Degradable Polymers

Principles and Applications

2nd Edition

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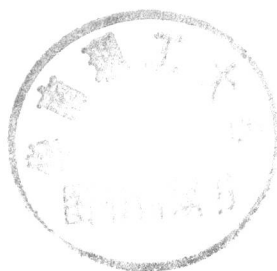
Degradable Polymers

Principles and Applications

2nd Edition

Edited by

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WHY DEGRADABLE POLYMERS?

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1   Polymers in modern society

Polymers have gained a unique position in modern materials technology for a number of quite different reasons. The development of the inflatable rubber tyre in modern transport would not have been possible without the use of natural, and later synthetic, rubbers as the energy absorbing components. 'Plastics', have largely replaced traditional materials used in packaging because of their better physical properties, notably strength and toughness, lightness and barrier properties. Their ability to protect perishable commodities against spoilage at minimal cost has led to a revolution in the distribution of foodstuffs to the extent that they are now indispensable in modern retailing [1].

Plastics are also energy-efficient compared with traditional materials [1]. It takes twice the weight of paper to effectively protect goods than in the case of polyethylene and if all the plastics currently used in packaging were to be replaced by paper, the effect on the environment would be catastrophic in terms of forest depletion, increased energy utilisation and damage to the environment [2,3]. This ecologically important characteristic of the polyolefins will be discussed in more detail in Section 4.

2   The management of polymer wastes

The volume of plastics, synthetic fibres and rubber that appear as wastes presents disposal authorities with an increasingly serious problem. At one time it was relatively inexpensive to dispose of domestic and industrial wastes in holes in the ground on the peripheries of towns and cities. The reduction in the number of such sites, coupled with the increasing bulk of the wastes means that the cost of transporting packaging wastes to available landfill sites has increased unacceptably. There is also an increasing recognition that society should treat waste as a resource to be re-utilised by 'recycling' to useful products rather than by burying them. Consequently the disposal of packaging waste has become the responsibility of the producer of the packaging. Landfill taxes have

been introduced in the developed countries to recover materials that would have originally gone to landfill from the waste stream for recycling [4].

It is now accepted, for reasons that will become apparent in the following discussion, that the term 'recycling' must be broadened to include not only reprocessing or **mechanical recycling**, but also other methods of conserving the intrinsic value of the materials, including **energy recycling** and **biological recycling**. The alternative ways of constructively utilising waste will be discussed in more detail in Chapter 14. It now seems likely that before the end of the second decade of this century, domestic and industrial wastes will be reused by a combination of these methods and that only wastes with little or no potential value will be disposed of in sanitary landfill [4-6].

2.1 MECHANICAL RECYCLING

During the past decade it has been recognised that the initial enthusiasm shown for mechanical recycling by environmental enthusiasts [7-9] was somewhat misplaced [4]. It was assumed that plastics could be recycled to the original products in the same way as metals and glass. Some industrial products such as automotive components (e.g. battery cases and bumpers) and some packaging (e.g. crates and shrink-wrap film) can be readily recovered from the waste stream [10] and, because they are generally well protected from environmental degradation by antioxidants and stabilisers in their first life, they may be recycled in a 'closed loop' [4]. However, plastics packaging and other disposable products such as plastics plates and cutlery from domestic wastes and retail outlets comprises over 60% of the post-user plastics wastes generated and it is technically much more difficult to reprocess this waste to useful products [10,11]. There are two associated reasons for this. The first is that they are normally highly contaminated by non-polymer components, notably fats, oils and transition metal ions that reduce the quality of the recycled products. The high surface area to mass ratio of packaging makes it difficult and generally quite uneconomic to segregate and cleanse them after collection. 'Kerb-side' collection of individual polymer components of packaging already segregated by the householder offers a potential solution to this practical problem, particularly for the more expensive packaging materials such as the polyesters (PET).

