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Green chemistry and the plastic pollution challenge Towards a circular economy

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Green chemistry and the plastic pollution challenge: towards a circular economy

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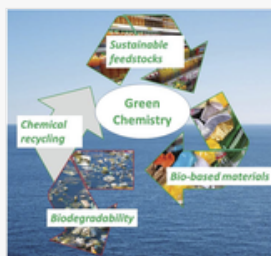
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The solution to plastic pollution is not less chemistry but more, greener chemistry in a circular bio-based economy.

Abstract

The linear economy for plastic packaging, which currently leads to excessive carbon dioxide emissions and leakage into the environment, needs to be reformed to a greener circular model which is resource efficient and environmentally benign. This requires a system-wide redesigning of rules and incentives that apply to the plastics value chain, from product design to recycling and end-of-life options. This article identifies areas where green chemistry can contribute. Substituting plastics derived from fossil resources, with bio-based alternatives from renewable resources can reduce emissions of greenhouse gases, produce plastics that are easier to recycle to the virgin polymer and, at the end of their useful life, biodegrade in the environment. The underpinning chemo- and biocatalytic technologies for the production and recycling of plastics are reviewed and priorities suggested for future development.

Introduction: the scale and complexity of the problem

It is difficult to imagine a world without the ubiquitous plastics. They are inexpensive, lightweight, durable materials which can be molded into various products for use in, for example, food packaging, biomedical devices and electronics. We use them because they have unique properties and future technologies will continue to depend on them.

However, plastics are a double-edged sword: a boon to modern society but at the same time a major source of environmental pollution. Indeed, one of the grand challenges of the 21st century is to solve the environmental problem caused by plastic litter-including single-use plastics (SUPs) used as packaging materials. Pollution of the environment, in particular of the earth's oceans, by plastic litter is a problem of global proportions. The enormity of the problem was brought home by, *inter alia*, the 2017 documentary series Blue Planet II of David Attenborough and by pictures of

turtles tangled in plastic debris, stomachs of whales and sea birds full of plastic and the great pacific garbage patch, a gyre of plastic waste in the northern Pacific Ocean.

The plastic pollution problem is a result of a systems failure in the roles and incentives between the various stakeholders in the plastics value chain – comprising the chemical industry, product designers, marketing departments, consumers (and their behaviour) – all the way to the recycling and disposal industries. This system was analysed, and policy recommendations made for its improvement, in a recent report¹ – Packaging plastics in a circular economy – from Europe's scientific academies (EASAC)[†].

In this Perspective we consider the potential of green chemistry to address the many challenges that emerge from the analysis described in the EASAC report and from the associated politicisation in debates on how to regulate the plastics life cycle.² The goal is to identify key areas for technical innovation and make proposals for change on the road to a sustainable circular plastics economy for optimised resource efficiency and minimal environmental pollution.

The plastics market

It is estimated^{3,4} that 8300 mio tonnes of plastics were cumulatively produced globally, from 1950 to 2015, of which 6300 mio tonnes ended up as waste. Roughly 800 mio tonnes (12%) of this waste was incinerated and 600 mio tonnes (9%) recycled, only 10% of which was recycled more than once. Roughly 60% (4900 mio tonnes) of all the plastics ever produced was discarded, ending up as landfill or as litter in the natural environment. If current practices regarding plastic use and waste management are perpetuated this will lead, inevitably, to the accumulation of 12 000 mio tonnes of plastics in the environment by 2050. Obviously, this cannot be allowed to happen. A sustainable solution must be found.

Plastics are divided into thermoplastics (pliable on heating and hard on cooling), thermosets and fibres. Global production of plastics, mainly from the fossil resource derived hydrocarbons, ethylene, propylene and aromatics, was 382 mio tonnes in 2015. It consisted of plastics derived from the basic polymer resins of polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET) and polyvinyl chloride (PVC) in addition to polyamide, polyester and acrylic (PP&A) fibres and polyurethanes (PUR). The plastics industry is an important part of the European economy, with a turnover of €360 billion in 2018.

The main uses for PE, PP, PS and PET are in packaging plastics that offer many possibilities to manufacturers when designing shape, colour or labels to convey marketing messages to the consumer. The basic polymer resins can be adjusted with fillers, and additives to provide many desirable properties such as high strength to weight ratios, durability, barrier capabilities, antimicrobial and UV-resistance-all at a cost/performance ratio that is difficult to achieve with alternative materials.

The unintended consequences of single use plastics (SUPS)

Packaging is the dominant application of PE, PP, PS and PET resins and most applications are discarded after use. Such 'single use plastics (SUPs)' represent 36% of all plastics used and are a major source of leakage into the environment, where their long life (a desirable characteristic during storage and use), leads to the majority remaining in some form in terrestrial, freshwater or marine environments. Effects tend to be categorised in terms of macro-plastics (*e.g.* plastic bags and bottles), micro-plastics (small fragments below 5 mm size) and nano-plastics (below 0.1 mm). The latter are now detectable in almost all aquatic media,⁵ including drinking water,^{6–8} beer and sea salt,⁹ in snow,¹⁰ and in the atmosphere of cities¹¹ where they can be inhaled.¹² It is also worth noting in this context that an important source of micro-plastics in the aquatic environment is formed by the plastic microbeads that are contained in many personal care products. These micro-plastics are subsequently further transformed into nano-plastics¹³ Cosmetic products containing plastic microbeads were banned from the EU as from January 1st 2018.

The socio-economic factor

Littering of our natural environment by SUPs is primarily a socio-economic problem and is mainly governed by social behaviour of consumers and the economics of the plastic value chain. It is a so-called social trap: it is not the intention of people or organisations to litter the environment with plastics but it is nevertheless happening on an enormous scale.

The role of consumer behaviour

Consumer behaviour is not only important at the end-of-life of plastic goods. Leakage of SUPs into the environment arises both from purchasing decisions, *e.g.* whether or not to purchase a plastic product, and from post-consumer behaviour, *e.g.* to reuse a plastic bottle or throw it away. Customers who buy plastic goods have a potentially important role in avoiding plastic pollution.

