Macromol. Symp. **144**, *113–125 (1999)*

Antioxidant control of polymer biodegradation

Gerald Scott
Aston University, Birmingham, UK

SUMMARY: Hydrocarbon-based synthetic polymers are versatile and cost-effective materials in packaging and agriculture. Unstabilised polyolefins are known to biodegrade through peroxidation initiated by both abiotic and biotic and mechanisms. Both abiotic and biotic peroxidation can be accelerated and controlled by specially designed antioxidants and this has resulted in their commercial use in packaging, mulching films and baler twines. They are currently being evaluated in controlled release fertilisers.

Introduction

Hydrocarbon polymers are the materials of choice for packaging and agricultural applications [1,2]. They offer very considerable advantages over biologically based polymers (e.g. paper and cellulose derivitives) because, due to the very large scale on which they are manufactured, they are cheap and unlike agricultural and forestry crops, they do not use large areas of land in their production. Energy utilisation of hydrocarbon polymers during manufacture is lower than traditional materials and they cause less environmental pollution during manufacture than cellulose-based materials. Hydrocarbon polymers also have very good barrier properties against water and water-borne organisms. They are readily recycled if uncontaminated and on incineration they have a calorific value similar to fuel oil [3]. When released into the environment as litter, hydrocarbon polymers biodegrade in a process which is controlled by their rate of peroxidation and the mechanisms by which this occurs and how it can be controlled will be discussed in this paper.

Peroxidation, a prelude to biodegradation

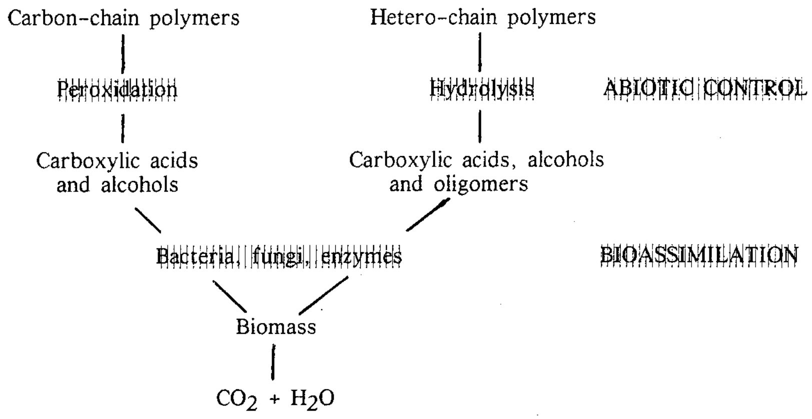
A **biodegradable polymer** has been defined by an earlier Workshop [4] as

'A polymer in which the degradation is mediated at least in part by a biological system'

In the case of the synthetic poymers, abiotic hydrolysis and/or peroxidation normally precede biotic attack (Fig. 1). However, the time-scale over which hydrocarbon-based polymers biodegrade may vary by many orders of magnitude.

CCC 1022-1360/99/$ 17.50+.50/0

Figure 1 Biodegradation mechanisms of synthetic polymers



A typical natural polymer, *cis*-poly(isoprene), as it comes from the tree *Hevea Braziliensis* is highly peroxidisable and biodegradable and is absorbed into the environment in a matter of weeks. However, the same polymer when incorporated into a truck tyre is stable and non-biodegradable in the out-door environment for many decades. Futhermore, it makes no difference if the polymer is natural *cis*-poly(isoprene) as produced by nature or synthetic *cis*-poly(isoprene) as it comes from a chemical plant.

The reason for the extraordinary biological stability of the natural rubber in a truck tyre has nothing to do with the 'intrinsic biodegradability' of the rubber molecule since synthetic *cis*-polyisoprene behaves in exactly the same way but it has everything to do with the incorporation of highly effective antioxidants during manufacture. Moreover, this phenomenon is not limited to the hydrocarbon polymers. The sequoia tree can survive for many hundreds of years in a forest environment after being felled where other trees would survive for only a few years. This is because the cellulose in the sequoia is protected from biological hydrolysis and peroxidation by the tannic acids which are both antioxidants and biostats. The distinction between synthetic polymers and 'natural' polymers is thus an artifical one.