The second reason is not quite so obvious. Approximately one third of the fossil fuel energy that goes into the initial manufacture of plastics products is used in transforming the polymer from pellets to the final product [6,12]. Even more energy is used in recycling, since the recovered polymer has to be first cleansed and shredded or ground. The energy (and cost) of collection, segregation and cleansing, mechanical recycling of plastics packaging waste from domestic sources may be up to twice that used in the fabrication of the original package [13,14]. Since the energy used in manufacture is at present almost entirely derived from fossil fuel resources, mechanical recycling of single-component plastics packaging from domestic sources may actually waste fossil resources rather than save them.

Mechanical recycling of mixed plastics wastes is an even more contentious issue due to the poor mechanical properties and durability of blends of mixed plastics [10,11]. The first can be overcome to some extent by using expensive solid phase dispersants ('compatibilizers') but most recyclers of mixed plastics cannot afford to use this technology and instead rely on thick sections of the recycled product to provide acceptable mechanical performance (e.g. as wood substitutes for park benches, docks, road signs, etc). However, it has been shown in a critical study of the Duales

Deutschland System (DSD) [13] that to compete with conventional materials such as wood and concrete, plastics recycled from domestic waste would have to last 3.3 times as long as the materials they replace. From the known properties of recycled mixed plastics it is most unlikely that this could be achieved [10].

2.2   ENERGY RECYCLING

Polyolefins differ from metals and glass in that when incinerated they produce energy equivalent to the oil from which they were originally manufactured [12]. This then in principle gives them a second life as a source of energy. Unfortunately incineration is looked upon with considerable suspicion in most developed societies since there is evidence that dioxins and other toxic products may be present in the atmosphere downwind from incinerators [4], often situated in or near conurbations. This has been attributed particularly to chlorine-containing polymers that are also difficult to incinerate as a result of the formation of highly corrosive hydrogen chloride in the plant. Polyolefins and other hydrocarbon polymers are rather different since they produce only carbon dioxide and water on complete incineration. There is therefore considerable potential for utilising waste polyolefins in energy generation, particularly in cement or steel furnaces [13].

Alternatives to incineration with energy recovery are to pyrolyse or hydrogenate waste plastics to give liquid fuels or new polymer feed-stocks [4]. The advantage of this approach is that the wastes can be processed under controlled industrial conditions to give portable liquids for use elsewhere. The disadvantages are that substantial amounts of thermal energy have to be used to obtain useful chemicals.

2.3.   BIOCYCLING

It will be evident from the above discussion that neither mechanical recycling nor energy recycling provides a complete solution to the problems of plastics wastes in modern society. In particular, plastics litter is normally found in locations that make it prohibitive to collect wastes for mechanical or energy recycling. In this situation, the concept of reabsorbing plastics into the biological cycle is an attractive ecological alternative to locking away polymer wastes in expensive landfill. Technologies for achieving this with the polyolefins were pioneered in universities some time before mechanical or energy recycling were considered to be viable alternatives to landfill disposal.

3   Biodegradable polymers

During the 1960s percipient environmentalists became aware that the increase in volume of synthetic polymers, particularly in the form of one-trip packaging, presented a potential threat to the environment. This was particularly evident in the appearance of persistent plastics packaging litter in the streets, in the countryside and in the seas. Not only was this aesthetically undesirable but it presented a potential threat to animals and birds both on land and in the sea. The first practical response to this threat came from academe rather than industry. Several university groups, as part of their research

programmes into polymer stabilisation were aware of the basic scientific reasons for the environmental instability of polymers and were able to develop technologies to induce polymer degradation in existing commercial polymers in a controlled way. Because of the well-understood mechanisms of polymer degradation and stabilisation, the hydrocarbon polymers were selected as the basis for polymers with enhanced but controlled degradation. However, this solution was not well received by industry since considerable research had been invested in developing antioxidants and light stabilisers to produce polymers as environmentally stable as natural products such as metals, glass and wood. It was argued that the way forward was to recover the original materials by recycling and that the development of degradable polymers would threaten the recycling strategy.