The overwhelming evidence that consumers are influenced more by prices than by behavioural measures is particularly relevant in this context.¹⁴ For example, considerable success has been achieved in altering customer behaviour by the simple measure of charging for plastic bags.¹ A second market-based instrument, which has achieved high collection rates for PET bottles in several EU member states, is the use of deposit return schemes (DRS), where reverse vending machines provide an economic motive for return. The EASAC report¹ recommended that DRS should be extended to a wider range of containers, *e.g.* high density PE containers and coffee cups. Indeed, it was suggested that such containers should be viewed as being on loan and retailers should have a duty to provide on-site collection points.

Alternatives, substitution and prohibition

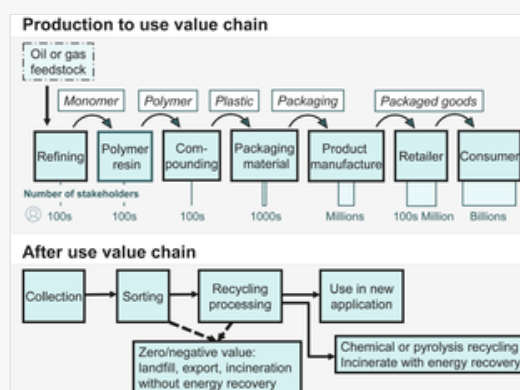
A 2011 study¹⁵ of the impact of plastic packaging on life-cycle energy consumption and greenhouse gas (GHG) emissions in Europe concluded that if plastic packaging would be substituted by other materials, the mass of the packaging material would increase on average by a factor of 3.6. The life cycle energy demand would increase by a factor of 2.2, corresponding to 1240 million GJ per year or 27 million tonnes of crude oil or 20 million heated homes. GHG emissions would increase by a factor of 2.7, equivalent to 61 million tonnes of CO₂ equivalents per year or to 21 million cars on the road. Interestingly, of the seven plastic packaging sectors studied, beverage bottles showed the most positive difference. In short, the use of alternatives for plastics in packaging is not the answer to the pollution challenge.

Nonetheless, for some applications of SUPs, environmentally friendlier alternatives are available in the market and the European Commission has a Directive to restrict and in some cases apply an outright ban on such SUPs (including cotton bud sticks, plastic cutlery and plates, plastic straws and stirrers and beverage containers made of expanded polystyrene).¹⁶

Extended producer responsibility (EPR)

The packaging plastics value chain is depicted in Fig. 1. The starting point has historically been the petrochemical refinery where crude oil is refined to produce the olefins, aromatic hydrocarbons and derivatives thereof that are the raw materials for producing the polymer resins. The raw resin is then 'compounded' by addition of additives to the molten polymer base to produce a material with the desired properties for a particular application. The material is then cooled and extruded to give pellets of the raw plastic which are converted to the required packaging format. The packaged good then enters the retail system where the consumer decides to purchase it. After the consumer has finished with the packaging (often after only one use), it is discarded. Some of the discarded packaging is recycled, but the majority has historically gone for incineration or landfill or has leaked into the environment.

Fig. 1



The packaging plastics value chain (reproduced with permission from the EASAC report¹).

The quantities of plastics leaking into the environment and ultimately entering the oceans were estimated by Jambeck and co-workers¹⁷ to be between 5 and 13 million tonnes (1.5 to 4% of global plastics production) each year; the majority of which has originated in Asia and Africa. We note, however, that some of this may have resulted from imported plastic waste (see below). According to the Plastics Europe 2019 report,¹⁸ 62 mio tonnes of plastic (17% of global production) were produced in Europe in 2018. Approximately 40% of this was for plastic packaging. In the same period, 29.1 million tonnes of post-consumer plastic waste were collected. 17.8 million tonnes of this total were plastic packaging waste, 18.5% of which went to landfill, 39.5% to incineration (with or without energy recovery) and 42% was destined for recycling (which includes export to non-EU countries). Overall, the amount of plastic re-entering the value chain as raw material is just 6% of European plastics demand.¹⁹

Profitability in the plastics recycling sector is also low, impeding investment in new recycling capacity; the lack of capacity has led in the last decade to increased reliance on export as a means of 'recycling' waste. While in theory, export to lower-income countries may render some recycling methods economic, many high-income countries (whether in the EU, USA, Japan or elsewhere) have depended on export to other countries with insufficient attention to the fate of the waste in the receiving country. China used to be the main destination for such exports, but stopped accepting import of mixed plastics waste in 2017. As a result, export shifted to other countries such as Malaysia, Vietnam and Thailand despite the limited recycling facilities in such countries. Mishandling and abandonment of such wastes has successively led to further restrictions on imports and it is self-evident that this does not represent a global solution to the plastic waste challenge.

As a whole, the plastics value chain is an example of the linear 'take-make-use-dispose' economy.²⁰ The environmental costs of natural resource extraction, pollution and end of life disposal of products remain largely external costs borne by society and the environment. The prices of virgin plastics thus don't incorporate the full costs of disposal or contribute sufficiently to an efficient recycling system.

EASAC's analysis also pointed to conflicts between different parts of the value chain because the motives of the various stakeholders are not aligned. Feedstock producers are motivated to expand production capacities, in the flawed paradigm of perpetual growth, while the objective of circularity is to reduce material flows. Moreover, there doesn't appear to be sufficient motivation for designers of packaging plastics to design for recycling. One striking example is that often three different plastics may be used for a plastic bottle, one (PET) for the bottle, another one (PE) for the cap and yet another (PP) for the label. This makes recycling more difficult in comparison with a PET bottle containing a PET cap and a PET label, so why do it? Because it is slightly less expensive. Even more disruptive to recycling is the deliberate use of fillers to make the bottle opaque and white-for instance as milk containers.

The solution to such problems associated with the classical linear economy is clear: Extended Producer Responsibility (EPR). The costs of plastic waste collection and recycling must be incorporated in a charge added to the price of the virgin resin to provide financial incentives to increase recycling.

