

**REVIEW OF BIODEGRADABLE
POLYOLEFINE TECHNOLOGY**

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A. Background and History of Biodegradable Plastics and Standards

From the time of their discovery and commercialization plastics were designed to be long lasting and persistent and the plastics industry developed techniques and additives to support this requirement. Apart from some early cellulosic derivatives, which were not necessarily thermoplastic, the first work on “biodegradable” plastics started in the 1970s with the work of Griffin in the UK with granular starch in polyethylene (1), the developments with gelatinized starch by Otey at the USDA in Peoria (2) and the evaluation of polycaprolactone (PCL) biodegradability by Potts at Union Carbide (3). There was some commercial development of these findings, but the technologies only came under public scrutiny in the late 1980s.

From 1985 a number of plastic products were introduced to the market with claims of biodegradability and some stating how they would help save diminishing landfill space. The U.S. Federal Trade Commission, some States Attorneys General, State legislators and the U.S. Congress became very concerned over some of the claims. In the United States 48 separate legal actions were initiated for misleading environmental advertising, including the most notorious against Archer Daniels Midland (ADM) and Mobil, which resulted in fines around \$1 million each. The latter was making claims for the biodegradability of Hefty bags in landfill when they included a photodegradation additive!

The resulting bad publicity set the biodegradable plastics industry back several years. Another consequence was the setting up of Committee D 20.96 by the American Society of Testing and Materials (ASTM) to standardize test methods and standards. Because of the background to this Committee there was also an overreaction against degradable plastics based on polyethylene and a deliberate focus on rapid mineralization (conversion of the polymers by microorganisms to carbon dioxide, water and biomass).

The Committee developed the test method ASTM D 5338, which is a laboratory procedure to determine carbon dioxide evolution under simulated compost conditions. This became the basis for similar test methods in Europe and Japan. This test method has several drawbacks, the most significant being that it does not take account of the amount of the plastic polymer that is biodegraded and assimilated into the biomass.

Recently a Standard Guide, D 6954-04, for Exposing and Testing Plastics that Degrade in the Environment by a Combination of Oxidation and Biodegradation was drawn up and, whilst this is a significant step forward on the acceptance of the oxo-biodegradable technologies, it is not yet in the form of a Standard.

Although the oxo-biodegradable plastics require the first oxidation step before the polymer or polymer fragments can be metabolized by microorganisms, similarly “biodegradable” polyesters need a hydrolysis step before they can be mineralized. This is particularly true of polylactic acid, which in composting is first hydrolysed and then mineralised; the polylactic acid is not directly attacked by the microorganisms.

B. Types of Biodegradable Plastics Technologies

1. Naturally derived polymers

There are many naturally derived polymers that have been tried in plastic applications and some of these have been rendered thermoplastic. Since the polymers derive from nature there are generally enzymes widely available to metabolise them, but their properties are not necessarily compatible with typical plastic processes nor are their properties comparable to the synthetic polymers.

Cellulose and its derivatives have been used for many years and cellulose can be made thermoplastic by chemical treatment. The main derivatives, cellulose acetates, unfortunately become less biodegradable the higher the degree of substitution by acetate which improves processibility.

Starch, derived from corn, wheat or many other cereal sources, is readily and widely available and has been the target of many attempts at commercialization in the plastics industry. The problem with starch is that it decomposes at a lower temperature than it melts and therefore, for conventional processing, needs to be plasticized, for example with water, glycerol or urea as in Otey's work (2). Because of its properties, particularly its humidity sensitivity, for many applications it needs to be blended with other more processible polymers, such as polycaprolactone. Its widest use in the biodegradables industry is in loosefill, where it is often blended with small amounts of polyvinyl alcohol, and can be used to replace expanded polystyrene.

Granular starch has been used as an additive to enhance the biodegradability of materials such as polyethylene (1), but by itself it does not render the synthetic polymer biodegradable.

The biodegradability of natural starch has not been questioned and it has been shown to mineralize rapidly in aerobic or anaerobic conditions. However, like cellulose, with increasing substitution by acetyl groups, the biodegradation rate falls.

Several other natural polymers have been proposed for biodegradable plastics, such as chitin/chitosan, proteins, particularly those derived from soy or wheat, but the performance has not yet been good enough to commercialise these materials fully. However, with the spiraling cost of fossil fuel derived polymers, they could have a future.