3.1 BIODEGRADABLE POLYMERS BASED ON POLYOLEFINS

Table 1 shows some commercial degradable plastics based on polyolefins originally developed in the in the 1970s. In some cases they have been successfully used in agriculture and to a more limited extent in packaging applications for more than 20 years. Regular polyolefins are not biodegradable in an acceptable time, since they are protected by antioxidants and stabilisers incorporated during processing to provide durability during use. However, polyolefins can be made sensitive to heat or light in the presence of oxygen after use to give bioassimilable products [3,16-20]. In the **oxo-biodegradation** process bioassimilation is controlled by abiotic (and occasionally biotic) peroxidation and is mechanistically distinguished from **hydro-biodegradation** in which bio-assimilation is preceded by hydrolysis (e.g. in polysaccharides, polyesters, etc.) [18,21].

Table 1. Early commercial degradable polyolefins

Photolytic polymers

Ethylene-carbon monoxide copolymers: E-CO, Ethylene-vinyl ketone copolymers: Ecolyte[TM] (J.E.Guillet) [3,15,16]

Oxo-biodegradable polymers

Antioxidant controlled, transition metal-catalysed photo- and thermooxidisable polymers:
Plastor[TM] (G.Scott-D.Gilead) [17-20]

PE-Starch blends

PE blended with starch (and in later developments with prooxidants):
Coloroll, St.Lawrence Starch (G.J.L.Griffin) [22]

It is instructive to explore in more detail the reason why polyolefins were initially selected for development as degradable polymers rather than natural products such as cellulose, which was already available commercially in derivatized form as cellulose

acetate. The latter was known to be slowly biodegradable but suffered from a number of technical deficiencies, of which the most important was that the extraction of cellulose from natural products was both energy intensive and polluting compared with the polyolefins [4]. Furthermore the modification of cellulose by acetylation to give technologically acceptable products sharply reduced the environmental biodegradability of the base polymer [18]. Consequently it is difficult to achieve an acceptable balance between the required technological performance and ultimate biodegradability. More recent experience has shown that this is a significant problem with other hydro-biodegradable polymers of biological origin and indeed it is in the nature of hydrophilic natural polymers such as cellulose and starch to be rapidly bioassimilated by hydrolytic microorganisms and any attempt to improve technological properties by chemical or physical modification interferes with nature's intention. The hydrophobic polymers such as natural rubber and the synthetic polyolefins stand at the other end of a spectrum of technological and ecological properties (Fig.1) [23]. Synthetic plastics have achieved a central position in the distribution of consumer goods because of their combination of flexibility, toughness and excellent barrier properties, which has made them the materials of choice for packaging applications. The polyolefins have been found to be particularly important in blown film and injection moulding technologies because of their ease of conversion and low cost. The present-day efficient distribution of perishable foodstuffs is a direct consequence of the low cost of polyolefin packaging and its resistance to water and water-borne microorganisms during use [1].

Increase in biodegradability
——➤

Polyolefins Hydrophobic Bio-inert	Oxidation ⟶	Oxo-bio-degradable acids,alcohols		
		Hydro-bio-degradable saccharides, acids,alcohols	Modification ⟵ Hydrolysis	Polysaccharides Polyesters Hydrophilic Intrinsically biodegradable

⟵——
Increase in technological usefulness
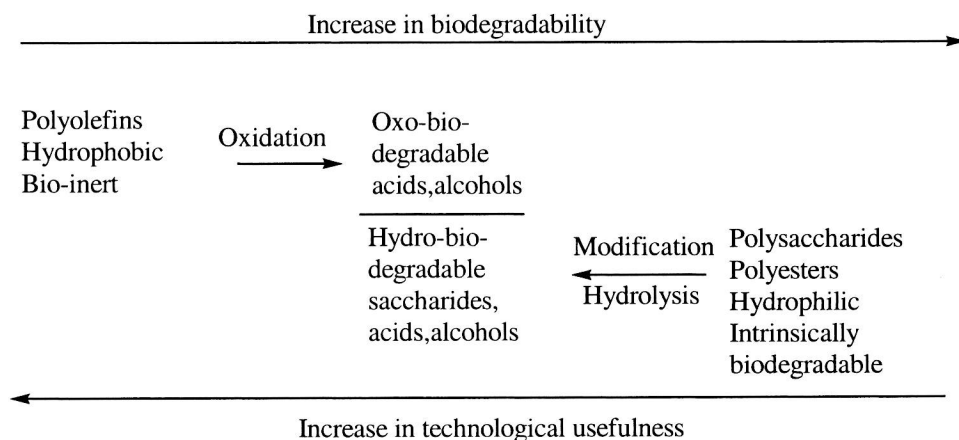
Fig. 1. Alternative approaches to environmentally acceptable polymers [23]

