Reviews

Programmed-Life Plastics from Polyolefins: A New Look at Sustainability[†]

Gerald Scott*,[‡] and David M. Wiles[§]

Aston University, Birmingham, United Kingdom, and EPI, Environmental Products Inc., Vancouver, BC, Canada

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The term "sustainable" is often assumed to be synonymous with "renewable". However, polymers made from renewable natural resources are not necessarily eco-efficient. Cellulose-based polymers utilize more nonrenewable fossil fuels and are more polluting during manufacture than petro-based polymers. Sustainable polymers also have to be industrially acceptable, and although ultimate biodegradability in the natural environment is important, polymer-based products are required to biodegrade in a controlled way. Service life may be a year or more before the commencement of environmental degradation occurs. Many natural polymers such as rubber, lignin, and humus, like the synthetic polyolefins, biodegrade by an oxidative mechanism (oxo-biodegradation), and consequently much of nature's biological waste cannot satisfy the rapid mineralization criteria currently advocated by standards committees for synthetic polymers. Although biometric tests are more convenient to use than full composting tests, they are meaningless when applied to hydrocarbon polymers, whether natural or synthetic, since oxo-biodegradation is a slower process than hydro-biodegradation at ambient temperatures. Biodegradation standards currently proposed are unrealistic and will need to be modified on the basis of recent scientific evidence.

Technological Advantages of the Polyolefins

Degradable polyolefins have a long history. During the 1970s, a number of products based on polyethylene were commercialized (Table 1). It was recognized at that time that polyolefins as produced were oxidatively unstable in the environment, and early investigations showed that the reason for their instability was the presence of sensitizing impurities in the polymer.[1–4] The most important of these were carbonyl ($>C=O$)[1,3,4] and hydroperoxide groups ($-OOH$)[1,5–8] formed during manufacture of plastics products. This led to extensive studies in the polymer industries and later in universities directed toward extending the lifetime of polymers by using heat and light stabilizers.[5–12] The consequent understanding

Table 1. Commercial Degradable Polyolefins

photolytic polymers
    ethylene−carbon monoxide copolymers: E-CO
    ethylene−vinyl ketone copolymers; Ecolyte (J. E. Guillet)
oxo-biodegradable polymers
    antioxidant-controlled, transition-metal-catalyzed photo- and
        thermooxidizable polymers; Plastor (G. Scott−D. Gilead),
        TDPA (EPI)
PE−starch blends
    PE blended with starch (and subsequently with prooxidants)
    Coloroll, St. Lawrence Starch (G. J. L. Griffin)

of how the effects of sensitizers resulting from peroxidation could be controlled in polymers was subsequently applied to the opposite problem of accelerating the bioassimilation of polymers in a controlled way after they had served their useful purpose. The development of the degradable polymers listed in Table 1 resulted from these studies.[13–27]

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* Corresponding author. E-mail: scott@rogat.fsnet.co.uk.
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‡ Aston University.
§ EPI.

Table 2. Energy Used and Pollution Generated during the Manufacture of 50 000 Carrier Bags[a]

| environmental burden	polyethylene	paper
energy (GJ) during manufacture	29	67
air pollution (kg)		
SO_2	9.9	28.1
NO_x	6.8	10.8
CH_x	3.8	1.5
CO	1.0	6.4
dust	0.5	3.8
water burden (kg)		
chemical oxygen demand	0.5	107.8
biological oxygen demand	0.02	43.1

[a] Reference 31.

It is relevant to ask why the polyolefins were selected as a basis for biodegradable polymers rather than natural products such as cellulose, already used as cellulose acetate in packaging. Cellulose acetate 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. Furthermore, the modification of cellulose by acetylation to give technologically acceptable products sharply reduced the environmental biodegradability of the polymer so that the correct balance between technological acceptability and ultimate biodegradability was difficult to achieve.

