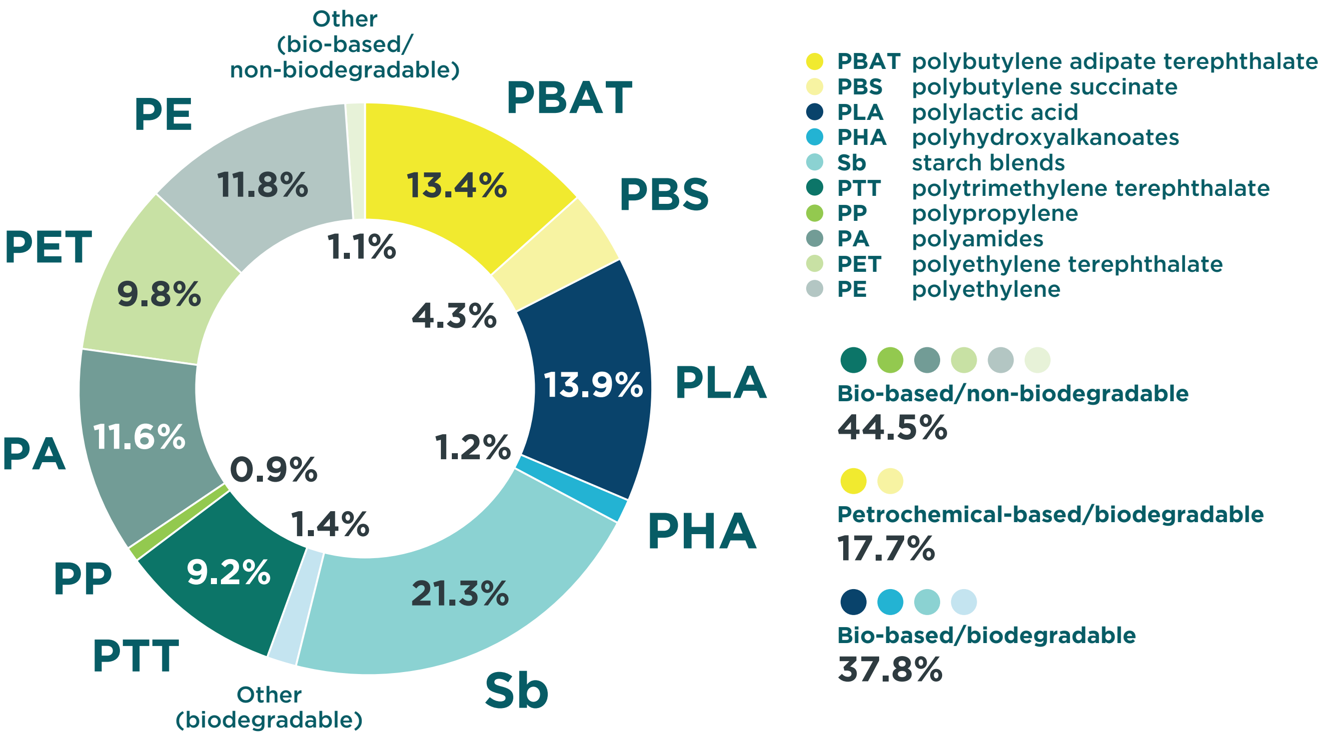
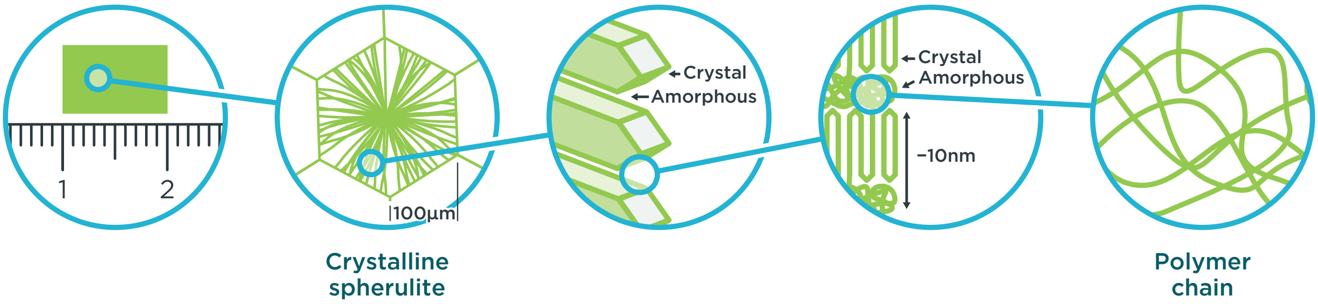


Figure 4.2: **Structure of plastics at different scales**



Plastics have different structural features at different scales – these parts of the material do not degrade in the same ways, or at the same rate. Plastics often contain tough crystalline grains called spherulites that can be a few hundred micrometres wide and strengthen the material. Within these spherulites, some polymer chains are highly organized into crystalline regions that may be tens of nanometres thick; these are separated by amorphous regions where the polymer chains are more tangled and are generally easier to break down.