In agriculture, the new technology of plasticulture, based on polyethylene, has led to a revolution in the growing of soft fruits and vegetables. Polyolefins do not hydrolyse under any practical conditions but, as already indicated, they do oxidise rapidly in the environment unless protected by antioxidants and particularly in the presence of the oxygenase enzymes they are bioassimilated. A major advantage of the polyolefins is then

that oxo-biodegradation can be degraded in a controlled way involving both prooxidant and antioxidants. This will be discussed in more detail in Chapter 3.

During the 1980s, trade associations such as the British Plastics Federation, the Industry Committee for Packging and the Environment (INCPEN) in the UK and the Council for Solid Waste Solutions in the USA positively campaigned against degradable plastics, primarily on the grounds that that induced degradability would interfere with recycling [24-26]. Consequently the subsequent development of polyolefins with induced degradability was developed by polymer additive companies in association with universities and the outcome of these development will be discussed in later chapters in this book.

## 3.2 BIODEGRADABLE POLYMERS BASED ON RENEWABLE RESOURCES

The search for biodegradable polymers based on renewable resources, which began in the 1980s, has been compared to the search for the holy grail [27]. It has been embraced with enthusiasm by the 'green' movement [28] and has in turn influenced the scientific community and subsequently the even the sceptical polymer manufacturing industry itself. The following are the stated objectives of this search [27];

1.   To replace polyolefins (PO) and polyvinyl chloride (PVC) regardless of which properties are looked for.
2.   To match the production costs of PO and PVC.
3.   The reduce the full 'metabolic burning time' to two composting cycles (30 days) in a technical composting unit.

The renewability concept, which is frequently confused with sustainability (see Section 4), has now been embraced by the polymer industries. The first fully bio-synthetic/biodegradable polymer, poly-(3-hydroxy-butyrate) (PHB), although originally discovered in 1925 [29], was developed on a semi-technical scale by ICI in the 1980s by microbial fermentation of sugar. The development of this and related polyesters, the poly(alkanoates) (PHAs) was described by Hamond and Liggat in the first edition of this book [30] and has stimulated a search for other bio-based biodegradable polymers. Poly(lactic acid) (PLA), a hydro-biodegradable polymer synthesised from corn sugar by conventional abiotc chemistry, is now made on a small commercial scale. Its properties have been intensively studied and the mechanical behaviour of PLA is reported to be similar to that of polyethylene. However, cost and performance still lack the economic attractions of the polyolefins. The PHAs similarly have so far not had an easy technological development as they have been passed from one company to another. Progress toward the development of sustainable PHAs that satisfy the consumer market still lies in the future and scientific approaches to this objective will be discussed in Chapters 9 and 10.

$$\begin{array}{cc}
R & CH_3 \\
| & | \\
[\text{-OCHCH}_2\text{CO-}]_n & [\text{-OCHCO-}]_n \\
\end{array}$$
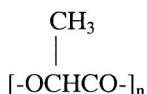
PHA , PHB, $R = CH_3$ PLA

Starch, normally obtained from cereals, is of little value to the plastics industry in its natural form. However, by the process of extrusion cooking, it can be made into a plastic which, when plasticised, approaches the properties of the commodity plastics (see Chapter 6}. The ideological argument for using starch as a base material for plastics is that it hydro-biodegrades rapidly in the environment. Corn starch, is a relatively cheap commodity and producers in the more affluent counties would like to find an outlet for current excess capacity. However, the fact that it is renewable and cheap does not necessarily mean that it is sustainable and if the requirements of the above paradigm are to be met, then the agricultural production of starch for the plastics industry must soon come in conflict with the production of food (Section 4). The production of commodity plastics from a temporary excess of food is not then a long-term sustainable policy for an already overpopulated world. This does not mean that polymers based on carbohydrates will not find niche applications and, if the vast amounts of waste cellulose could be utilised by means of 'green' chemistry, cellulose-derived product could make a substantial impact on the packaging industry.

