

The Efficacy of Oxo-biodegradable Technology

Considerable controversy is attached to the subject of oxo-biodegradability. Even describing this oxidative process as biodegradable can cause an explosive reaction on the part of hydro-biodegradable technology advocates.

For the one or two readers that are not familiar with the oxo-biodegradable technology let me briefly describe the process.

A masterbatch (additive contained in a pellet of polyolefin) is introduced at the processing stage of a petro-chemical derived plastic material. The inclusion rate is small being 1 or 2%. Thus, the impact on processing parameters and finished material properties is negligible.

The additive typically consists of a transition metal salt and stabilisers. The salt has a catalytic action that causes a free radical reaction causing chain cleavage, in turn leading to the creation of hydroperoxides which are precursors to complete bio assimilation –these include esters, alcohols, aldehydes and carboxylic acids. The stabilisers retard this action under the elevated temperatures of processing and in the environment –typically geared to match the required time scale of functionality of the finished packaging item.

There are a number of papers and test results that confirm the biodegradability of these materials.

Ironically some scientific verification of the process took place as long ago as the 1970's. It is the classic scenario of context when related to scientific papers. A good example of this is the late Professor James Guillet's work at Toronto University in 1976 (1). His work illustrated that carbon derived from oxidised polyolefin could be sequestered by plants – albeit very slowly. In fact, so slow that it could only be studied using radio-labelled polymers. Biodegradation of carbon-14 labelled polymers has also been studied by Albertsson (2) at KTH, Stockholm, Kostyniak at the State University New York at Buffalo (3), and Bartha at Rutgers University (4).

However, with the newer technologies 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 (5) and Chiellini at the University of Pisa (6). For photodegraded polyethylene mineralization, has been shown by Lemaire and others (7).

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

Aside from carbon labelling there are currently a number of ways of measuring and/or detecting the degradation and ultimate biodegradation of oxo'technology treated polyolefin. Closely associated with the assessment of biodegradation is the measurement of molecular mass. We all know that polyolefin materials such as polyethylene and polypropylene have huge molecular structures –reflected by their large molecular weights - in the order of 100 to 200 thousand units.

There is no single molecular weight at which a hydrocarbon polymer can be said to be suitable for microbiological digestion. Associated waxes and paraffins, which are low molecular weight hydrocarbons, are readily biodegradable. The microbial species involved in this biodegradation have been summarized (8). 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. This was demonstrated in the 1994 work by Arnaud et al (7) to be around 40,000 Mw.

The work in Table 1. by Michèle Weiland at the Université Libre de Bruxelles is typical.

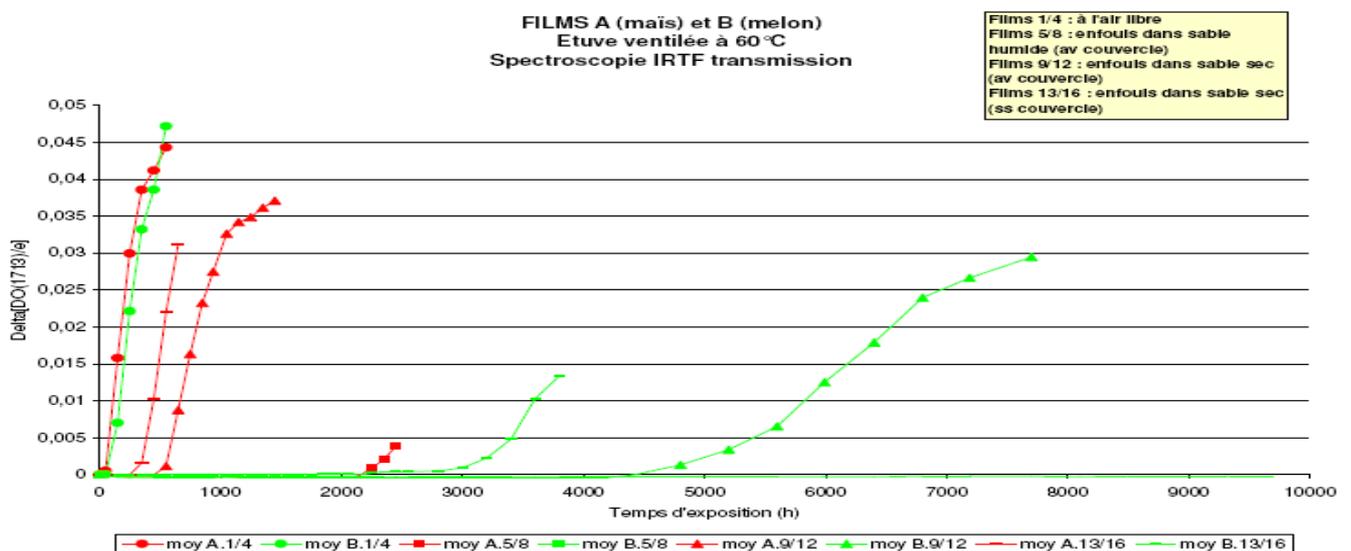
Temperature	Time (days)	Mw	Mn	Mw/Mn	n
	0	94,900	17,600	5.4	-
70	2	11,800	2,100	5.6	7.4
	5	3,510	1,090	3.2	15.1
	12	2,380	780	3.1	21.6
	20	2,080	690	3.0	24.5
	28	1,840	610	3.0	27.9
60	2	17,200	3,730	4.6	3.7
	5	4,620	1,240	3.7	13.2
	10	3,060	930	3.3	17.9
	25	2,170	710	3.1	23.8
	40	2,000	660	3.0	25.7
40	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 transition metal salt 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. 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.



