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REINVENTING

A rising tide of public awareness about plastic waste and its impact on the environment is spurring the development of new polymer chemistries and routes to recycle polymers. Anthony King reports

Two years ago, wildlife photographer Justin Hofman shocked visitors to the Natural History Museum in London with his image of a miniscule seahorse carrying a waste cotton bud by its tail. The disturbing photo was snapped in a reef off Borneo and exemplified the horrors of ubiquitous plastic waste.

Today, >350m t of plastics are made every year, but only 15% is recycled. Around 9 m t/year of plastic goes into the sea. However, the vast majority of polymers are not biodegradable and take decades to decompose, explains Mark Miodownik, a materials scientist at University College London, UK: 'They are compact and don't have the functional side chains that microbes need to get hold of.'

Waste sustainability has re-emerged as a hot topic in the past two and a half years, says Paul Bjacek, a market consultant at Accenture. Plastic production consumes around 6% of global oil production, while about 40% of plastics are incinerated in Europe for energy, which the EU regards as unsustainable; 31% is landfilled, and 30% recycled. A 2018 study estimated that of the 8.3bn t of plastic produced, just 9% has been recycled and 79% accumulated in landfills or the natural environment.

PLASTICS

GETTY

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Haritz Sardon *University of the Basque Country, Spain*

26%

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Single use plastics

Single use plastics have been a particular area of concern. In landfill sites, for example, polyethylene terephthalate (PET) used in bottles can take 400 years to decompose at landfill. In a 2016 report, consultants at McKinsey estimated the market for single use plastics at between $80bn and $120bn/year. Media pressure has forced a rethink, driving greater investment in R&D to discover new environmentally benign plastics or recycling solutions.

First off, Miodownik argues there is a need to harmonise recycling facilities across the UK and restrict packaging to three polymers: PET, polypropylene (PP) or polyester. Plastics that are unrecyclable should just be legislated or taxed out of existence for packaging. 'Expanded polystyrene should just be illegal, except if used in buildings,' says Miodownik.

Plastic packaging represents 26% of the total volume of plastics used. Laminated films used to cover food are, unfortunately, not recyclable. Often made from two different plastics, they can also contain metals such as aluminium which help to keep food fresher and sterile. An example is the iconic crisp bag. 'They are polypropylene and polyethylene with a film of aluminium. You get crispy crisps and it is an amazing achievement,' says Miodownik. Without new materials, however, such laminated films are never going to be recyclable, he adds.

'These plastics don't interact with foodstuffs and they have the right chemical properties,' says David Rooney, a chemical engineer at Queen's University Belfast, UK. 'Coming up with new polymers to penetrate that market is a very big ask.' This remains one of the trickiest waste problems, since plastic packaging has upsides in human health and reduced food waste. Over 300m people in China suffer foodborne illnesses every year. The emphasis in China in packaging is on quality, says Bjacek. 'Plastic has value.'

In the UK, plenty of plastics are recyclable right now, but are incinerated or buried. Reasons include inconsistent or complicated local disposal instructions and unclear coding on packaging, says Carl Redshaw, polymer chemist at the University of Hull, UK. 'If people have to think about disposal too much, then it becomes a barrier,' he adds. Also, 'if economics is the driver, the near 50% drop in the value of recycled materials is clearly detrimental'.

One hurdle for PET bottle mechanical recycling is coloured dyes, which camouflage plastics for automated sorters but also generates greyish pellets that are far less valuable than new PET. 'Brands are opposed to having the same colour packaging, but it has happened in some countries,' says Miodownik. In Japan, where all plastic drink bottles must be made of transparent PET, recycling rates have gone up – one example of how government policy can incentivise recycling.