2. Polyesters

There are many varieties of polyesters proposed for biodegradable plastic applications. Some are produced microbiologically, particularly polyhydroxy butyrate/valerate (PHBV). Until now this has not been a cost-effective process and Monsanto with Biopol (formerly the technology belonged to ICI) withdrew from the business. Metabolix jointly with ADM are proposing to commercialise these polymers as is Procter and Gamble with Nodax.

Biodegradable aliphatic polyesters have been produced in Japan by companies such as Dowa Highpolymer with Bionolle and in Korea by Ire Chemical . The problem with these materials is their cost.

Biodegradable aliphatic/aromatic polyesters have been developed by Eastman with Eastar (the technical know-how is currently owned by Novamont) and BASF with Ecoflex. These also have the problem of high cost. Another version of an aromatic polyester is Biomax from Dupont; this material is only slowly biodegradable and does not mineralize in less than 180 days in many tests.

Polylactic acid has been produced for many years mainly for medical applications and only in the last ten years has it been proposed for commodity type applications. Much of this thrust has come from Cargill which has built a 140,000 ton/yr. plant. Inevitably because the production includes a very specific fermentation followed by formation of the dimer and then polymerization, the cost is high. There are several other polylactic acid producers, mainly in Japan.

Other polyesters include materials such as polyglycolic acid, but these are not used in thermoplastic applications.

3. Vinyl polymers

The two main biodegradable vinyl polymers are polyvinyl alcohol (PVAL) and ethylene vinyl alcohol (EVOH). The degradation of both these polymers requires oxygen and they will not biodegrade anaerobically. The speed of biodegradation depends on several factors – for polyvinyl alcohol the degree of hydrolysis, whether it is predissolved in water and whether the microbial population has been acclimatized to the material. For EVOH the speed of biodegradation depends on the ethylene content (the higher the ethylene content the slower the rate of degradation).

There has been considerable commercial activity with polyvinyl alcohol in the past few years particularly in Europe with companies such as Idroplast, Polyval, Aquafilm (now part of Monosol) and the Environmental Polymer Group (now part of Stanelco) promoting mainly PVAL film.

Because of the strength of PVAL it can be cost competitive on the basis of simple strength, but it requires plasticization (like starch), is difficult to work with and is susceptible to moisture and changes in humidity. Its biodegradability can be very slow and depends critically on the conditions.

Polyvinyl chloride (PVC) has been suggested as a biodegradable material but the degradation is usually due to loss of plasticizer resulting in embrittlement, although it can be made oxidatively degradable.

4. Oxidatively degradable and biodegradable systems

Rather than designing special biodegradable polymers technology has been developed to provide suitable additives for commodity polyolefines, such as polyethylene and polypropylene. These polymers are typically susceptible to oxidative degradation and generally have to be stabilized to prevent this. Polymers such as linear low density polyethylene and polypropylene need anti-oxidants for processibility and stability in use.

By selecting a suitable commodity polymer and designing an appropriate additive the necessary stability in use and degradation in the designated environment can be tailor made – “programmable life”. Because the additive, generally at low levels, is added to a standard polymer the processing is straightforward and no changes are necessary to the manufacturing procedure. The physical properties of the product are the same or insignificantly different from the standard. Furthermore the cost of the finished product is very close to the standard.

5. Others

Other biodegradable polymers include Polyox, poly(ethylene oxide), which is water soluble and environmentally degradable due to oxidation and aerobic biodegradation. Polyox has been used to make films.

C. Summary of Shelf Life, Performance, Cost and Biodegradation

The advantages and shortcomings of the various biodegradable plastics technologies can be summarized as follows:

Technology	Shelf Life	Performance	Cost	Biodegradation
Natural polymers	Generally satisfactory	Weaker than conventional plastic materials. Processing is often difficult	Basic polymer cost is low but it needs additives and additional processing	Very fast
Polyesters	Mostly satisfactory, but there can be problems with low melting polymers such as PCL	Generally satisfactory, but processing can require special procedures	A multiple of conventional plastics	Variable from slow to fast depending on the polyester type
Vinyl	Satisfactory	Humidity dependent. Processing is difficult	Higher than commodity plastics	Oxygen dependent and generally slow
Oxidative/ Biodegradable	Adequate	Excellent – as good as conventional plastics	Very close to commodity plastics	Following oxidation slow biodegradation is achieved

D. Degradation and disintegration with oxidative/biodegradable technology

The Add-X oxo-biodegradable technology is designed to ensure satisfactory performance in use and degradation followed by biodegradation in appropriate environments. In addition different degrees of oxidative photodegradation can be built in. The technology is used with conventional polyolefines, such as polyethylene and polypropylene as well as with polystyrene.