Product designers can be incentivised to pay more attention to the need for facile recycling when EPR differentiates between readily recyclable and difficult to recycle plastics (so-called eco-modulation). The EASAC report found huge differences between the charges and their basis in EU member states. Some charges were so low they could effectively be ignored but on the other hand some were high-of the order of €250 per tonne of packaging plastic used and offered rewards for easily recycled materials and substantial penalties for materials not able to be recycled.

These financial incentives provide a framework within which technical changes can be encouraged by the development of greener chemistry and engineering to enable the design, manufacture and recycling of plastics. Opportunities also exist to apply green chemistry to reduce the environmental impact of any plastics that leak into the environment – for example through enhanced biodegradability.

Designing for circularity

The goal of circularity is to optimise resource utilisation and, by doing so, minimise the generation of waste. It involves prioritisation according to the '6Rs':

1. Reduce (raw material use)

2. Redesign (to enable reuse or recycling)
3. Remove (*e.g.* avoiding SUPS when practical)
4. Reuse (*e.g.* through returnable uses or refurbishment)
5. Recycle (preferably closed loop where the recycled product can be used in the same application)
6. Recover by extracting chemicals or fuels or by recovering energy by incineration.

A key enabler of circularity is to (re)design products for longevity and circularity from the beginning. The transition from a linear to a circular economy for plastics will be facilitated by excluding, in the design phase, properties which hinder recycling and including those which facilitate recycling. For example, composites and multi-layer products involving multiple plastics and the use of coloured and opaque plastics, and additives, should be avoided as much as possible as they present problems for sorting and recycling of plastics. New polymer resins should have superior properties, *e.g.* easier to process to plastic end-products and to recycle to virgin polymer.

In short, *the goals of all stakeholders, from production to the end-of-life, disposal phase, must be aligned towards a common goal of resource efficient and waste-free circularity with no externalised costs borne by society.*

Plastics and green chemistry: towards a circular economy

It is abundantly clear that the socially and economically redundant linear take-make-use-dispose economy is drastically in need of replacement by a circular economy. The latter is a framework for an industrial economy, such as in chemical products²¹⁻²³ in general and plastics in particular,^{24,25} that is restorative and regenerative by intention and design, the main aim of which is to reduce material flows.²⁶ It can be defined as:

*A circular economy is based on the principles of designing out waste and pollution, keeping products and materials in use, and regenerating natural systems.*²⁷

A succinct definition of Green Chemistry is:

*Green chemistry efficiently utilises (preferably renewable) raw materials, eliminates waste and avoids the use of toxic and/or hazardous reagents and solvents in the manufacture and application of chemical products.*²⁸

It is also described by the 12 principles of green chemistry, first published by Anastas and Warner²⁹ in 1998:

- (1) Waste prevention instead of remediation
- (2) Atom efficiency
- (3) Less hazardous materials
- (4) Safer products by design
- (5) Innocuous solvents and auxiliaries
- (6) Energy efficient by design
- (7) Preferably renewable raw materials
- (8) Shorter synthesis (avoid derivatization)
- (9) Catalytic rather than stoichiometric reagents
- (10) Design products for degradation
- (11) Analytical methodologies for pollution prevention
- (12) Inherently safer processes

The overall guiding element is “benign by design” which aligns admirably with the aims of the circular economy. The earlier mentioned EASAC report¹ made a number of recommendations that are designed to stimulate the transition from the current linear take-make-use-dispose plastic economy to a sustainable circular economy: for example, to

- support an effective ban on exports of plastic waste to countries outside the EU.
- adopt a target of zero plastic waste to landfill at an early date.
- apply differentiated EPR fees to all packaging, combined with eco-modulation which rewards easily recyclable plastics and penalises difficult-to-recycle materials.
- consider extending DRS to a wider range of plastic containers.

Priorities in recycling: the hierarchy of recycling

If export and landfill options are no longer available it is critical to develop more integrated recycling systems that can handle all plastic waste while, at the same time, achieve net savings in emissions and use of resources. According to the EASAC report, advanced recycling/reprocessing of plastics should follow the hierarchy:³⁰

1. **Closed-loop recycling** for use in the same product, *e.g.* PET bottles to PET bottles or the PET monomers.
2. **Downcycling** is open-loop recycling for use in another product, generally a lower value product.
3. **Molecule recycling** could comprise conversion to valuable commodity chemicals through chemical treatment or pyrolysis.
4. **Energy recovery through** incineration.

The technical and economic viability of recycling can be improved by limiting the number of polymer resins and the range of additives used, both of which are hindrances to recycling. For example, the polymers used in large volume applications could be limited to PET (generally devoid of additives) and PE (generally includes only antioxidants). Multilayer packaging materials comprising different polymers could also be replaced with multilayer packaging with the same resin. In this context, it is worth noting that, according to Groh and co-workers,³¹ of the 906 chemicals likely associated with plastic packaging, 63 rank highest for human health hazards, 68 for environmental hazards and 7 are classified in the EU as persistent, bio-accumulative, and toxic.

A fundamental barrier to widespread recycling is the difficulty in competing with virgin raw materials which are low-priced, particularly with the historically low prices of crude oil which also do not include the external social and environmental costs. On the contrary, fossil fuel users continue to receive government subsidies, both outside and inside the EU. Consequently, measures are under discussion in the EU concerning the introduction of a plastics tax or a requirement for a minimum recycled content.

Recycling technologies

Recycling plastics makes good sense, both environmentally and economically, by reducing pollution and optimizing the use of resources. Thus, a large number of life-cycle assessments of plastics have been carried out and the general conclusion is that recycling has a significantly smaller GHG footprint than incineration or landfill.³² According to one report¹³ recycling of plastics (in 2011) led to a reduction of 24% in life-cycle energy demand and 27% in GHG emissions.