The mechanism of peroxidation of *cis*-polyisoprene was elucidated by Farmer, Bolland and Bevilaqua over 50 years ago and it was shown to give rise to low molar mass biodegradable carboxylic acids [5] (Scheme 1). This is the classical peroxidation chain reaction which is normally summarised as;

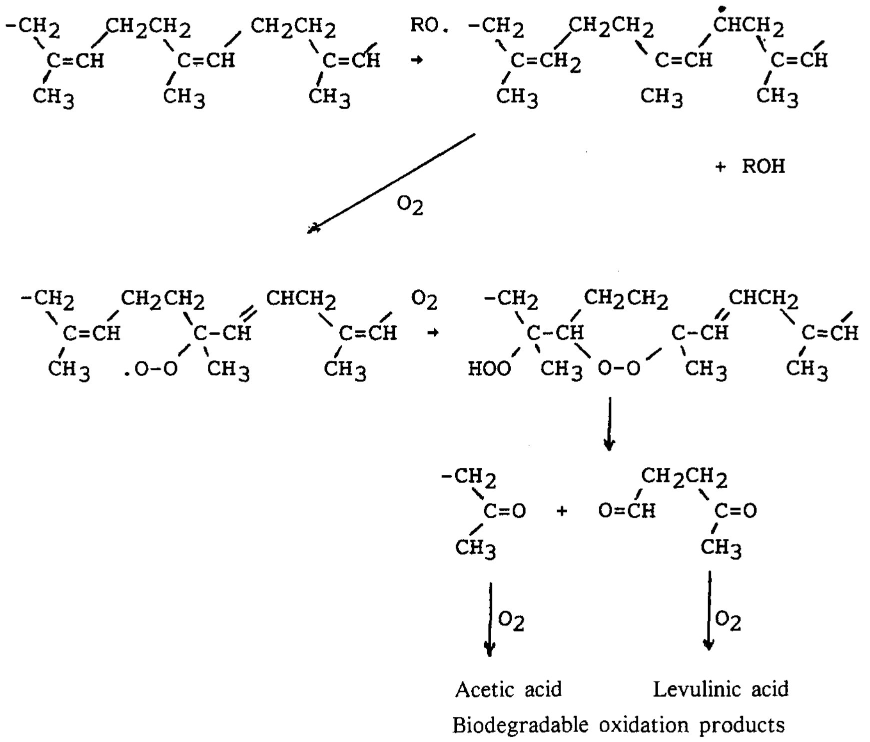
$$\mathrm{P\cdot} + \mathrm{O_2} \rightarrow \mathrm{POO\cdot} \qquad (1)$$

$$\mathrm{POO\cdot} + \mathrm{PH} \rightarrow \mathrm{POOH} + \mathrm{P\cdot} \qquad (2)$$

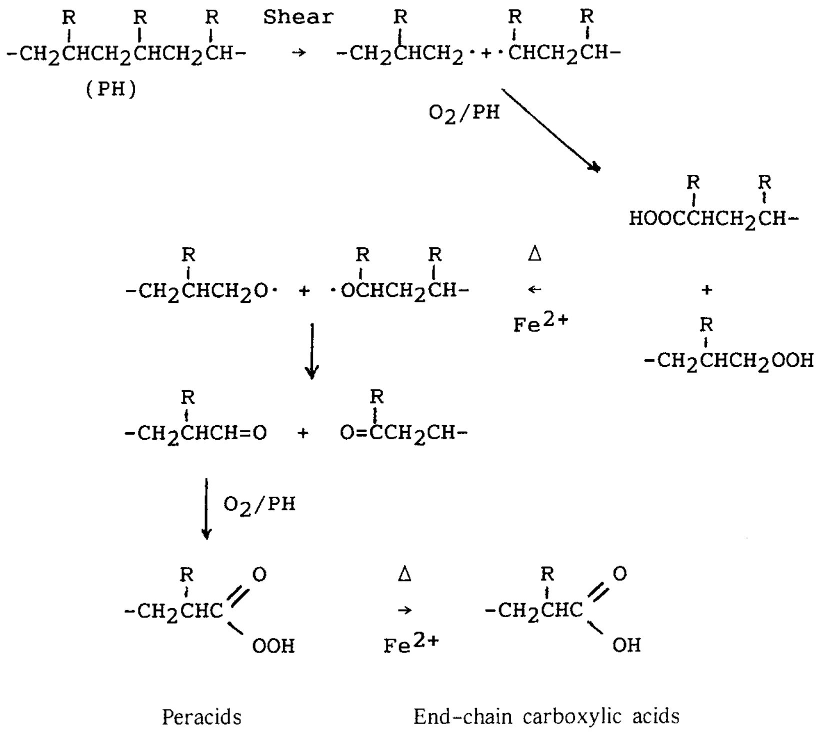
$$\mathrm{POO\cdot} + \mathrm{>C{=}C<} \rightarrow \mathrm{POO}\overset{|}{\mathrm{C}}\overset{\bullet}{\mathrm{C}}< \qquad (3)$$

