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BIODEGRADABLE PLASTICS

& MARINE LITTER

MISCONCEPTIONS, CONCERNS AND IMPACTS ON MARINE ENVIRONMENTS

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BIODEGRADABLE PLASTICS & MARINE LITTER

MISCONCEPTIONS, CONCERNS AND IMPACTS ON MARINE ENVIRONMENTS

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PHOTO: ©LAURA BILLINGS / CREATIVE COMMONS

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ABBREVIATIONS LIST

ABS	Acrylonitrile butadiene styrene
AC	Acrylic
AcC (CTA, TAC)	Acetyl cellulose, cellulose triacetate
AKD	Alkyd
ASA	Acrylonitrile styrene acrylate
DECP	Degradable and electrically conductive polymers
EP	Epoxy resin (thermoset)
PA	Polyamide 4, 6, 11, 66
PAN	Polyacrylonitrile
PBAT	Poly(butylene adipate-co-teraphthalate
PBS	Poly(butylene succinate)
PCL	Polycaprolactone
PE	Polyethylene
PE-LD	Polyethylene low density
PE-LLD	Polyethylene linear low density
PE-HD	Polyethylene high density
PES	Poly(ethylene succinate)
PET	Polyethylene terephthalate
PGA	Poly(glycolic acid)
PHB	Poly(hyroxybutyrate)
PLA	Poly(lactide)
PMA	Poly methylacrylate
PMMA	Poly(methyl) methacrylate
POM	Polyoxymethylene
PP	Polypropylene
PS	Polystyrene
EPS (PSE)	Expanded polystyrene
PU (PUR)	Polyurethane
PVA	Polyvinyl alcohol
PVC	Polyvinyl chloride
SAN	Styrene acrylonitrile
SBR	Styrene-butadiene rubber
Starch	Starch

Executive Summary

- The development and use of synthetic polymers, and plastics has conferred widespread benefits on society. One of the most notable properties of these materials is their durability which, combined with their accidental loss, deliberate release and poor waste management has resulted in the ubiquitous presence of plastic in oceans. As most plastics in common use are very resistant to biodegradation, the quantity of plastic in the ocean is increasing, together with the risk of significant physical or chemical impacts on the marine environment. The nature of the risk will depend on: the size and physical characteristics of the objects; the chemical composition of the polymer; and, the time taken for complete biodegradation to occur (GESAMP 2015).

- Synthetic polymers can be manufactured from fossil fuels or recently-grown biomass. Both sources can be used to produce either non-biodegradable or biodegradable plastics. Many plastics will weather and fragment in response to UV radiation – a process that can be slowed down by the inclusion of specific additives. Complete biodegradation of plastic occurs when none of the original polymer remains, a process involving microbial action; i.e. it has been broken down to carbon dioxide, methane and water. The process is temperature dependent and some plastics labelled as ‘biodegradable’ require the conditions that typically occur in industrial compositing units, with prolonged temperatures of above 50°C, to be completely broken down. Such conditions are rarely if ever met in the marine environment.

- Some common non-biodegradable polymers, such as polyethylene, are manufactured with a metal-based additive that results in more rapid fragmentation (oxo-degradable). This will increase the rate of microplastic formation but there is a lack of independent scientific evidence that biodegradation will occur any more rapidly than unmodified polyethylene. Other more specialised polymers will break down more readily in seawater, and they may have useful applications, for example, to reduce the impact of lost or discarded fishing gear. However, there is the potential that such polymers may compromise the operational requirement of the product. In addition, they are much more expensive to produce and financial incentives may be required to encourage uptake.

- A further disadvantage of the more widespread adoption of ‘biodegradable’ plastics is the need to separate them from the non-biodegradable waste streams for plastic recycling to avoid compromising the quality of the final product. In addition, there is some albeit limited evidence to suggest that labelling a product as ‘biodegradable’ will result in a greater inclination to litter on the part of the public (GESAMP 2015).

- In conclusion, the adoption of plastic products labelled as ‘biodegradable’ will not bring about a significant decrease either in the quantity of plastic entering the ocean or the risk of physical and chemical impacts on the marine environment, on the balance of current scientific evidence.

1

BACKGROUND

PHOTO: © AMANDA WYCHERLEY / CREATIVE COMMONS

BACKGROUND

The objective of this briefing paper is to provide a concise summary of some of the key issues surrounding the biodegradability of plastics in the oceans, and whether the adoption of biodegradable plastics will reduce the impact of marine plastics overall.

One of the principal properties sought of many plastics is durability. This allows plastics to be used for many applications which formerly relied on stone, metal, concrete or timber. There are significant advantages, for food preservation, medical product efficacy, electrical safety, improved thermal insulation and to lower fuel consumption in aircraft and automotives. Unfortunately, the poor management of post-use plastic means that the durability of plastic becomes a significant problem in mitigating its impact on the environment. Plastics are ubiquitous in the oceans as a result of several decades of poor waste management, influenced by a failure to appreciate the potential value of 'unwanted' plastics, the under-use of market-based instruments (MBIs), and a lack of concern for the consequences (GESAMP 2015).

The principal reasons plastic ends up in the ocean are:

- Inadequate waste management by the public and private sector;
- Illegal practices;
- Littering by individuals and groups;
- Accidental input from land-based activities and the maritime sector, including geological and meteorological events;
- A lack of awareness on the part of consumers, for example of the use of microplastics in personal care products and the loss of fibres from clothes when washed.

> Plastics are ubiquitous in the oceans as a result of several decades of poor waste management, influenced by a failure to appreciate the potential value of 'unwanted' plastics

Efforts to improve waste management and influence changes in behaviour, on the part of individuals and groups, face many challenges, and the results of mitigation measures may take many years to demonstrate a benefit (GESAMP 2015).

PHOTO: © CHESAPEAKE BAY PROGRAM / CREATIVE COMMONS

The degree to which ‘biodegradable’ plastics actually biodegrade in the natural environment is subject to intense debate.

It has been suggested that plastics considered to be ‘biodegradable’ may play an important role in reducing the impact of ocean plastics. Environmental biodegradation is the partial or complete breakdown of a polymer as a result of microbial activity, into CO_2, H_2O and biomasses, as a result of a combination of hydrolysis, photodegradation and microbial action (enzyme secretion and within-cell processes). It is described in more detail in section 3. Although this property may be appealing, it is critical to evaluate the potential of ‘biodegradable’ plastics in terms of their impact on the marine environment, before encouraging wider use.

A material may be labelled ‘biodegradable’ if it conforms to certain national or regional standards that apply to industrial composters (section 3.1), not to domestic compost heaps or discarded litter in the ocean. Equally important is the time taken for biodegradation to take place. Clearly the process is time-dependent and this is controlled by environmental factors as well as the properties of the polymer. The environmental impact of discarded plastics is correlated with the time taken for complete breakdown of the polymer. At every stage there will be the potential for an impact to occur, whether as a large object or a nano-sized particle.


PHOTO: © PETERCHARAF / RACEFORWATER

There is considerable debate as to the extent to which plastics intended to be biodegradable do actually biodegrade in the natural environment. This extends to the peer-reviewed scientific literature but is most intense between those organisations that can be thought to have a vested interest in the outcome, such as the producers of different types of plastics, the producers of additive chemicals intended to promote degradation and those involved in the waste management and recycling sectors.

