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Oxo-biodegradable Technology Applications in Agricultural Film

Certificate No. FM37939

Registered in England Number 2967867 - Address as above.
A wholly owned subsidiary of Symphony Environmental Technologies Plc.

SYMPHONY ENVIRONMENTAL LTD

CONTROLLED-LIFE PLASTIC TECHNOLOGY

1. Agricultural Applications and their benefit, performance

- **Mulch film advantages**

- Mulch film can be used to alter soil temperature. Dark and clear mulches warm the soil allowing for earlier planting and faster growth early in the growing season. White mulches reflect heat from the sun and therefore cool the soil. This can help establish plants mid-summer when cooler soil might be required.

- Mulch film reduces the amount of water required for irrigation as they reduce the amount of water lost due to evaporation. Mulch films also aid even water distribution which reduces plant stress.

- By preventing sunlight reaching the soil mulch films can inhibit most annual and perennial weeds. This reduction in weed growth reduces the need for cultivation and therefore eliminates root damage due to cultivation.

- Plastic mulches keep ripening fruits off the soil. This helps prevent fruit rot and keeps fruits and vegetables clean.

- The need for mechanical cultivation of the soil is reduced as plastic mulch decreases the crusting effects of rain and sunlight. Soil underneath the film is kept loose and well aerated, increasing the amount of oxygen in the soil and increasing microbial activity.

- **Silage wrap advantages**

- Protection against extreme weather conditions and climates

- Reduces the number of bales needed per/hectare

- Concentrates the sugars and maintains moisture content to improve fermentation, making it easier to achieve a stable silage

- Reduces the amount of effluent. Which is more environmentally friendly and also leads to a reduction in bale weight which saves fuel during transportation

- Increases the dry matter content of the material, which means less water, needs to be transported from the field to stocking area. A higher dry matter content will improve chances of achieving a better fermentation by reducing the amount of undesirable bacteria who can't survive under such dry conditions

- **Fruit sleeve advantages**

- Protect fruit from wind, rain, sunstroke and other climatic conditions. As well as diseases, and insects

- They allow the grower to advance or delay ripening of fruit to suit market conditions which is of great benefit

- Sleeves provide better light and temperature conditions for banana growth. The sleeve has a buffering effect when in high temperatures. Thermal variations between night and day are limited, maintaining a more constant growing temperature

- Studies have demonstrated an increase in fruit firmness and peel hardness, as well as fruit length and average grade (+2 to 8%), depending on the environmental conditions and on the position of the hand (M. Jannoyer, M. Chillet, 1998, ISHS 490:127-134)

2. The impact of oxo-biodegradable plastic technology on Agricultural Applications

- Why is it beneficial to use oxo-biodegradable plastic film in agricultural applications?

Conventional agricultural film costs time, intensive labour effort and money to collect and dispose of after use.
Where the products are discarded or lost due to weather conditions they create major environmental issues.

Symphony's d_2w oxo-degradable prodegradant additive allows agricultural film to degrade naturally after its useful life. The abiotic degradation products resulted, are inherently biodegradable once reduced to a significantly low molecular weight.

- How it works

Abiotic degradation:

Polyethylene is a non-polar, hydrophobic polymer, made of only carbon and hydrogen, with a large molecular size (200k–300k Daltons). The microorganisms can't consume these molecules in their trophic process. Besides that, the microorganisms can't settle onto the plastic surface as they need a wet environment where they can thrive.

During the abiotic degradation process, polymers undergo free radical oxidation reactions which result in chain cleavage, to produce reduced molecular weight oxidation products. So the long chains break down in short fragments and organic functional groups form at the ends of these fragments. The molecular weight of the original chains reduces dramatically and the fragments become polar and hydrophilic. The chemical composition of these fragments changes, as oxygen is accumulated due to the oxidation process. The d2w pro-oxidant additive will act as catalyst for this process, reducing the time period for degradation.

This process is initiated in ambient conditions when exposed to oxygen in the air and accelerated by exposure to UV light and/or increased temperature. This is well documented by Koutny et al (Chemosphere 64 1243-1252 2006).