By contrast, the polyolefins had already 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. They were particularly important in blown film technology and injection moulding because of their ease of conversion and low cost. The present-day efficient distribution of perishable foodstuffs is a direct consequence of the resistance of the polyolefins and other carbon-chain polymers to water and water-borne microorganisms,[25] and in agriculture, the new technology of plasticulture based on polyethylene was already making an impact on the growing of soft fruits and vegetables.[16,20,28,29]

Eco-Efficiency of Petro-Based and Bio-Based Polymers

Three main factors have to be considered when evaluating the life-cycle eco-efficiency of polymers (Figure 1).[30] The first is energy input during manufacture and disposal that is in turn reflected in the life-cycle cost of products. Low energy utilization during manufacture is of course an ecologically desirable objective since it also minimizes carbon dioxide generation. The polyolefins are based on low value oil fractions, and the energy utilized in the production of the same volume container is much lower than for paper (Table 2). The polyolefins can also be recycled for second-life use in a number of ways.[30] If the waste is clean, it can be mechanically recycled, and if incinerated with energy recovery, waste polyolefins have a calorific value almost identical to the oil from which they are manufactured. In this respect, they are less polluting than fossil fuels. As will be discussed below, hydrocarbon polymers also make a positive contribution to compost by biological recycling.

Bio-based polymers such as cellulose and starch are not so conducive to mechanical recycling, and they also have a lower calorific value on incineration. Nevertheless, biomass from energy crops grown on marginal land is an increasingly important source of fuel, and it seems that it may be possible some time in the future to close the energy loop for the manufacture of biopolymers from renewable resources by using fast-growing grasses and soft wood crops as a source of fuel during manufacture thus conserving fossil resources for polymer manufacture (Figure 1).
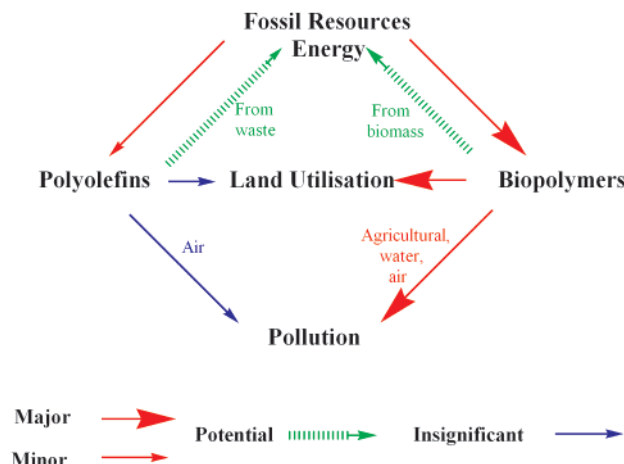
Figure 1. Eco-efficiency of polymers during manufacture and disposal.

The second criterion of eco-efficiency is the minimization of unwanted byproducts and associated pollution (Table 2). This is generally less during the manufacture of polyolefins than during the production of paper.[31] Solid waste and water-borne pollution is particularly severe in the case of agricultural-based polymers. Since the disposal of wastes and the purification of water are themselves energy-absorbing processes, they also contribute to the wastage of fossil resources.[30]

The third factor is land utilization. Although little information has so far been published on the areas and qualities of land that would be utilized if and when bio-based polymers were ever to approach the scale of production of the polyolefins, some reasonable estimates can be made from data already available: If the total U.S. plastics production were to be based on cellulose, a land area equivalent to seven states the size of Michigan, Louisiana, and Virginia would be required.[31] At 30% yield of PHA from an oilseed crop, 7% of the total worldwide land area at present used for the production of oilseed food crops would be required to produce only 7% of the U.S. requirements for packaging plastics.[32]

This suggests that crops for the manufacture of chemicals and polymers would very quickly come into competition with food crops. The argument that plastics could be made from surplus crops is of course parochial, applying primarily to some developed and relatively affluent countries. It is not a basis for the sustainable development of polymers worldwide. By contrast, the land utilization of the petrochemical and polymer industries is negligible in comparison and it seems probable that biopolymers will be restricted to the manu-

facture of speciality polymers, particularly for biomedical applications for the foreseeable future, and that petrochemicals will remain the basis of commodity plastics provided they are environmentally acceptable after discard.