where PH is any hydrocarbon polymer. Hydroperoxides are the normal initiators in hydrocarbon peroxidation and in the case of most commercial polymers they are formed during processing due to the mechanooxidation processes that occur in a screw extruder [6]. This is shown typically for the polyolefins in Scheme 2 where hydroperoxides and peracids initiate the kinetic chain during environmental exposure, particularly in the presence of transition metal ions of which ubiquitous iron compounds are abundant.

Scheme 1 Abiotic peroxidation of cis-polyisoprene



Scheme 2 Peroxidation of polyolefins during processing

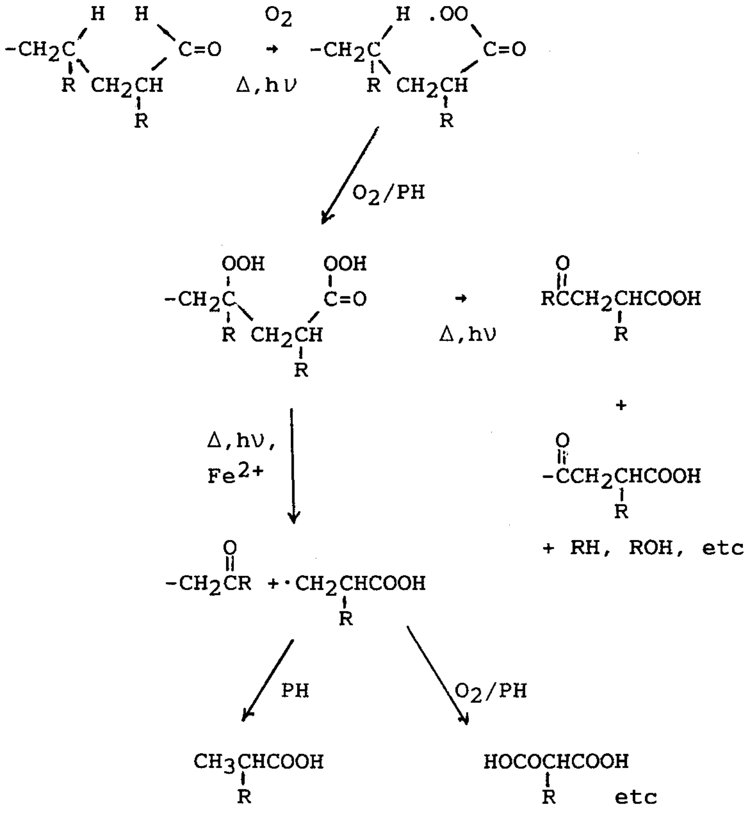


Low molar mass carboxylic acids are also formed by the peroxidation of the polyolefins [7-9]. Many have been identified, particularly during photooxidation [10]. This results from the attack of peracyl radicals on neighbouring C-H bonds with the formation of vicinal hydroperoxides (Scheme 3) which further photolyse or thermolyse to give biodegradable carboxylic acids and alcohols.