Depending on the particular grade of Add-X's Addiflex additive there can be three mechanisms involved in the degradation of products containing the additives:

- The oxidation of the polyolefine
- The microbial digestion of the directly biodegradable polymer (where added)
- The microbial digestion of the polyolefin fragments

Although these mechanisms can be studied separately they usually occur simultaneously and there is often synergy between them.

Polyolefines, such as polyethylene and polypropylene are known to oxidize during processing and slowly degrade during their lifetime. The chemical processes are accelerated by heat – thermal oxidation – and by UV light – photodegradation. For this reason anti-oxidant stabilizers are added to polyolefine materials to prevent, or at least slow down, this breakdown.

With Addiflex modified products chemicals are added to accelerate the polymer breakdown, but, in order to achieve stability during use, the polymers selected often need to contain some anti-oxidant. These additives, particularly at the low levels used are totally safe for the environment and are approved for products in contact with food.

The free radical oxidation mechanisms for the breakdown of polyolefines are well understood (4-7). The results of these oxidation reactions can be studied at the molecular level and the changes in physical properties measured with standard testing equipment.

One of the effects of the oxidation is breaking of the polymer chain and therefore reduction in molecular weight./ There have been numerous studies measuring the molecular weight change during the catalysed oxidation of polyolefines. For illustration the following table from the studies of Michèle Weiland at the Université Libre de Bruxelles (8) is typical.

Temperature °C	Time (days)	M _w	M _n	M _w /M _n	n
	0	94,900	17,600	5.4	-
70	2	11,800	2,100	5.6	7.4
	5	3,510	1,090	3.2	15.1
	12	2,380	780	3.1	21.6
	20	2,080	690	3.0	24.5
	28	1,840	610	3.0	27.9
60	2	17,200	3,730	4.6	3.7
	5	4,620	1,240	3.7	13.2
	10	3,060	930	3.3	17.9
	25	2,170	710	3.1	23.8
	40	2,000	660	3.0	25.7
40	15	29,800	4,250	7.0	3.1
	25	14,900	2,590	5.8	5.8
	45	6,960	1,560	4.5	10.3
	95	3,390	940	3.6	17.7

Table 1. Molecular weight changes of LDPE film containing manganese as a degradation catalyst.

Another method of chemically studying the oxidation process is to measure the concentration of the molecules resulting from the reaction. Typically this is done using

FTIR (Fourier Transform Infra Red) and measuring the carbonyl group formation. The carbonyl group occurs in oxidation products such as aldehydes, ketones, esters and lactones and this group is chosen because of the strength of its absorption in the infra red. Typical results are shown below for films both thermally oxidized and photo-oxidised in the SEPAP apparatus at CNEP (Centre National d’Evaluation de Photoprotection) in Clermont Ferrand by Professor Lemaire (9). The SEPAP apparatus exposes the film to irradiation similar to sunlight.

Time (hours)	$\Delta DO, 1715 \text{ cm}^{-1}$
0	0
20	0.020
40	0.056
60	0.110
80	0.179
100	0.239
140	0.345

Table 2. Change in Optical Density (ΔDO) of a 30 μ film containing Addiflex exposed in the SEPAP apparatus.

Time (hours)	$\Delta DO, 1715 \text{ cm}^{-1}$
0	0
48	0.001
93	0.003
134	0.002
188	0.005
264	0.003
330	0.009
382	0.008
526	0.015
894	0.177
1006	0.570

Table 3. Change in Optical Density (ΔDO) of a 30 μ film containing Addiflex exposed in the oven at 60⁰C.

The degradation can be tracked by measuring the mechanical properties, but typically a ΔDO of 0.10 corresponds to a 50% drop in mechanical properties and by the time the film has a ΔDO of 0.30 it is too fragile to handle and spontaneously disintegrates.

