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Polyolefins with controlled environmental degradability

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Abstract

Antioxidants and stabilisers, developed to increase the durability of polyolefins, in combination with prooxidant transition metal complexes provide industrial products with widely variable but controlled lifetimes. The low molar mass oxidation products formed during photo-oxidation and thermal oxidation are biodegradable and oxo-biodegradable polyolefins are now widely used in agricultural applications and in degradable packaging as examples. The scientific basis for the performance of oxo-biodegradable materials is explained with reference to naturally occurring macromolecules. Comparison with hydro-biodegradable materials is made and the need is demonstrated for performance standards to be developed that mimic nature's resource recovery mechanism, that of oxo-biodegradation.
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1. Introduction

It is generally recognized that polyolefins are bioinert, that is, they are highly resistant to assimilation by microorganisms such as fungi, bacteria and the like. This is not surprising since the surfaces of materials and articles made from polyolefins are hydrophobic and thus inhibit the growth of microflora on them. Moreover, there are common mechanisms of biodegradation that involve bioassimilation from the "ends" of substrate molecules. Since commercial polyolefins have relatively high molar mass values, there are very few ends of molecules accessible on or near the surfaces of materials made from these resins. It has been observed, however, that the oxidation products of polyolefins are biodegradable [1–7]. Such products have molar mass values that are significantly reduced, and they incorporate polar, oxygen-containing groups such as acid, alcohol and ketone [8]. This is the basis for the term oxo-biodegradable polyolefins. This concept is used to distinguish polymers that biodegrade by a hydrolysis mechanism from those that are inert to hydrolysis but undergo oxidation [9,10]. Oxo-biodegradation

then denotes a two-stage process involving, in sequence, oxidative degradation, which is normally abiotic in the first instance, followed by the biodegradation of the oxidation products. It should be noted that, considering for the moment a given piece of polyolefin plastic in a microbially active environment, abiotic and biotic degradation will be occurring simultaneously owing to the normal range of molar mass values in commercial materials. The sequence of oxidative degradation followed by biodegradation applies to individual molecules. In reality, as each molecule undergoes oxidative degradation and is reduced in size, a point is reached when microbial degradation will commence. This situation conforms to the definition [10] that a biodegradable polymer is one "in which degradation is mediated at least in part by a biological system".

The rate-determining part of the two-stage process in oxo-biodegradation is the oxidation segment, commonly called peroxidation. It has been demonstrated [1–11] that the biodegradation of polar molecular fragments from polyethylene (PE) occurs relatively rapidly. However, in the conditions in which they are normally employed and disposed of, commercial polyolefin products used for packaging, for example, undergo peroxidation quite slowly. This is because of the presence of antioxidants and other stabilisers, and the

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relatively benign conditions in landfills into which many used plastics are dumped. Moreover, conventional plastics are a real problem in commercial composting operations because they do not undergo abiotic oxidation very rapidly even at the elevated temperatures encountered, and they cannot biodegrade as a result. The persistence of normal industrial plastics causes a visual problem in the compost product and reduces its applicability and hence its commercial value. In addition, although the use of PE as agricultural mulch film is common, the requirement for mechanical property retention by the films until at or near harvesting time, followed by rapid embrittlement [11] cannot be met by simply omitting or even just adjusting the content of the stabiliser(s) added to the resin prior to fabrication. What is needed is a way of controlling the time during which the polyolefin retains its normal, useful properties as well as a way of having it undergo subsequent oxo-biodegradation at a much higher than normal rate that is commensurate with the application and with the disposal environment. The key to this control requirement is a sound understanding of the peroxidation mechanisms and kinetics.

2. Abiotic oxidation of polyolefins

Research stretching back several decades [12–14, and references therein] has established the sequence of reactions that are regarded as the essence of polyolefin peroxidation. Although the products of the oxidation initiated by heat are similar to those resulting from photo-oxidation, it was investigations of the latter which confirmed that it was the presence of sensitising impurities, generated during the fabrication of polyolefin products, that caused the instability of these plastics in the environment [15]. The most significant of these impurities are carbonyl groups [12,15–17] and hydroperoxide groups [12,15,18–20] with the latter of particular importance as a consequence of thermo-oxidation during processing. Scheme 1 illustrates one way of describing the formation of some of the products generated as a result of the peroxidation of PE. The starting point is shown here as a hydroperoxide, the formation of which resulted from shear stresses during extrusion, for example, that caused homolytic bond cleavage. The resultant carbon-centred radical reacted
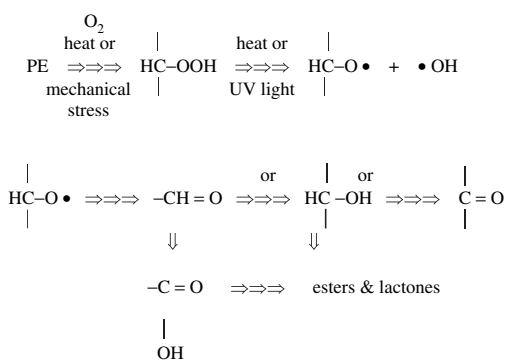
Scheme 1. A simplified scheme that illustrates the degradation, by peroxidation, of PE.

with the oxygen that is never removed completely from the system to form a peroxyl radical which, by hydrogen abstraction, is converted to a hydroperoxide group. This group is unstable to both heat and UV light, and its destruction will lead to the formation of several types of oxygen-containing products. One of the few differences between peroxidation initiated by heat and by light is that ketone products are stable to heat but not to UV light. In either case, one is dealing with a branching chain reaction sequence in which the reaction of the hydroperoxide group is the rate-determining step in peroxidation leading to molar mass reduction. Scheme 1 shows only a part of the reactions relevant to the oxidising system. The formation of low molecular weight biodegradable fragments is discussed in Section 5. However, the reader wishing more details on abiotic degradation is encouraged to consult Refs. [12,13,20,21, and references therein].

In order to focus on polyolefin disintegration, it is necessary to identify those parts of the overall peroxidation process that result in the breaking of C−C bonds in the main polymer backbone. Examples are the beta-scission of the alkoxyl radical (Scheme 1) to produce ketones and aldehydes, which are subsequently oxidised to form carboxylic acids.

Since the properties of PE (and other macromolecular materials) derive in large part from the relatively high molar mass values of the original molecules, molar mass reduction will lead to a reduction in elongation at break (EAB) and to a major reduction in tensile breaking strength. A PE film may, as formed, have an EAB value of 500% or more. After molar mass reduction resulting from significant peroxidation, however, the EAB will have fallen drastically. At less than 5% EAB of the original film, it is considered to be brittle and will fragment even with gentle handling.