Biooxidation of polyolefins

Albertsson noted many years ago [11] that the biooxidation of polyethylene in the presence of *Fusarium redolens* was much more rapid for unstabilised polyethylene than for polyethylene containing an antioxidant. More recently Wasserbauer et al. [12] have found that polyethylene which has been extracted to remove antioxidants peroxidises rapidly in the presence of *Pseudomonas putida* with the formation of CO_2. This process is inhibited completely by an antioxidant (Fig. 2).

Scheme 3 Low molar mass carboxylic acids by peroxidation of polyolefins



PH is polyolefin; PE, R = H; PP, R = CH_3

These studies have shown that the distribution of ketonic carbonyl (1720 cm^{-1}), ester (1740 cm^{-1}) and alcohol (1020-1170 cm^{-1}) formed during incubation was identical to that obtained by abiotic thermal peroxidation suggesting that enzymic oxidation is involved only in the initiation step of the peroxidation chain reaction. This was identified as the ferriprotoporphorin, Cytochrome P-450 which is widely distributed in a variety of bateria and fungi. In animals is is concentated in the liver where it hydroxylates and detoxifies xenobiotics. Not surprisingly, liver homogenates cause rapid bioerosion of unstabilised polyethylene films [13].

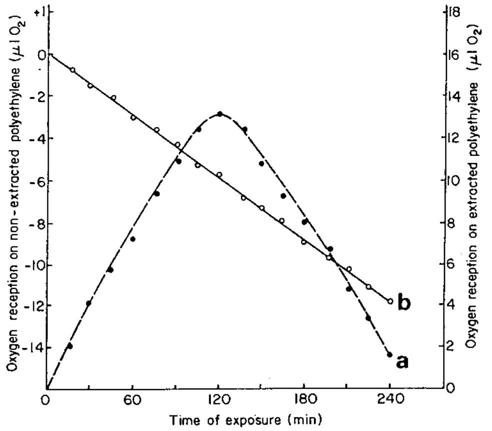
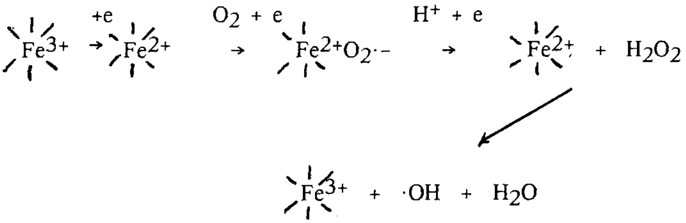


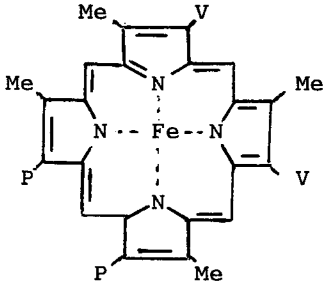
Fig. 2 Oxygen absorption of polyethylene in the presence of *Pseudomonas putida* at 37°C. Curve a without antioxidant and curve b stabilised with BHT. Measurements are relative to the endogenous 'breathing' of the microorganism. (Reproduced with permission from R.Wasserbauer et al., Biomaterials, **11**, 38 (1990)).

Oxidases and peroxidases contain the ferriprotoporphorin structure and involve the same redox mechanism [14]. Horseradish peoxidase (HRP) reacts readily with both phenolic [15] and arylamine [16-18] antioxidants in the presence of hydrogen peroxide and both antioxidants retard or inhibit the intermediate free radical species. The reaction of Fe(II) in Scheme 4 is analogous to the much slower abiotic 'Fenton' reaction. Both biotic and abiotic reactions are inhibited by the chain-breaking (CB-D) antioxidants found in commercial polyolefins.