Biological degradation:

The abiotic degradation creates the environmental conditions for biodegradation. The polymer fragments are hydrophilic, the microorganisms can settle and the chemical composition includes C, H, and O which are the food constituents. The low molecular weight oxidation products are consumed by microorganisms in the same way as degradation compounds produced by dead plants (Gerald Scott 1975 Polymer Age 6 54).
During the bio assimilation step, microorganisms convert some of the carbon compounds into CO_2 for energy generation and the rest into biomass by way of growth and multiplication. This biomass will eventually be converted into humic compounds in the soil, CO_2 and further biomass as it is consumed by other microorganisms (Gerald Scott 2002 Degradable Polymers 2nd Edition Chapter 3).

In Chiellini et al. (Polymer Degradation and Stability 81 341-351, 2003) a significant study is made into the biodegradation of these abiotic degradation products. High mineralization levels were observed, above 60%, comparable to those that occur for natural polymers in the environment.
A further study by Jakubowicz has illustrated more than 90% of polymer mineralization (Polymer Degradation and Stability 96 919-928, 2011).

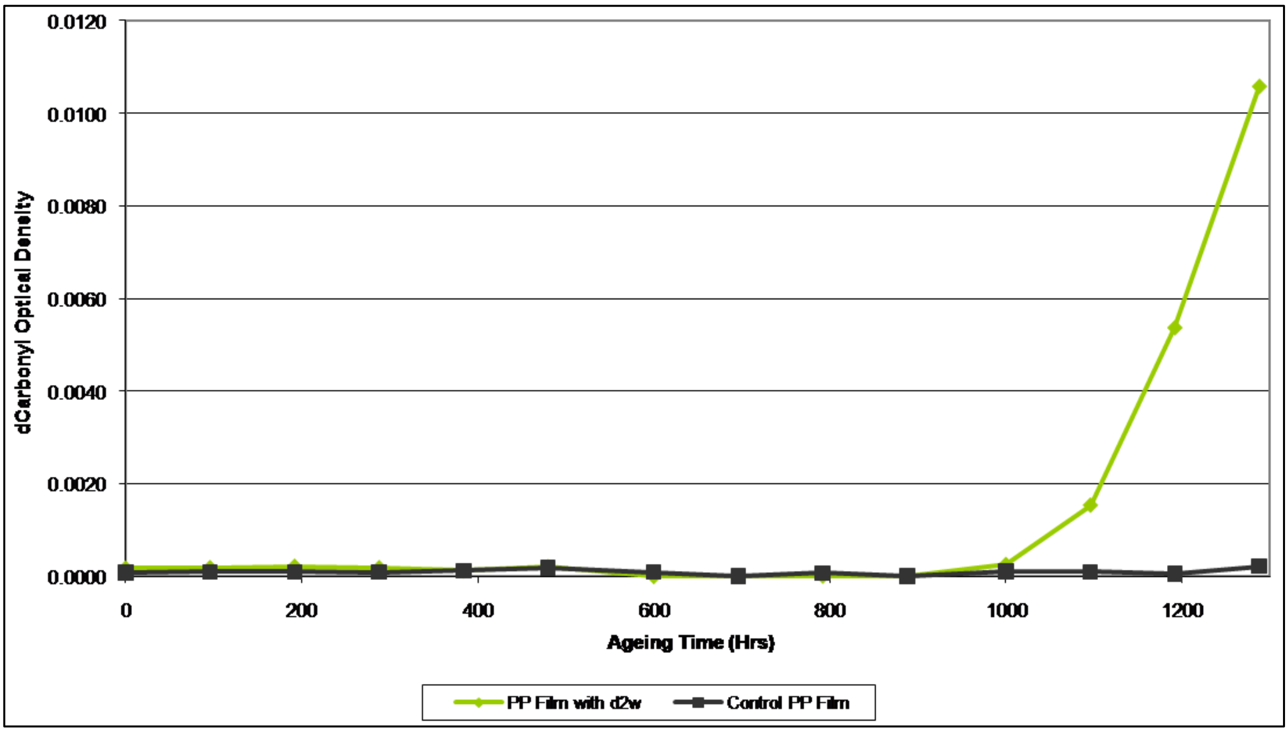
Shelf life and service life:

The optical density is defined by the magnitude of the carbonyl peak at 1713 cm^{-1} divided by the sample thickness. Measuring changes in carbonyl optical density is a useful technique for monitoring the rate of degradation of the sample. Carbonyl species (aldehydes, ketones, carboxylic acids, alcohols, esters, etc.) are reaction by-products of the oxidative degradation process and as such their accumulation is indicative of ongoing degradation.