3. Controlling peroxidation

It will be evident from the above that although biodegradable plastics are required to disintegrate rapidly followed by biodegradation at the end of their use life, it is equally important that their mechanical properties remain essentially unchanged during use. The rate of peroxidation of hydrocarbons, including polyolefins, depends on two primary parameters. The first is the rate of the free radical chain reaction of the polymer with oxygen, which is in turn governed by the rate of reaction of peroxyl radicals with polymers [12].

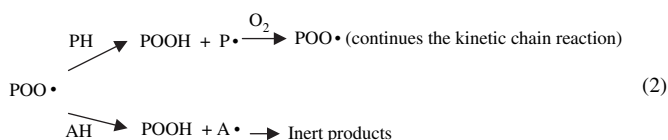$$PH + POO\bullet \rightarrow P\bullet + POOH \qquad (1)$$

where PH = polymer.

The second is the presence of initiators that lead to the formation of radicals, of which the most important are the hydroperoxides (POOH) that are the products of the chain reaction. From this it follows that antioxidants and stabilisers also fall into two categories; the *chain-breaking antioxidants* that deactivate alkylperoxyl radicals and the *preventive antioxidants* that destroy hydroperoxides or otherwise neutralise their action [22].

3.1. Chain-breaking antioxidants

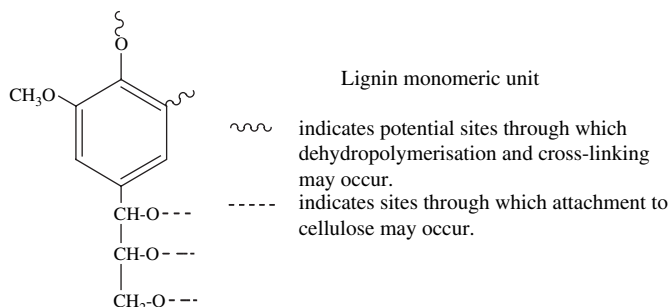Chain-breaking antioxidants can act by two complementary mechanisms.

(a) The *chain-breaking donor* (CB-D) antioxidants, depicted typically as AH, are generally phenols or arylamines that reduce alkylperoxyl radicals more rapidly than the latter can abstract a hydrogen from the substrate (PH), Reaction (2) [12]. A primary requirement is that the aryloxyl or aminoxyl radical (A•) produced should not continue the kinetic chain, Reaction (2). This is normally achieved by delocalisation of the unpaired electron in the aromatic ring and/or by steric hindrance of a group formally containing the unpaired electron.

$$
\begin{array}{c}
\text{PH} \rightarrow \text{POOH} + \text{P} \cdot \xrightarrow{\ O_2\ } \text{POO} \cdot \ (\text{continues the kinetic chain reaction}) \\
\text{POO} \cdot \\
\text{AH} \rightarrow \text{POOH} + \text{A} \cdot \rightarrow \text{Inert products}
\end{array}
\qquad (2)
$$

It is the combination of electronic and steric mechanisms that make the 2,6-di-*tert*-butyl phenols (e.g. BHT) so effective as antioxidants [12,21,22].
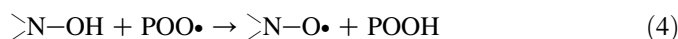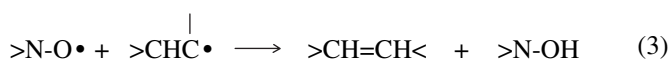

BHT
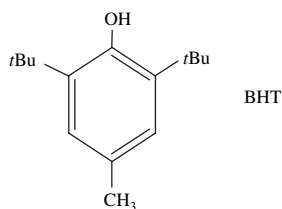
CB-D antioxidants are widely distributed in biological systems to protect substrates that are susceptible to peroxidation from attack by atmospheric oxygen [23]. The best known of these, because of its therapeutic value, is α-tocopherol, which is not a hindered phenol but does form a highly delocalised aryloxyl radical [23]. Other less well-known biological antioxidants that are present in natural products in very large quantities are the polyphenolic natural products such as lignin, the second most abundant polymer on the planet. Lignin contains a high concentration of aromatic structures linked through −C−O− and −C−C− bonds.