Deciding what constitutes best environmental practice through the choice of different plastics and non-plastics is not straightforward. Life Cycle Assessments (LCA) can be used to provide a basis for decisions about optimal use of resources and the impact of different processes, materials or products on the environment. For example, LCA could be employed to assess the use of plastic-based or natural fibre-based bags and textiles, and conventional and biodegradable plastics. In one LCA –based study of consumer shopping bags, conventional PE (HDPE) shopping carrier bags were considered to be a good environmental option compared with bags made from paper, LDPE, non-woven PP and cotton, but strictly in terms of carbon footprints (paper to cotton in order of increasing global warming potential; Thomas et al. 2010). This analysis did not take account of the social and ecological impact that plastic litter may have.

In contrast, an analysis of textiles - that included factors for human health, environmental impact and sustainability - placed cotton as having a much smaller footprint than acrylic fibres (Mutha et al. 2012). However, it is important to examine what is included under such broad terms as ‘environmental impact’. For example, a third study which also performed an LCA-based assessment of textiles concluded that cotton had a greater impact than fabrics made with PP or PET, and a much greater impact than man-made cellulose-based fibres (Shen et al. 2010). This was on the basis of ecotoxicity, eutrophication, water use and land use. Neither textile-based LCAs considered the potential ecological impact due to littering by the textile products or fibres. Clearly, the scope of an environmental LCA can determine the outcome. Ecological and social

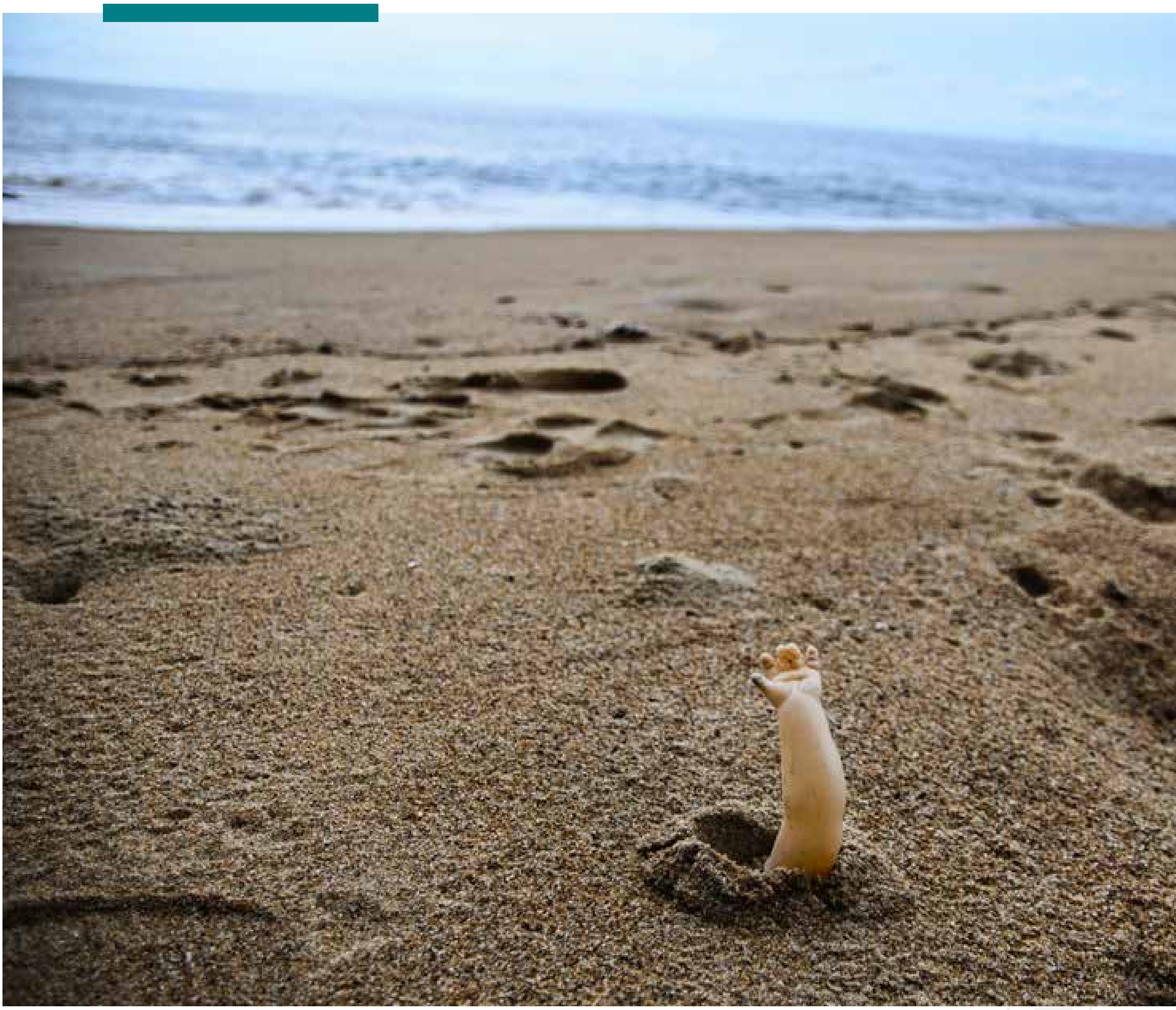


PHOTO: LUDWIG TRÖLLER / CREATIVE COMMONS

perspectives should be included in a comprehensive LCA approach, as well as the time-scales involved. Without such evaluation, decisions made in good faith may result in ineffective mitigation measures, unnecessary or disproportionate costs, or unforeseen negative consequences.

As with all such assessment studies, it is very important to consider the scope, assumptions, limitations, motivations, data quality and uncertainties before drawing conclusions about the study's validity and wider applicability.

The environmental impact of discarded plastics is correlated with the time taken for complete breakdown of the polymer.

2

POLYMERS AND PLASTICS TERMINOLOGY AND DEFINITIONS

PHOTO:GERAINT ROWLAND / CREATIVE COMMONS

POLYMERS AND PLASTICS - TERMINOLOGY AND DEFINITIONS

The term 'plastic', as commonly applied, refers to a group of synthetic polymers (section 2.3).

Polymers are large organic molecules composed of repeating carbon-based units or chains that occur naturally and can be synthesised. Different types of polymers have a wide range of properties, and this influences their behaviour in the environment.