The carbonyl optical density method allows direct correlation with the mechanical properties of the samples. An optical density of 0.001 is considered equivalent to an Elongation at Break (EaB) reduction of 50% in the sample, whilst a value of 0.01 equates to an EaB value of a 5%.

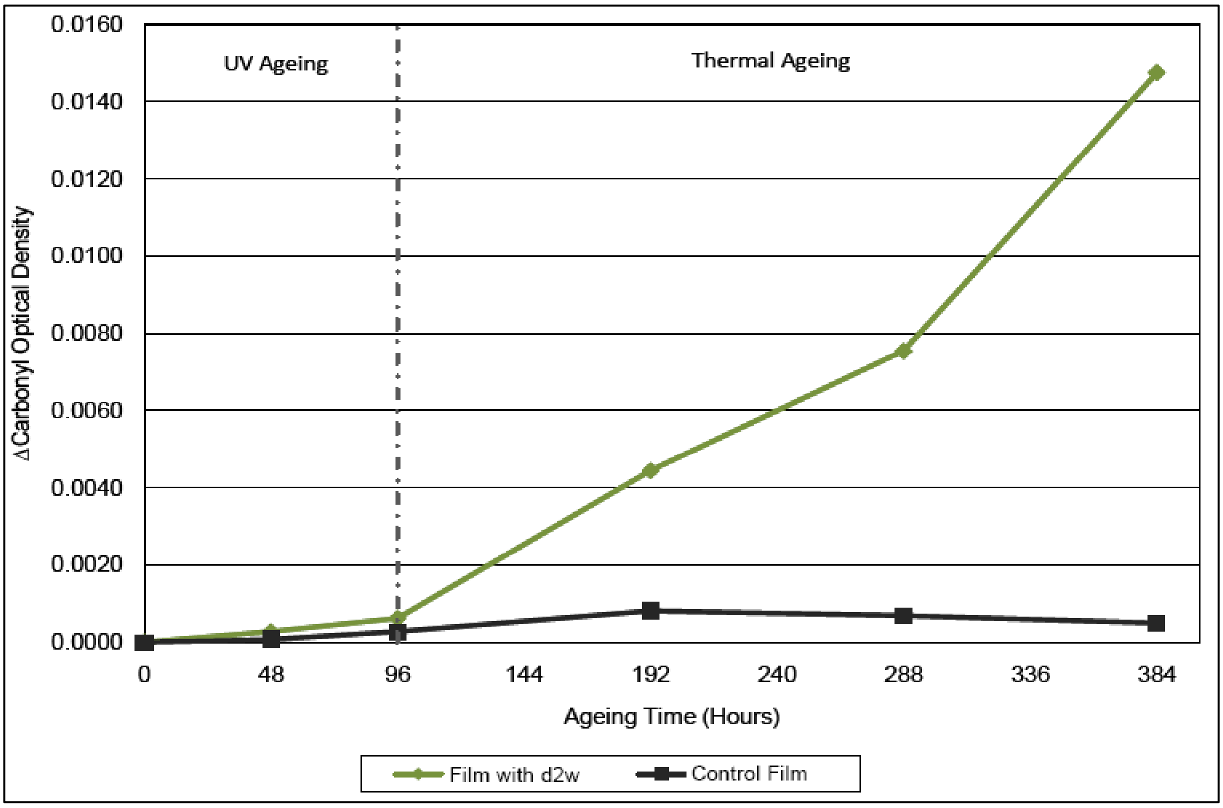
ASTM D3826 defines the polymer degradation in terms of an embrittlement endpoint at which the sample has achieved an elongation at break value of less than 5% for at least of 75% of specimens tested. Based on the correlation above, it thus follows that, when a sample achieves a carbonyl optical density of 0.01 it is similarly embrittled.

EXAMPLE 1 - Accelerated thermal ageing



The lack of degradation after 1000 hours demonstrates a product shelf life of 22 months.