Lignin monomeric unit

~~~ indicates potential sites through which dehydropolymerisation and cross-linking may occur.

----- indicates sites through which attachment to cellulose may occur.

Some of the hydroxyl groups in lignin are phenolic and the lower molar mass lignins are very powerful antioxidants that protect the lignocellulose substrate from destruction by molecular oxygen of the environment [24,25]. The lower molecular weight extracts of lignin have been shown to be effective antioxidants in polypropylene [26].

Another group of naturally occurring antioxidants is the tannic acids (tannin), which are biosynthesised from gallic acid by oxidation, Reaction (3) [27]. They contain up to three phenolic hydroxyl groups in the same aromatic ring and are consequently highly effective stabilisers for lignocellulose with which they are normally associated in nature. The outstanding durability of the ''red-wood'' sequoia trees is primarily due to the presence of high concentrations of tannic acids in the bark [28], the colour of the acid gives them their name (Scheme 2).

(b) The *chain-breaking acceptor* (CB-A) antioxidants are oxidising agents. More specifically they are ''stable'' radicals such as aminoxyls ($>$N−O•), which remove a hydrogen from the propagating radical to give a stable molecule, Reaction (3). An important commercial example is the cycloaliphatic hindered aminoxyls that are reversibly reduced by carbon-centred radicals and continuously re-oxidised by peroxyl radicals, Reaction (4) [15,22,29,30].

$$
>\!\text{N-O}\bullet \ + \ >\!\overset{|}{\text{CHC}}\bullet \ \longrightarrow \ >\!\text{CH}{=}\text{CH}\!< \ + \ >\!\text{N-OH} \qquad (3)
$$

$$
>\!\text{N}{-}\text{OH} + \text{POO}\bullet \rightarrow \ >\!\text{N}{-}\text{O}\bullet + \text{POOH} \qquad (4)
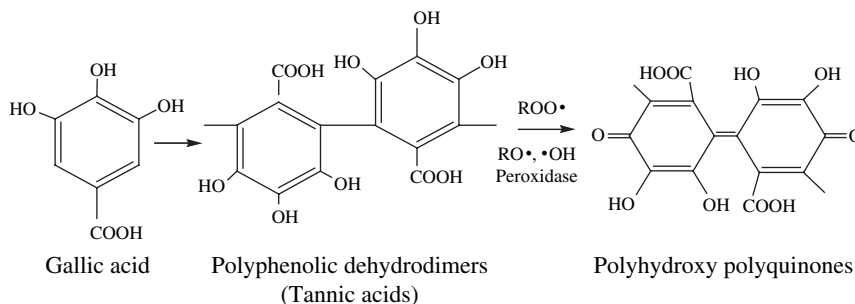$$

This type of chain-breaking antioxidant is particularly effective in the presence of UV light since aliphatic aminoxyls are not destroyed by the short wavelength of the sun's spectrum and the deactivation cycle continues over very many cycles until the redox (catalytic) system is slowly destroyed by side reactions [15,30]. For normal commercial polymers, this is a considerable advantage but it is a disadvantage in light-controlled photodegradable antioxidants where rapid disintegration is required at the end of the service life of the artifact (see Sections 3.2 and 4.2).

3.2. Preventive antioxidants

Peroxidation is normally initiated by the external environment and initiation involves a number of processes giving rise to free radicals. The most important of these are as follows.

(a) Photolysis or thermolysis of unstable compounds, of which hydroperoxides and ketones in the polymer structure (Section 2) are the best known photo-initiators. Consequently, the *peroxide decomposing* (PD) antioxidants are the most important preventive antioxidants [22].

(b) Transition metal ion catalysed hydroperoxide decomposition can be inhibited either by removing the hydroperoxides (see (a)) or by *metal deactivation* (MD), which generally involves metal ion chelation [31].

(c) Photolysis of hydroperoxides can be reduced or eliminated by the PD process or by screening the incident UV light. The latter is normally effected by light-stable *UV absorbers* (UVAs) [15] or by pigments such as carbon black and titanium dioxide, which screen the polymer from UV light.

Scheme 2. Biosynthesis and antioxidant function of the tannins.

In order to control both the lifetime of a degradable plastic during use as well as the rate of subsequent biodegradation in the environment, the onset of pro-oxidant activity must be controlled by appropriate antioxidants. Since the most successful pro-oxidants currently in use are transition metal ions that catalyse the decomposition of hydroperoxides, this can be achieved by the process (b) above. The successful use of such systems, particularly in plasticulture, has been widely discussed in the technical literature [3,8,9,22,32–37].

Some antioxidants act in cooperation to give the phenomenon of *synergism* [38]. In practice synergism is often achieved by the dual functionality of a single compound. For example some metal complexing agents are both MDs and PDs, resulting in the phenomenon of *autosynergism* [38]. Thus light-stable transition metal dithiocarbamates [R₂NCSS]₂M (e.g. when M = Ni, Co, Cu) are among the most powerful PD/MD antioxidants known [10,15]. With other transition metal ions, notably Fe, the metal complexes are highly effective "delayed action" photo-sensitisers [32]. In this case the "inversion" process from stabiliser to "activator" is facilitated by light and this system has been used for many years in agricultural mulching films [8,9,34,35] and in photo-biodegradable polypropylene twines.

4. Microbiology applied to waste reduction: specific disposal environments

Control of the lifetime of polyolefin plastics comes with control of the onset of peroxidation and the rate at which it occurs subsequently. Antioxidants, UV stabilisers and other protective additives have in the past been developed to improve the long-term durability of polyolefins, particularly in the out-door environment. Today the understanding of the basic science of oxidative degradation permits the use of these same additives in combination with prodegradant metal ions in polyolefins in applications for which a short but controlled lifetime is required. In general it is essential that the polyolefin retain its useful properties through one or more of a variety of fabrication procedures, e.g. blending, pelletising, extrusion, and injection moulding. The final product — film, bag, container, etc. — must have a reasonable storage life. And, of course, the customer expects to have a functional material or article that serves a useful purpose under a variety of

circumstances. It is at the end of the service life that the controlled-lifetime polyolefin must degrade in whatever environment it is discarded. As has been noted already, peroxidation of the plastic must begin after a specific use-time and should proceed relatively rapidly. The optimisation of the use-time/time-to-(bio)degrade ratio is best identified in terms of specific applications and these, in turn, involve specific disposal environments.

4.1. Litter

It is an unfortunate fact that packaging plastics (films, bags, bottles, etc.) are discarded carelessly outdoors after use by thoughtless people. Industrial plastic litter arises from the agricultural, shipping and fishing industries. Much of this litter is made of polyolefins, and it persists as an eyesore (or worse) for many months or years [10,39–41]. The high costs of collecting and disposing of discarded plastics preclude such activities in any consistent and widespread way. Careless and avoidable litter, particularly in urban areas should be controlled primarily by legislation and public education and degradable packaging should be employed as a safety net to reduce the accumulation of plastic litter. The use of oxo-biodegradable polyolefins and particularly those which photo-degrade in a controlled way followed by rapid bioassimilation can reduce or eliminate many chronic litter problems and is particularly valuable in places of high ecological significance, which are generally remote from centres of population (e.g. on the seashore or in the countryside). Early examples of this concept were copolymers which included a ketone carbonyl group alpha to the main chain [17,39,42], described as the Ecolyte™ process. Vinyl ketones were copolymerised with specific vinyl monomers to produce plastics having much greater sensitivity to terrestrial sunlight than the analogous homopolymer plastics containing no ketone groups. The same principles were applied to make photosensitive condensation polymers. Other examples of commodity plastics with enhanced sensitivity to oxidative degradation initiated by near-UV radiation are the ethylene–carbon monoxide copolymers [43]. These plastics are commonly used for the loop carriers for beverage-can 6-packs. Photosensitive co-polyolefins as described here begin to undergo peroxidation upon exposure to terrestrial sunlight at a rate that is adjustable by controlling the ketone content.