Nature's cellulose-based litter abounds on land and in the sea. Most of this is in combination with lignin and in principle there is the possibility of utilising these abundant materials as the basis of a genuinely sustainable polymer industry. However, useful products are not achieved at present without the input of fossil fuel energy (see Section 4). Renewability alone is then not a sufficient criterion of ecological acceptability. Packaging polymers are required not only to be compatible with the natural biocycle but they must also fulfil their intended function for the benefit of society [1] and at the same time be economic in the use of fossil resources [4]. The ideal renewable polymer has so proved to be difficult to achieve for these purely practical reasons.

3   Custom design of biodegradable polymers

3.1   END-OF-LIFE DESIGN

It is now recognised for the reasons discussed above that the design of biodegradable polymers depends on the end-of-life environment as well as on service requirements. Typical examples are items intended to end up primarily in sewage [18], which should be substantially converted to CO_2 and associated cell biomass during the time it is in the sewage plant. Some, but not all bio-based polymers (modified starch and aliphatic polyesters) satisfy this requirement and are suitable for the manufacture of short-lived personal hygiene products such as diapers, etc.

Agricultural products such as mulching films and tunnels have quite different service requirements and end-of-life requirements from domestic packaging (Chapter 14). Garden waste sacks and some food packaging may appear in municipal compost where a longer biodegradation time is not only reasonable but is also ecologically desirable (see Section 4). Agricultural mulch, silage films and fertilizer sacks and animal feed bags, either deliberately or inadvertently remain on the land as litter. To fulfil their design purpose, all these products require a safety period in use before they begin to biodegrade. There are also very important applications for biodegradable polymers in the body either in controlled drug release or in sutures and related applications where very specific durability requirements apply.

The long-term effects of man-made materials in the environment are as important, if not more important than their initial impact as litter. The use of degradable materials in consumer products, in agriculture and in prostheses should not lead to the generation of toxic or otherwise environmentally unacceptable chemicals in the human environment. For example the polyolefins that contain only carbon and hydrogen are converted by peroxidation to low molar mass carboxylic acids, hydroxy acids and alcohols that are nutrients for microorganisms. They thus appear ultimately as carbon dioxide and water (Chapter 3). Chlorinated polymers and other polymers containing hetero-atoms other than oxygen and nitrogen by contrast must be viewed with some suspicion. Low molar mass organo-chlorine compounds represent a particular threat to the environment due to their persistence and it is critically important that new polymers that are intended to biodegrade rapidly in the environment should be carefully assessed by standardisation organisations for eco-toxicity effects before being allowed into general application in waste and litter control. This will be discussed in Chapter 14.

3.2   DESIGN FOR SERVICE-LIFE

The applications of biodegradable polymers fall into two distinct categories. In the first, biodegradability is an essential part of the function of the product. Examples are temporary sutures in the body during surgery or the therapeutic controlled release of drugs (Chapter 10). In both, cost is relatively unimportant provided that the artefacts fulfil their intended purpose. Similarly in agriculture where very thin films of photo-biodegradable polyolefins (mulching films) are used to increase soil temperature, ensuring earlier harvest. A major ecological benefit of plastics mulch is to reduce the use of irrigation water and fertilisers, an increasingly important objective in parts of the world where water is scarce and becoming scarcer [19]. An important requirement is that no significant quantity of plastics residues must persist in the soil in subsequent seasons since these interfere with root growth and reduce productivity. The technological design and use of biodegradable polymers in agriculture is motivated by economics since the need to remove films from the land is eliminated [18-20,31,32] (see Chapter 14).