In order to be technically and commercially viable the entire recycling process needs to be optimised and this process begins with collection and sorting of the waste plastic. The switch towards recycling of plastic waste, as opposed to export, incineration or landfill, is stimulating the development of ‘smart’ sorting of plastic waste for recycling.^{33,34} For example, PRISM (Plastic Packaging Recycling using Intelligent Separation Technologies for Materials), a consortium of UK companies, developed fluorescent markers to be used to recover food grade PP and HDPE.³⁵ Similarly, Germany-based INEOS Styrosolutions, together with equipment firm Tomra, used near infrared sensor technology, to separate polystyrene in 99.9% purity from post-consumer plastic waste.³⁶

Plastic packaging generally involves thermoplastic polymers which, in principle, can be recycled to the virgin polymer resin through simple thermo-mechanical means under relatively mild conditions which is the method of choice.^{37,38} Unfortunately, it often leads to lower grade resin and can't be used for many recycles. The second choice is then closed-loop recycling back to the feedstocks (monomers) which can be used to produce new virgin resin.^{39,40}

Recycling polyolefins

The discovery of efficient catalytic systems for the polymerisation of ethylene and the stereo-regular polymerisation of propylene, by Ziegler in 1953 and Natta in 1954,⁴¹ respectively, marked the advent of the polyolefin thermoplastics industry. Unfortunately, they could not foresee the global environmental pollution problem that these wonderful materials would cause several decades later and, hence, they saw no reason to invent an efficient process for their depolymerisation to regenerate the constituent olefins. PE and PP waste can be mechanically recycled to the original resin but this soon leads to molecular breakdown and off-spec material. A common limitation on the ability to mechanically recycle polyolefins is the thermal degradation and reduction in molecular weight affecting the resin's mechanical properties.

The preferred option to mechanical recycling is closed-loop recycling, *via* depolymerisation back to ethylene, but this is a difficult proposition. PE and PP are essentially long-chain alkanes with unreactive C–C and C–H bonds and a method for their selective depolymerisation is hard to find.

The olefin monomers for PE and PP are produced in oil refineries by catalytic cracking of the naphtha fraction (C₄–C₁₁) of crude oil. An interesting alternative is, therefore, closed-loop recycling by pyrolysis to a naphtha equivalent mixture of hydrocarbons which can be cracked back to the olefin monomers. Several companies have developed pyrolysis processes for PE and PP. Plastic Energy, for example, is working together with SABIC to use what they call Tacoil, produced by heating the polyolefin waste at low pressure, as the feedstock for a catalytic cracker.⁴² A 20 000 tonne demonstration unit is planned at the SABIC site in Geleen, the Netherlands for 2021 with plans for 10 plants in operation by 2023. Similarly, Recycling Technologies,⁴³ and Mura Technology⁴⁴ have developed pyrolysis technologies for closed-loop recycling of polyolefins to a naphtha equivalent fraction for cracking back to the olefin feedstocks for PE and PP.

Polystyrene, on the other hand, is more reactive than PE and PP and can be directly depolymerised back to styrene. For example, a process for polystyrene-to-styrene, in a fixed-bed catalytic reactor, was already described in 2012.⁴⁵ More recently, the US company, Agilyx, has reportedly commercialised a polystyrene-to-styrene process.⁴⁶

An alternative approach is recycling to functionalised molecules which may themselves be industrial monomers. For example, microwave-assisted oxidation of PE with a mixture of dioxygen and nitrogen dioxide at 170 °C affords a mixture of short-chain dicarboxylic acids comprising predominantly succinic, glutaric and adipic acids.⁴⁷ However, it requires the marketing of a mixture of products, with different applications to the original polymer, and recycling to virgin polymer remains the preferred option.

In short, although there is not yet a viable technology for the depolymerisation of PE and PP there are other economically and environmentally sound methods for recycling.⁴⁸ Moreover, there are various bio-based alternatives for polyolefin packaging plastics such as PHAs (see later). Chem. Eng. News recently published a Discovery Report focusing on new polyolefin recycling technologies, including many of the examples discussed above, which are being developed by 32 different companies.⁴⁹

Recycling polyesters and polyamides

The facile recycling of aliphatic polyesters, such as polybutylene succinate (PBS), polylactide (PLA) and poly- β -hydroxybutyrate (PHB), to the corresponding alcohol and carboxylic acid raw materials *via* hydrolytic cleavage of the ester functionality can be performed under acid or alkaline conditions.⁵⁰

An interesting, green alternative is recycling of polyesters *via* enzymatic cleavage.⁵¹ For example, the lipase catalysed synthesis and depolymerisation of polyesters has been known for at least two decades, as reviewed by Matsumura in

2002.⁵² In particular, thermostable enzymes, *e.g.* *Candida antarctica* lipase B (CalB), are interesting because they can be used above the melting point of some polyesters, such as PBS, even under reactive extrusion conditions.⁵³ The French company, Carbios, is developing enzymatic processes for the depolymerisation of polyesters and polyamides.⁵⁴

The most abundant polyester plastic, the iconic PET, is usually recycled mechanically but this generally leads to lower grade material. A variety of chemical methods for PET depolymerisation have been described but they generally involve harsh conditions and/or afford a lower grade product.⁵⁵ In contrast with aliphatic polyesters, the aromatic PET is not susceptible towards enzyme catalysed hydrolysis using commercially available ester hydrolases although lipases, esterases and cutinases catalysed functionalisation of the PET surface.⁵⁶

The isolation in 2016 of an enzyme, appropriately named petase, secreted by a bacterium present in soil from an industrial waste PET recycling facility, which catalysed the hydrolysis of PET,⁵⁷ precipitated a flourish of activity in developing aromatic polyesterases for enzymatic depolymerisation of PET.⁵⁸ Petase contained structural features common to both lipases and cutinases⁵⁹ The latter are plant cell-wall degrading enzymes and have been shown to catalyse PET depolymerisation *via* hydrolysis^{60,61} or glycolysis with ethylene glycol⁶² In one example, a cutinase catalysed the hydrolysis of PET in polymer blends with PE or polyamide.⁶³

Kanaya and co-workers⁶⁴ used a metagenomic approach to identify a cutinase, from leaf-branch compost (LCC) in a Japanese public park, which catalysed the hydrolysis of PET at 70 °C. The temperature is important because of the rather high glass transition temperature of around 75 °C of PET. More recently, the LCC enzyme, which was already at least 33 times as effective as other cutinases tested, was further optimised by protein engineering using directed evolution with site-specific saturation mutagenesis to afford a variant which catalysed the depolymerisation of PET waste at 72 °C to 90% conversion in less than 10 h, with a mean Space Time Yield of 16.7 g l⁻¹ h⁻¹ at a PET concentration of 20% using 0.3 wt% enzyme.⁶⁵ These metrics are commensurate with commercial viability.⁶⁶ The cost was estimated to be *ca.* 4% of the cost of virgin PET and the produced terephthalic acid was converted to virgin PET and subsequently blown to PET bottles. It would appear that this development forms the basis for a commercial process for recycling PET waste in a circular economy.