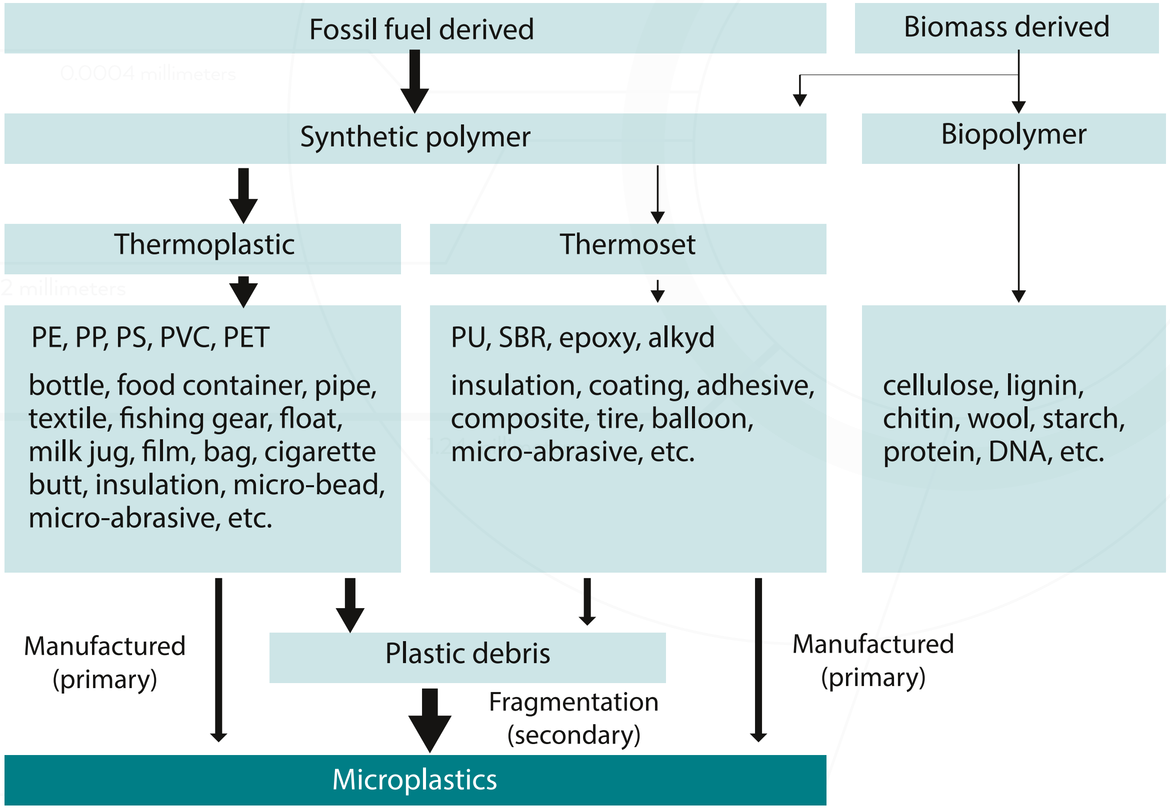
Some biodegradable plastics are made from fossil fuels, and some non-biodegradable plastics are made from biomass

2.1 The need for precise definitions

There is great scope for confusion in the terminology surrounding 'plastic' and its behaviour in the environment. Section 2 provides some definitions to terms used in this report.

Assessing the impact of plastics in the environment, and communicating the conclusions to a disparate audience is challenging. The science itself is complex and multidisciplinary. Some synthetic polymers are made from biomass and some from fossil fuels, and some can be made from either (Figure 2.1). Some polymers derived from fossil fuels can be biodegradable.

Fig. 2.1 Schematic illustrating the relationship between primary materials source, synthetic and natural polymers, thermoplastic and thermoset plastics and their applications: from GESAMP, 2015



Conversely, some polymers made from biomass sources, such as maize, may be non-biodegradable.

Apart from the polymer composition, material behaviour is linked to the environmental setting, which can be very variable in the ocean. Terms are sometimes not defined sufficiently, which can lead to confusion or misunderstanding (Table 2.1)

The conditions under which 'biodegradable' polymers will actually biodegrade vary widely. For example, a single-use plastic shopping bag marked 'biodegradable' may require the conditions that commonly occur only in an industrial composter (e.g. 50 °C) to breakdown completely into its constituent components of water, carbon dioxide, methane, on a reasonable or practical timescale. It is important, if users are to make informed decisions, for society to have access to reliable, authoritative and clear guidance on what terms such as 'degradable' or 'biodegradable' actually mean, and what caveats may apply.

Table 2.1 Some common definitions regarding the biodegradation of polymers

TERM	DEFINITION
Degradation	The partial or complete breakdown of a polymer as a result of e.g. UV radiation, oxygen attack, biological attack. This implies alteration of the properties, such as discolouration, surface cracking, and fragmentation
Biodegradation	Biological process of organic matter, which is completely or partially converted to water, CO_2/methane, energy and new biomass by microorganisms (bacteria and fungi).
Mineralisation	Defined here, in the context of polymer degradation, as the complete breakdown of a polymer as a result of the combined abiotic and microbial activity, into CO_2, water, methane, hydrogen, ammonia and other simple inorganic compounds
Biodegradable	Capable of being biodegraded
Compostable	Capable of being biodegraded at elevated temperatures in soil under specified conditions and time scales, usually only encountered in an industrial composter (standards apply)
Oxo-degradable	Containing a pro-oxidant that induces degradation under favourable conditions. Complete breakdown of the polymers and biodegradation still have to be proven.

> The conditions under which 'biodegradable' polymers will actually biodegrade vary widely.

2.2 Natural (bio)polymers

Bio-polymers are very large molecules with a long chain-like structure and a high molecule weight, produced by living organisms. They are very common in nature, and form the building blocks of plant and animal tissue. *Cellulose* $(C_6H_{10}O_5)n$ is a polysaccharide (carbohydrate chains), and is considered the most abundant natural polymer on Earth, forming a key constituent of the cell walls of terrestrial plants. *Chitin* $(C_8H_{13}O_5N)n$ is a polymer of a derivative of glucose (N-acetylglucosamine) and is found in the exoskeleton of insects and crustaceans. *Lignin* $(C_{31}H_{34}O_{11})n$ is a complex polymer of aromatic alcohols, and forms another important component of cell walls in plants, providing strength and restricting the entry of water. Cutin is formed of a waxy polymer that covers the surface of plants.

Other types of natural polymers are poly amides such as occur in proteins and form materials such as wool and silk. Examples of common natural polymers and their potential uses by society are provided in Table 2.2.

Single-use plastic shopping bag marked ‘biodegradable’ may require the conditions that commonly occur only in an industrial composter

PHOTO: © VWASTE BUSTERS / CREATIVE COMMONS

Table 2.2 Examples of common natural polymers and uses by society.

POLYMER	NATURAL OCCURRENCE	HUMAN USES
Chitin	Exoskeleton of crustaceans: e.g. crabs, lobsters and shrimp Exoskeleton of insects Cell walls of fungi	Medical, biomedical (lattices for growing tissues) Agriculture
Lignin	Cell walls of plants	(Ligno-cellulose) Construction timber Fuel as timber Newsprint Industrial – as a dispersant, additive and raw material
Cellulose	Cell walls of plants, many algae and the secretions of some bacteria	Paper Cellophane and rayon Fuel - Conversion into cellulosic ethanol
Polyester	Cutin in plant cuticles	
Protein fibre (e.g. fibroin, keratin)	Wool, silk	Clothing

2.3 Synthetic polymers and plastics

There are two main classes of synthetic polymers: thermoplastic and thermoset (Figure 2.1). Thermoplastic has been shortened to 'plastic' and, in lay terms, has come to be the most common use of the term. In engineering, soil mechanics, materials science and geology plasticity refers to the property of a material able to deform without fracturing. Thermoplastic is capable of being repeatedly moulded, or deformed plastically, when heated. Thermoset plastic material, once formed, cannot be remoulded by melting; common examples are epoxy resins or coatings. Many plastics often contain a variety of additional compounds that are added to alter the properties, such as plasticisers, colouring agents, UV protection, anti oxidants, and fire retardants. Epoxy (EP) resins or coatings are common examples of thermoset plastics. Synthetic polymers are commonly manufactured from fossil fuels, but biomass (e.g. maize, plant oils) are increasingly being used. Once the polymer is synthesised, the material properties will be the same, whatever the type of raw material used.

In terms of volume, the market is dominated by a limited number of well-established synthetic polymers (Figure 2.2 below). However, there is a very wide range of polymers produced for more specialised application, with an equally wide range of physical and chemical properties (Table 2.3). In addition, many plastics are synthesised as co-polymers, a mixture of two or more polymers with particular characteristics. Objects may be produced using more than one type of polymer or co-polymer. All these factors result in, for the non-specialist, a bewildering array of materials. Although their characteristics and behaviour may be well understood with regard to the designed application (e.g. insulation slabs, shopping bags, fishing line) their behaviour in the marine environment may be poorly understood.