It is clear then that the long-term eco-sustainability of plastics based on renewable resources has not yet been established. It is equally clear that the socioeconomic benefits of the synthetic hydrocarbon polymers also have to be taken into account in comparing synthetic polymers with natural polymers (see below). However, it is instructive to see how the present attitude to synthetic plastics has arisen.

The Popular Image of Plastics

Plastics made from petrochemical feedstocks are portrayed by the "green" lobby as ecologically undesirable because they are made from fossil carbon resources and it is assumed that they are very resistant to biodegradation in the environment. It is ironical that the very physical properties (water and microbe resistance) that have made the polyolefins so commercially successful are a disadvantage when the materials appear in the waste stream.

In the 1960s, a well-known environmentalist, Barry Commoner, suggested that because no biological organisms were known that could attack plastics, the earth would soon be buried in 10 feet of plastics waste! Thirty years later, he expressed the same views in rather a different way when he stated in a report for Greenpeace,[33]

> "Materials made from naturally occurring or biologically produced polymers are the only truly biodegradable 'plastics' available. Since living things construct these materials, living things can metabolise them."

However, many naturally produced materials also persist in the environment for very long periods. For example, certain types of wood such as the sequoia can survive for 500 years in the biotic environment after being felled due to the high concentration of the antioxidant/antibacterial tannin in the bark.[32] Natural rubber (*cis*-polyisoprene) is a hydrocarbon polymer, which oxo-biodegrades naturally in the form of latex as it comes from the rubber tree. However, it can also be synthesized in a chemical plant, and synthetic *cis*-polyisoprene shows exactly the same behavior in a bioactive environment. The same is true of other hydrocarbon rubbers (e.g., polybutadiene) not found in nature. Strikingly, however, both natural and synthetic rubbers after formulation with antioxidants in automotive tires, like sequoia wood, do not detectably biodegrade for many decades in the outdoor environment. This is because the antioxidants added during manufacture inhibit the formation of low molar mass oxidation products that are absorbed and utilized as a source of energy by bacteria and fungi. The nonbiodegradability of commercial rubber products is then not a consequence of the nonbiodegradability of the rubber molecule whether natural or synthetic but of the inhibition of its oxidation by antioxidants.[32]

Polyolefins are hydrophobic hydrocarbon polymers similar to the rubbers, and like the rubbers, they are very resistant

to peroxidation and biodegradation as commercial products due to the presence of antioxidants and stabilizers.[34−36] They are also highly resistant to hydrolysis, and for this reason they cannot hydro-biodegrade. However, it has been shown that they can be made oxo-biodegradable by the use of prooxidant additives[11−17,19−27,32] leading to hydrophilic surface modification friendly to microorganisms that are thus able to bioassimilate the low molar mass oxidation products (see below).

Balancing Environmental Acceptability against Technological Utility

The polyolefins and the polysaccharides stand at the opposite ends of a spectrum of polymer properties (Figure 2).
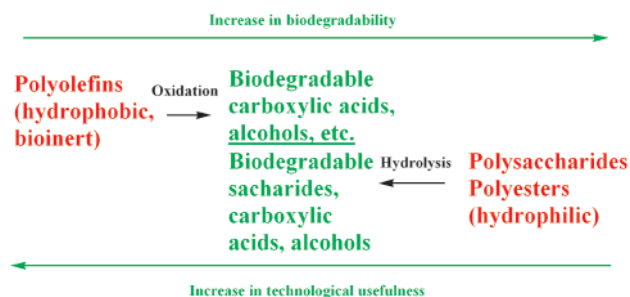

Figure 2. Technologically and environmentally acceptable polymers from polyolefins and natural products.