Scheme 4 Radical generating mechanism of the ferriprotoporphorin enzymes



Fe^{3+} is the hexacoordinate ferriprotoporhorin;



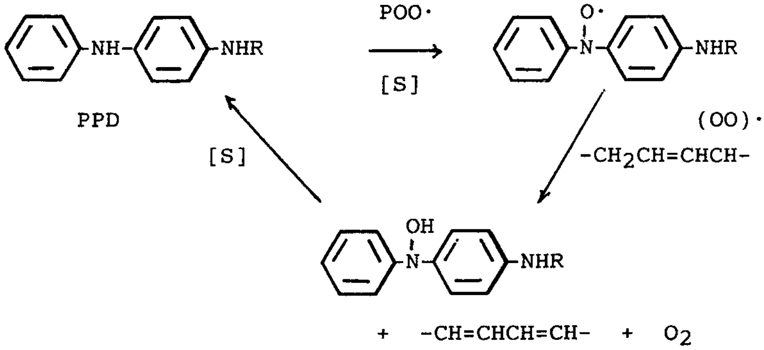
Ferriprotoporphorin

Me = methyl
V = vinyl
P = γ-propionyl

Antioxidant specificity in the control of bio-degradation

The theory and mechamisms of antioxidant action have been extensively reviewed in the literature [19,20] and will not be discussed in detail here. Antioxidants are used commercially to extend the life of polymer artefacts as long as possible but not all antioxidants provide a controllable induction period. It has already been noted that tyre antioxidants delay the peroxidation of *cis*-poly(isoprene) to the point where tyres become a burden on the environment after discard. This is partly due to the UV protective affect of carbon back but it also results from the exceptional effectiveness of the *p*-phenylenediamine (PPD) antioxidants. PPDs are catalytic in rubber due to the continuous regeneration from their oxidation products by sulphur species present in vulcanised rubber [21] (Scheme 5). Hindered amine light stabilisers (HALS) are also regenerated in a similar way in polyolefins during out-door exposure [22]. In general chain-breaking donor (CB-D) antioxidants (phenols and arylamines) are converted by oxidation to higher molecular weight species with similar CB-D activity [23,24] and the rate of polymer deterioration depends profoundly on the environmental conditions. By contrast, transition metal anioxidants acting by a peroxidolytic mechanism are very sensitive to UV light, and they consequently produce a very sharp and definable embrittlement time in polyolefins [25]. The inversion of activity of the transition metal dithiocarbamates (MDRCs) was first observed in rubber where copper dithiocarbamates were shown to be powerful short-term antioxidants, becoming thermal prooxidants after an induction period [26]. In the 1970s we were able to adapt this to the hydrocarbon plastics to produce light sensitive antioxidants that showed a UV controlled inversion to photo-prooxidants.

Scheme 5 Reversible oxidation and reduction of *p*-phenylenediamines during ageing of rubber.



The nickel dialkyldithoicarmamates (NiDRCs) were known to be highly effective light stabilisers due to their abilty to destroy hydroperoxides catlytically [27] and to absorb UV light [28]. The FeDRCs, although initially photoantioxidants were found to be photolysed by UV in the region of 315 nm and underwent inversion after an induction period to give ionic iron [29] (Fig. 3). The mechanism of this process is shown in Scheme 6.