Fig. 2.2 European plastics demand (EU27 + Norway & Switzerland) by resin type and industrial sector in 2012. Polyamide (mainly Polyamide 6 and 6.6) in fishing gear applications and polystyrene, polyurethane foams used in vessel insulation and floats, are employed extensively in the marine environment. Figure courtesy of PlasticsEurope (PEMRG)/Consultic/ECEBD

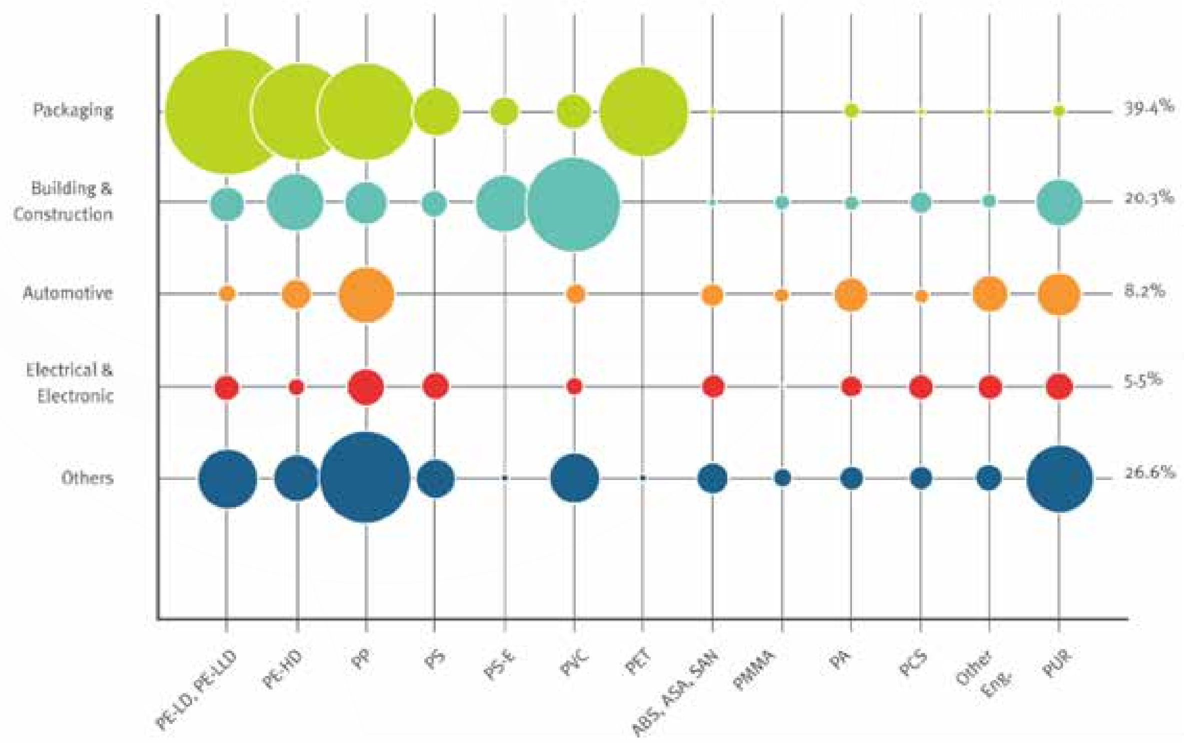


Table 2.3 Common synthetic polymers – source, use and degradation properties

ABBREVIATION	FULL NAME	COMMON SOURCE	EXAMPLES OF COMMON USES	BIODEGRADATION PROPERTIES IN TERRESTRIAL ENVIRONMENT (INCLUDING MEDICAL APPLICATIONS)	BIODEGRADATION PROPERTIES IN AQUATIC/MARINE ENVIRONMENT	REFERENCE
ABS	(acrylonitrile butadiene sytyrene) Copolymer	Fossil fuel	Pipes, protective headgear, consumer goods, Lego™ bricks			
AC	Acrylic	Fossil fuel	Acrylic glass (see PMMA)			
AcC (CTA, TAC)	Acetyl cellulose, cellulose triacetate	Biomass	Fibres, photographic film base	Biodegradability depends on degree of acetylation[1]		[1] Tokiwa et al. 2009
AKD	Alkyd	Partly biomass	Coatings, moulds			
	Cellophane	Biomass (cellulose)	Film for packaging			
DECP	A group of degradable and electrically conductive polymers	Biomass & fossil fuel	Biosensors and tissue engineering	Degradable within living tissues[2]		[2] Guo et al. 2013
EP	Epoxy resin (thermoset)	Fossil fuel	Adhesives, coatings, insulators			
PA	Polyamide e.g. Nylon™ 4, 6, 11, 66; Kevlar™	Fossil fuel	Fabrics, fishing lines and nets,			
PAN	Polyacrylonitrile	Fossil fuel	Fibres, membranes, sails, precursor in carbon fibre production			
PBAT	Poly(butylene adipate-co -teraphthalate	Fossil fuel	Films	Biodegradable[7]		[7] Weng et al., 2013

ABBREVIATION	FULL NAME	COMMON SOURCE	EXAMPLES OF COMMON USES	BIODEGRADATION PROPERTIES IN TERRESTRIAL ENVIRONMENT (INCLUDING MEDICAL APPLICATIONS)	BIODEGRADATION PROPERTIES IN AQUATIC/MARINE ENVIRONMENT	REFERENCE
PBS	Poly (butylene succinate)	Fossil fuel	Agricultural mulching films, packaging	Biodegradable[1]	Some degradation after 12 months but retains 95% tensile strength[3] Some degradation after 2 years[4]	[1] Tokiwa et al. 2009 [3] Sekiguchi et al. 2011 [4] Kim et al. 2014a,b
PCL	Polycaprolac-tone	Fossil fuel	3D printing, hobbyists, biomedical applications	Biodegradable by hydrolysis in the human body Biodegradable[1]	Some degradation after 12 months[3]	[1] Tokiwa et al. 2009 [3] Sekiguchi et al. 2011
PE	Polyethylene	Biomass & fossil fuel	Packaging, containers, pipes		Extremely limited, potential minor effect in Tropics due to higher temperature, dissolved oxygen and microfauna/flora assemblages[5]	[5] Sudhakar et al. 2007
PES	Poly(ethylene succinate)	Fossil fuel	films	Biodegradable[1]		[1] Tokiwa et al. 2009
PET	Polyethylene terephthalate	Fossil fuel, fossil fuel with biomass	Containers, bottles, 'fleece' clothing			
PGA	Poly (glycolic acid)		Sutures, food packaging	Biodegradable by hydrolysis in the human body		
PHB	Poly (hyroxybutyrate)	Biomass	Medical sutures	Biodegradable[1] Some degradation after 12[3]		[1] Tokiwa et al. 2009 [3] Sekiguchi et al. 2011
PLA	Poly(lactide)	Biomass	Agricultural mulching films, packaginzg, biomedical applications, personal hygiene products, 3D printing	Biodegradable[1] Compostable[5]		[1] Tokiwa et al. 2009 [5] Pemba et al. 2014

