

# Biodegradable polyolefins

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## How do biodegradable polyolefins work?

There are two types of biodegradable polymer. The first type, of which cellulose, starch and aliphatic polyesters are typical, is rapidly converted to carbon dioxide and water in compost, in landfill and on the surface of the soil by a process of hydro-biodegradation. The second type is the oxo-biodegradable polymers, which includes naturally occurring polymers such as natural rubber and lignocellulose. The latter, in the form of wood, twigs, peat, straw, etc. is the most abundant polymer on the earth and in some cases, for example in the oak or the sequoia trees it may take many hundreds of years for the lignocellulose to be returned to the environment as CO<sub>2</sub>. Even straw takes up to ten years to be fully converted to carbon dioxide in biologically active soil. Oxo-biodegradable polymers, unlike cellulose and starch, do not hydrolyse rapidly and they are protected from oxidation in the environment by antioxidants present as natural components of their structure. Typical of these are the tannins, which, of course, have been traditionally used by the leather industry to preserve leather.

The polyolefins fall into the latter category. As normally manufactured, they are formulated with antioxidants that, like tannin, protect them from environmental degradation. Polyolefins could not be used for the normal industrial purposes that are commonplace in modern industrial technology without the use of antioxidants. Not only do unstabilised polyolefins oxidise rapidly, in the environment, but they also biodegrade rapidly in compost, particularly after exposure to sunlight. Thus, unstabilised polyethylene loses 20% of its mass due to bioassimilation in five months in compost and polypropylene loses 80% of its mass in the same time. Laboratory experiments have demonstrated that, due to the formation of low molecular weight biodegradable compounds such as formic acid, acetic acid, succinic acid, etc. by abiotic oxidation, microorganisms are able to colonise on the surface of the polymer, utilizing in the first place the compounds produced by abiotic peroxidation. However, as in the case of the lignase enzymes, they then produce extra-cellular enzymes that themselves continue the peroxidation process. The rate at which these processes occur depend very critically on how the polymers are formulated and on the conditions to which they are exposed.

A good deal is known about the kinetics of abiotic peroxidation and stabilisation of carbon-chain polymers. Since oxidation is the rate-determining step in the case of the polyolefins, it is now possible to extrapolate from laboratory experiments to predict the time taken for ultimate oxidation and hence biodegradation under known conditions.

## Practical and ecological advantages of biodegradable polyolefins in packaging

It is not by chance that the polyolefins have achieved a unique position in packaging. They combine a spectrum of technological properties that makes the ideal for packaging. They are flexible, tough and tear resistant, while at the same time providing good barrier properties to environmental influences such as water, oxygen and above all, microorganisms. Unlike the bio-based polymers such as starch, the polyolefins do not require extensive modification to fulfill their technological function. Consequently, they are relatively cheap to manufacture. They are not in their normal commercial formulations rapidly bioassimilated into the environment but, by the use of an appropriate combination of prooxidants and antioxidants added during the normal processing procedure, they can be given a lifetime commensurate with their application, which may vary from weeks to years. They thus stand at the opposite end of the spectrum from the bioplastics (Figure 1)

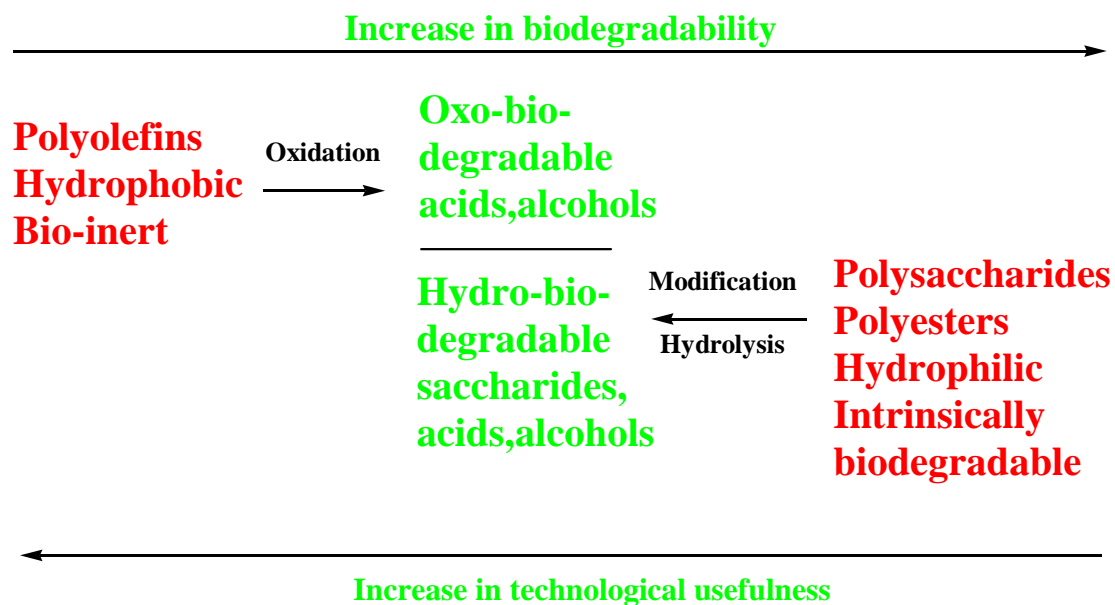


Fig. 1. The competing manufacturing technologies of hydro-biodegradable and oxo-biodegradable plastics.  
(G. Scott in *Degradable Polymers: Principles and Applications*, Ed. G. Scott, Kluwer Academic Publishers, 2002, Chapter 1)