The use of additives, rather than the copolymer approach described above, has been shown to provide the necessary control of the shelf life, use life and degradation time for polyolefin products in a variety of applications. The first of these that really did provide controlled lifetimes was the Scott–Gilead technology [44]. It was demonstrated more than 30 years ago [45,46] that some metal complexes are efficient photo-pro-oxidants for polyethylene which, when photo-oxidised, not only fragment but the oxidation products biodegrade in any biologically active medium.

Another technology that addresses the litter problem is based on the work of EPI, Environmental Plastics Inc. Once again, an additive approach is used. TDPA® formulations added to polyolefins provide for conventional fabrication techniques, controlled storage- and use-lives and relatively rapid oxidative degradation after disposal [47]. All these time periods can be controlled by altering the additive formulation to suit different applications and different disposal conditions in a variety of geographic locations.

There may be readers who regard the use of oxo-biodegradable plastics as potentially encouraging the litterers amongst us, and who prefer the use of "education" and fines to address the problem. This concern is unfounded. Guillet has published [39] an analysis of this problem and has shown that "the most effective way to deal with the litter problem is by reducing the 'lifetime' of the littered object".

4.2. Agricultural plastics

Conventional PE films have been used for crop protection and enhancement for several decades, but owing to the persistence of these films after their service life is over, problems with harvesting and planting equipment occur. Visual pollution (litter) is also a serious problem with film residues. The requirement for a controlled service life of several months up to a year or more for mulch and silage films followed by a rapid loss of mechanical properties is called for [34]. At the end of the crop growth and/or protection period, the film must disintegrate readily, and the molecular fragments should biodegrade readily in arable soil. Plastor, a commercial PE mulching film based on Scott–Gilead technology, contains iron dithiocarbamate which functions initially as an antioxidant to maintain mechanical properties throughout the growing season. At the end of that period, photo-oxidation to embrittlement occurs, and the film fragments strongly support microbial growth in the absence of any other source of carbon [1]. A variety of induction times can be obtained, and several agriculturally useful products [11,35,36,40] have met with widespread commercial success on the basis of this science. The Scott–Gilead technology is so versatile that it can be used in the production of two consecutive, fast-growing vegetable crops with the single mulching film timed to degrade as the second crop is being harvested [11,37,41].

Likewise, commercially viable, degradable PE mulch film can be based on the TDPA® technology developed by EPI Environmental Plastics Inc. In a comparison trial at the SAC Crichton Royal Farm in Scotland, TDPA®-PE film was evaluated against two other commercial products, with forage maize as the crop. All three films increased crop values but the TDPA® product showed the lowest costs per unit weight for dry matter, metabolisable energy, and starch. The crop protection/disintegration timing was also superior for the product developed by EPI. Products for agricultural applications based on EPI formulations are being developed and marketed by Ciba Specialty Chemicals, under the trade name Envirocare™. Details of a comparison between the results of laboratory experiments and field trials demonstrated [48] that successful results are obtained with mulch films containing Envirocare™ additives for different crops in different countries. Field trials are also running for solarisation films, small tunnel films, seedling bags and banana bags.

4.3. Compost bags

No laboratory-scale test has yet been devised that really duplicates the conditions in a commercial composting plant. This is unfortunate because, with such a procedure, it would be possible to identify materials suitable for inexpensive, one-way containers for the collection and composting of food and garden waste, indeed, of any organic matter in municipal solid waste. Oxo-biodegradable PE bags, with a prodegradant included in the additive formulation, meet all of the requirements including high wet strength. Compost bags produced using EPI's TDPA® technology were evaluated by Raninger (Loeben University, Austria) using the municipal composting plant of Vienna Neustadt. Detailed results have been published [49] but the overall results may be summarised as follows:

- The TDPA®-modified PE bags did not interfere with the biodegradation of the normal input to the plant – about 10,000 tons annually of mixed household and green garden waste.
- The TDPA®-modified PE bags underwent biodegradation during the composting operation.
- The resulting compost product, which contained particulate and partially biodegraded plastics, was premium quality material and passed all the usual ecotoxicity tests. These included seed germination, plant growth and organisms' survival (daphnia, earthworms) tests carried out in accordance with DIN V 54900-3, ON S 2200 and ON S 2300 national standards.

It is clear that heat generated microbially in composting is the "trigger" that causes oxidative degradation of the PE, and that this happens relatively rapidly because of the prodegradant. Molar mass decreases cause polymer embrittlement, mechanical stresses from windrow turning speed up PE film fragmentation, and polymer surface area increases. The microorganisms in the compost biodegrade the oxidised plastic at molar mass values at least as high as 40,000 [1], more rapidly as M_w values are reduced further. This is the two-stage process referred to earlier, and it seems to proceed at a rate comparable to that of naturally occurring plant material.

It is evident that oxo-biodegradable plastics based on polyolefins contribute to the amount and nutritive value of the compost because much of the carbon from the plastic is in the form of intermediate oxidation products, humic material and cell biomass [50]. This is in contrast to plastics, such as hydro-biodegradable polyesters that biodegrade at rates comparable to purified cellulose. At the end of the commercial composting process, all of the carbon from the latter has been converted to CO_2, so there is a contribution to greenhouse gas levels but not to the value of the compost (see Section 6).

4.4. Landfill disposal