Adapted from a figure by Keiji Numata.

These steps depend on physical and chemical processes, such as weathering and abrasion, water, ultraviolet light, oxygen, heat, various chemical mechanisms, or biological organisms such as microbes.

Ultimately, the polymers undergo complete biological degradation to form small molecules, which are naturally processable or readily metabolized. In some circumstances, this kind of environmental degradation may be the best way to deal with plastics and to reduce pollution from plastics. Nevertheless, a thorough life cycle assessment is always needed to offer a useful comparison of the impact of different waste management strategies.

To design new environmentally degradable plastics, chemists can incorporate chemical groups into polymers that enzymes can attack. But researchers must also consider how these enzymes will access the polymer molecules and take account of different degrees of crystallinity or surface treatments. Further research into the chemical mechanisms of polymer degradation should help to guide that discovery process, as will studies on the residues produced by such breakdown processes. Crucially, it is important to study these processes in the natural environment, as well as the laboratory.

This research should identify the molecular weights and chemical structures of degradation products, but it should also consider intermediate breakdown products, including shorter polymer chains and nanoparticles. We also need biological assays to study what effects these molecules have on living organisms, using techniques such as *in vitro* enzyme assays.

A slow process

Any new environmentally degradable plastics should be completely assimilated into the environment within a defined time, and without generating ecotoxic degradation products. Defining this time scale will depend upon application. Today's hydrocarbon plastics generally break down far too slowly, and degradation often stops once the plastic has reached the size of microparticles or nanoparticles, which may themselves cause environmental problems (see chapter 1: **The impact of plastics**).

Current European Union regulations state that a plastic is considered compostable if, after 12 weeks of composting, no more than 10% of the plastic's mass is caught by a sieve with holes 2 millimetres wide. That means the material that passes through the sieve may contain microscopic fragments of plastic particles. If this residue is applied to agricultural land, which is common in most countries (*Sci. Adv*. 2018, DOI: 10.1126/sciadv.aap8060), it is important for scientists to establish whether soil microbes can complete the breakdown of these particles. This may also allow some materials that are never likely to fully degrade to be confused with fully degradable structures, for example oxo-degradable polyethylene.

PLA is a fully hydrolyzable polymer and its degradation product, lactic acid, is a natural metabolite and can be bio-processed to CO_2 and water. Nonetheless, understanding the time scale for complete degradation is important and defining acceptable rates for degradation will depend on applications. For example, PLA has been shown to break down over the course of months in a field, but after one year visible flakes of material may remain and take much longer to fully degrade. This underscores the need for more environmental testing to understand the times taken and the fate of breakdown products, work that will require chemists to collaborate more closely with biologists and ecologists. It also requires a molecular perspective that looks at the bonding and structure of the polymers, and the mechanisms involved in disassembling them.

Designing environmental degradability into plastics does not mean that environmental degradation should be the default option for dealing with that waste. Indeed, the degradation mechanisms increase the end-of-life options available to society. For example, PLA is an aliphatic polyester that can easily be depolymerized, so it can be managed through closed-loop chemical recycling (*ChemSusChem* 2019, DOI: 10.1002/cssc.201902755).

Since enzymes are usually less effective at attacking crystallites, it may be possible to promote environmental degradation by using polymers that have amorphous regions by design yet retain the required physical and mechanical properties. Blending different polymers together, or creating composites with other materials, could help to maintain the strength of the amorphous plastics during their use. For example, branched aliphatic polyesters tend to form more amorphous materials that degrade more rapidly than crystalline variants. Early-stage research suggests that blending linear and branched polyesters may help to fine tune the physical properties of the finished plastic so that it still performs well during use.

Polyhydroxyalkanoates (PHAs) are another promising class of polymer that are both bio-based and biologically degradable. The start of PHA production involves bacterial production of the polymers – as much as 90% of the weight of dry cells can be polymer. There are already some PHAs in commercial production and alternative chemical routes to the materials are also feasible in the future.