## Life-cycle assessment of biodegradable polymers

It is sometimes assumed that bioplastics are by definition ‘environmentally friendly’, or in modern parlance, ‘sustainable’ because they are produced from renewable resources. One definition of “sustainable” suggests that the development of new products for the benefit of society should not have an unacceptable effect on resource depletion and

environmental pollution. However, 'acceptable' is a relative term and invites comparison of one material with another by life-cycle assessment (LCA).

It is often not realised by the general public that a great deal of energy goes into the production of agricultural products. For example, tilling the ground involves energy input, as does the manufacture of fertilisers, the harvesting of the crop, the disposal of waste in such a way that it does not cause pollution. When the crop is required as a feedstock for polymer manufacture, it has to be transported to the factory and the required polymer purified from plant waste before the process of chemical modification described above can begin. The energy from all these processes is at present derived from fossil resources and not renewable resources.

Companies engaged in the development degradable polymers from renewable resources have initiated life-cycle assessment (LCA) comparisons of their products with the commodity synthetic polymers - notably polyethylene. These have not so far shown that bio-based polymers are more environmentally sustainable than the present range of commodity plastics. This results from the same reason that led to concern in the 1980s; namely lack of consistency and uniformity of the assumptions used in LCA. In some cases they actually contradict one another.

The definition of LCA in the 'Green Report' of the Attorneys General of the USA given below is the basis of life cycle assessment of degradable plastics as currently practiced.

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

The most important measures of the sustainability of biodegradable plastics are minimisation of energy and environmental pollution during manufacture. However, they must also be capable of being utilised as wastes in one or more of the main recycling procedures (i.e. mechanical recycling, energy recovery and composting) and land utilisation during manufacture and disposal must be minimised.

## ENERGY BALANCE DURING MANUFACTURE AND RECOVERY

LCAs of degradable polymers published by bioplastic producers assume that PE can only be disposed of in landfill or by non-energy incineration. There is no recognition that PE can be "recovered" from the waste stream by composting, by pyrolysis to give monomers and fuels or by incineration to give energy. In practice, since the calorific value of PE (43 GJ/t) is almost identical to that of the oil from which it was manufactured so that, if the waste is incinerated with energy recovery, the carbon content of the plastic is ecologically neutral. The total non-recoverable energy used in the manufacture of PE is 21.6 GJ/t. This compares with the estimates of energy used in the manufacture of starch (Mater-Bi) products, which vary between 25.4 GJ/t and 52.5 GJ/t, depending on the oil-base co-agent used in the formulations. Although the carbon energy input is assumed to be zero, since it is biosynthesised and returned to the carbon cycle by biodegradation, this does not apply to blends with fossil-based additives or polymers. If waste biopolymers are used as a source of fuel in waste-to-energy

incineration, the energy produced is considerably less than that from PE and the ecological energy balance favours the biodegradable polyolefins.

Although biodegradable polymers may sometimes be mechanically recycled, it is important to recognise that the energy required for the reprocessing operation is about one third of the energy that goes into the manufacture of polyolefins from fossil resources. Furthermore, if the waste polymer is contaminated and has to be transported for substantial distances, the energy used in making new products from waste may be equal to or greater than that for manufacture from oil or gas. In these circumstances incineration with heat recovery is the only ecologically acceptable alternative to recovery as compost.

## LAND RESOURCE UTILISATION

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

## Biodegradation time-scale

It is generally accepted that the primary measure of the ultimate return of materials to the carbon cycle is carbon dioxide formation. However, the assumption that polymers must mineralise rapidly is not only unnecessary it is also counter-productive, since carbon in the environment, as carbon dioxide is ecologically undesirable. Furthermore, the assumption that fossil-based polymers do not biodegrade in the environment is not valid since as was discussed above polyolefins like lignocellulose can be returned to the soil, either through composting or directly when used as mulching films, thus contributing to the fertility of the earth. It does a disservice to nature's versatility to draw a sharp distinction between natural and synthetic organic polymers. There is no intrinsic difference between the biodegradation of natural and synthetic rubbers. Both oxo-biodegrade when first manufactured and both become highly resistant to biodegradation when formulated with antioxidants, for example in motor car tyres. The non-biodegradability of fully formulated engineering rubbers, whether natural or synthetic, as in the case of the commodity synthetic plastics, has much more to do with the presence of antioxidants, than with the "non-biodegradability" of the polymers themselves. As already noted, much of nature's litter is very resistant to degradation in a biotic environment. Lignocellulose is an important component of compost. In the form of straw, roots, twigs, etc. it acts as soil conditioners before being slowly converted to humus, the most valuable end product of nature's waste.