The second use of biodegradable polymers is in applications such as packaging where their use brings social benefit but does not bring overt economic gains to the manufacturer or user [33]. Biodegradable plastics do not add to the technological performance of a packaging material and manufacturers are reluctant to invest in new materials that do not bring cost-benefit. Consequently few developments in degradable packaging have established a position the marketplace during the past 15 years. Ethylene-carbon monoxide co-polymer (E-CO) is used in six-pack collars and has made a significant contribution in the protection of birds and animals from entrapment by carelessly discarded packaging [16,34] (see Chapter 13).

4   Life-cycle assessment

During the 1970s there was a popular but rather naive belief in industry that the incorporation of biodegradable materials such as starch into synthetic polymers such as polyethylene would transform these relatively intractable materials into environ-mentally biodegradable products. This was subsequently shown not to be the case but it

resulted in serious over claiming by industrial companies wishing to take advantage of public enthusiasm for "environmentally friendly" packaging materials. This was categorised as "deceptive" by legislators. A timely and valuable investigation was carried out into "green marketing" by a Working Group of the Attorneys General of the USA. Their conclusions were summarised in "The 'Green Report' in 1990 [35], which subsequently provided a basis for standards for degradable polymers. The salient conclusions as to the purpose of such standards may be summarised as follows.

1.   To protect the environment
2.   To provide a 'level playing field" for business
3.   To clarify competing claims for the benefit of the consumer

The basis proposed for the 'level playing field' is that "environmental claims must be uniform and supported by competent and reliable scientific evidence". The use of the term "environmentally friendly" was particularly criticised as being a vague term in normal use that was not based on objective criteria. It was concluded that this term should not be used unless product was first subjected to life-cycle assessment. The definition of LCA in the 'Green Report' given below is now the basis of LCA techniques as currently practiced.

"Product life-cycle assessment involves consideration of environmental effects at every stage in the products life-cycle, including the natural resources and energy consumed and the waste created in the manufacture, distribution and disposal of a product and its packaging......Such assessments will only provide useful comparative information about how to reduce environmental problems associated with products if they are conducted using uniform and consistent assumptions"

The term "environmentally friendly" has more recently been superseded by its modern equivalents "renewable" and "sustainable". As already discussed, it is sometimes assumed that polymers from renewable resources are by definition 'sustainable'. One definition of "sustainable" suggests that the development of new products for the benefit of society should not have an unacceptable effect on resource depletion and environmental pollution. However, 'acceptable' is a relative term and invites comparison of one material with another by life-cycle assessment (LCA) [4]. Companies engaged in the development degradable polymers from renewable resources have initiated life-cycle assessment comparisons of their products with the commodity synthetic polymers; notably polyethylene. As will be seen in the following Sections, these have not so far shown unambiguously that bio-based polymers are more environmentally sustainable than the present range of commodity polymers [36]. This results from the same reason that led to the "Green Report"; namely lack of consistency and uniformity of the assumptions made. In some cases they actually contradict one another.

4.1 ENERGY BALANCE DURING MANUFACTURE AND DISPOSAL

Energy input data for the manufacture of polyethylene quoted in the literature vary between ca. 65 GJ/t and 80 GJ/t [37]. . However, Dinkel et al. on behalf of Carbotech, in

an LCA comparison of starch polymers with that of low density polyethylene [38], assumed a value of 92 GJ/t producing an immediate bias toward starch polymers.

Published LCAs of degradable polymers [14,38-42] assume that PE is disposed of only in landfill or by incineration. There is no recognition that PE can be "recovered" from the waste stream by composting (see Section 4.2), by pyrolysis to give monomers and fuels or by incineration with energy recovery. In practice, since the calorific value of PE (43 GJ/t) is almost identical to that of the oil from which it was manufactured, the carbon content of the plastic is ecologically neutral. The total non-recoverable energy used in the manufacture of PE is thus 21.6 GJ/t [12], not 65 GJ/t. This compares with the energy used in the manufacture of starch (Mater-Bi) products, which vary between 25.4 GJ/t and 52.5 GJ/t, depending on the co-agent in the formulations. Although the carbon energy input is assumed to be zero, since it is biosynthesised and returned to the carbon cycle by biodegradation, this does not apply to blends with fossil-based additives or polymers (co-agents) [36]. If biopolymers are used as a source of fuel in waste-to-energy incineration, the energy produced is considerably less from polysaccharides than that from PE. These data cast some doubt on the ecological benefits of bio-based polymers and emphasises the importance of using the same assumptions to produce the "level playing field".