The thermal measurements above were carried out in a dry oven, and it has been suggested that in damp conditions (such as might occur in a compost pile) the rate of thermal degradation is reduced. This has been investigated at SP (The Swedish National Testing and Research Institute) by Henrik Petersen and was the subject of his thesis for the Högskolan I Borås and the findings were reported by Dr. Jakubowicz at the CEES Workshop (Confederation of European Environmental Engineering Societies) in 2004

(10). Broadly speaking it was found that PE film disintegrates faster in humid conditions (60 and 100%RH) compared with dry conditions, but in a compost environment disintegration was retarded from 16 days to around 22 days, still adequate for commercial composting.

To determine all the compounds produced by the thermal oxidation of polyolefines the greatest detail is provided by identifying the degradation products by separating them using gas chromatography (GC) and identifying the molecules by mass spectrometry (MS). One such study has been undertaken at the Department of Polymer Technology at the Royal Institute of Technology in Stockholm (11).

A summary of the compounds identified is below (there were only very small differences observed using different transition metal catalysts):

- **Carboxylic acids:** formic acid to octadecanoic acid, benzoic acid
- **Ketoacids:** 4-oxopentanoic acid, 5-oxopentanoic acid
- **Lactones:** butyrolactone to 2(3H)-furanone
- **Ketones:** 2-pentanone to 2-heptanone
- **Hydrocarbons:** heptane to heneicosane
- **Aldehydes:** 3-methyl-pentanal to 2-propyl-5-oxohexanal
- **Esters:** hexanoic acid ethyl ester to undecanoic acid methyl ester

These benign bio-assimilable compounds are only present at very low levels and have no negative toxicological effect.

The physical effect on the plastic product as a result of the oxidative breakdown and reduction in molecular weight of the polyolefine is to reduce the strength of the material so that it becomes brittle and disintegrates. For film this is usually measured by determining the change in elongation, because this tends to be more progressive than tensile strength which can drop off suddenly during degradation. In order to obtain results in a relatively short time the degradation is carried out at elevated temperatures (not elevated by comparison with composting and some other applications). Below is a table showing the change in elongation of a film containing a degradation catalyst system compared with one without:

Time (days)	HDPE Film with Oxidative Catalyst System	HDPE Film with no Oxidative Catalyst
0	500.1	452.1
1	31.5	440.7
2	7.0	511.8
3	1.4	435.1
4	0	480.2
5	0	470.8
6	0	446.8
7	0	463.1
8	0	460.5

Table 4. Elongation (%) of two films stored in an oven at 80°C.

Although it depends to some extent on the polymer, the value of the average molecular weight (M_w) which corresponds to embrittlement of a film is in the region of 10,000 to 20,000. When degraded to this point the film disintegrates. This is also the molecular weight region in which biodegradation of the film can start.

E. Biodegradation of Products containing Addiflex

It is generally agreed that high molecular weight hydrocarbons ($M_w \sim 100,000$) such as polyethylene and polypropylene are not directly biodegradable because of their hydrophobicity and inaccessibility to microorganisms and their enzyme systems. It has been suggested that the wood rotting fungi, that are known to attack the high molecular weight lignin in wood by a “random” oxidation mechanism, might be capable of degrading high molecular weight polyolefines.

There have been studies in Japan (12) and Israel (13) that suggested direct biodegradation of polyethylene, but it was not definitely proven that some oxidative degradation had not preceded the biodegradation.

There is no singular molecular weight at which it can be said hydrocarbons or polymer fragments from the breakdown of hydrocarbons can be biodegraded. The metabolism of these fragments depends on several factors:

- The presence of a functional group, such as a carboxylic acid chain ending which is readily accessible to enzymatic attack and makes the polymer chain more hydrophilic
- Length of the polymer chain
- Morphology of the polymer matrix
- Degree of chain branching

There is also no single molecular weight at which a hydrocarbon polymer can be said to be suitable for microbiological digestion. Waxes and paraffins, which are low molecular weight hydrocarbons, are readily biodegradable. The microbial species involved in this biodegradation have been summarized (14). Typically when the molecular weight is less than 10,000 the polymer can be attacked, but with a functional group, such as a carboxylic acid, this can be higher.

