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How do oxo-degradable polyolefins biodegrade?

Environmental degradation of polymers

Polymers have been known to lose mechanical properties due to peroxidation by atmospheric oxygen since the discovery of the commercial applications of natural rubber in the 19th century. This was controlled by the addition of synthetic antioxidants so that the modern automobile tyre degrades by abrasion and mechanical damage rather than loss of strength. When the petro-based hydrocarbon polymers, polyethylene (PE), polystyrene (PS) were developed in the early part of the 20th century, they suffered from similar problems, particularly in sunlight, and light stabilisers were used in combination with processing stabilisers to provide the necessary durability in the environment. The chemistry of polymer peroxidation, leading to mechanical degradation (oxo-degradation) and in particular the chemical kinetics (the rate at which changes occur) were studied in some detail in industrial and academic laboratories, beginning in the 1940s and this research has been reviewed in standard text books [1]. During the course of this research, it was realised that there are always two opposing components contributing to the durability of commercial hydrocarbon polymers. The first is the presence of prooxidants, notably transition metal ions, which are opposed by a variety of antioxidants and stabilisers.

Time-controlled biodegradation of polyolefins

In the late 1960s, environmentalists woke up to the fact that commercial polyolefins were increasingly a cause of packaging litter on land, in the streets and in the sea. The scientific principles developed above were applied to this problem and in the early 70s the first process to control the lifetime of polyolefins in the environment was published as a patent [2]. It was immediately realised that, since the products of the peroxidation of rubber and polyolefins were biodegradable, the oxo-degraded polyolefins would be rapidly bioassimilable. This was studied by the author in collaboration with biologists at the University of Aston in Birmingham and it was confirmed that under thermophilic conditions, photo-oxidised polyethylene was indeed used as a food-source by thermophilic fungi [3,4]. Agro-technologists went on to apply this process to agricultural mulching films in the secure knowledge that there would be no accumulation of partially degraded plastics in agricultural soils and that all the carbon would be converted within two seasons to cell biomass and CO₂ in exactly the same way as natural polymers such as rubber or wood in soil. In order to be sure that this was indeed happening, the fields to which the mulching films were applied continuously for up to 15 years were monitored for fertility and no adverse effects were noted.

Later studies of polyolefin biodegradation

As a consequence of the extensive field trials in the 1980s discussed above, which were widely reported in the technical press, it was not thought to be important to develop laboratory tests to reproduce the biodegradation of polyolefins in the environment. However, in the late 1980s, new biodegradable plastics based on hydro-biodegradable natural polymers began to appear. These were characterised by their proponents as “truly” biodegradable plastics. His topic became an important element in EU funded research programmes and we were invited to collaborate in a joint EU project with the University of Clermont-Ferrand in France to investigate the mechanisms by which oxo-degradable polyolefins were bioassimilated and in particular to demonstrate that soil microbes could utilise peroxidised polyolefins as the only source of carbon. This objective was completely successful. Photooxidised polyethylene films were found to be rapidly colonised by both bacteria and fungi found in the soil in the absence of any other source of carbon. Removal of the microorganisms showed that the degraded polymers in the surface of the plastics were bioassimilated leaving an eroded surface with mass loss of the polymer film [5]. The extent of surface peroxidation was found to be related to the rate of bioassimilation but since the antioxidants had been destroyed during photooxidation, peroxidation was able to continue, although more slowly in the absence of light due to the continued action of the prooxidant metal ion (Fe^{3+}). A subsequent study in the same laboratories [6], using plastic films identical to Symphony’s products showed that a very similar process occurred after thermal peroxidation of similar oxo-biodegradable plastics. In this case the growth of bacteria on the surface of the plastic could be observed and the rate of colonisation of the microfilms was measured. The identity of the microbes was characterised by surface FTIR analysis, which showed the presence of both nitrogen and phosphorus species characteristic of bacteria.

These studies showed without any doubt that aged or weathered polyethylene was used as a source of carbon nutrients by bacteria and fungi. The rate-controlling process is the initial peroxidation, controlled by specific antioxidants, since microorganisms can only colonise on a hydrophilic surface. This is why commercial polyolefins that have been protected against peroxidation do not biodegrade, since they are hydrophobic.

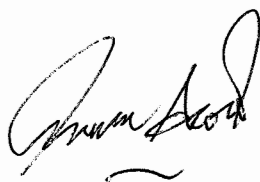
Standardised tests for oxo-biodegradable plastics

Unfortunately culture tests as described above are not acceptable to traditional biologists as indicators of complete biodegradability. Many do not recognise that abiotic processes may and generally do, play an important part in the process of bioassimilation. For example, the hydro-biodegradable aliphatic polyester polylactic acid (PLA) is known to degrade by hydrolysis in the complete absence of microorganisms and the low molar mass carboxylic acids and alcohols, subsequently biodegrade. This is entirely analogous to the oxo-biodegradation process, the only difference being the rate at which the abiotic breakdown of the polymer occurs. However, two independent research groups, on the basis of the above work, undertook a more extensive study of the conversion of the carbon in polyethylene to carbon dioxide and water. The first study by Jakubowicz at the Swedish National Standards Research Institute [7] showed that after exposure of a degradable polyethylene film containing Mn stearate as prooxidant in an air oven at 70°C for 1 month immediately evolved CO_2 in the presence of soil microorganisms and after 6 months, 60% of the carbon had been converted to CO_2 . In the second study on films

similar to Symphony's biodegradable packaging plastic [8], thermal pre-treatment was carried out at 55°C, and was followed by a biometric test at the same temperature. The latter showed an auto-accelerating rate of CO₂ evolution in the presence of soil microorganisms, which again reached more than 60% after 18 months. In both cases the CO₂ evolution continued after the test was finished. 60% mineralisation is considered to be an acceptable level to demonstrate biodegradation of a homogeneous polymer by ASTM [9].

References

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