Aliphatic polycarbonates also have potential as degradable plastics and may show a lower carbon footprint than conventional petrochemical polymers, because they can be made by reacting epoxides with CO_2 (see chapter 2: **New sustainable plastics**). The properties and manufacturing processes of these polycarbonates still need optimization, including improvements to their thermal and mechanical strength. For example, it is been shown that CO_2-derived polypropylene carbonate (PPC) film has a very low permeability to water vapour, and may be useful as an agricultural mulch film (see chapter 1: **The impact of plastics**). In 2018, a field trial in China using PPC mulch film showed that some crops, including potato and quinoa, were just as successful as when conventional polyethylene film was applied. The PPC film was less successful for cotton, largely because the film degraded too quickly on the field, and further research to strengthen the film is ongoing.

Recyclable mail wraps and degradable food packaging.

In academic laboratories, a wide range of other degradable polymers are being explored, with the majority of research focused on aliphatic polyesters, polyamides, polycarbonates and polyacetals. Another area for investigation is the use of modified amino acids to build synthetic polymers that mimic natural materials such as spider silk, and to make fabrics and foams.

Conclusion

Despite the immense potential for these innovative new polymers, it is difficult for them to compete with conventional petrochemical polymers that have been in mass production for 60 years. So one of the most immediate challenges for chemists is to find cost reductions and performance enhancements for existing biologically degradable polymers, to help them gain market share. This will require new routes to monomers, new catalysts to stitch them together, and new ways to enhance the physical properties of these plastics – for example, by blending polymers or increasing cross-linking between polymer chains. It is also essential to stimulate more fundamental research and innovation in the development of degradable polymers. This exploratory science needs to begin quickly because new materials technology pipelines require significant optimization of technology and processes to deliver new products.

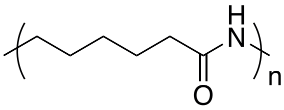
As degradable plastics become more common, we need much better understanding and information regarding the different types of degradation and the products formed by degradation. Developing the emerging field of degradation in the environment will require the input of chemistry, as will setting standards and legislation in this sector. As part of this work, effective communication of the results to the general public will be vital and chemists must engage in outreach activities to improve public awareness of how plastic waste is currently managed, and the different ways it can be sustainably managed in the future.

Decisions about whether researchers should design plastics to be degraded in chemical recycling facilities, industrial composting units, or in the environment, must be guided by life cycle assessments and a full awareness of the fate and activity of breakdown products. It is also important to note that adding degradable linkages and chemistries into polymers will likely facilitate recycling of those materials, thus offering two benefits. Ultimately, chemists should be aiming to design polymers for ‘degradation on demand’, so that waste plastic can be handled in the most sustainable way possible.