The naturally occurring hydro-biodegradable polymers such as cellulose, starch, and so forth are water wettable or water swellable. Consequently, to be technologically useful, they have to be made less hydrophilic with sacrifice of biodegradation rate. The properties of synthetic hydrocarbon polymers are a mirror image of this.[25] They are resistant to water, which is their main attribute in packaging, but in their conventional commercial versions, they do not biodegrade at a practically acceptable rate in the natural environment and they in turn have to be made more oxo-biodegradable by prior thermo- or photooxidation. Between these two extremes are the hydro-biodegradable aliphatic polyesters such as polylactic acid (PLA) and the poly(hydroxyalkanoates) (PHA). These, like the hydro-biodegradable polysaccharides are on a "knife-edge" balance between the achievement of useful technological performance and end-of-life biodegradability. The polyolefins, by contrast, can be given a programmed lifetime by the use of antioxidants. Sustainability must in practice be a compromise between commercial viability (i.e., cost-performance) and environmental acceptability. This must ultimately mean adaptability, namely, the potential for adapting polymers (both bio-based and petro-based) to the needs of the environment and to the needs of society. Bio-based polymers have already found important niche applications (for example in medicine) where cost is much less important than function. However, cost with environmental acceptability will continue to dominate the consumer market, and it seems very unlikely that biodegradable petro-based polymers will be displaced from their current role in packaging and agriculture.

Programmed-Life Polyolefins

It is implicit in the above discussion that bioassimilation of plastics residues in the environment is an essential but not the only requirement of technologically useful packaging plastic. In most cases, plastics require a controlled lifetime before physical degradation commences. Figure 3 shows the behavior of an ideal degradable plastic.
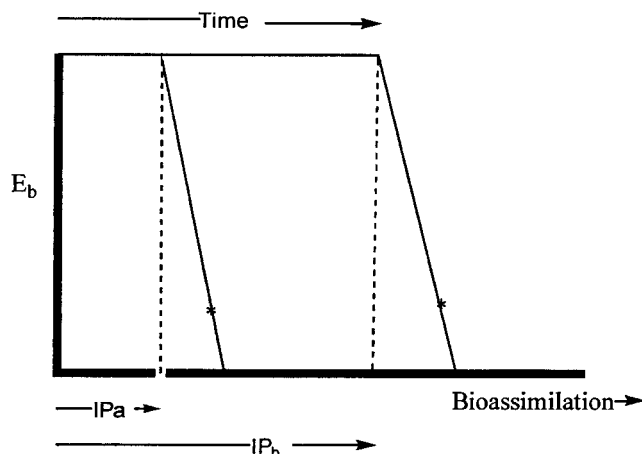

Figure 3. The ideal behavior of a degradable plastic in the environment (ref 32). E_b = elongation at break; IP_a and IP_b are induction periods during which no change in chemical, physical, or mechanical properties should occur; * is the point at which the sample disintegrates (generally ~85–90% loss of E_b).

There should be no change in the physical and mechanical characteristics of the polymer during the induction period (IP). Moreover, the IP must be variable (IP_a, IP_b) and controllable in the end environment if the full potential of the plastics is to be realized.[23] Photolysis and thermolysis of peroxidation products (notably, $>C=O$ and POOH) is the primary cause of the loss of mechanical properties of hydrocarbon polymers in the environment.[1,10,14,21,23,24] In many applications and particularly in plasticulture, mulching films and tunnels used to control the microenvironment of the plant[20,28,29,32,34–36] must be timed to disintegrate ($E_b <$ 10%) under slight pressure at the end of their useful life. If the films break too early, there will be a significant loss in crop yield, and if they break down too late the partially degraded plastic will clog the automatic harvester.

The photographs in Figure 4 illustrates two different grades of polyethylene mulching film that differ only in the induction period before physical disintegration commences. In this case, the IP of #131 is 5 times that of #221 which enables a second crop to be grown over the same film the following season. The subsequent physical fragmentation and ultimate bioassimilation occurs at a similar rate.

Many auxiliary plastics products used in agriculture and horticulture also require an extended lifetime before losing mechanical strength. Important examples are polypropylene baler twines, polyethylene stretch-wrap silage films, bird protective netting, and agricultural packaging.[32] It is crucially important then to understand how the hydrocarbon polymers degrade in the environment by a combination of peroxidation and bioassimilation and how the free radical chain mechanism can be controlled by antioxidants.

28 days after laying (October 27 1999)

92 days after laying (Dcember 30 1999)

Figure 4. Programmed-life mulching films in Taiwan. Printed with the kind permission of Dr. S-R. Yang at the Tainan District Agricultural Station.