Most packaging plastics and many other types of plastic items and containers are disposed off in landfills. The costs of collecting, cleaning and sorting all these post-consumer plastics are high, and the market for mechanically recycled plastics is limited, partly for this reason. Proper incineration of waste plastics would enable the recovery of most of the energy stored in them (polyolefins are excellent fuels) but modern incinerators are expensive and the "NIMBY" principle also applies [10]. It seems that waste plastics will continue to be sent to landfills where their inherent bioinertness could be an asset, except for the following considerations. Many waste materials (e.g. food wastes, garden wastes, paper) that are known to be biodegradable persist in the landfill environment for many years in spite of significant microbial activity therein. This is partly because so much of this waste is enclosed in bioinert, impervious plastic bags and wrappers which impede the flow of gases and liquids and reduce the possibilities for aerobic biodegradation. All landfills change from aerobic to anaerobic conditions at any given place as the depth of garbage above that place increases. There are several advantages to encouraging as much aerobic biodegradation as possible of the organic matter disposed off in landfills before anaerobic conditions develop. Conversion of the carbon in the waste to carbon dioxide instead of methane [10 (p. 75–6)] and rapid reduction of the waste volume in order to prolong the useful life of the landfill are two such advantages. There is much to be said, therefore, for using oxo-biodegradable polyolefins in virtually all plastic applications for which disposal in landfills is probable after use [51].

The situation for polyolefins with controlled degradability in a landfill environment may be summarised as follows. These materials must have the familiar excellent mechanical properties during use, but they must embrittle and fragment much more rapidly in landfill conditions after disposal than do ordinary PE bags and films. Initiation of oxidative degradation (peroxidation) is the result of heat generated microbially in landfills. Disintegration of these plastics follows molar mass reduction as a result of the mechanical actions (compaction, settlement) that occur during normal landfill operations. The fragmentation of the films and bags allows the vertical flow of liquids and gases which enhances the aerobic biodegradation of food and "green" garden wastes, paper and the like. PE films that have been manufactured using EPI's TDPA® technology have been evaluated in several independent trials, using landfills in Canada, China and England. Tensile and spectroscopic measurements clearly showed the oxidative and mechanical deterioration of these films in a matter of months, even during the winter [52].

A further application of oxo-biodegradable TDPA®-based PE is as a daily cover for the active face in landfill operations. In many parts of the world it is mandatory to apply a daily cover to minimise the spread of refuse, odour and microorganisms, and 15 cm of soil has often been used for this purpose. Such a cover is wasteful of space and hence expensive…., and it is increasingly common to use a PE film. In order to avoid the problems inherent with the landfilling of conventional packaging plastics (described above), EPI's Enviro®Cover [52] is being used in a number of countries as an inexpensive replacement for soil. As is required, the Enviro®Cover provides the necessary cover protection but undergoes relatively rapid peroxidation to embrittlement after about 12 months, or less.

4.5. Toxicity

It has been important to establish that nothing harmful to the environment is generated or left behind by the use and disposal of polyolefins with controlled environmental degradability. It should be noted that the additives used to promote peroxidation of oxo-biodegradable polyolefins do not alter the normal oxidation chemistry of these materials but only speed up the slowest (rate-determining) of the individual reactions. The intermediate and final products of oxidation remain the same as those from ordinary polyolefins. Peroxidation involves the incorporation of oxygen (in combination with the carbon and hydrogen of the as-fabricated polyolefins), embrittlement and reduction of the original article to powder. This powder is harmless to humans, animals and plant life [35,36] and molecular oxidation and breakdown continue "until the polymer is ultimately returned to the natural carbon cycle as simple compounds such as water and carbon dioxide".

Of all the "disposal" environments discussed above, that of commercial composting encompasses the most rapid environmental degradation because the temperatures are highest and the microbial activity is greatest. The compost product from the Raninger trial [49] would have contained a wide spectrum of intermediate products of oxo-biodegradation from TDPA®-PE, and this material showed no contamination or harmful effects in the following tests: "heavy metals", plant tolerance and propagules, cress, summer barley plant growth, daphnia, and earthworm. As a result of exposure to near-UV light as well as to moderate temperatures and significant microbial activity, oxo-biodegradable polyolefins are most affective in agricultural applications. Photo-biodegradable PE films based on Scott–Gilead technology are widely used as mulching films (Plastor™ in Europe; Plastigone™ in the USA). They have been used in the same fields for 15 years or more, and there has been no accumulation of the plastic or its degradation products [3]. Calculation has shown [35] that continuous use of Scott–Gilead mulching film (containing a nickel
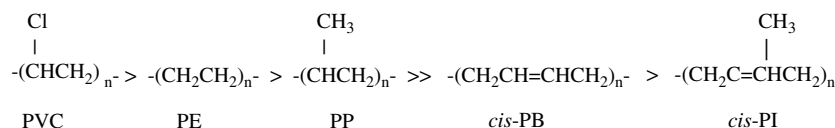
dialkyldithiocarbamate additive) for 500 years could increase the nickel content of the soil by one part per million, and the soil could contain up to 300 ppm to begin with. Moreover, it has been demonstrated [36] that water-soluble nickel corresponding to 180 years of continuous mulching had no effect on the ''assimilable'' nickel in the soil or on the amount of nickel incorporated in growing plants.

In the remaining applications (referred to earlier) of environmentally degradable polyolefins, the same degradation mechanisms prevail, the same peroxidation products are formed, and they are bioassimilated in the same way. Items made from oxo-biodegradable polyolefins that end up as litter will undergo primarily photo-initiated oxidation leading to biodegradable oxidation products. Likewise, packaging plastics made from such polyolefins that are discarded in landfills will (like Enviro®Cover daily landfill cover) oxidise abiotically as a result of the warmth generated by microorganisms. Film fragmentation has been observed to occur in less than a year. How long the biodegradation of oxidation products requires in soil or in landfills is not particularly important, but it is expected to be comparable to the times for paper, leaves, and other lignocellulosics. It has already been proven that no toxic residue formation occurs.

In the latter connection, there has been considerable negative publicity about the residual transition metal ions, often mistakenly referred to as ''heavy metals'' used to accelerate the abiotic degradation of the polyolefins. These are primarily carboxylates of Fe, Co, Ni and Mn, and are normally used at very low concentrations in the polymer. As discussed above, the agronomic effects of Ni have been particularly studied because of its reputation as a carcinogen. It has been demonstrated that, although small amounts of nickel are taken up by growing plants, this is not related to the concentration of nickel in the soil even at levels that could be reached if plastic films were used on the same soil for a century or more [34]. In fact the reputations of nickel and, to a lesser extent cobalt, were based upon studies of inhalation of dusts by miners. In practice, there is no evidence that aqueous nickel and cobalt salts are toxic. Indeed cobalt and manganese are widely distributed in drinking water and are required dietary supplements. They are taken in to the human diet through cereals, nuts and leafy vegetables and the plants receive these from the soils via water [37].

5. Scientific evidence for the oxo-biodegradation of hydrocarbon polymers