ABBREVIATION	FULL NAME	COMMON SOURCE	EXAMPLES OF COMMON USES	BIODEGRADATION PROPERTIES IN TERRESTRIAL ENVIRONMENT (INCLUDING MEDICAL APPLICATIONS)	BIODEGRADATION PROPERTIES IN AQUATIC/MARINE ENVIRONMENT	REFERENCE
PMMA	Poly(methyl) methylacrylate	Fossil fuel	Acrylic glass, biomedical applications, lasers	Biodegradable[3]		[3] Cappitelli et al. 2006
POM	Poly(oxymethylene) Also called Acetal	Fossil fuel	High performance engineering components e.g. automobile industry			
PP	Polypropylene	Fossil fuel	Packaging, containers, furniture, pipes			
PS	Polystyrene	Fossil fuel	Food packaging			
EPS	Expanded polystyrene	Fossil fuel	Insulation panels, insulated boxes, fishing/aquaculture floats, packaging			
PU (PUR)	Polyurethane	Fossil fuel	Insulation, wheels, gaskets, adhesives			
PVA	Poly(vinyl alcohol)	Fossil fuel	Paper coatings	Biodegradable		
PVA	Poly(vinyl acetate)	Fossil fuel	Adhesives			
PVC	Poly (vinyl chloride)	Fossil fuel	Pipes, insulation for electric cables, construction			
Rayon	Rayon	Biomass (cellulose)	Fibres, clothing	Biodegradable	Biodegradable	
SBR	Styrene-butadiene rubber	Fossil fuel	Pneumatic tyres, gaskets, chewing gum, sealant			
Starch	Starch	Biomass	Packaging, bags, Starch blends e.g. Mater-Bi™	Biodegradable in soil and compost[6]	Minimal deterioration in littoral marsh of seawater[6]	[6] Accinelli et al. 2012

Utilising waste material can be seen as fitting into the model of the circular economy, closing a loop in the resource, manufacture, use, waste stream.

2.4 Bio-derived plastic

Bio-based plastics are derived from biomass such as organic waste material or crops grown specifically for the purpose (Table 2.4). Utilising waste material can be seen as fitting into the model of the circular economy, closing a loop in the resource-manufacture-use-waste stream. The latter source could be considered to be potentially more problematic as it may require land to be set aside from either growing food crops, at a time of growing food insecurity, or from protecting sensitive habitat, at a time of diminishing biodiversity. One current feature of biomass-based polymers is that they tend to be more expensive to produce than those based on fossil fuels (Sekiguchi et al. 2011, Pemba et al. 2014).

Perhaps the two most common bio-based plastics are bio-polyethylene and poly(lactide). While most of the conventional polyethylenes are produced from fossil fuel feedstock, bio-polyethylene a leading bio-based plastic is produced entirely from biomass feedstock. Similarly, bio-polyamide11 is derived from vegetable oil and poly(lactide) is a polyester produced from lactic acid derived from agricultural crops such as maize and sugar cane.

2.5 Bio-based plastics

The term bio-plastic is a term used rather loosely. It has been often described as comprising both biodegradable plastics and bio-based plastics, which may or may not be biodegradable (Figure 2.3; Tokiwa et al, 2009). To avoid confusion it is suggested that the description 'bio-plastic' is qualified to indicate the precise source or properties on the polymer concerned.

Table 2.4 Examples of common bio-based plastics

POLYMER	DERIVATION	APPLICATIONS
Cellophane	Cellulose (e.g. wood, cotton, hemp)	Sheets – packaging Base layer for adhesive tape Dialysis (Visking) tubing
Chitosan	Chiton	Tissue engineering, wound healing, drug delivery
Rayon	Cellulose (e.g. wood pulp)	Threads – clothing

§ *most types of polyamide are derived from fossil fuels*

PHOTO: DOUG BECKERS / CREATIVE COMMONS

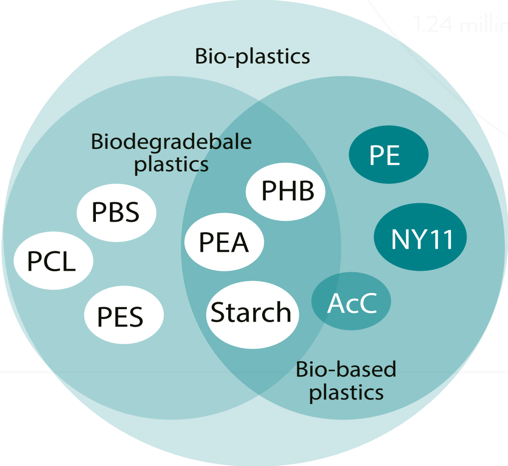


Fig. 2.3 Bio-plastics comprised of biodegradable and bio-based plastics (taken from Tokiwa et al. 2009; available under the Creative Commons Attribution license).

One current feature of biomass-based polymers is that they tend to be more expensive to produce than those based on fossil fuels

3

FRAGMENTATION, DEGRADATION AND BIODEGRADATION

PHOTO: © RALPH AICHINGER / CREATIVE COMMONS

FRAGMENTATION, DEGRADATION AND BIODEGRADATIONTS

3.1 The degradation process

Fragmentation

The degree to which synthetic polymers degrade depends on both the properties of the polymer and the environment to which it is exposed (Mohee et al. 2008). At the point when the original polymer has been completely broken into water, carbon dioxide, methane and ammonia (with proportions depending on the amount of oxygen present), it is said to have been completely mineralised (Eubeler at al. 2009).

Fragmentation and biodegradation proceeds through a combination of photo- (UV) and thermal-oxidation and microbial activity. In the marine environment UV radiation is the dominant weathering process. It causes embrittlement, cracking and fragmentation, leading to the production of microplastics (Andrady 2011). This means that fragmentation is greatest when debris is directly exposed to UV radiation on shorelines. Higher temperatures and oxygen levels both increase the rate of fragmentation, as does mechanical abrasion (e.g. wave action). Once plastics become buried in sediment, submerged in water or covered in organic and inorganic films (which happens readily in seawater) then the rate of fragmentation decreases rapidly. Plastic objects observed on the deep ocean seabed, such as PET bottles, plastic bags and fishing nets, show insignificant deterioration (Pham et al 2014). In addition, the inclusion of additive chemicals such as UV- and thermal-stabilizers inhibit the fragmentation process.

Biodegradation

Biodegradation is the partial or complete breakdown of a polymer as a result of microbial activity, into carbon, hydrogen and oxygen, as a result of hydrolysis, photodegradation and microbial action (enzyme secretion and within-cell processes). The probability of biodegradation taking place is highly dependent on the type of polymer and the receiving environment. The literature on the biodegradation of a wide range of synthetic polymers has been extensively reviewed by Eubeler et al. (2009, 2010). Partial biodegradation can lead to the production of nano-sized fragments and other synthetic breakdown products (Lambert et al. 2013).

> If a products is marketed as biodegradable it should conform to a recognised standard defining compostability, for example ASTM 6400 (USA) , EN 13432 (European) or ISO 17088 (International)

A number of national and international standards have been developed, or are under development, to cover materials designed to be compostable or biodegradable (e.g. ISO, European Norm - EN, American Society for Testing and Materials - ASTM International). These standards are appropriate for conditions that occur in an industrial composter, in which temperature are expected to reach 70 °C. The EN standard requires that at least 90% of the organic matter is converted into CO_2 within 6 months, and that no more than 30% of the residue is retained by a 2mm mesh sieve after 3 months composting[1]. A recent literature review, commissioned by PlasticsEurope, concluded that most

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[1] EN 13432:2000. Packaging. Requirements for packaging recoverable through composting and biodegradation. Test scheme and evaluation criteria for the final acceptance of packaging; http://www.bpiworld.org/page-190437, accessed 10th February 2015.

plastic packaging marketed as biodegradable meets the EN 13432 or equivalent standard (Deconinck and De Wilde 2013). Test procedures include weight loss and production of CO_2. However, the plastic may still retain important physical appearance such as overall shape and tensile strength even with significant weight loss.