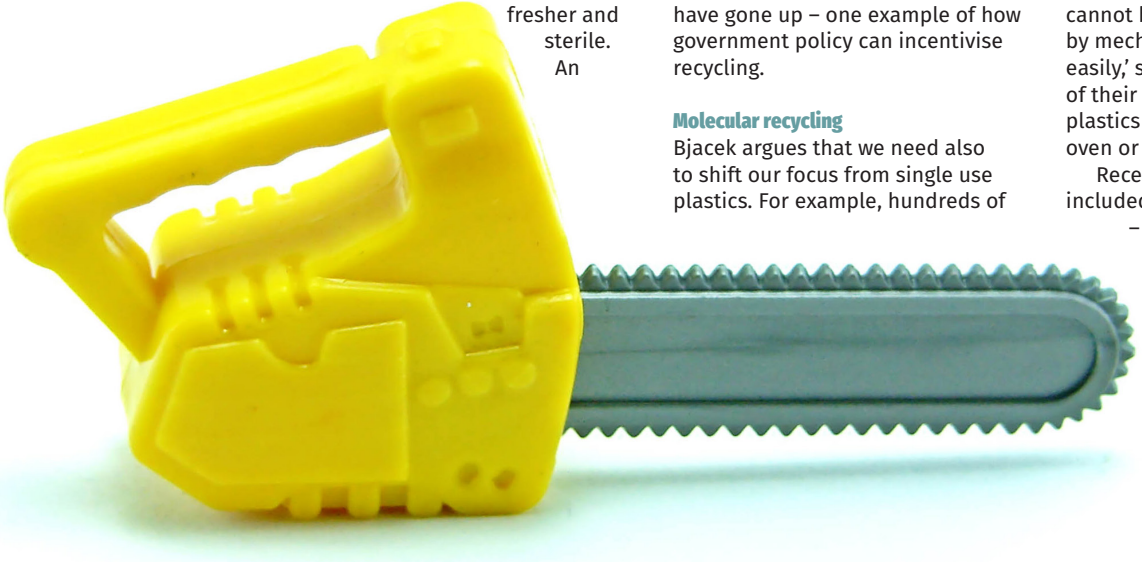
Molecular recycling

Bjacek argues that we need also to shift our focus from single use plastics. For example, hundreds of tonnes of wind turbine blades made from plastics, graphite and carbon fibre will have to be recycled soon. While 16% of cars is now organic matter such as polymers or rubber, this is predicted to hit 26% by 2040. That's a significant ramp up in volume considering how much lighter they are than metals. While sorting out billions of lightweight crisp bags is impractical, structural plastics will come in large volumes and should be recoverable. 'What happens now with auto shredder residue is that it goes to landfill. Society is not going to accept that in future,' says Bjacek; this is where smart chemistry is needed.

'One current trend in the plastic community is to not consider plastic as waste but to consider it as new reagents,' says Haritz Sardon, a polymer chemist at the University of the Basque Country, Spain. Plastic waste could be chemically broken down into monomers and re-polymerised as a substitute for virgin polymer material made from petroleum. Other approaches include attacking polyester bonds to get carboxylic acid, which when reacted with methanol yields useful precursors such as methyl ester. Meanwhile there is a lot of research going into technologies to sort polymers by type, which would facilitate chemical recycling. 'We need to design new chemistries,' says Sardon. 'Until now, we have designed plastics for their properties, but without considering end of life. This is now changing.'

Thermoset plastics account for 15 to 20% of global plastic production. They are essential for high-performance applications, but are especially challenging to recycle because they cannot be reprocessed easily. 'Thermosets are crosslinked by covalent bonds and cannot be melted or reprocessed by mechanical means or dissolved easily,' says Sardon. This is part of their attraction and why some plastics can readily be used in an oven or in car and airplane parts.

Recently, however, a US group included a special – diketoenamine – bond in a thermoset, which allows the polymer to break down when treated with a strong acid (*Nature Chemistry*, doi: 10.1038/s41557-



019-0249-2). The process takes less than 12 hours and generates excellent monomer yields. 'They are really strong thermosets, but at the same time the material is easily recyclable,' notes Sardon, who co-authored a commentary on the paper in *Nature*.

Responsibility call

Sardon argues for incentives for companies to increase the amount of recycled plastics in products. 'There has to be some regulation to push companies to change,' he says. Miodownik believes producers need a shove too. 'The polymer industry is so optimised for taking crude oil and refining it, that there needs to be a market push to get other technologies up and running,' he says. One example is the producer responsibility tax being mooted in the UK: if a consumer item cannot be recycled, then a waste tax must be paid. Until now, the costs for managing waste have generally been carried by governments and consumers, not companies.

Others call for greater responsibility from plastic and consumer companies. Firms already take product stewardship of hazardous chemicals and of potential precursors that could be used for illegal drug manufacture. 'Why give away a plastic toy for free with a meal, when you have no idea whether it will ever be recycled. Especially if it has electronics inside it, that is a failure of design,' Miodownik argues.