Products Formed by Peroxidation of Polyolefins

The mechanism of abiotic peroxidation of hydrocarbons has been extensively studied over the past 50 years.[1,2,5,8–12,33–35,48] The primary products of the peroxidation chain reaction in (1) and (2) are hydroperoxides which either thermolyze (Δ) or photolyze ($h\nu$), particularly in the presence

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

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

of transition metal ions (see below) with chain scission and the production of biodegradable low molar mass oxidation products such as carboxylic acids, alcohols, aldehydes, and ketones (Scheme 1). Many of these oxidation products are lost by volatilization during thermal oxidation in an open atmosphere, and carbon dioxide has been recognized to be a significant product under these conditions.[38–44] Albertsson, Karlsson, and co-workers have recently paid particular attention to the low molar mass products, and a wide range of carboxylic acids, alcohols, hydroxy alcohols and esters, and low molar mass hydrocarbon waxes have been identified in the thermal and photooxidation of commercial degradable polyethylenes.[43,44] The process involves the formation of vicinal hydroperoxides by the well-established "back-biting" mechanism,[45,46] and in the case of polypropylene, 90% of

the hydroperoxides are present as hydrogen-bonded vicinal hydroperoxides.[45] However, both isolated (non-hydrogen-bonded) and vicinal (hydrogen-bonded) hydroperoxides are present in polyethylene, and Albertsson et al. have concluded that the same mechanism is responsible for the low molar mass biodegradable products they have identified during peroxidation of PE.

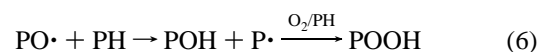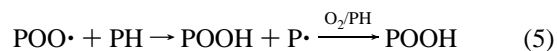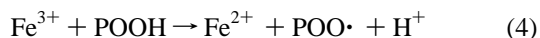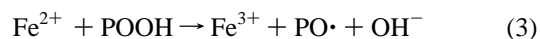**Scheme 1.** Formation of Biodegradable Carboxylic Acids by Peroxidation of Polyethylene

An interesting consequence of the above mechanism is that in the presence of microorganisms the concentration of carbonyl compounds is very much reduced,[43] indicating that they are assimilated by the microbial cells as they are formed. This is consistent with the findings of Lemaire, Scott, et al.[47] that microorganisms can utilize oxidized polyethylene as the sole source of carbon, leading to bioerosion of the polymer surface while leaving M_w of the bulk plastic essentially unchanged.

As mentioned earlier, antioxidants inhibit the chain reaction that leads to hydroperoxide formation and the subsequent biodegradation of hydrocarbon polymers.[32,34,35] Thus, chain-breaking (hindered phenol) antioxidants inhibit the oxo-biodegradation of the polyolefins under thermooxidative conditions during service. However, to simply omit antioxidants and stabilizers during conversion to commercial products is not a viable technological solution to the environmental persistence of hydrocarbon polymers since they are added to protect the polymer against mechanooxidation during the processing operation and to provide the required shelf life.[48] Furthermore, commercial processing stabilizers such as the hindered phenols or phosphite esters considerably extend the life of the polyolefins in the outdoor environment[49] even though they are not normally considered to be light stabilizers.

It has been known since natural rubber became a technological product that many transition metal ions are effective accelerators for peroxidation and hence for the biodegradation of the hydrocarbon polymers (Scheme 2) and that this can be retarded by certain types of antioxidant.[5,37,50,51] Hindered phenols control the metal-catalyzed melt degradation of polyolefins during processing but are relatively ineffective in controlling photodegradation.[51] Photodegradable polyolefins based on transition metal compounds and processing stabilizers are thus very effective in short-term applications such as garden waste bags that are intended to biodegrade in aerobic compost but not in programmed-life products such as mulching films, silage film, or baler twines where an outdoor service life of up to 12 months may be required. Some of the naturally occurring oxygenases (e.g., Cytochrome P450) act in a similar way to initiate an abiotic peroxidation process, and this has been shown to occur when

polyethylene contains no protective antioxidant.[22] The evidence suggests that the combination of abiotic and biotic initiation of peroxidation causes a cooperative bioassimilation of the polymer.