Alternatively, an anaerobic thermophilic bacterium, *Clostridium thermocellum* was genetically engineered to enable high-level secretory expression of LCC.⁶⁷ The whole cell biocatalyst was able to depolymerise PET at 60 °C. Interestingly, *C. thermocellum* also catalyses the efficient hydrolysis of cellulose and, hence, could be used in the recycling of mixed textile waste containing both polymers.

Another possibility is to use organocatalysis instead of enzyme catalysis. For example, the simple and inexpensive tetramethyl ammonium methyl carbonate catalysed the transesterification of various polyesters – PLA, PET, PCL (polycaprolactone), and poly carbonates (PC) – with methanol or ethanol.⁶⁸ The reactions are conducted in organic solvents, including 2-methyltetrahydrofuran and dimethyl carbonate, at 50 °C and afford monomeric esters that can be recycled back to the virgin polymer.

The B factor

In the preceding section we have seen that biocatalytic methods are playing an increasingly important role in the recycling of plastics. In this section we are more concerned with the origin of the plastic. The negative environmental impacts of plastics have led to serious efforts to find materials which have more environmentally benign properties in their production or if they leak into the environment. The term ‘bio-plastics’ is often used to describe such materials but the term is ambiguous. The more preferred term, bio-based plastics refers to plastics that are produced from renewable resources as part of the general transition from a fossil resource-based chemical industry to a more sustainable bio-based economy in which renewable biomass is the feedstock.

We can call this the B factor, *i.e.* the percentage of the carbon in the plastic originating from renewable rather than fossil resources. This percentage is readily determined by measuring the carbon 14 content of a sample using the ASTM-D6866 standard test method.⁶⁹ Any raw material formed directly from plant biomass, *e.g.* methane derived

from rotting vegetation, consists of renewable carbon. By the same token plastics formed by direct conversion of carbon dioxide consist of renewable carbon[‡].

In principle, the calculation of B should also include the energy used in the production process. Indeed, in a bio-refinery a certain fraction of the biomass feedstock will often be used for energy generation. However, in practice the term bio-based generally refers to the raw materials but not the energy used.

The primary objective of developing bio-based chemicals in general, and bio-based plastics in particular, is to contribute to the transition to a low carbon economy with minimal net CO₂ emissions. This is crucial in connection with climate change mitigation and preservation of the earth's natural resources. Bio-degradable plastics, on the other hand, are plastics that break down under biological conditions, generally involving bacteria, encountered in the natural environment (see the next section). It is important to note that not all bio-based plastics are biodegradable and not all biodegradable plastics are bio-based.

Bio-based plastics

The bio-based economy is concerned with the use of renewable biomass to replace the unsustainable use of fossil resources – oil, coal and natural gas – as raw materials for the manufacture of fuels, commodity chemicals and materials, such as plastics. This must also mesh well with the conditions for sustainable development: (i) natural resources should be used at rates that do not unacceptably deplete supplies over the long term and (ii) residues should be generated at rates no higher than can be readily assimilated by the natural environment.^{70,71}

In addition^{72,73} bio-based development could also enable the substitution of existing petrochemical-based products by inherently safer bio-based alternatives with reduced environmental footprints, such as recyclable and biodegradable packaging plastics. Indeed, sustainable polymers from renewable resources can be viewed as the macromolecular materials of the 21st century.^{74,75}

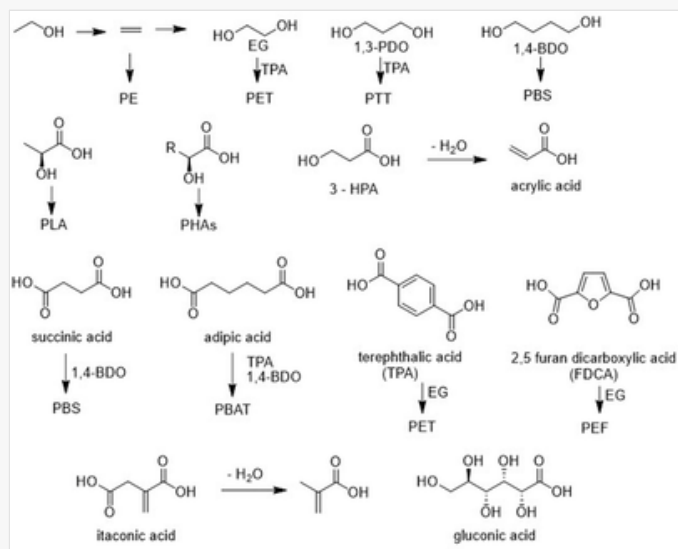
The primary motivation for making bio-based plastics is to reduce GHG emissions but the use of renewable resources should not compete with food production, as is the case with first generation (1G) biomass, or result in deforestation and loss of biodiversity.⁷² The key is to use unavoidable waste as the feedstock. For example, second generation (2G) biomass, comprising lignocellulosic waste in agricultural and forestry residues^{76,77} and food supply chain waste,⁷⁸ can serve as a raw material for production of plastics. This could mean, however, that in the short term bio-based plastics are produced from, for example, corn starch while such second generation feedstock based methods are not fully commercialised.