Carbon-chain polymers vary remarkably in their ability to resist peroxidation [53]. The following sequence shows some common commercial hydrocarbon polymers in order of decreasing oxidative stability.
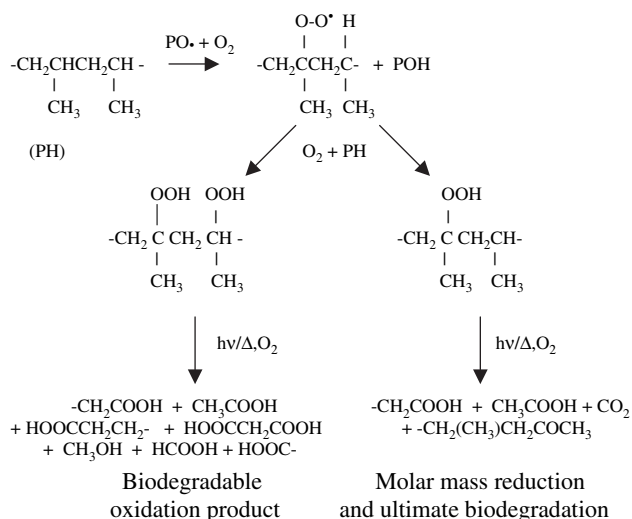
This sequence reflects the ease of hydrogen abstraction by peroxyl (see Section 3). Because of its ease of oxidation and loss of mechanical properties, the peroxidation of natural rubber (*cis*-poly(isoprene)) has been studied for many years and it is relatively recently that this process has been associated with its relatively rapid biodegradation and the inhibition of rubber biodegradation with the presence of antioxidants rather than with the polymer structure [27]. Contrary to the popular belief that synthetic polymers do not biodegrade like natural polymers, it has been shown [54,55] that naturally occurring *cis*-(polyisoprene) (NR) and synthetic *cis*-(polyisoprene) (IR) biodegrade at a similar rate in the presence of *Pseudomonas aeruginosa*. NR gloves were 26% mineralised in 6 weeks compared with 21% for IR gloves. This slight difference is probably due to the difference in the antioxidants used in the formulation [27]. Berekaa et al. [56] in a similar study showed that removal of antioxidants by extraction markedly increased the rate of microbial growth. It is clear, however, that there is no intrinsic difference between natural and synthetic polymers.

Less readily peroxidisable polymers do not biodegrade as rapidly as the polydienes in normal soils. Commercial nitrile and neoprene rubbers showed insignificant loss after 48 weeks and plasticised PVC showed mass loss (11.6%) that was due entirely to the biodegradation of the plasticiser and not to the polymer itself [57]. By contrast, NR gloves showed 54% loss of thickness after 4 weeks in soil at 25 °C and 94% mass loss after 48 weeks.

Abiotic peroxidation of the polyolefins (Scheme 3) gives rise to some vicinal hydroperoxides and this process is particularly favoured in the poly-α-olefins, such as polypropylene due to the susceptibility of the *tertiary* carbon atom to hydrogen abstraction via a hydrogen-bonded intermediate. A major proportion of the peroxidic products are hydrogen-bonded vicinal hydroperoxides that break down to small biodegradable molecules such as carboxylic acids, alcohols and ketones [4,28] as well as longer chain oxygen-modified breakdown products (Section 2), which oxo-biodegrade more slowly. The decomposition of the vicinal hydroperoxides is also facilitated by internal hydrogen bonding and the low molar mass products of this self-induced degradation are small biodegradable molecules such as acetic and formic acids.

In the case of the polyolefins, random chain scission is initially the dominant process (Scheme 3). However, some low molar mass oxidation products are formed via vicinal hydroperoxides even in PE [4,28]. The alkoxyl radicals formed by decomposition of the hydroperoxides contain weak carbon–carbon bonds in the α positions to the hydroperoxide groups, which lead to the formation of low molecular weight aldehydes and alcohols that rapidly oxidise further to carboxylic acids. These are biodegradable species, similar to products formed by hydrolysis of aliphatic polyesters and, as in the

$$-(CHCH_2)_n\text{-} > -(CH_2CH_2)_n\text{-} > -(\underset{\underset{CH_3}{|}}{C}HCH_2)_n\text{-} \gg -(CH_2CH=CHCH_2)_n\text{-} > -(CH_2\underset{\underset{CH_3}{|}}{C}=CHCH_2)_n$$
with Cl on first group

PVC   PE   PP   *cis*-PB   *cis*-PI

Scheme 3. Formation and breakdown of hydroperoxides in polypropylene.

case of *cis*-PI, they are rapidly bioassimilated to give cell biomass (see below).

The conclusion from the above work, which has been reviewed in more detail elsewhere [29], is that the biodegradation of the polyolefins occurs by a combination of abiotic and biotic oxidation and that it is controlled by the rate of initiation of the abiotic peroxidation. The products of the abiotic peroxidation of the polyolefins are very similar to those formed in the abiotic hydrolysis of the aliphatic polyesters, such as poly(lactic acid), whether produced from biological resources or not and the two routes are complementary strategies to the biodegradation of synthetic polymers.

6. Science-based standards for biodegradable polymers

In the development of international standards for biodegradable polymers, it is generally considered essential that these are based on objective published scientific research in order to provide a "level playing field for business" [27,58,59]. This principle has so far not been in evidence in the International Standardization Organisations. In practice new standards for biodegradable plastics are almost entirely directed toward bioplastics that have achieved a high profile because they are derived from "renewable" materials. They are claimed to be more "sustainable" than polymers based on fossil fuels. This concept has been questioned [27,59] on the grounds that at least an equivalent amount of fossil resources is used during the manufacture of bioplastics as that required for the carbon content of the fossil-based synthetic hydrocarbons. Furthermore less than 10% of the fossil fuels used in energy production are used in plastics manufacture. The benefits of bio-based plastics, then, have to be made on the basis of their frequently claimed unique ability to be returned to the carbon cycle by biodegradation.

There is no question that some plastics made from natural resources are rapidly converted to carbon dioxide and water. However, there is no obvious ecological or practical advantage

in rapid mineralisation. Rapid elimination of CO_2 to the environment is not considered by environmentalists to be an advantage because of its effect on the "greenhouse effect". Ideally, the carbon should be retained in the soil as a seed-bed for growing plants similarly to lignocellulose in the natural environment [60,61]. Furthermore, there is a general concern about the premature degradation of polymers, particularly when used in critical applications such as agricultural films, where their *reason d'etre* depends on their ability to resist the effects of the environment until they have fulfilled their intended purpose, which may mean that they have to be intact in contact with the soil for up to 12 months [3,37,41,62]. The behaviour of biodegradable polyolefins satisfies both of these requirements. Current progress in the development of standards for the biodegradation of polyolefins in Europe and America is discussed in the following sections.

6.1. Comité Européen de Normalisation (CEN)

CEN, the European Standards Organisation considers degradable materials under two different headings controlled by different Working Groups, TC 261/SC4/WG2 and TC 249/WG9.

6.1.1. CEN TC 261/SC4/WG2: Degradability and organic recovery of packaging and packaging waste

As the name implies, the mandate of this Working Group is not limited to plastics since it also embraces wood products, notably paper and cardboard. The remit of WG2 is primarily the recovery of packaging materials through composting. Other Working Groups of TC 261/SC4 are concerned with waste minimisation, mechanical recycling, energy production, etc. which in principle have to be regarded as alternatives to and in competition with composting as a means of recovering benefit from waste [62].

As indicated above, the primary target for compostability legislation has so far been the bioplastics (hydro-biodegradable plastics) because of their "green" image. The primary standard governing composting is EN 13432:2000 *Packaging – Requirements for packaging recoverable through composting and biodegradation – Test scheme and evaluation criteria for final acceptance of packaging*. This embraces the following essential criteria

1 *Characterisation*: Identification of packaging constituents, dry solid content, ignition residues, and hazardous metal residues.