In addition, ASTM produced a standard for 'Non-floating biodegradable plastics in the marine environment' (ASTM D7081-05). It has been withdrawn but is currently being subjected to ASTM's balloting process for reinstatement[2]. An additional standard (ASTM WK42833) is being developed that will cover 'New Test Method for Determining Aerobic Biodegradation of Plastics Buried in Sandy Marine Sediment under Controlled Laboratory Conditions.

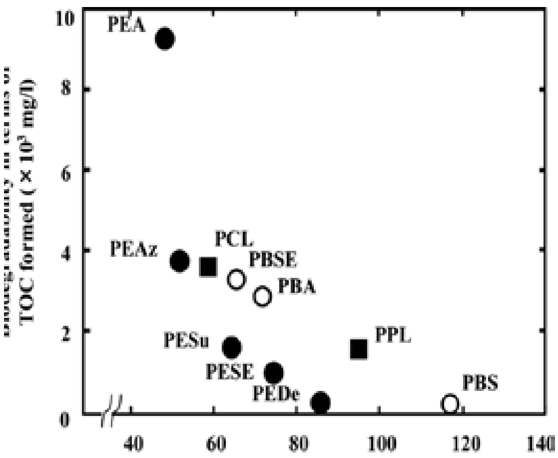

Fig.3.1 The relationship between melting temperature (Tm°C) and biodegradability (TOC - Total Organic Carbon mg l^{-1}) by the enzyme lipase of the fungus Rhizopus delemar. (taken from Tokiwa et al. 2009; available under the Creative Commons Attribution license).

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[2] http://www.astm.org/Standards/D7081.htm

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The biodegradability of polymers is influenced by a range of intrinsic factors. A higher molecular weight (Eubeler et al. 2010), higher melting temperature and higher degree of crystalinity all reduce the degree to which the polymer is likely to biodegrade (Figure 3.1, Tokiwa et al. 2009).

3.2 Non-biodegradable plastics:

Many common polymers can be considered as effectively non-biodegradable. This means that complete mineralisation, requiring a process of gradual fragmentation, facilitated by UV, higher temperature and an oxygenated environment, will happen so slowly as to be considered negligible in the natural environment. Conditions of UV exposure, which occur more frequently on land, or the coastal margins in tropical or sub-tropical climates, may result in the fragmentation of some material, such as non-UV-stabilised PE sheeting (Figure 3.2). However, as soon as plastics become buried in sediment, submerged, or covered by organic and inorganic coatings, the rate of fragmentation declines rapidly. Common examples include: PE, PET, PA (Polyamide 11), PS, EP, PU, PVA, PVC and SBR (see Table 2.3).

3.3 ‘Biodegradable’ plastics

Biodegradable plastics are polymers that are capable of being broken down quite readily by hydrolysis, the process by which chemical bonds are broken by the addition of water (GESAMP 2015). This process is influenced by the environmental setting and is facilitated by the presence of microorganisms.

Some polymers have been designed to be biodegradable for use in medical applications (Table 2.3). They are capable of being metabolized in the human body through hydrolysis catalysed by enzyme activity. Some polymers, such as poly (glygolic acid) and its copolymers, are used as temporary sutures while others have been designed for slow-release drug delivery used, for example, in the treatment of certain cancers, or the delivery of vaccines (Pillay et al. 2013, Bhavsar and Amiji 2007). Others have been designed to form temporary lattices for cell growth (Woodruff and Hutmacher 2010). Despite these engineered properties it does not mean that all such

Fig. 3.2 Fragmentation of PE with exposure to UV in a cool temperate climate at 61.6 °North; (a) standard PE sheeting, (b) PE sheeting with UV stabilizer added, for horticultural use. © Peter Kershaw

A higher molecular weight, higher melting temperature and higher degree of crystalinity all reduce the degree to which the polymer is likely to biodegrade

> Outside the human body the degree or rate of biodegradation becomes very dependent on the surrounding environment, which will show a much greater variability

polymers will be rapidly biodegraded in the external environment. Outside the human body the degree or rate of biodegradation becomes very dependent on the surrounding environment, which will show a much greater variability (e.g. temperature, humidity, oxygen levels, microbe assemblages, UV irradiation). For example, polycaprolactone and polylactide are both used for 3D printing and producing hard durable components, as well as for time-limited medical applications.

Plastics made from the same initial polymer can show differences in material properties and rates of biodegradation. For example, a study of cellulose-based fabrics demonstrated that biodegradation was greatest in rayon and decreased in the order rayon > cotton >> acetate (Park et al 2004). The tests used were soil burial, activated sewage sludge and enzyme hydrolysis. Biodegradability was related to the crystalinity of the fibres (rayon had lowest crystalinity) and the fabric weave. The bio-plastic PLA is a polyester, produced from lactic acid derived from agricultural crops such as maize and sugar cane, and it can be biodegraded by a variety of micro-organisms (Eubeler et al. 2010). However, despite the biological origins degradation under natural environmental conditions is very slow and it requires industrial composting for complete biodegradation (GESAMP 2015).

A polymer may be marketed as 'biodegradable' but this may only apply to a limited range of environmental conditions, which are probably not encountered in the natural environment (Figure 3.3). This can lead to misunderstandings and confusion as to what constitutes biodegradability. For example, some items, such as plastic shopping bags supplied for groceries, may be labelled as 'biodegradable'. However, it is quite possible that the item will only degrade appreciably in an industrial composter (section 3.1). Such polymers will not 'biodegrade' in domestic compost heaps or if left to litter the environment. This lack of clarity may lead to behaviours that result in a greater degree of littering (Section 5.0). The State of California has passed legislation that covers the use of the terms 'biodegradable' and 'compostable' on consumer packaging.

3.4 Oxo-degradable plastics

These are conventional polymers, such as polyethylene, which have had a metal compound (e.g. manganese) added to act as a catalyst, or pro-oxidant, to increase the rate of initial oxidation and fragmentation (Chiellini et al. 2006). They are sometimes referred to as oxy-biodegradable or oxo-degradable. Initial degradation may result in the production of many small fragments (i.e. microplastics), but the eventual fate of these is poorly understood (Eubeler et al. 2010, Thomas et al. 2010). As with all forms of degradation the rate and degree of fragmentation and utilisation by microorganisms will be dependent on the surrounding environment. There appears to be no convincing published evidence that oxo-degradable plastics do mineralise completely in the environment, except under industrial composting conditions. The use of a catalyst will invariably tend to restrict the applications the plastic can be used for as it will alter the mechanical properties.

The conclusions of the present paper are based on evidence presented in the peer-reviewed literature. But, it should be appreciated that the degree to which oxo-degradable plastics really do offer a more 'environmentally-friendly' option over traditional polymers is the subject of intense debate. This appears to be influenced, at least in part, by commercial interests, both for those supporting the use of oxo-degradable plastics and for those opposing them. For example, a position paper issued by European Bioplastics (European Bioplastics 2012), an industry association of European bioplastics producers, strongly challenged the conclusions of an LCA of oxo-degradable bags commissioned by a producer of pro-oxidants (Edwards and Parker 2012). Without wishing to be drawn into this debate, it should be pointed out that decision-makers are unlikely to be influenced solely by reliable, independent and peer-reviewed scientific evidence.