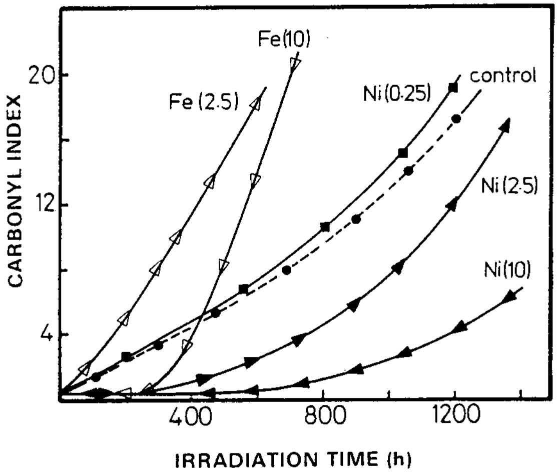
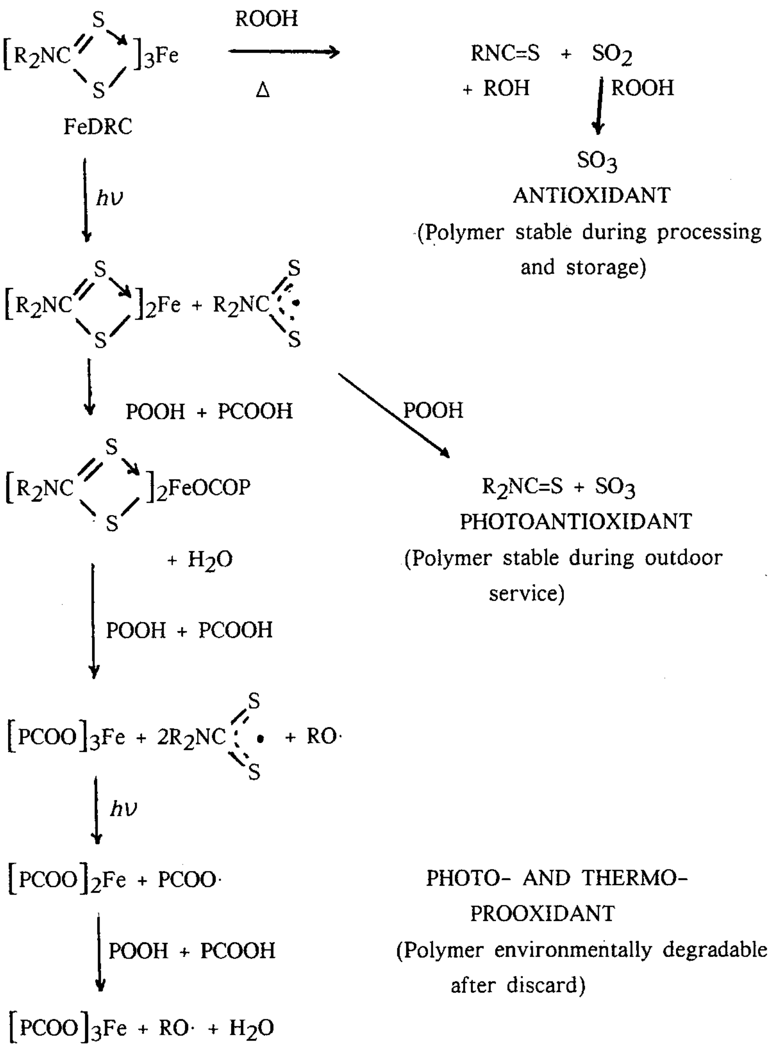


Fig. 3 Inversion of photoantioxidant activity of iron dithiocarbamates (Fe) in light. (figures in parenthesis are concentrations of FeDRC and NiDRC in mol/100g x 10^4). (Reproduced with permission from *J.App. Polym. Sci.*, 31, 688 (1986).

Scheme 6 Iron dithiocarbamate (FeDRC) antioxidant-prooxidant inversion in a poyolefin (P represents a polyolefin chain)



By combining an iron dithiocarbamate with a UV stabilising MRDC (e.g. NiDRC) in varying proportions, a wide range of useful polymer lifetimes can be obtained. This system was developed and commercialised during the 1970s by Dan Gilead of Plastopil Hazorea for mulching films as the Scott-Gilead (S-G) system [30,31].

Typical mulching film lifetimes vary between 2 months and 8 months, depending on the crop. More recently, the S-G system has been developed for other agricultural application. These include hay baling twines, generally polypropylene, which have largely replaced sisal and are designed to last for about one year before being absorbed into the environment. Another application which has received considerable attention in Japan is as a means of controlled release of fertilisers in order to reduce pollution by fertilisers in ground waters and associated eutrification of rivers and lakes. This not only improves the environment but also leads to economies in fertiliser usage. The science and technology of these applications will be discussed in other papers at this Workshop.

Peroxidation of hydrocarbon polymers must precede bioassimilation

It was noted above that peroxidation of hydrocarbon polymers appears to proceed by the same radical-chain mechanism whether the initiation process is abiotic or biotic. Recent evidence suggests [32,33] that the two initiation mechanisms can operate in parallel (Figure 4) and once peroxidation is in progress, both contribute to the formation of low molar mass carboxylic acids and alcohols which are nutrients for the growth of microorganisms. However, when polyolefins are exposed to the environment, abiotic initiation and in particular UV initiated peroxidation in the presence of transition metal ions is almost certainly a necessary precursor to the colonisation of microorganisms on the surface of the polymer.