2 *Biodegradability*: 90% of the total theoretical CO_2 evolution in compost or simulated compost in 6 months.
3 *Disintegration*: Not more than 10% shall fail to pass through a >2 mm fraction sieve.
4 *Compost quality*: No negative effects on density, total dry solids, volatile solids, salt content, pH, total nitrogen, ammonium nitrogen, phosphorus, magnesium and potassium. Ecotoxicity effects on 2 crop plants.
5 *Recognisability*: "Must be recognisable as compostable or biodegradable by the end user by appropriate means".

Of these, criterion 1 is intended to identify potentially toxic components and 3–5 are to facilitate the commercial interests of the composting industry and are concerned with subjective judgements associated with the understanding of how normal commercial plastics behave. The main problem from a scientific standpoint is criterion 2, which utilises a biometric test derived from earlier ISO standards, originally intended to demonstrate the short-term biodegradability of detergents in aqueous media (ISO 14851, ISO 14852). Although this may be an appropriate test for water-soluble plastics that end up in a sewage plant, it has been strongly criticised by the European Association for the Co-ordination of Consumer Representation in Standards (ANEC) on the grounds that it really has nothing to do with composting [63]. Nature deals with its voluminous lignocellulosic wastes in quite a different way. It is also quite clear from the data presented in Sections 4 and 5, that the CEN "biodegradability test" is not compatible with the EU "Waste Framework Directive" 1991, [64] which defines "recovery" of materials as:

"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".

However, if 90% of the total theoretical CO_2 were evolved during the composting operation in 6 months, the residue would have minimal value as a soil improver and would contribute almost nothing to the "land carbon sink". This is an important concept that has been highlighted in a number of documents from scientific organisations [65–68]. The following statement [68] emphasises the importance of organic carbon to the fertility of soil.

"Organic matter maintains a central role in soil function, in its fertility and its ability to hold water and to diffuse pollution. Moreover, it is the organic matter in soil which holds its carbon and enables it to act as a carbon sink".

The sequestration of carbon in the soil is equally important in the context of mitigating global climate change by minimising the release of CO_2 to the environment [65,67]. Consequently, slow release of carbon to the soil as microbial biomass, which acts as a nutrient for growing vegetation, is clearly the more ecologically acceptable option than rapid conversion to CO_2 [27,29,41]. Complete mineralisation of plastics is favoured by parts of the composting industry because it provides a convenient means of disposing of packaging wastes rapidly to the environment. However, it is not "recovery" as defined in the Directive and in practice nature does not dispose of the enormous quantities of lingocellulosic wastes in this way. As discussed in Section 5, cellulose is stabilised by association with lignin and the slow biodegradation of natural lignocellulose serves as a model for the disposal of man-made wastes. Moreover, EN 13432 does not validate wood products as biodegradable since they do not comply with the rapid mineralisation requirement. This fact has been rationalised in retrospect [41] on the basis that, because lignocellulose is a natural product, it is not necessary to require that

it must mineralise within 6 months. As seen earlier, there is no basic distinction between the biodegradation of natural and synthetic polymers (Section 5) and any distinction on grounds of origin are scientifically meaningless [29].

6.1.2. CEN TC 249/WG9 Characterisation of biodegradability

This Working Group is concerned with non-packaging applications of plastics. Because the range of applications of biodegradable plastics in the environment is so wide, they may terminate in quite different environments. For example agricultural products remain on the soil as litter after use for a relatively short period and terminate in the soil along with nature's litter. This is very different from biodegradable body bags, which are not intended to be exposed to the outdoor environment and which rely entirely on sub-soil bacteria to both initiate and terminate biodegradation. This is a long-term process, which unlike mulching films and tunnels that are required to disintegrate sharply to match the requirements of the farmer, there is no specified limit to the initiation or ultimate biodegradation of body bags.

A second application that requires a different time-scale again is for products that end up in sewage systems where disintegration and biodegradation must take place in a very short time to avoid clogging of pipes, etc. Products that comply with the rapid mineralisation test outlined in EN 13432:2000 are well suited to select materials that are required to be substantially biodegraded over a period of a week in a sewage plant. However, they are not at all suitable for plastics mulching films and protective tunnels or silage films, plant pots etc., which normally require a "safety period" in use in a biological environment of up to 12 months. Other applications of polyolefins, for example in baler twines, agricultural packaging or silage films may require an even longer induction period before disintegration commences [35–37,41].

The present proposal is to limit the scope of each standard to a single industrial sector. A standard for "Biodegradable plastics materials suitable for manufacturing mulch films for agriculture" has been proposed as a commercial priority [69]. However, although litter from mulching films, controlled release fertiliser capsules and related products can be classified as "socially beneficial" because of its benefit to the farming industry, it ends up in the same environment as "anti-social" litter from animal feed bags, fertiliser sacks, silage films and baler twines that end up as litter in the countryside. Similarly, litter from the shipping industry that terminates on the seashore in remote areas cannot be collected and recovered economically for more conventional recycling procedures. Generally biodegradable social litter is based on the same technology as biodegradable anti-social litter and there is no obvious reason why the appropriate standard should not be designed to cover both.

Plastics on soil are subjected to two synergistic influences: light and heat. The envisaged protocol for oxo-biodegradable litter should then utilise pre-treatment in a typical weatherometer in which both heat and UV light are generated. A filtered mercury arc developed by Professor Jacques Lemaire at the

University of Clermont-Ferrand has been found to be satisfactory for this purpose, but other standard weatherometers such as the xenon arc may also be adapted to simulate exposure on soil. In the draft standard it is envisaged that this pre-treatment will be optional if bioplastics are not light activated.
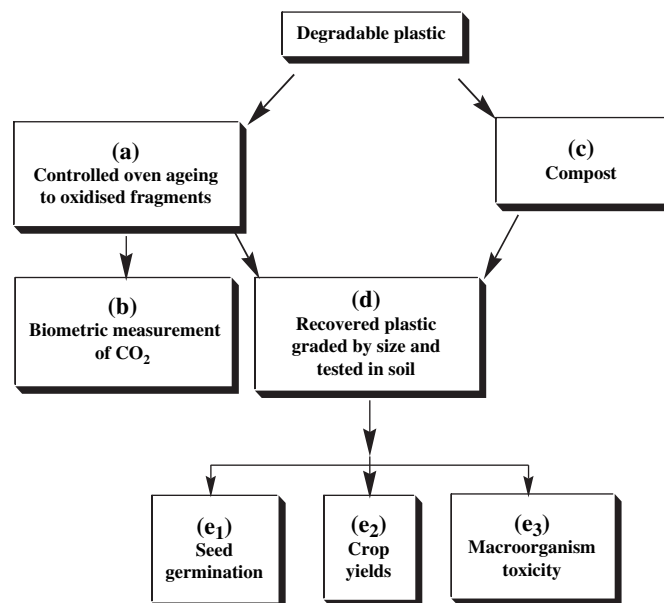
7. British Standards Institution

7.1. BSi PKW/0: Packaging and the environment