EXAMPLE 2 - Accelerated UV/thermal aging



The graph above demonstrates that the film sample containing the d_2w prodegradant additive has degraded to a greater extent than the control sample. This is representative of conditions in the open environment.

Biodegradation

I. Jakubowicz et al. / Polymer Degradation and Stability 96 (2011) 919–928

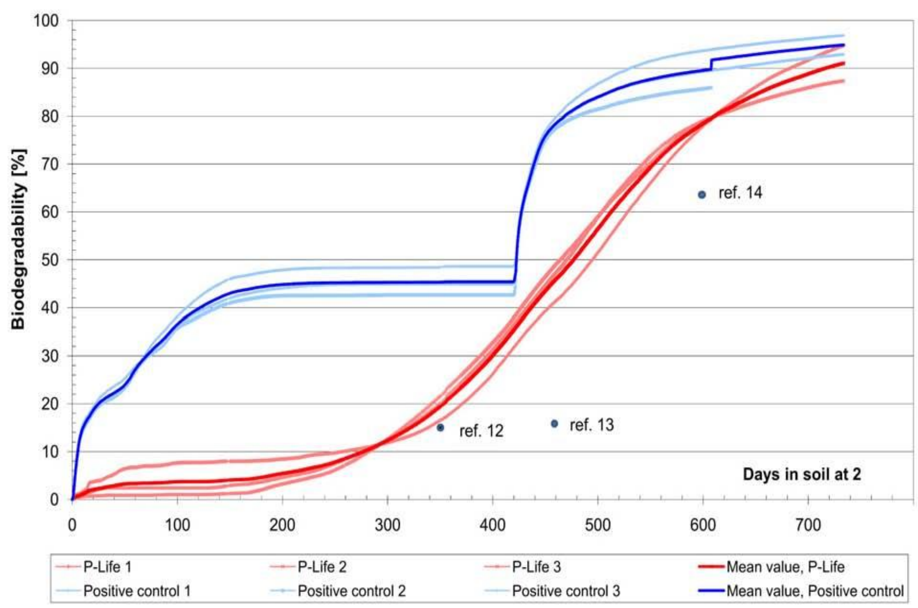


Fig. 3. Mineralization profiles of thermally oxidized test material (red/lower curves) and reference material (blue/upper curves) in the soil test at 23 °C.

This result illustrates more than 90% mineralization of an aged polymer film containing a prodegradant additive. The missing 10% is accounted for as biomass.

- **Ecotoxicity**

Ecotoxicology refers to the potential for biological, chemical or physical stressors to affect ecosystems. Therefore to define any of the abiotic degradation products produced by polymer degradation as ecotoxic, their presence in an ecosystem must cause some element of disruption in comparison to an equivalent ecosystem, or a blank system.

Two separate studies were commissioned by Symphony and performed by 'Organic Waste Systems', an independent third party certified laboratory in Belgium. The degraded polymer material was intimately mixed with a sample of compost, and two species of plants were grown in this environment. The same species of plants were also grown in blank compost samples.

These studies were executed in line with the OECD 208 Guideline for Testing of Chemicals (2006): "*Terrestrial Plant Test: Seedling Emergence and Seedling Growth Test*" and the ASTM International standard ASTM D 6954-04 "*Standard Guide for Exposing and Testing Plastics that Degrade in the Environment by a Combination of Oxidation and Biodegradation*"

Both studies illustrated similar germination rates between the two compost samples with and without degraded polymer material present, which suggests that the degraded polymer samples had no effect on the ecosystem the plants existed in.

- **Heavy metals**

Oxo-degradable additives contain transition metal ions which are required to initiate thermo and photo oxidation reactions. Concern has been expressed in the past about the effects of 'heavy metals' on plants and on humans who eat the plants. However it is normally overlooked by environmental pressure groups that many agricultural soils contain substantial concentrations of these same metal ions and that they are slowly leached into agricultural and drinking water.

Humans require metal ions like cobalt, iron, manganese and nickel for their normal metabolism and most of these are sourced from plants, which in turn obtain them from the soil.

The tables below are an abstract of data from an Expert Group Report. They are associated with the essential requirements of trace elements in the diets of humans and animals. The latter are often fed cobalt salts as part of their diets.