Waste refineries

Australian company Licella claims to have the only process that can handle end-of-life mixed plastics at very high yield and low cost. 'We are putting plants up around the world to deal with that problem,' says technology inventor Thomas Maschmeyer at the University of Sydney. Licella's process uses water at or near supercritical temperatures to crack carbon bonds in waste plastic and generate shorter chain hydrocarbon products at a pilot facility in New South Wales, Australia. A 20,000t/year recycling facility based on the technology is being built at the old ICI site in Wilton, UK, and is scheduled to start up in late 2019.

Waste plastics will be broken down into component molecules and used to build chemicals and recycled oils. 'If it is a high polyethylene stream, we can make a fair few high value waxes,' Meschmeyer explains. 'If it is a more polystyrene situation, then we are making more aromatics.' Aided by various catalysts, even a mix of plastics can generate hydrocarbon streams that will fit into a petrochemical refinery.

While lots of start-ups are eyeing the new markets for chemically recycling plastics and developing new processes, Bjacek says large petrochemical and chemical companies must consider integrating plastic waste into their facilities.

It is estimated that 40% of plastics might be recycled or reprocessed by 2040, which could eat up demand for hydrocarbons. 'Existing producers, especially oil companies, could lose control of the molecule unless they get involved in recycling hydrocarbons,' says Bjacek. For now, he says, refineries are understandably reluctant to tailor their processes to incorporate plastic waste, but market and regulatory pushes would lead to a rethink.

Biodegradables

Biodegradable plastics and bioplastics are another area of growing interest, but as yet there often isn't a system for collecting them. 'Flooding the market with biodegradables, all it does at the moment is contaminate other recycling systems,' says Miodownik. He points to packaging made from all sorts of plant starches, although ingredients are usually unspecified. 'Unless you are composting in well-defined conditions, you have no idea if these materials will break down. They could end up in the sea for hundreds of years.' In the oceans, temperatures might be too cold and required microbes absent to degrade these polymers. Some commentators predict that the bioplastic market will grow at 30%/year to 2030, compared with 3% for fossil-based plastics.

Redshaw views biodegradable polylactide (PLAs) polymers positively, partly because they can be upgraded to new high-value resources. A report in *Chemical Communications* (doi: 10.1039/c9cc02861g) showed how waste plastic drinking cups can be used to make a new lactide-containing metal organic framework, MOFs. These are polymers consisting of metal modes and organic linkers, which show promise for applications such as sensing and separations. 'Such strategies are becoming increasingly important in the light of the recent move by China to stop taking our plastics [waste] because it wasn't clean enough,' comments Redshaw. Others fear the introduction of yet more plastics onto the market. 'If there was just one type of plastic, recycling would be easy enough,' says Rooney. But with ten different types in circulation it becomes a lot trickier.

In 2019, eight new projects funded by the UK's Plastics Research Innovation Fund were launched, including a University of Hull project to develop biodegradable biopolymers that can be repurposed following disposal. This fund has been a catalyst for Renshaw's group to engage with other disciplines and talk to supermarkets, local councils and various industries.

A prime challenge, for example, is moving from grams of biodegradable polymer to kilograms, so that the bulk properties can be tested and applications identified. 'Locally there are few if any companies with the necessary facilities for scale-up,' Redshaw explains. His method relies on a chemistry trick called ring opening polymerisation of cyclic esters, which builds biodegradable polymers using a cheap and efficient catalyst.

Ultimately, it may be that nature's enzymes provide the blueprint to solve our plastic problems, Redshaw believes. 'Maybe in the years ahead, we will learn from bacteria and worms that possess the ability to break down and degrade plastics, even stuff like polyethylene carrier bags, and design large artificial worms that can eat their way through our plastic waste.'

Meanwhile, consumer frustration over the problems continues to grow. In a recent survey, Accenture reports that over 80% of 6000 consumers said it was important for companies to design products that can be reused or recycled. Almost three-quarters said they were buying more environmentally friendly products than five years ago.

40%

Estimated amount of plastics that might be recycled or reprocessed by 2040. Today, >350m t of plastics are made every year, but only 15% is recycled. Around 9 m t/year of plastic goes into the sea.

20,000t

Annual capacity of a recycling facility based on novel mixed plastics technology being built at the old ICI site in Wilton, UK, and scheduled to start up in late 2019. The technology, developed by Australian company Licella, is claimed to be the only process that can recycle end-of-life mixed plastics at very high yield and low cost.

$80–120bn

Estimated value of the annual market for single use plastics, according to a 2016 report by consultancy firm McKinsey