Scheme 2. Iron Catalyzed Peroxidation of Hydrocarbon Polymers[a]

$$Fe^{2+} + POOH \rightarrow Fe^{3+} + PO\cdot + OH^- \qquad (3)$$

$$Fe^{3+} + POOH \rightarrow Fe^{2+} + POO\cdot + H^+ \qquad (4)$$

$$POO\cdot + PH \rightarrow POOH + P\cdot \xrightarrow{O_2/PH} POOH \qquad (5)$$

$$PO\cdot + PH \rightarrow POH + P\cdot \xrightarrow{O_2/PH} POOH \qquad (6)$$

[a] PH = hydrocarbon polymer, POOH = macromolecular hydroperoxide.

Since the sequence of reactions shown in Scheme 2 leads to the rapid buildup of hydroperoxides in the polymer, peroxidation cannot be controlled by chain-breaking antioxidants such as the hindered phenols since the latter are rapidly destroyed by hydroxyl and peroxyl radicals. By contrast, some peroxidolytic antioxidants such as the metal dithiocarbamates, $(R_2NCSS)_2M$, are able to catalytically destroy hydroperoxides as they are formed in the polymer in a process not involving the formation of radicals.[9−12,16,22] Consequently, peroxydolytic antioxidants based on transition metal ions inhibit peroxidation until the antioxidant has been depleted by the action of light or heat, liberating the prooxidant metal ion in a controlled manner. This process has been discussed in a number of reviews of antioxidant-controlled biodegradation of carbon-chain polymers[15−17,23,32,34−36] and will not be discussed further here.

The Effect of the Biodegradation Environment

The two alternate mechanisms of polymer biodegradation, summarized in Figure 5, cut across the biopolymer−petropolymer divide. Hydro-biodegradation is the well-known process that gives bioassimilable products from cellulose, starch, polyesters, etc. Oxo-biodegradation also leads to the generation of biodegradable carboxylic acids, alcohols, ketones, etc. by peroxidation, initiated by heat or light. It should be noted that although photolysis of C=O modified polymers is a precursor to peroxidation in the case
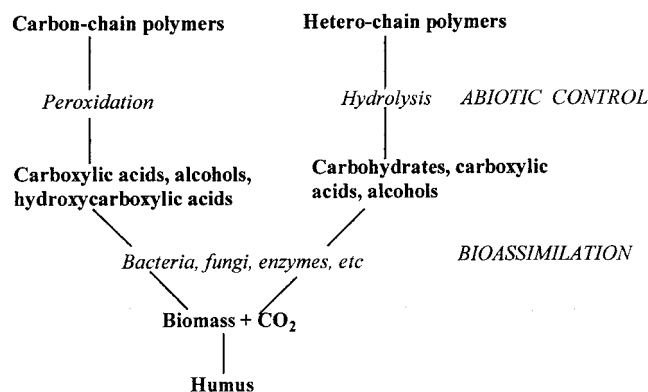

Figure 5. Alternate mechanisms for the biodegradation of the synthetic polymers (ref 32).

of the Ecolyte polymers,[31] E-CO plastics do not appear to biodegrade rapidly after photolysis.[47]

Like the hydrolysis products from hydro-biodegradable polymers, the low molar mass oxidation products formed by peroxidation of the polyolefins can also be utilized by microorganisms as nutrients to produce cell biomass.[43,44,47,52] Rubbers, if they do not contain antioxidants, oxo-biodegrade much more rapidly than the polyolefins. Aliphatic polyesters are more oxidatively stable, but they are hydrophilic and are hydrolyzed and bioassimilated rapidly in an aqueous biotic environment in much the same way as starch and cellulose.

The development of standard tests to measure the rate of biodegradation of polymers is necessary in order to ensure that residues from plastics packaging do not create a long-term pollution problem in the environment. Unfortunately, carbon-chain polymers, including many natural products, do not pass the tests laid down by the American Society for Testing Materials (ASTM) in the U.S. and Comité Européen de Normalisation (CEN) in Europe. Quite unscientific explanations are put forward to explain why synthetic polymers, but not natural polymers, must be shown to be mineralized within a very short time, for example, in compost. It is argued that there is no need to demonstrate that natural materials such as leaves and twigs (which contain the relatively slowly oxo-biodegrading lignin) do not need to mineralize during composting but that synthetic hydro-carbon polymers are "different".[54] The following rationale is given by CEN to explain why this distinction can be made.