Bio-based plastics are of two types: (i) drop-in, that is existing plastics but produced from renewable raw materials, *e.g.* PE from bioethanol *via* bioethylene, and (ii) entirely new plastics produced from renewables, *e.g.* polyhydroxyalkanoates (see later). The advantage of drop-ins is that they can easily substitute for the fossil-resource based monomer without the need to change equipment and production processes and the product is already known in the marketplace. In contrast, when the bio-based feedstock produces a different resin such as PLA, to replace PET, for example, different additives and processing technology may be required and a different product obtained in terms of mechanical and barrier properties to small molecules such as water and oxygen.⁷⁹ Such problems can sometimes be solved by using polymer blends.⁷⁹

Bio-based plastics are produced in three different ways:⁸⁰ (i) polymerisation of bio-based monomers, *e.g.* PLA from lactic acid produced from glucose by fermentation (ii) polymers produced directly by fermentation, and (iii) modification of natural polymers such as starch and cellulose.

Examples of bio-based monomers, produced by fermentation or chemocatalytic conversion of glucose, and the polymer resins derived from them and their equivalent fossil resource derived plastics are depicted in Fig. 2. They can be produced in 2nd generation biorefineries from waste lignocellulose or, broadening our horizon, from 3rd generation (3G) polysaccharide feedstocks, namely algae, which have the advantage that arable land and fresh water are not necessary for their cultivation. Polysaccharides from seaweed (macroalgae), such as alginate and carrageenan, for example, can be used as feedstocks for bio-based plastics.⁸¹

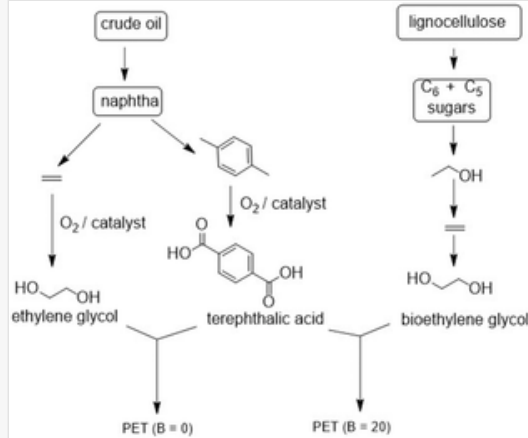
Fig. 2



Bio-based monomers for thermoplastics.

Drop-in bio-based PET is the overall market leader⁸² and currently consists of partly bio-based PET (20% bio-based carbon content) produced from bioethanol (2 C atoms) and fossil *p*-xylene (8 C atoms) as shown in Fig. 3. Considerable research effort is being devoted to the synthesis of bio-based terephthalic acid in order to enable the production of 100% bio-based PET but as yet these processes have not been reduced to industrial practice.^{83,84}

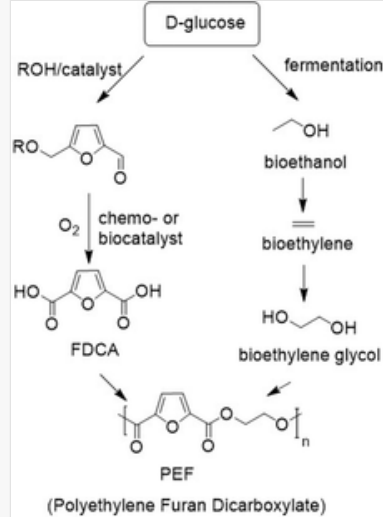
Fig. 3



Production of fossil- vs. biobased PET.

A 100% bio-based alternative to PET, polyethylene furandicarboxylate (PEF), that is derived from ethylene glycol and furan-2,5-dicarboxylic acid (FDCA), has been developed by Avantium.⁸⁵ The process has been demonstrated at pilot plant scale but still has to be commercialised. FDCA is prepared by chemo-⁸⁶ or biocatalytic oxidation⁸⁷ of 5-hydroxymethylfurfural that is in turn obtained by acid catalysed dehydration of glucose (Fig. 4). PEF also has superior mechanical, thermal and gas barrier properties compared to PET.⁸⁸ In a life-cycle assessment study, PEF showed a reduction in GHG emissions of up to 55% compared with petrochemical-derived PET.⁸⁹ Similarly, a 100% biobased equivalent of polytrimethylene terephthalate (PTT) can be produced from FDCA and bio-based 1,3-propane diol.⁹⁰

Fig. 4



Production of PEF.

Polyhydroxyalkanoates (PHAs) are one example of bio-based polymer produced directly by fermentation. In acetogenic bacteria, PHAs function as a source of energy and carbon and can reach up to 90% of the dry weight of the microbe. They can be produced by the fermentation of, for example, paper mill waste water,⁹¹ municipal waste water,^{92,93} and waste polystyrene.⁹⁴ PHAs have diverse properties depending on the structure and various applications including biodegradable plastics for packaging purposes. The physical properties of PHAs are comparable with those of PE and PP, making them suitable for various single-use products. Indeed, it was noted³⁸ that PHA development appears to be limited only by imagination and commonly applied practices. Interestingly, ~~the~~ Newlight Technologies produced a PHA by fermentation of a mixture of methane or biogas from landfills and air. The product was processed to a thermoplastic which was named 'AirCarbon'. Newlight licensed AirCarbon to the retailer, IKEA, for use in home furnishing products.⁹⁵ Composites of PHAs with inexpensive natural fibres, including bio-waste such as agave fibre, are readily produced and can exhibit enhanced physico-mechanical properties.⁹⁶ Indeed, various biotech companies, such as Kaneka in Japan and CJ CheilJedang in South Korea are investing in commercial production of PHAs. This led one observer to comment that "the world is finally ready for PHAs".⁹⁷

Global production of bio-based plastics was estimated⁹⁸ at 2.11 million tonnes in 2016 which is less than 1% of that of fossil based plastics. We note, however, that it does not include bio-based polyurethanes which are not used in packaging but account for more than 40% of the bio-based plastics market.⁹⁹ The various bio-based plastics – both biodegradable and non-biodegradable – are summarised in [Table 1](#).

Table 1

Bio-based plastics market

Bio-based plastic	B (% renewable C)	% of total ^a	Equivalent resin
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Non-biodegradable			
PET	20	25.6	
PA	40–100	11.6	
PE	100	9.5	
PTT	27	9.2	PET
PEF	100	0	PET
Other		0.9	
Total		56.8	
Biodegradable			
Starch blends	40–100	18.2	PE, PP, PS, PVC
PLA	100	10.2	PE, PP, PS, PVC, PET
PBS	Up to 100	4.6	PE
PBAT	50	7.2	PE
PHA	100	1.4	PE, PP, PET
Other		1.5	
Total		43.2	

Table Footnotes

^a% of 2.11 mio tonnes per annum.