A literature review (Deconinck and De Wilde 2013) of publications on bio- and oxo-degradable plastics, commissioned by Plastics Europe, concluded that the rate and level of biodegradation of oxo-degradable plastics 'is at least questionable and reproducibility'.

Fig. 3.3 Examples of single-use plastic products marked as either 'oxo-degradable' or '100% biodegradable'.

The lack of consensus on the desirability or otherwise of oxo-degradable plastics is evident from the disputed entry in the on-line Wikipedia dictionary[3]. A useful commentary on many of the disputed claims is available. (Narayan 2009).

Meanwhile, a review commissioned by the UK Government, published in 2010, concluded that oxo-degradable plastics did not provide a lower environmental impact compared with conventional plastics (Thomas et al. 2010). The recommended solutions for dealing with end-of-life oxo-degradable plastics were incineration (first choice) or landfill. In addition, the authors observed that:

> '… as the [oxo-degradable] plastics will not degrade for approximately 2-5 years, they will still remain visible as litter before they start to degrade'.
>
> (Thomas et al. 2010)

There has been debate on the need for legislation to control the marketing of products made with oxo-degradable polymers

Plastics containing pro-oxidants are not recommended for recycling as they have the potential to compromise the utility of recycled plastics (Hornitschek 2012). There has been debate on the need for legislation to control the marketing of products made with oxo-degradable polymers in the state of California and within the European Union.

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[3] Accessed 9th February 2015

4

THE BEHAVIOUR OF 'BIODEGRADABLE' PLASTICS IN THE MARINE ENVIRONMENT

PHOTO: © JENNYVIDS / CREATIVE COMMONS

THE BEHAVIOUR OF 'BIODEGRADABLE' PLASTICS IN THE MARINE ENVIRONMENT

4.1 The composition of plastic litter in the ocean

Plastics are ubiquitous in the marine environment. A number of studies have been published illustrating the wide range of polymer compositions found in seawater, sediments and biota (Table 4.1). There does not appear to have been any attempt to analyse the proportion of 'non-biodegradable' and 'biodegradable' plastics in the ocean. Much of the biodegradable plastics market is focussed on packaging, single-use consumer products, and horticultural applications. This suggests that the input of biodegradable plastic into the ocean will be broadly similar to the overall plastic input when adjusted for regional differences in uptake of biodegradable plastics. As the quantity and types of plastic entering the ocean is unknown it follows that the quantity of biodegradable plastics entering the ocean is also unknown.

The exact quantities of different polymers observed in the marine environment will depend on the nature of local and regional sources, long-distance transport pathways, material properties (size, shape, density) and conditions experienced at each location (e.g. UV irradiance, temperature, oxygen level, physical disturbance, biological factors). Sampling methods commonly under-sample material < 330 microns in diameter, and identification is usually restricted to the major polymer types. Sampling at mid-water depths and at or near the seabed is much more resource intensive than sampling the sea surface or shoreline, and is conducted much less frequently.

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4.2 The fate of biodegradable plastic in the ocean

Degradation processes

Biodegradable plastics in the marine environment will behave quite differently than in a terrestrial setting (soil, landfill, composter) as the conditions required for rapid biodegradation are unlikely to occur. Plastics lying on the shoreline will be exposed to UV and oxidation and fragmentation will occur, a process that will be more rapid in regions subject to higher temperatures or where physical abrasion takes place. Once larger items or fragments become buried in sediment or enter the water column then the rate of fragmentation will slow dramatically. Experimental studies of biodegradation of polymers in seawater are rather limited in number, and the results have to be placed in the context of natural conditions (UV, temperature, oxygen, presence of suitable microbiota), as well as the characteristics of the polymer. For example, PE degradation rates may be a little higher in tropics due to higher temperatures, higher dissolved oxygen and a favourable microbial assemblage, but they remain very low (Sudhakar et al. 2007).

Table 4.1 Selection of reported polymer compositions in a variety of media (GESAMP 2015).

MATRIX	SIZE	POLYMER COMPOSITION	REFERENCE
sediment/ shoreline	< 1 mm	PES (56%), AC (23%), PP (7%), PE (6%), PA (3%).	Browne et al. (2011)
sediment/ sewage disposal site	< 1 mm	PES (78%), AC (22%)	Browne et al. (2011)
sediment/ beach	< 1 mm	PES (35%), PVC (26%), PA (18%), AC, PP, PE, EPS	Browne et al. (2008)
sediment /Inter- and sub-tidal	0.03-0.5 mm	PE (48.4%), PP (34.1%), PP+PE (5.2%), PES (3.6%), PAN (2.6%), PS (3.5%), AKD (1.4%), PVC (0.5%), PVA (0.4%), PA (0.3%)	Vianello et al. (2013)
sediment/ beach	1-5 mm (pellet)	PE (54, 87, 90, 78%), PP (32, 13, 10, 22%)	Karapanagioti et al. (2011)
water/ coastal surface microlayer	< 1 mm	AKD (75%), PSA (20%), PP+PE (2%), PE, PET, EPS	Song et al. (2013)
water/ sewage effluent	< 1 mm	PES (67%), AC (17%), PA (16%),	Browne et al. (2011)
fish	0.13-14.3 mm	PA (35.6%), PES (5.1%), PS (0.9%), LDPE (0.3%) AC (0.3%), rayon (57.8%)	Lusher et al. (2012)
bird	-	PE (50.5%), PP (22.8%), PC and ABS (3.4%), PS (0.6%), not-identified (22.8%)	Yamashita et al. (2011)

Bacteria capable of degrading PCL have been isolated from deep seawater off the coast of Japan (Sekiguchi et al. 2011). Pitting and loss of structural integrity was observed when PCL was exposed to species of the genera *Pseudomonas, Alcanivorax,* and *Tenacibaculum*. The time-dependence and extent of biodegradation was expected to be influenced by competition from other colonizing bacteria as well as temperature and oxygen levels. The addition of PLA to PUR was shown to increase the rate of degradation in seawater (Moravek et al. 2009). However, the reaction was very temperature dependent and the results have limited applicability to natural conditions. Experimental studies on carrier bags composed of the starch-based Mater-Bi™ led to the conclusion that such bags would not automatically reduce or provide a solution to the environmental impacts caused by marine litter, on the basis of the slow rate of degradation observed in marine ecosystems (Accinelli et al. 2013). Biodegradation of plastics that are considered recalcitrant, such as PE, can take place in the marine environment at an extremely slow rate. There is limited evidence suggesting that microbial degradation of the surface of PE particles happens in the marine environment (Zettler et al. 2013).

Interactions with species

Many species are affected by interaction with marine plastics, either by ingestion or by entanglement. Toothed whales, sea turtles and seagulls commonly are found to contain large quantities of plastic within their guts during necropsies of beached specimens. It is thought that plastic items are mistaken for prey and, when swallowed, block the gut and cause starvation. The degree to which the presence of plastic causes the death of the specimen is difficult to quantify but it does appear to have been a significant factor in many cases. Conditions within an organism may be very different from the ambient environment (e.g. gut chemistry, enzyme activity, microbial action). Differences in the behaviour of some polymers within an organism, compared with externally, *may occur* but this has not been documented sufficiently and is likely to be species-specific.