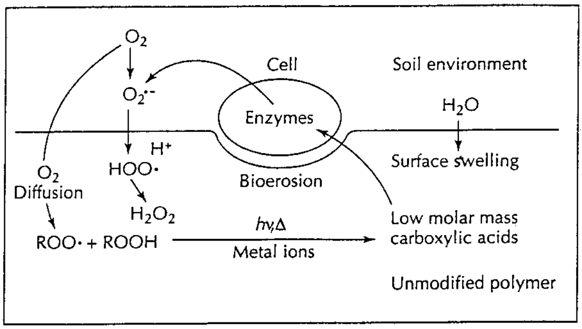


Fig. 4 Synergistic abiotic and biotic initiation in the bioassimilation of hydrocarbon polymers (Reproduced with permission from G.Scott, *Trends in Polymer Science*, 5, 365 (1997))

Colonisation results partly from the fact that an unmodified hydrocarbon polymer surface is hydrophobic and hostile to microorganisms. Modification by oxidation leads to a high concentration of hydrophilic groups in the polymer surface which in turn leads to water swelling and the rapid diffusion of low molar mass nutrients that can be assimilated by the cell. At this stage the Cytochrome enzymes come into play, providing an additional initiation mechanism. The overall effect is rapid bioerosion from the polymer surface which leaves the molecular weight distribution in the bulk of the polymer essentially unchanged [32].

The rate of bioassimilation of polymer products, then depends not only on the presence of antioxidants or on the presence of catalysts for peroxidation but also on the profile of the polymer artefact. Thick sections of polymer may take many years to bioassimilate unless they undergo fragmentation due to mechanical property change. Thin mulching films, on the other hand, which undergo rapid fragmentation under the influence of the same catalyst, cannot be distinguished from the decayed vegetable biomass after one season of environmental exposure [30]. Bioegradable mulching films conserve irrigation water and fertilsers during the growing season [3,31] and are returned to the biosystem, initially as biomass but eventually as carbon dioxide when they have served their primary purpose.

Environmental requirements of biodegradable polymers

Hydro-biodegradable polymers originating domestically fequently end up in sewage and are required to mineralise to CO_2 very rapidly (generally within days rather than weeks). Packaging polymers (e.g garden waste bags, hay-wrap, etc.) require a longer service life and must not lose their mechanical properties while in use. Since they are most likely to end up in the fields or in a municipal compost it is essemtial that they fragment rapidly and subsequently convert to biomass. Ultimate mineralisation may take months or even years and is not a critical factor in their bioassimilation (Table 1). Agricultural polymers may require a still longer life but again immediate mineralisation after fragmentation is neither necessary nor desirable. The primary requirement is that the plastic residues do not accumulate from season to season. The biomass generated from from hydrocarbon polymers actually contribute beneficially to the quality of the soil.

Table 1 Time scale for bioassimilation in different environments

Fate of waste	Time scale, products and preferred materials
Sewage (toilet products nappies, etc.)	Days, mineralisation essential. Preferred materials, cellulose, plasticised starch, some polyesters
Compost (garden waste bags, etc.)	Weeks to biomass. Preferred materials, peroxidisable polyolefins, starch composites or polyesters.
Soil (agricultural packaging, mulch films, twines)	Weeks or months to physical disintegration. Months to biomass, years to complete mineralisation. Preferred polymers, polyolefins.

Testing methods and protocols have to match the user environment. It is counter-productive and environmentally unnecessary to require that hydrocarbon polymers must nineralise within days of exposure to microorganisms. Biological waste materials do not behave in this way in compost or as agricultural litter.

Acknowledgement

I am grateful to Dr.R.Wasserbauer for helpful discussions, for details of unpublished work and for permission to reproduce Figure 2.