4.2 LAND RESOURCE UTILISATION

None of the LCA studies have so far considered land utilisation in the ecological balance. At present bio-based polymers such as PHA, PLA and starch are produced from food crops. This does not present a problem in the short-term if the polymers are to be used in specialised 'niche' applications on the basis of a temporary surplus of food crops but it cannot be used as the basis of long-term sustainable development of bio-based plastics to replace polyolefins in packaging (Section 3.2). For example the anticipated scale of production of PLA during the present decade (not more than 500,000 tonnes/annum worldwide) is less than 1% of the worldwide production of polyolefins and, if the production of food-based biodegradable polymers was to increase toward the level of the fossil-based polymers, there would be serious competition between polymer and food production [18]. However, if, as discussed for cellulosic materials, bio-based feedstocks could be based on biological wastes or on crops grown on marginal land, then the situation would be changed. This represents a major challenge to the bioengineering industry and will be discussed further in later Chapters.

4.3 BIODEGRADATION TIME-SCALE

The final criterion of sustainability is the ultimate return of the materials to the carbon cycle. However, the assumption that fossil-based polymers do not biodegrade in the environment is not valid since polyolefins can be returned to the soil where they contribute to the fertility of the earth. It does a disservice to nature's versatility to draw a sharp distinction between natural and synthetic organic polymers. There is, for example, no intrinsic difference between the biodegradation of natural and synthetic rubbers. Both oxo-biodegrade in exactly the same way when first manufactured and both become highly resistant to biodegradation when formulated with antioxidants, for example in motor car tyres. The non-biodegradability of fully formulated engineering rubbers, whether natural or synthetic, as in the case of the commodity synthetic plastics, has much

more to do with the presence of antioxidants, than with the inherent biodegradability of the polymers themselves. The process of oxo-biodegradation will be discussed in more detail in Chapter 3, but it is important to note here that some of nature's products, notably sequoia wood, are very resistant to degradation in a biotic environment [18]. This again is due to protection by powerful antioxidants and antibacterials (e.g. tannic acids).

5   Biodegradation test methods and standards

Many environmentalists are suspicious of all man-made materials that do not biodegrade rapidly in the environment after they have served their primary purpose. The reason for this is understandable. During the latter half of the twentieth century, it became evident that many industrial and agricultural chemicals have undesirable effects on the environment that could not have been anticipated when they were first introduced. However, this is often also applied to materials that are essentially inert because of their physical form. Polymers fall into this category. Polyvinyl chloride (PVC) has been denigrated because it contains chlorine. In fact PVC is physiologically inert, although vinyl chloride from which it is manufactured is highly toxic. No one knows at present what products are formed from PVC if and when it is induced to biodegrade. It must be assumed, until it is demonstrated otherwise, that the chlorine is only 'safe' in the environment in the form of the commercial undegraded high polymer.

Other carbon-chain polymers, particularly the polyolefins, when used in packaging, again present no toxicity hazard as high molar mass materials. However hydrocarbon polymers, unlike the halogenated polymers, when biodegraded or incinerated, produce only carbon dioxide and water. Even when they are pyrolysed they produce small molecule consisting mainly of a mixture of paraffins (methane, ethane etc) and olefins (ethene, propene, etc.). This process is safe when carried out under controlled conditions in a petrochemical plant [4]. In the environment, polyolefins are broken down by oxygen to a mixture of alcohols, carboxylic acids, hydroxy-carboxylic acids and the lower molar mass homologues are bioassimilated very rapidly *in situ* (see Chapter 3).