This committee is concerned with the environmental impact of packaging and its recovery. It is clear from the work described in the last section that oxo-biodegradable plastics cannot and indeed should not comply with rapid mineralisation tests without peroxidation after use, leading to biodegradable oxidation products. Moreover, it would be counterproductive if they did so, since their mechanical properties have to be maintained during their service life before disintegrating and biodegrading. These attributes have been considered by BSi PKW/0, the UK "mirror group" of CEN TC 261/SC4/WG2 [70]. It is proposed that, since hydrocarbon polymers are quite different from the materials covered by CEN TC 261/SC4/WG2, oxo-biodegradable polymers should be subjected to the same environmental influences experienced by plastics during composting (i.e. 60–70 °C in the presence of air). In practice, this transforms the polymer to a hydrophilic material that supports microbial biofilm formation. It is standard procedure for polymer technologists to apply accelerated ageing and weathering tests to polymers to predict their service life and this procedure must then precede conventional biometric measurements in order to replicate the complete life cycle of the plastic. This proposal is outlined in Scheme 4 [70]. Recent published work by Jakubowicz [7] has shown that oxo-biodegradable polyethylene films subjected to 70 °C undergo over 60% conversion to carbon dioxide in just over 6

months. Independently, Chiellini et al. [6] showed that after relatively mild thermal oxidative conditions (55 °C) oxo-biodegradable polyethylene was substantially converted to CO_2 within 18 months when incubated with both soil and with mature compost and extrapolation of result so far obtained suggest that this will be complete within 3 years. This time is actually rather shorter than the time required for the mineralisation of straw on soil [71]. The carbon content of the polyolefins cannot in their nature be converted to any toxic carbon compounds since CO_2 is the only carbon end product. The purpose of ecotoxicity tests outlined in Scheme 4 is to establish that plastics residues in soil do not interfere with the germination and growth of plants or migrate into the soil environment.

8. American Society for Testing and Materials (ASTM)

ASTM is a large organisation focused on establishing "voluntary full consensus standards for materials, products, systems, and services by providing a forum for producers, users, ultimate consumers and those having a general interest". It began to consider biodegradable plastics following the ill-advised introduction in the 1980s of starch-filled polyolefins as supposedly biodegradable and compostable. Since such materials were neither, ASTM requested its research arm, the Institute for Standards Research (ISR) to conduct research which could and did provide the basis for a *Standard Specification for Compostable Plastics* – ASTM D 6400-99. Over a 6-year period, the ISR investigated the requirements with participation from industry, government and academe. A major element of this program was a comparison of the results from laboratory-scale, pilot-scale and full-scale composting trials. A fundamental tenet of the work was that "the only direct measurements of biodegradability are measurements of mineralisation, the conversion of carbon from the test

Scheme 4. Biometric and ecotoxicity evaluations for oxo-biodegradable polymers [70].

substance into gaseous carbon: CO_2 in aerobic processes or CO_2 plus CH_4 in anaerobic processes'' [72].

The emphasis in the laboratory-scale test was on the biometric measurement of the conversion of carbon to carbon dioxide, a test (as noted in Section 6.1) that derived from a test for the biodegradability of detergents in water treatment situations. This commonality between the approaches used by CEN and ASTM is not surprising in view of the continuing liaison between the two organisations. Among the important results of the ISR investigation was the finding that the laboratory-scale test was more conservative than the pilot-scale test which in turn was more conservative than the full-scale test [73]. In other words, the laboratory-scale test will ''fail'' plastics that actually biodegrade in full-scale composting.

Under the jurisdiction of ASTM D20 on plastics, Subcommittee D20.96 on Environmentally Degradable Plastics has produced three standards that are immediately relevant to the evaluation of degradable plastics: D 5338-98 *Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions* (originally published as D 5338-92); D 6002-96 *Standard Guide for Assessing the Compostability of Environmentally Degradable Plastics*; and D 6400-99 (re-approved in 2004) referred to above. Careful consideration of all three of these publications leads to the conclusion that a plastic which yields not less than 60% of its carbon as carbon dioxide in an incubation flask up to 5 L in volume at a temperature that may be kept at 58 °C over a period of up to 180 days may be considered to be biodegradable and compostable. The reader is directed to the standards for a full account of how the testing must be performed, and reported. The ASTM testing protocol does indeed identify plastics and other polymers, primarily hydro-biodegradable polymers, that can meet the designated criteria, although many of these do not biodegrade solely as a result of microbial activity.

Criticisms of the arbitrary assertion that only those plastics that meet the requirements spelled out in D 6400-99/D6002-02/D 5338-98 can be considered to be compostable tend to centre on the following facts: (1) this testing protocol requires a high rate of mineralisation that is actually a disadvantage in composting; (2) the protocol does not reproduce actual commercial composting conditions in regard to temperature, and microbial population profiles; (3) the positive control specified in D 5338 is purified cellulose, which is neither a naturally occurring substance nor a plastic; (4) no account is taken of the amount of carbon that is converted to biomass although this is an important product of biodegradation. ASTM's ISR recognized that the laboratory-scale test is more conservative than full-scale composting but the former is still the mandated requirement for compostability. This, in spite of the recognition by Subcommittee D20.96 that biodegradation processes, the conversion of carbon in materials into carbon dioxide by microorganisms in the environment, are expected to continue long after the compost has passed the curing stage and been applied to the soil.

There is widespread recognition that there is a legitimate requirement for a method to evaluate properly oxo-biodegradable plastics, since to date neither CEN nor ASTM has published standards that do that. Subcommittee D20.96 (now referred to as the Subcommittee on Biodegradable Plastics and Biobased Products) produced D 6954-04 with the title *Standard Guide for Exposing and Testing Plastics that Degrade in the Environment by a Combination of Oxidation and Biodegradation*. This new Standard Guide, approved and published in May 2004, ''uses a tiered, criteria-based approach to assess the consecutive oxidation and biodegradability of plastic products and ecological impacts in defined applications …. The tiered approach is chosen in the laboratory for convenient separation of oxidative degradation, biodegradation and ecological impact stages even though in the real world all three are likely to be concurrent rather than consecutive''. D 6954-04 is a useful addition to the ASTM Standards dossier dealing with degradable plastics since there are a number of important applications for biodegradable plastics for which those that meet D 6400-04 are unsuitable. During 2005, work was begun on preparing Standard Methods, based on D 6954-04 for landfill and litter disposal environments. Clearly, the search is not over for a laboratory-scale composting test that duplicates the actual conditions in full-scale composting. Perhaps the requirement will be met by simply reducing the rate at which carbon in the plastic is required to be converted to carbon dioxide. Time will tell.

Acknowledgements

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