Considering their relatively early stage of commercial development, compared with the more than half a century for fossil-based plastics, it is inevitable that the manufacturing processes are not optimised and that they are more expensive (*e.g.* PLA is around twice and PHA about 3–4 times as expensive as PE¹⁰⁰). With process refinement and scale up this difference is decreasing and the number of applications increasing, albeit not fast enough to have an impact on the grand plastic pollution challenge. This situation could rapidly change, however, if EPR with eco-modulation is incorporated in the pricing of polyolefins.

Alternatively, bio-based plastics can be produced directly from natural biopolymers, such as polysaccharides. Well established examples are starch-based plastics and cellulose acetate fibres. In 2018 the Finnish company, Stora Enso, began production of Durasense, cost and resource-efficient wood-based bio-composites, comprising a blend of wood fibre and polymers (fossil, bio-based or recycled) with up to 98% renewable content, and marketed as more eco-friendly and sustainable alternatives for plastic packaging with a reduced carbon footprint.¹⁰¹

Other, less explored polysaccharides are also potential sources of packaging plastics. For example, nanofibers of chitin,¹⁰² the second most abundant natural polymer after cellulose, can be processed into useful materials with low permeability to oxygen and carbon dioxide, combined with flexibility and optical transparency, which make them ideal candidates for sustainable barrier packaging.¹⁰³

A range of polyamide and polyurethane plastics can be produced from the long-chain fatty acids present in plant oils (*e.g.* castor oil, sunflower oil).¹⁰⁴ Waste proteins also constitute interesting raw materials for producing novel bio-based materials. For example, large amounts of waste keratin are available from wool, hair and chicken feathers.¹⁰⁵

Looking further afield, why not cut out the middleman (biomass) by going directly from carbon dioxide to plastics? This will be enabled by future availability of an economically and environmentally attractive source of hydrogen, *e.g.* from water electrolysis.¹⁰⁶ The carbon dioxide can be reduced by hydrogen to carbon monoxide and a mixture of the latter with hydrogen (syn gas) can be converted to commodity chemicals, including monomers for plastics, by existing

petrochemical technologies or by fermentation.¹⁰⁷ Interestingly, Newlight's Aircarbon technology can convert carbon dioxide to polyurethanes and thermoplastics.⁹⁵

Environmental impact of bio-based plastics

While the label of 'bio' is sometimes used as an indication of lower environmental impact, assessing whether overall environmental impacts are positive or negative requires full life cycle assessments, including effects due to direct or indirect land use change. A detailed review of such studies of bio-based plastics¹⁰⁸ led to the conclusion that meeting two thirds of the global plastics demand with bio-based plastics could save 241–316 million tonnes of CO₂ equivalents annually. Furthermore, it was noted that all three pillars of sustainability (environmental, social and economic) have to be balanced and specific needs of vulnerable stakeholders have to be supported and protected by governments and NGOs.

Using renewable biomass for the production of plastics is crucial for lowering GHG emissions. For example, producing PLA from corn-starch led to a 27% reduction in GHG emissions compared with PE from fossil resources.¹⁰⁹ Similarly, production of PET bottles from bio-based PET emits on average 25% less GHG than PET from petrochemical feedstocks.^{110,111}

Biodegradable and compostable plastics

In Callenbach's 1978 novel¹¹² *Ecotopia*, the Ecotopians used huge amounts of plastics but they were 100% derived from plants, *i.e.* bio-based. Moreover, they were all biodegradable and could be returned to the field to nourish new crops which in turn could be used to produce new plastics in what they called a "stable-state system". This concept forms the basis of using biodegradable plastic mulches in agriculture, a technology which also dates back to the 1970s.

¹¹³ Biodegradable plastic films are designed to be tilled into the soil after use where they are degraded by resident microorganisms. This offers an alternative¹¹⁴ to PE currently used in mulches and silage bales that are difficult and expensive to collect and recycle and persist in the soil. There they can interfere with cultivation and harvesting and becoming a major source of micro- and nano-plastics in agro-ecosystems.^{115,116}

A number of polyester plastics can be used in mulching, *e.g.* PHAs, PBS and PBAT, as well as films based on starch. Tests in large scale applications show that when ploughed in, they can subsequently degrade in the soil. However, their widespread introduction is hampered by higher costs per hectare compared with PE film. This situation can be rectified by the application of differentiated EPR fees combined with eco-modulation to internalise the costs of waste management.¹¹⁷

Biodegradable polyester plastics, such as PBS, PHAs and PLA, have been used in biomedical applications¹¹⁸ where the temperature and humidity of the human body provide stable conditions for their degradation. However, there are several socio-economic and technical factors that may limit broad applications of biodegradable plastics in packaging:

- Most packaging applications require durability, and clearly a plastic that degrades in the environment should not degrade during its shelf life.
- The diversity of natural environments (*e.g.* in temperature, humidity, degrading microorganisms, *etc.*) make it difficult to engineer biodegradability into the plastic molecule¹¹⁹
- Even plastics that ultimately degrade in marine environments can still maintain their integrity for months with the risk of entanglement and ingestion.
- Biodegradability could have a negative effect on consumer behaviour if the label biodegradable is taken as implying that littering is environmentally benign.

A key question is what is the fate of the plastic when it ends up in the environment? Owing to their persistence, current plastics accumulate and degrade (fragment) in the environment into micro-plastics (and ultimately nano-plastics) which migrate *via* rivers to the oceans. The ideal environmentally-benign plastic would be one that breaks down to nutrients through biological processes under the range of conditions in the natural environment.¹²⁰ Potentially, such plastics can

be produced either from crude oil or renewable resources and there is no general rule that 'bio'-based materials are more degradable than those derived from fossil fuels; some may exhibit some degree of biodegradability while others may not be biodegradable at all.