> "Natural products (leaves, wood, small stones are...generally known to be non-toxic. They are universally recognised as biodegradable. On the other hand, residues of synthetic polymers would be perceived by the general public as being contamination of the compost"

The basis for this statement is that

> "The accumulation of lignin in the environment is a natural event which is beneficial for the fertility of the soil. On the other hand, the accumulation of other foreign materials cannot be encouraged because, while it is well known that lignin is ultimately degradable and helps environment and soil structure, this cannot be claimed for synthetic products whose behaviour in the environment is not known"

From this, it is reasoned that

> "the CEN scheme considers lignin and the natural non-chemically modified materials as biodegrad-able *by definition*"

This extension of the popular views of Greenpeace discussed above is not a good basis for the development of science-based standards. In particular, it ignores the extensive studies on the oxo-biodegradation of polyolefins. Nor does it recognize that lignin, a major constituent of natural products, is also an oxo-biodegradable polymer similar in structure to the synthetic phenol-formaldehyde resins and like the latter, it is very stable due to the presence of the polyphenolic antioxidant functions in the polymer chain.

Thus, polyethylene, PF resins, lignin, humic acid, and tannic acid oxo-biodegrade relatively slowly but all are ultimately converted to carbon dioxide and water. Humus is a complex mixture of polyphenolic and quinonoid compounds, and the slower mineralization occurs, the more beneficial is this organic matter to the fertility of the soil.

The Time Scale for Bioassimilation into the Environment

Biodegradable plastics may end up in sewage systems, in compost, or on the soil as litter (Figure 6). The CEN standard for synthetic polymers in compost, EN 13432, stipulates that they must be substantially (i.e., >90%) converted to carbon dioxide and biomass in an aqueous biotic environment within 6 months.[55] This is to simulate the behavior of pure cellulose which is rarely found as such in nature. The presence of lignin in natural products such as leaves and twigs slows down this process in an ambient biotic environment for the reasons already discussed.
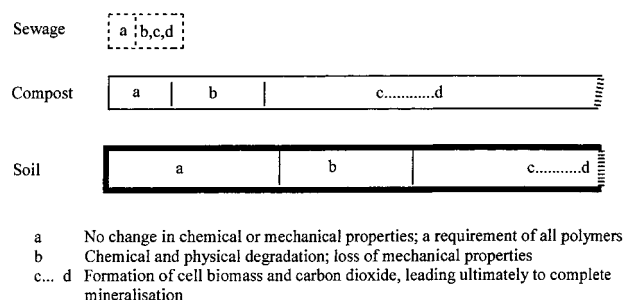

a	No change in chemical or mechanical properties; a requirement of all polymers
b	Chemical and physical degradation; loss of mechanical properties
c... d	Formation of cell biomass and carbon dioxide, leading ultimately to complete mineralisation

Figure 6. Biodegradation time scale for polymers in different environments (ref 32).

A good deal of packaging based on cellulose in combination with lignin and/or other bonding agents does not satisfy this requirement, raising serious doubts about the ecological validity of this test.

In reality, rapid mineralization brings no benefit to compost or to the soil since it increases the CO_2 "greenhouse" effect. Rapidly mineralizing polymers are not therefore "recoverable" in the sense required by the European Directive since carbon dioxide is not a useful product. Rapid mineralization is thus a waste of resources, and to make it a requirement that synthetic polymers entering the compost or soil environment must be rapidly mineralized is ecologically counterproductive.

The proposed standards are causing a great deal of concern to manufacturers of degradable polyolefins because of their arbitrary nature. No oxo-biodegradable polymers including those found in nature can possibly pass the mineralization test demanded by EN 13432. The effect of this standard will be to discriminate in the future against the manufacturers of degradable hydrocarbon polymers throughout the countries of the enlarged European Union. At the same time, it will favor less ecologically efficient bio-based polymers with consequent detrimental effects on the environment.