Appendix

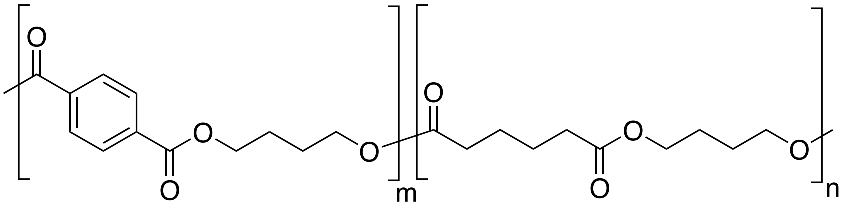
Glossary of acronyms

PA polyamide

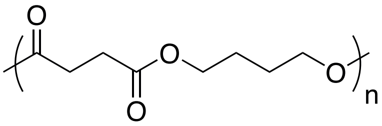


Illustrated with Nylon 6

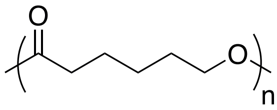
PBAT polybutylene adipate terephthalate



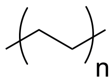
PBS polybutylene succinate



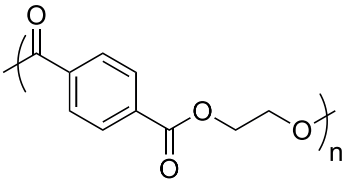
PCL poly ε -caprolactone



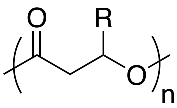
PE polyethylene



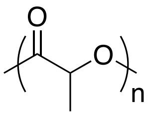
PET polyethylene terephthalate



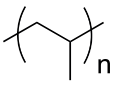
PHA polyhydroxyalkanoate



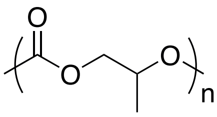
PLA polylactic acid/polylactide



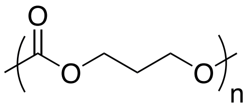
PP polypropylene



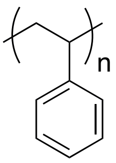
PPC polypropylene carbonate



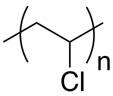
PPT polytrimethylene carbonate



PS polystyrene

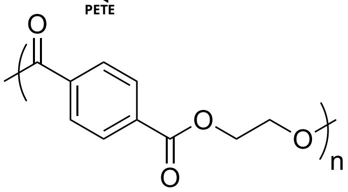


PVC polyvinyl chloride

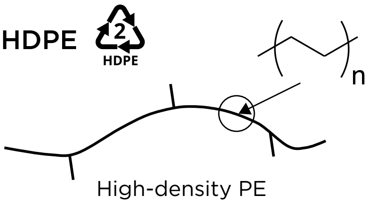


Structures of common polymers and their recycling symbols

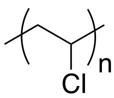
PET 1 PETE



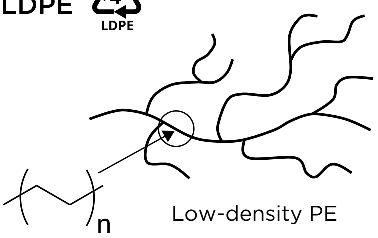
HDPE 2 HDPE



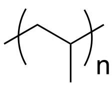
PVC 3 V



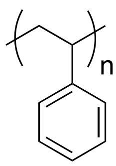
LDPE 4 LDPE



PP 5 PP



PS 6 PS



OTHERS 7 OTHER

Other plastics, including acrylic, acrylonitrile butadiene styrene, nylon, polycarbonate, and polylactic acid.

Further reading

United Nations Environment Programme ‘Biodegradable Plastics & Marine Litter: Misconceptions, Concerns and Impacts on Marine Environments’ 2015. Available at **wedocs.unep.org/handle/20.500.11822/7468**

Suschem ‘Plastics Strategic Research and Innovation Agenda in a Circular Economy’ 2018. Available at **suschem.org/publications**

PlasticsEurope ‘Plastics – the Facts’ 2019. Available at **plasticseurope.org/en/resources/publications/1804-plastics-facts-2019**

House of Commons Library, Briefing Paper number 08515 ‘Plastic Waste’ 2020. Available at **commonslibrary.parliament.uk/research-briefings/cbp-8515/**

The National Academies of Sciences, Engineering and Medicine ‘Closing the Loop on the Plastics Dilemma: Proceedings of a Workshop in Brief’ 2020. Available at **doi.org/10.17226/25647**

CS3 participants

China

Zhibo Li (Chair)	Qingdao University of Science and Technology
Zheng Huang	Shanghai Institute of Organic Chemistry, CAS
Hua Lu	Peking University
Xianhong Wang	Changchun Institute of Applied Chemistry, CAS
Changrong Yan	Chinese Academy of Agricultural Sciences
Jun Zhang	Institute of Chemistry, CAS
Zhigang Shuai	Chinese Chemical Society (CCS)
Lidong Han	Chinese Chemical Society (CCS)

Germany

Andreas Greiner (Chair)	University of Bayreuth
Markus Biesalski	Technical University of Darmstadt
Christian Laforsch	University of Bayreuth
Stefan Mecking	University of Konstanz
Brigitte Voit	Leibniz Institute of Polymer Research Dresden (IPF)
Markus Behnke	German Research Foundation (DFG)
Hans-Georg Weinig	German Chemical Society (GDCh)

Japan

Atsushi Takahara (Chair)	Kyushu University
Hirofumi Hinata	Ehime University
Keiji Numata	RIKEN Center for Sustainable Resource Science
Kotaro Satoh	Tokyo Institute of Technology
Toshiaki Yoshioka	Tohoku University
Satoshi Miyashita	Japan Science and Technology Agency (JST)
Ryoji Nakamura	Japan Science and Technology Agency (JST)
Mitsuo Sawamoto	Chemical Society of Japan (CSJ)

United Kingdom

Charlotte Williams (Chair)	University of Oxford
Matthew Davidson	University of Bath
Andrew Dove	University of Birmingham
Tamara Galloway	University of Exeter
Jennifer Garden	University of Edinburgh
Steve Howdle	University of Nottingham
John Hand	Engineering and Physical Sciences Research Council (EPSRC)
Jennifer Channell	Engineering and Physical Sciences Research Council (EPSRC)
Sarah Thomas	Royal Society of Chemistry (RSC)
Stuart Govan	Royal Society of Chemistry (RSC)
Rebecca Quine	Royal Society of Chemistry (RSC)

Thomas Graham House
Science Park, Milton Road
Cambridge CB4 0WF, UK
T +44 (0)1223 420066

Burlington House
Piccadilly, London
W1J 0BA, UK
T +44 (0)20 7437 8656

rsc.li/progressive-plastics

To quote this report, please use the following reference:
Science to enable sustainable plastics – A white paper from the 8th Chemical Sciences and Society Summit (CS3), 2020, rsc.li/sustainable-plastics-report

Registered charity number: 207890