Cobalt				
Fish (mg/kg)	Nuts (mg/kg)	Cereals (mg/kg)	Fresh water (mg/l)	Average Daily intake (mg/day)
0.01	0.09	0.01	0.01	0.12

Manganese					
Green Vegetables (mg/kg)	Nuts (mg/kg)	Bread (mg/kg)	Other Cereals (mg/kg)	Tea (mg/kg)	Water (mg/l)
2.00	15.00	8.00	6.80	2.70	0.01

Nickel			
Oats (mg/kg)	Nuts (mg/kg)	Water (mg/l)	Average Daily intake (mg/day)
0.18	1.80	Variable	0.016

In spite of the large quantities of transition metal ions in common soils, the evidence suggests that edible plants, like humans, take up only the very small amounts they require. Furthermore, it has been calculated, based on known parameters, that if the same field was to be covered every year with Ni-containing degradable plastic mulch, it would take 500 years to increase the content of the top-soil by 1 mg/kg (or ppm).

The growth of vegetables in fields to which particulate degraded polyethylene containing transition metal compounds has been added has been studied in Taiwan for five years. The Table below follows the yields of lettuce with and without plastic debris over this period. No increase in the concentration of transition metals was observed in the plants.

Planting Date	Yields (kg/15.6m^2)	
	Without Debris	With Debris
January 1992	37.8	39.3
January 1994	35.2	38.2
February 1995	32.4	34.5
December 1995	52.0	55.4
October 1996	32.5	38.7
October 1997	40.1	40.5

3. Examples - Agricultural Applications incorporating d_2w additives

- Mulch film

  - Silage Maize Mulch Film - 12 micron LLDPE transparent, exposed in France

At start

After 10 weeks (target life-time)

The lifetime of the film article is controlled by the appropriate selection of type and concentration of the additives used, taking into account the type of plastic (e.g. polymer, thickness, presence of pigments) and environment-related parameters (e.g. mechanical stress, wind, humidity, temperature, solar irradiance etc.).

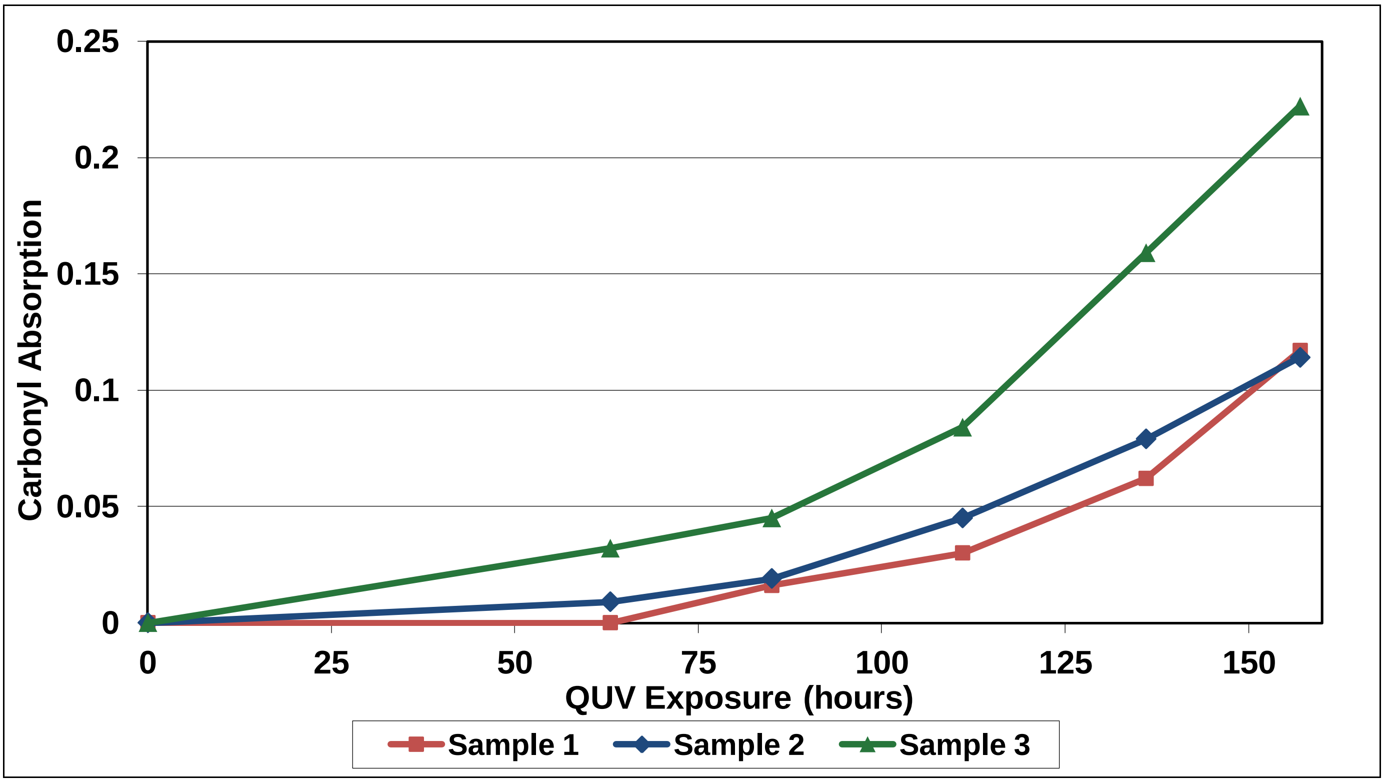
Degradable mulch film becomes brittle after desired lifetime