Polyolefins behave in the same way as lignocellulose. The formation of carbon dioxide during biodegradation has been clearly demonstrated, as has the generation of cell biomass from the organic nutrients formed. Based on the kinetics of the abiotic peroxidation of these polymers, the time scale for the ultimate oxo-biodegradation has been estimated to be about ten years. However, the time to complete liberation of CO<sub>2</sub> is less important than the potential eco-toxicity of partially degraded plastic particles in the soil, which is safeguarded by international standards for biodegradable plastics.

The time scale for the biodegradation of waste plastics then depends on the environment of their disposal (Fig. 2). It is clear that hydro-biodegradable plastics such as cellulose or starch products satisfy the requirement of disposal requirement of a sewage plant or of a watercourse that the material disappears by mineralisation within a few weeks. Compost is quite different since the primary purpose of compost is to provide a nutritious environment for growing plants in the form of biomass and humus. Provided, then that the degradable plastic does not in any way retard the germination and growth of plants its presence may be beneficial as a soil conditioner.

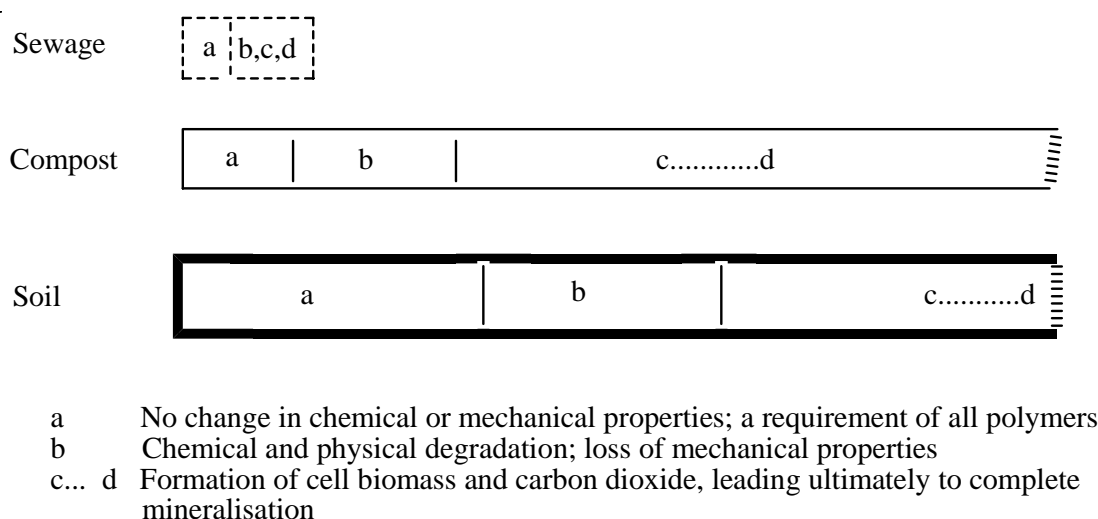


Fig. 2 Relative time-scale for biodegradation of degradable plastics in different environments

G.Scott, *Polymers and the Environment*, Royal Society of Chemistry, 1999, Chapter 5

When plastics are spread on land (for example in the form of mulching films or tunnels), the primary requirement is that they should protect the growing plants during the growing period, which depends entirely on the crop. It should then break down to small particles that can be ploughed into the soil to biodegrade over a much longer period

However, the popular perception that “Natural polymers” are “good” and “Synthetic polymers” are “bad” has influenced the Standards Organisations and has led to the unreasonable requirement that all synthetic polymers must be converted rapidly to carbon dioxide to be considered ‘biodegradable’. All “natural” materials are automatically exempted from this requirement because they are “by definition biodegradable”. Biometric tests, such as the Sturm test for the measurement of the carbon dioxide were originally developed as test methods for water-soluble and hydrophilic polymers in sewage systems at ambient temperatures. This type of test is very convenient for measuring the biodegradability of hydro-biodegradable polymers, but it quite in-appropriate for hydrophobic polymers degrading by oxo-biodegradation.

The requirement that polymers undergo rapid mineralisation in compost is inconsistent with the concept of 'reclamation'. The European Union 'Waste Framework Directive' 1991 defines "recovery" as follows;

"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"

## **Biodegradation in landfill**

Although it is often assumed that biodegradation of polyolefins cannot occur in landfill, this is in fact incorrect since the temperature may rise to 50-60° and there is always sufficient oxygen present to break down the polymer into small particles. This then leads to the disintegration of biodegradable polyethylene bags and the release of biodegradable garden or domestic waste, which has the beneficial effect of rapidly increasing the free space in the landfill.

## **Further reading**

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