In spite of the scientific evidence, the popular perception that "Natural" is "good" and "Synthetic" is "bad" has led to a climate of fear of man-made materials. This has influenced the standards organisations and has resulted in the unscientific requirement that all synthetic polymers must be converted rapidly to carbon dioxide to be considered 'biodegradable'. At the same time, "natural" materials are exempted from this requirement because they are considered to be "by definition biodegradable" [43]. Biometric tests, such as the Sturm test for the measurement of the carbon dioxide produced during biodegradation of water-soluble chemicals are very convenient and easy to use in simple laboratory equipment. They were originally developed as test methods for hydrophylic polymers in sewage systems at ambient temperatures. This type of test is very convenient for measuring the biodegradability of hydro-biodegradable polymers, but it quite inappropriate for hydrophobic polymers degrading by oxo-biodegradation.

Lignocellulose, an abundant oxo-biodegradable aromatic polymer containing C-C and C-O bonds (see Chapter 3), does not biodegrade rapidly in an aqueous environment so it is unreasonable to require that man-made carbon-chain oxo-biodegradable polymers should do so. Furthermore, the requirement that polymers undergo rapid mineralisation in compost [44] is inconsistent with the concept of 'reclamation'. The European 'Waste Framework Directive' 1991 defines "recovery" as follows [45];

"Recycling/reclamation of organic substances…..use as fuel to generate energy and spreading on land resulting in benefit to agriculture or ecological improvement, including composting and other biological processes"

As discussed in Section 4, carbon dioxide generation is considered by LCA to be a negative parameter. CO_2 is an ecological deficit and does not improve the environment. Indeed it is much more beneficial to agriculture and the environment to retain the carbon in the soil as an available nutrient as happens naturally with lignocellulose. Composting standards [44] are much more concerned with the easy disposal of biodegradable plastics than with recovering their value as biomass. The usefulness of plastics as soil improvers would be lost before the compost ever reached the soil. The mechanism of biodegradation of lignocellulose and other naturally occurring carbon-chain polymers will be discussed in Chapter 3 but it should be noted here that similar microoganisms are involved in the biodegradation of the polyolefins, providing a model from which to develop composting test methods to alleviate popular concerns about the biodegradation of man-made polymers. The bioassimilation of carbon-chain polymers will be discussed in more detail in Chapter 14 when the applications of degradable polyolefins will be discussed.

6 Conclusions

During the first half of the twentieth century, the emphasis in the developing plastics industries was to make polymers as resistant as possible to environmental degradation. This tended to obscure the fact that most polymers as manufactured are relatively unstable materials when exposed to the outdoor environment. Consequently, when it became clear that synthetic packaging materials posed a threat to the environment, popular folklore categorised the commodity polymers as "indestructible" and "non-biodegradable".

A scientific understanding of polymer degradation, based on fundamental research on the abiotic environmental degradation of naturally occurring *cis-polyisoprene* rubber provided a rational explanation of why and how natural rubber and later the synthetic hydrocarbon polymers biodegraded and this in turn provided an explanation of how antioxidants inhibited this process in technological applications. It was recognised in the 1960s and 1970s that there was no fundamental difference between natural rubber and its synthetic analogue or in principle between natural rubber and the polyolefin plastics. In the absence of antioxidants, they all peroxidise and biodegrade at predictable rates. An extension of these studies was to use the scientific knowledge gained to develop degradable polyolefins with controlled rates of biodegradation.

However, the popular belief that "natural is good" and "synthetic is bad" has led to the subsequent obfuscation and neglect of this fundamental knowledge and the use of the term "sustainable" has come in recent years to mean polymers made from renewable resources, preferably by biological processes. The use of renewable resources is believed to reduce the exploitation of fossil resources and reduce the "greenhouse" effect. A deeper reflection on these objectives has raised considerable doubt about the premises on which they are based. All chemical processes require an energy input and today the source of this energy is fossil fuels, so that the lower the energy input and the less the associated pollution, the 'greener' is the product [19]. Life cycle assessment provides in