Perhaps the most relevant study examined the degradation of plastic carrier bags in gastrointestinal fluids of two species of sea turtle: the herbivore Green turtle (Chelonia mydas) and carnivore Loggerhead turtle (Caretta caretta) (Műller et al. 2012). Fluids were collected from the stomach, the small intestine and large intestine of freshly dead specimens. Three types of polymer were used: conventional HDPE, oxo-degradable, and a biodegradable PBAT/Starch blend (Mater-Bi™).

Changes in polymer mass were measured over 49 days (standard test procedure) after which weight losses were as follows: HDPE – negligible, oxo-degradable – negligible, and biodegradable – 4.5 – 8.5%. This is much slower that the degradation rates claimed by the manufacturers for industrial composting. The study demonstrated that degradation of plastic was much slower than for normal dietary items. The lower rate of degradation in the Loggerhead may be due to differences in diet and associated enzyme activity.

Biodegradable polymers and ghost fishing

Many fisheries use pots or small fixed nets. For example, there are estimated to be approximately 77,000 fishing vessels operating in the waters of the Republic of Korea using this type of gear (Kim et al. 2014a). These are frequently lost due to gear conflicts or adverse weather conditions. In the Gulf of Maine alone, it is estimated that 175,000 lobster traps are lost each year[4].

Some studies have examined the feasibility of using biodegradable polymers in the design of fishing gear to reduce the impact of 'ghost fishing', a term used to describe the tendency for lost or discarded fishing gear to continue to trap marine organisms, leading to an unnecessary depletion of populations. Kim et al. (2014b) tested the performance of conger eel pots by comparing commercial pots used in the Republic of Korea with pots constructed with biodegradable (PBS) polymers for key components, using a number of mechanical tests as well as their effectiveness. The fishing performance was similar, although the biodegradable pots caught fewer smaller individuals, which was an unexpected bonus. In the commercial fishery the pots are usually replaced every two years, and so the durability of the biodegradable components would be sufficient. The main advantage would be for pots that were not recovered, as the efficacy of the biodegradable components, specifically designed to have a limited life in the marine environment, would be expected to decline and reduce the extent of continuing ghost fishing. The main disadvantage is that the biodegradable pots are more expensive so it is unlikely they will be exploited by the industry without financial incentives.

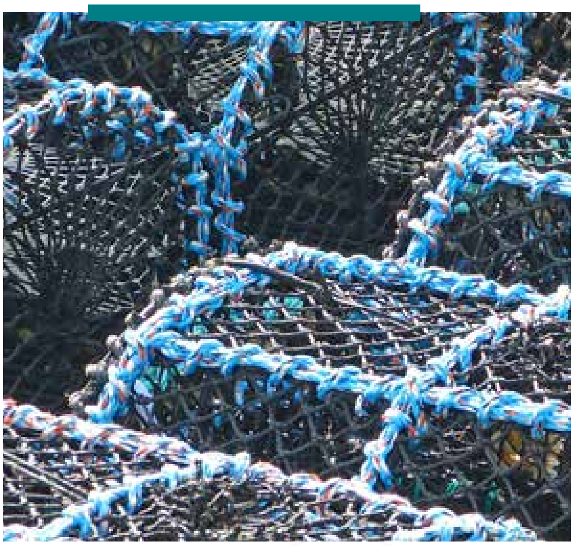

PHOTO: © CHRISTOPHER DART / CREATIVE COMMON

Table 4.2 Weight loss of three types of plastic bag in the gastrointestinal fluids of Green turtle (Chelonia mydas) and Loggerhead turtle (Caretta caretta) (Műller et al. 2012)

POLYMER TYPE	POLYMER SOURCE	WEIGHT LOSS AFTER 49 DAYS
HDPE	Shopping carrier bag	negligible
Oxo-degradable	Shopping carrier bag – PE with pro-oxidant (d2w™ technology)	negligible
Biodegradable	Shopping carrier bag – starch-based Mater-Bi™ from BioBag®	Green turtle 8.5% Loggerhead turtle 4.5 %

Experiments using PE and biodegradable (PBS) components for pot nets in the Korean octopus fisheries (Octopus minor) produced more mixed results, with fishing performance significantly lower using biodegradable polymers (Kim et al. 2014a). Octopus are very sensitive to the softness of the twine used in the trap, which shows that an understanding of species behaviour and the characteristics of the fishery is essential before making recommendations of what design is most 'environmentally friendly'. The modified pot nets were also more expensive than those made with standard PE.

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[4] Gulf of Maine Lobster Foundation http://www.geargrab.org/

5

PUBLIC PERCEPTIONS, ATTITUDES AND BEHAVIOURS

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PUBLIC PERCEPTIONS, ATTITUDES AND BEHAVIOURS

A number of studies have shown that attitudes towards the marine environment are influenced by age, educational level, gender and cultural background. Very few studies have been conducted on attitudes to marine litter and on the factors that contribute to littering behaviour (Whyles et al. 2014). A study of attitudes of European populations found that Governments and policy were considered to be most responsible for the reduction of marine litter, whereas environmental groups were considered to be most capable of making a difference (Bonny Hartley pers. comm.).

Human perceptions influence personal behaviour, legislative and commercial decisions. Some, albeit limited evidence suggests that some people are attracted by 'technological solutions' as an alternative to changing behaviour. In the present context, labelling a product as biodegradable may be seen as a technical fix that removes responsibility from the individual. A perceived lower responsibility will result in a reluctance to take action (Klöckner 2013). A survey of littering behaviour in young people in Los Angeles revealed that labelling a product as 'biodegradable' was one of several factors that would be more likely to result in littering behaviour (Keep Los Angeles Beautiful, 2009). Whether similar attitudes occur in different age and cultural groups and in different regions globally is unknown, and more research is justified.

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Labelling a product as biodegradable may be seen as a technical fix that removes responsibility from the individual.

6

CONCLUSIONS

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CONCLUSIONS

- Plastic debris is ubiquitous in the marine environment, comes from a multitude of sources and is composed of a great variety of polymers and copolymers, which can be grouped into a relatively limited number of major classes.
- Polymers most commonly used for general applications, with the required chemical and mechanical properties (e.g. PE, PP, PVC) are not readily biodegradable, especially in the marine environment.
- Polymers which will biodegrade in the terrestrial environment, under favourable conditions (e.g. AcC, PBS, PCL, PES, PVA), also biodegrade in the marine environment, but much more slowly and their widespread use is likely to lead to continuing littering problems and undesirable impacts.
- Biodegradable polymers tend to be significantly more expensive. Their adoption, in place of lower-cost alternatives, for well-justified purposes (e.g. key components of a fishing trap) may require financial inducement.
- The inclusion of a pro-oxidant, such as manganese, in oxo-degradable polymers is claimed to promote fragmentation by UV irradiation and oxygen. The fate of these fragments (microplastics) is unclear, but it should be assumed that oxo-degradable polymers will add to the quantity of microplastics in the oceans, until overwhelming independent evidence suggests otherwise. The current usage of these polymers is very limited.
- Oxo-degradable polymers do not fragment rapidly in the marine environment (i.e. persist > 2-5 years) and so manufactured items will continue to cause littering problems and lead to undesirable impacts.
- Some of the claims and counter-claims about particular types of polymer, and their propensity to biodegrade in the environment, appear to be influenced by commercial interests.
- Some evidence albeit limited suggests that public perceptions about whether an item is biodegradable can influence littering behaviour; i.e. if a bag is marked as biodegradable it is more likely to be discarded inappropriately.
- On the balance of the available evidence, biodegradable plastics will not play a significant role in reducing marine litter.

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