Normal Mulch film remains intact after use

Sample: 25 microns LLDPE/LDPE transparent mulch film
Exposure: WOM weathering: Atlas Weather-Ohmmeter Ci 65 @ 65°C, 0.35 W/m^2 at 340, no water sprays. Failure when tensile elongation is less than 10%.

	WOM weathering (< 10% tensile strain at break)
Control Sample	660 hours
Degradable Sample	280 hours

Sample: 12 micron LLDPE transparent mulch film
Exposure: ASTM D5208: QUV (UV-A 340 nm lamp at 0.8 W/m^2, 5 hours UV at 50°C, 1 hour condensation at 40°C



Sample: 12 micron LLDPE transparent mulch film
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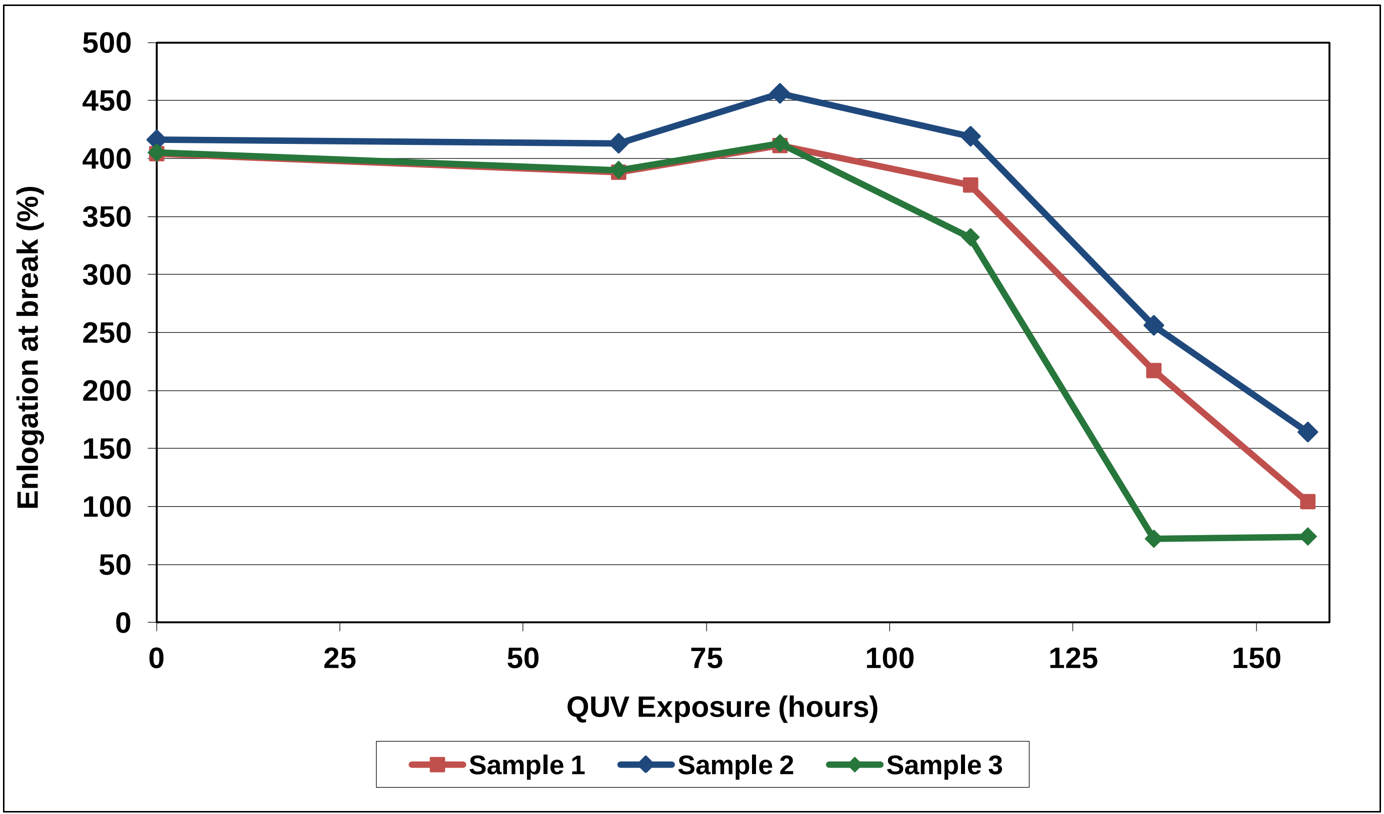