(Above) Extract from Sevar Laboratory Testing Exercise, Bandol, France 2008. Mulch films exposed in and on soil.

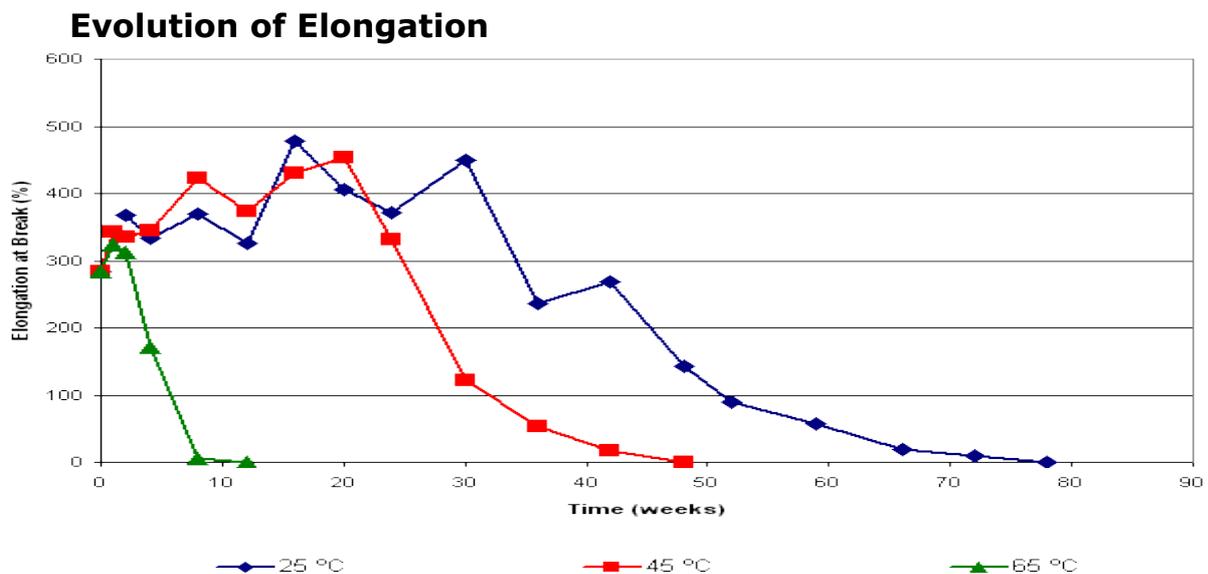
The free radical process instigated by oxo-technology produces intermediate compounds. These pre-cursors to ultimate biodegradation are hydroperoxides and by using gas chromatography (GC) and identifying the molecules by mass spectrometry (MS) they can be fully identified. One such study has been undertaken 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 polyolefin 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.



Study carried out by CRIQ Quebec Canada 640-PE36987
(Centre of Industrial Research Quebec)

The above papers and tests are only a small portion of the data constantly growing that substantiates the claims associated with oxo'technology.

The unique aspect of this technology is the ability to provide a controlled shelf life –or window of functionality –for a packaging material. Thus, a bread bag can be geared to remain functional for a shorter period than a snack food bag. After the guaranteed period of functionality, the material will degrade and ultimately bio-degrade. The time scale for that process is dependant upon the disposal method. If the disposal is before the functional time scale has elapsed the resultant elevated levels of heat and/or UV exposure –will accelerate the process.

Further information can be obtained from the various manufacturers of oxo-degradable materials on the Internet. I recommend checking out these sites. There is considerable evidence to be gained there.

References.

1. J. E. Guillet, T. W. Regulski and T. B. McAneney.
Biodegradability of Photodegraded Polymers. II. Tracer
Studies of Bio-oxidation of Ecolyte PS Polystyrene
Environmental Science and Technology, 8, 923-25 (1974)
2. A.-C. Albertsson, S. O. Andersson, S. Karlsson, Polymer Degradation and
Stability, **18**,73, (1987)
3. P. Kostyniak, Toxicology Department, State University of New York at
Buffalo, Applied Science Publ. 1976
4. M. Reich and R. Bartha, Journal Paper of the New Jersey Experimental
Station, Rutgers, The State University of New Jersey, (1997)
5. I. Jakubowicz, Polymer Degradation and Stability, **80**, 39 (2003)
6. E. Chiellini, A. Corti, G. Swift,
Polymer Degradation and Stability, **81**, 341, (2003).
- 7 R. Arnaud, P. Dabin, J. Lemaire, S. Al-Malaika, S. Chohan, M. Coker,
G. Scott, A. Fauve and A. Maaroufi, Polymer Degradation and Stability,
46, 2, 211, (1994).
8. M. Weiland, Ph.D. Thesis, Université Libre de Bruxelles, 1995
9. I. Jakubowicz, CEEES Workshop, November 4th, 2004. “Which Polymers
Are Biodegradable?”, Brussels, Belgium.
10. A.-C. Albertsson, C. Barenstedt, S. Karlsson, Journal of Chromatography
A, 690 (1995), 207