For many years it was thought that the mineralization of polyethylene fragments was so slow that it could only be studied using radio-labeled polymers. Biodegradation of carbon-14 labeled polymers was studied by Albertsson (15) at KTH, Stockholm, Kostyniak at the State University of New York at Buffalo (16), Guillet at the University of Toronto (17) and Bartha at Rutgers University (18).

However, with the newer technologies, such as Addiflex, the rate of mineralization is sufficiently fast to be studied directly. Proof of this type of mineralization has been provided by studies by

Jakubowicz at SP in Sweden (19) and Chiellini at the University of Pisa (20). For photodegraded polyethylene mineralization has been shown by Lemaire and others (21).

The Jakubowicz study carried out at SP in Sweden together with Kaiser at EMPA in Switzerland showed mineralization of the polyethylene containing Addiflex (as measured by carbon dioxide evolution) of 60% in 180 days.

F. Toxicology

Apart from meeting the requirements for having a useful service life and disintegration at the appropriate time, it is important that biodegradable plastics have no toxicological effects in manufacture, use and during and after degradation. Manufacture of these products is the same as for normal plastics processes, e.g. compounding and film blowing, with no release of toxic chemicals. In manufacture and use of plastics containing Addiflex there is no problem with toxicity.

When plastics modified with Addiflex are discarded into the environment, for example by use in composting or agriculture or inadvertently littered, the requirements can be separated as follows:

- No heavy metal contaminants
- No toxic amounts of organic compounds
- No long term residual polymer or polymer fragments.

The metals used in Addiflex are benign transition metals that are necessary nutrients for plants and are well below the inclusion rate – even in the pure film – that could cause a problem. In fact it has been shown that repeated applications of degradable PE films in agriculture have no negative effect on crop growth (22).

Because of the mechanism described above no organic compounds that can give rise to a toxicology problem are likely to be formed during the oxidative or biodegradation of plastics containing a pro-oxidant system. The ability of microorganisms to grow on the degraded fragments (19) indicates the absence of toxicity and is further supported by toxicity tests using other organisms (23).

G. Comparison with Natural Biodegradable Materials

Although the rate of mineralization for the new generation degradable polyolefines shows that rapid rates can be achieved, they will not evolve carbon dioxide as quickly as materials such as starch. Many natural materials do not biodegrade very rapidly and this is essential for providing nutrients in the soil and allows the carbon to be assimilated into biomass. Humus is generated from the slow breakdown of organic matter, such as leaves and wood. If all the organic matter were rapidly mineralized there would be no soil

replenishment and all the carbon present in organic matter would be transformed into a greenhouse gas. Containment of the process is necessary.

Using a degradable polyolefine allows the control of the process to provide some organic matter for soil rather than have all the carbon released into the atmosphere as CO₂. Rapid mineralization, as happens with some polymers, does not allow this.

The incorporation of carbon derived from degradation of the carbon polymer backbone in polyethylene into Amaranth plants grown on soil containing degraded polyethylene has been qualitatively demonstrated using carbon-14 labeled polyethylene (16). The report concludes:

“These studies demonstrate the ability of common grain plants, as exemplified by Amaranth, to incorporate metabolites originating from the linear polyethylene chain of LLDPE”.

The similarity of degradable polyethylene with natural materials is illustrated in the review paper by Haider (24). In one study using carbon-14 labeled straw distributed in soil, 40% was remaining after two years and confirmed the very slow mineralization. Using carbon-14 labeled lignin they still found unaltered lignin after 150 days. This illustrates Nature's other method of holding carbon for subsequent re-use in soil without the release into the atmosphere and subsequent incorporation into plants by photosynthesis. Evidence for this with oxo-biodegradable polyolefines has started to be accumulated by Chiellini and his group at the University of Pisa.

H. Summary and Benefits of Oxidative/Biodegradable Plastics

The above report illustrates the benefits of oxidative/biodegradable technology for biodegradable plastics applications. These can be summarized as:

- Cost-effective – only a very small increase in price over products based on commodity polymers
- Proven performance in use and controlled disintegration to meet the needs of composting, agriculture, inadvertent littering and other applications
- Biodegradation as required
- No adverse toxicological effects
- The ability to retain some of the carbon for incorporation into soil humus.

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