- Black Mulch Film, New York, June/July 2003

Before degradation

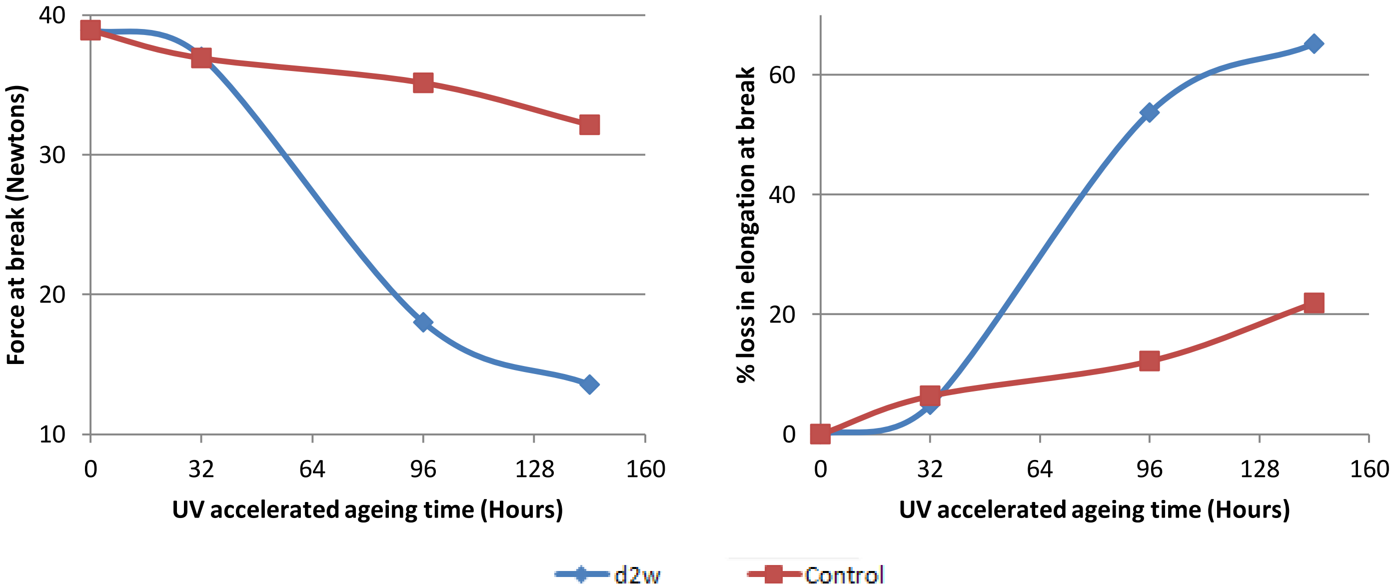
Degradation begins

At 4 weeks

At 7 weeks

- White Banana Tree bags, Dole, April 2004

The results below are, from degradation tests carried out at Symphony's testing laboratory