A number of specialists in polymer degradation have pointed out that EN 13432 does not take into account research carried out during the past 10 years on the biodegradation of the polyolefins. Laboratory biometric tests are based on CO_2 evolution or oxygen absorption at ambient

temperatures in an aqueous environment. These tests (e.g., the Sturm test) were originally developed to evaluate the biodegradability of aqueous detergents, and while they are entirely satisfactory for characterizing polymers that have to biodegrade rapidly in sewage systems (Figure 6) they are not effective in characterizing the behavior of polymers in compost at elevated temperatures. The compost environment accelerates the peroxidation of the oxo-biodegradable poly-olefins and also permits the assessment of ecotoxicity on the final product in the field under real conditions. Equally important tests are laboratory measurement of abiotic per-oxidation and the rate of subsequent bioassimilation of low molar mass oxidation products. These provide complemen-tary information that can be used to assess the time scale for ultimate absorption of the polyolefins into the environ-ment. The following is an excerpt representing the views of scientists active in the field of polymer degradation.[56]

> "Biodegradability tests that have been developed largely reflect the behaviour of hydro-biodegradable polymers (e.g. aliphatic polyesters, modified starch). These materials are ideal for rapid biodegradation in sewage sludge where a maximum rate and extent of mineralisation is required. The fundamental characteristic and most positive value of compost or mulches is the presence of biomass. Without biomass, there simply would be no product.

> "Rapid mineralisation is not ideal for polymers in compost where the carbon in the original plastic should be converted over a longer period of time to biomass and only slowly to carbon dioxide. The oxo-biodegradable polymers (e.g. the polyolefins) are ideal for this purpose since controlled peroxi-dation is the *rate-determining* step in the overall process. Furthermore they cannot give toxic or otherwise objectionable by-products during bio-assimilation"

Similar concerns have been expressed by the European Commission Directorate for Industry and the Environment.[57]

> "ISO 14851 (0xygen consumption) and ISO 148 (Sturm test) do not simulate composting conditions

> "What is really needed is to know what is the fate of materials under composting conditions and what happens once it is released to the soil

> "If the packaging material does not completely biodegrade during the composting process, it should be demonstrated that it eventually degrades in the soil"

This demands an early revision of EN 13432 to take into account scientific studies on the biodegradation of polyolefins carried out during the past eight years. This should be based upon the hierarchy of tests shown in Table 3 and the scientific basis for them.

A number of basic scientific studies have already been published which are relevant to the oxo-biodegradation of

Table 3. Hierarchy of Tests

full scale composting trials
    particle size reduction
    visual impact
ecotoxicity measurements
    plant germination and growth rate
    accumulation of transition metals in stems, leaves and fruit
    effect on macroorganisms (worms, daphnia, etc.)
background scientific studies
    rate of abiotic peroxidation at composting temperatures
    rate of biomass formation and polymer weight loss
    biometric measurements on peroxidized polymer
    correlation of bioerosion with extent of peroxidation

polyethylene in the environment. For example, it has been shown that soil bacteria and fungi can utilize peroxidized polyethylene in the absence of any other source of carbon leading to bioerosion of the polymer surface.[47] Biometric tests (oxygen absorption) have confirmed that the thermal peroxidation products formed on the surface of the polymer are rapidly mineralized.[52] There is also growing evidence that polyethylene can biodegrade in the body.[58,59] Studies are currently in progress to correlate the extent of peroxi-dation of polyolefins with polymer weight loss both during abiotic and biotic assimilation processes.

Conclusions

Nature uses a combination of abiotic and biotic processes to return its own waste to the natural carbon cycle. Abiotic peroxidation and hydrolysis of man-made polymers normally precede the bioassimilation of low molar mass products in the environment. Consequently, International Standards must reflect this fact and incorporate the relevant abiotic processes into test methods and protocols.

The polyolefins have been shown to satisfy the same oxo-biodegradability criteria that characterize biopolymers such as natural rubber and lignin, and as they are more eco-efficient during manufacture and effective during use than bio-based polymers, it seems certain that they will remain the materials of choice for packaging and agricultural applications.

References and Notes

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