References

1. J.Guillet, *'Degradable Polymers: Principles and Applications'*, eds. G.Scott and D.Gilead, Chapman & Hall, 1995, Chapter 12.
2. G.Scott and D.Gilead, *'Degradable Polymers: Principles and Applications'*, eds. G.Scott and D.Gilead, Chapman & Hall, 1995, Chapter 13.
3. G.Scott, *'Polymers and the Environment'* Royal Society of Chemistry, 1998.
4. R.M.Ottenbright, A-C.Albertsson and G.Scott, *'Biodegradable Polymers and Plasticss'*, eds. M.Vert et al., Royal Society of Chemistry, 1992, p.87.
5. G.Scott, *'Atmospheric Oxidation and Antioxidants'*, Elsevier, 1965, p.386-389.
6. G.Scott, *'Atmospheric Oxidation and Antioxidants'*, Vol.II, ed. G.Scott, Elsevier, 1993, Chapter 3.
7. E.M.Bevilacqua, E.S.English and J.S.Gall, *J.App. Polym, Sci.*, 8. 1691 (1964).
8. M.B.Neiman, *Russ. Chem. Rev.*, 33, 13 (1964).

9. V.B.Miller, M.B.Neiman, V.S.Pudov and L.I.Lafer, *Vysolomol., Soedin*, **1**, 1690 (1959).
10. S.Karlsson, M.Hakkarainen and A-C.Albertsson, *Macromolecules*, **30**, 7721 (1997).
11. A-C.Albertsson, PhD Thesis, Kungl. Tekniska Högskolan, Stockholm, p.V18.
12. R.Wasserbauer, M.Beranová, D.Vancurová and B.Doležel, *Biomaterials*, **11**, 36 (1990).
13. M.Beranová, R.Wasserbauer, D.Vančurová and H.Prachařová, *Internat. Biodet.*, **27**, 297 (1990).
14. D.Metodiewa and H.B.Dunford, *'Atmospheric Oxidation and Antioxidants', Vol. III*, Elsevier, 1993, Chapter 11.
15. W.W.Westerfield and C.Lowe, *J. Biol. Chem.*, **145**, 463 (1942).
16. D.G.H.Daniels and B.C.Saunders, *J. Chem. Soc.*, 2112 (1951).
17. B.C.Saunders and P.J.G.Mann, *J. Chem. Soc.*, 769 (1940).
18. B.C.Saunders and G.H.R.Watson, *Biochem. J.*, **46**, 629 (1950).
19. *'Atmospheric Oxidation and Antioxidants'* , Vol. I, ed. G.Scott, Elsevier, 1993.
20. G.Scott, *'Antioxidants in Science, Technology, Medicine and Nutrition'*, Albion, Chichester, 1997.
21. H.S.Dweik and G.Scott, *Rubb. Chem. Tech.*, **57**, 735, 908 (1984)
22. Ref. 20, p.117.
23. J.Pospíšil, *'Developments in Polymer Stabilisation-1'*, ed. G.Scott, App. Sci. Pub., 1979, Chapter 1.
24. J.Pospíšil, *'Developments in Polymer Stabilisation-7*, ed. G.Scott, Elsevier App. Sci., 1984, Chapter 1.
25. G.Scott, *'Degradable Polymers: Principles and Applications'*, eds. G.Scott and D.Gilead, Chapman & Hall, 1995, Chapters 1 & 9.
26. B.N.Leyland and R.L.Stafford, *Chem. Canada*, 45 (1959).
27 J.D.Holdsworth, G.Scott and D.Williams, *J. Chem. Soc.*, 4692 (1964).
28. G.Scott, *'Atmospheric Oxidation and Antioxidants'*, Elsevier, 1965, p.290.
29. S.Al-Malaika, A.Marogi and G.Scott, *J. App. Polym. Sci.*, **31**, 685 (1986).
30. D.Gilead, *'Degradable Polymers: Principles and Applications'*, eds. G.Scott and D.Gilead, Chapman & Hall, 1995, Chapter 10.
31. A.Fabbri, *'Degradable Polymer: Principles and Applications'*, Chapman & Hall, Chapter 11.
32. R.Arnaud, P.Dabin, J.Lemaire, S.Al-Malaika, S.Chohan, M.Coker, G.Scott, A.Fauve and A.Maaroufi, *Polym. Deg. Stab.*, **46**, 211 (1994).
33. G.Scott, *Trends in Polymer Science*, **5**, 361 (1997).