Another question is how to define biodegradability? According to the International Union of Applied Chemistry (IUPAC)¹²¹ biodegradable polymers are: 'polymers susceptible to degradation by biological activity, with the degradation accompanied by a lowering of its mass'. Biodegradable polymers are supposed to mineralise into water, carbon dioxide and microbial biomass once they end up in the environment.

However, as Wurm and co-workers¹²² have pointed out in their review of the impact of biodegradable polymers on the environment and on society, 'biodegradable' is a confusing term. Plastics labeled as biodegradable are often not as 'biodegradable' as claimed by producers who use the term as a marketing tool. Biodegradability is very much dependent on the prevailing conditions: humidity, temperature and the presence and amount of degrading microorganisms. The label "biodegradable" must, therefore, have a clear sign of the environment in which the test was performed. A general claim of biodegradability is unlikely to be valid if not accompanied by details of the conditions required for biodegradation.¹¹⁹

For example, PLA, is touted as 'the' biodegradable plastic but degradation after land littering or in seawater is actually very slow. PBS, in contrast, is biodegradable and is used in mulch film and packaging film. For example, PBS and PBS-Starch films were degraded by 1–7% after 28 days in soil with an initial bacterial biomass of 1.4×10^9 cells per g soil whereas PLA was not degraded at all.¹²³ In fact, PLA is a 'compostable' polymer that is degraded by thermophilic bacteria at higher temperatures in industrial or home composting facilities. PET is not biodegradable but the copolyester of 1,4-butane diol, adipic acid and terephthalic acid (PBAT) is eminently biodegradable. PHAs are reportedly biodegradable in seawater.⁹⁴

Conclusions and outlook

Hopefully, we have shown in this review that, notwithstanding the enormity of the problem, there is good reason for optimism in tackling the plastic pollution challenge. Technologies to facilitate waste-free production, sorting, recycling and disposal of packaging plastics are, to a large extent, already available albeit not yet fully implemented. To facilitate implementation in the short term stimulation by appropriate legislation and differentiated EPR fees is needed. The situation is reminiscent of the introduction of lead-free petrol in the 1970s. At the time it was slightly more expensive than leaded petrol and the opinion of producers, that is oil companies, was that it was doomed to fail because **customers** would not pay a few cents extra for unleaded petrol. So what happened? An extra tax was levied on leaded petrol to facilitate the introduction of lead-free petrol and we never looked back. The lesson is: epr with eco-modulation works.

The solution to plastic pollution is not less chemistry. It is more, greener chemistry, in a circular economy. Chemistry that is underpinned by recent advances in biology and biological chemistry. How can green chemistry be mobilised to facilitate the transition to more sustainable plastics? The following areas emerge from the foregoing discussion as research targets for technical innovation:

- Development of cost-effective and environmentally attractive chemo- and bio-catalytic methods for recycling. This is already quite advanced in, for example, chemo- and particularly biocatalytic recycling of polyester plastics.
- Design for circularity: new plastics need to be designed for facile disassembly and closed-loop recycling.
- Design bio-based plastics with recycling and end-of-life biodegradability in mind. PHAs as potential alternatives to polyolefins hold much promise in this respect.

However, the ideal plastic packaging which combines required mechanical properties and cost-effectiveness with rapid triggered end-of-life degradation into naturally recyclable components remains an elusive goal and remains a substantial challenge for future research and development.¹²⁴

Interestingly, a recently published Royal Society of Chemistry White Paper on 'Science to enable sustainable plastics' from the 8th Chemical Sciences and Society Summit (CS3)¹²⁵ discussed four major themes in sustainable plastics

which align well with the **e**Conclusions and **o**utlook of this Perspective. These are (i) to understand the impact of plastics throughout their life cycles, (ii) to develop new sustainable plastics, (iii) closed-loop plastics recycling and (iv) to understand and control plastics degradation.

As we enter the 3rd decade of the 21st century, confronted by the havoc of the Covid-19 pandemic, we appear to have reached a watershed moment in the history of humanity. A continuation of human activities in a 'business as usual' scenario, where time and effort is invested in propping up outdated, polluting technologies, is untenable. Now is the moment for a social, economic and technological reset to bring human activities and the planet back into equilibrium.

Conflicts of interest

There are no conflicts to declare.

Biography



Roger Sheldon


Roger Sheldon is a recognised authority on Green Chemistry and is widely known for developing the E factor for assessing the environmental impacts of chemical processes. He received the RSC Green Chemistry Award in 2010 in recognition of his role in the development of clean, catalytic technologies for waste minimisation and elimination of toxic/hazardous materials in chemicals manufacture, and the Biocat Lifetime Achievement Award for important and lasting contributions to biocatalysis. He was elected a Fellow of the Royal Society in 2015 and Honorary Fellow of the Royal Society of Chemistry in 2019. He has a PhD from Leicester University (UK) and was at Shell Research Amsterdam (1969–1980), DSM Andeno (1980–1990), Professor of Biocatalysis and Organic Chemistry at Delft University of Technology (NL) (1991–2007) and CEO of CLEA Technologies (2006–2015). He is currently Distinguished Professor of Biocatalysis Engineering at the University of the Witwatersrand in Johannesburg (RSA).



Michael Norton

Michael Norton obtained his Chemistry BSc and PhD at Bristol University, followed by postdoctoral research at the University of Alberta (Canada). He then joined the UK ICI Petrochemicals Division research group. This was followed by various positions in the UK Scientific Civil Service including the Ministry of Fisheries, the British Embassy in the US as the First Secretary (Science), and as founding Director of the Parliamentary Office of Science and Technology. From 1998–2004 he was Counsellor of Science and Technology in the British Embassy Tokyo. Since 2004, Michael

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Footnotes

[†] The European Academies Science Advisory Council is a consortium of all 28 of Europe's science academies that analyses issues emerging from science and which are on the European policy agenda.

[‡] In the petrochemical carbon cycle carbon dioxide is converted *via* photosynthesis into plant biomass which is transformed, over a period of millions of years in geological reservoirs, to fossil resources, and subsequently, in oil refineries, to liquid fuels which are burned to return the carbon dioxide to the atmosphere. However, the rate of formation of the fossil resources is about five orders of magnitude

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