- Fruit Sleeves

  - Banana film (sleeves) in Central America

Melt Flow Index for Clear Bags:

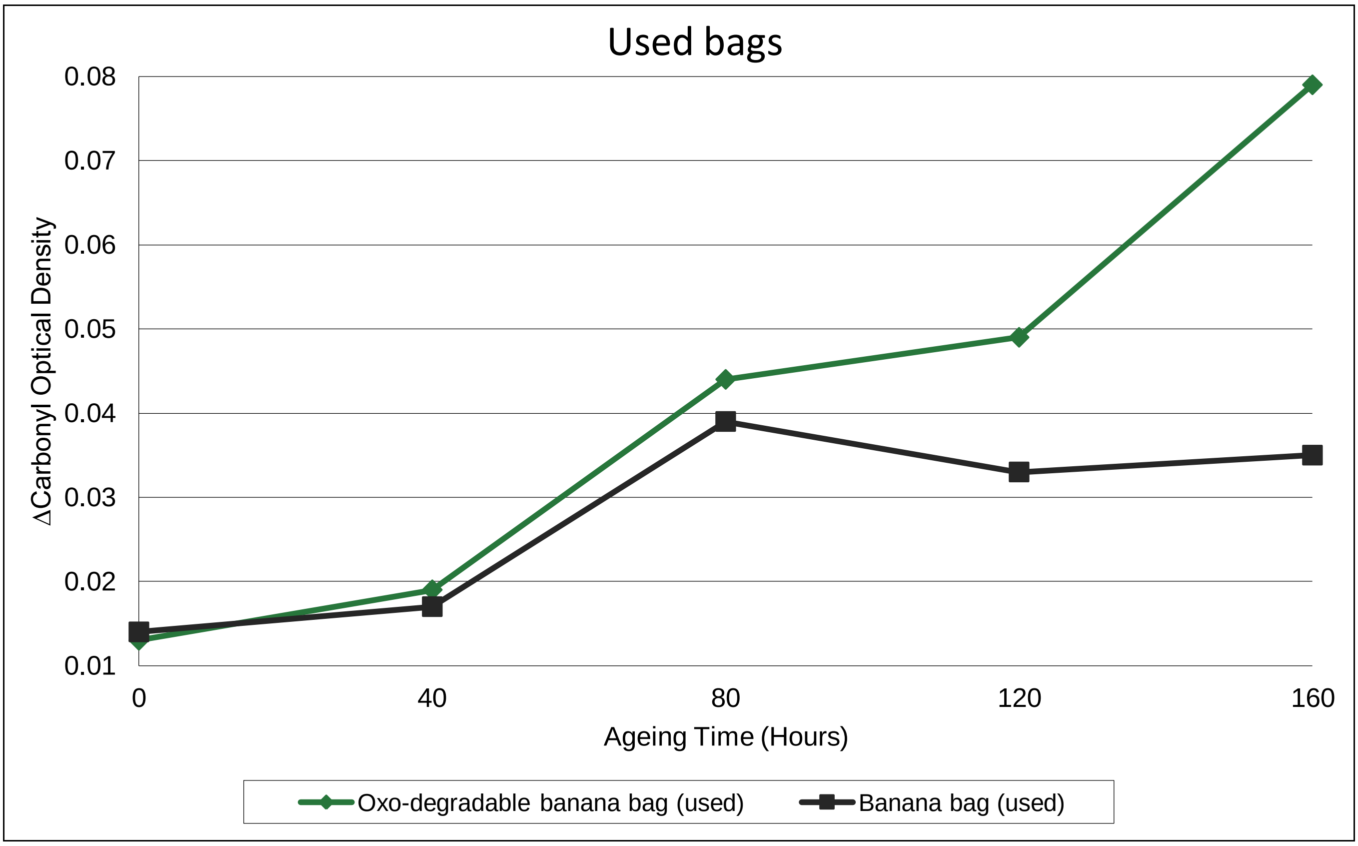
	Week 1 (g/10 mins)	After 15 Weeks (g/10 mins)
Non-degradable sample	2.86	3.92
Degradable sample	2.86	22.10

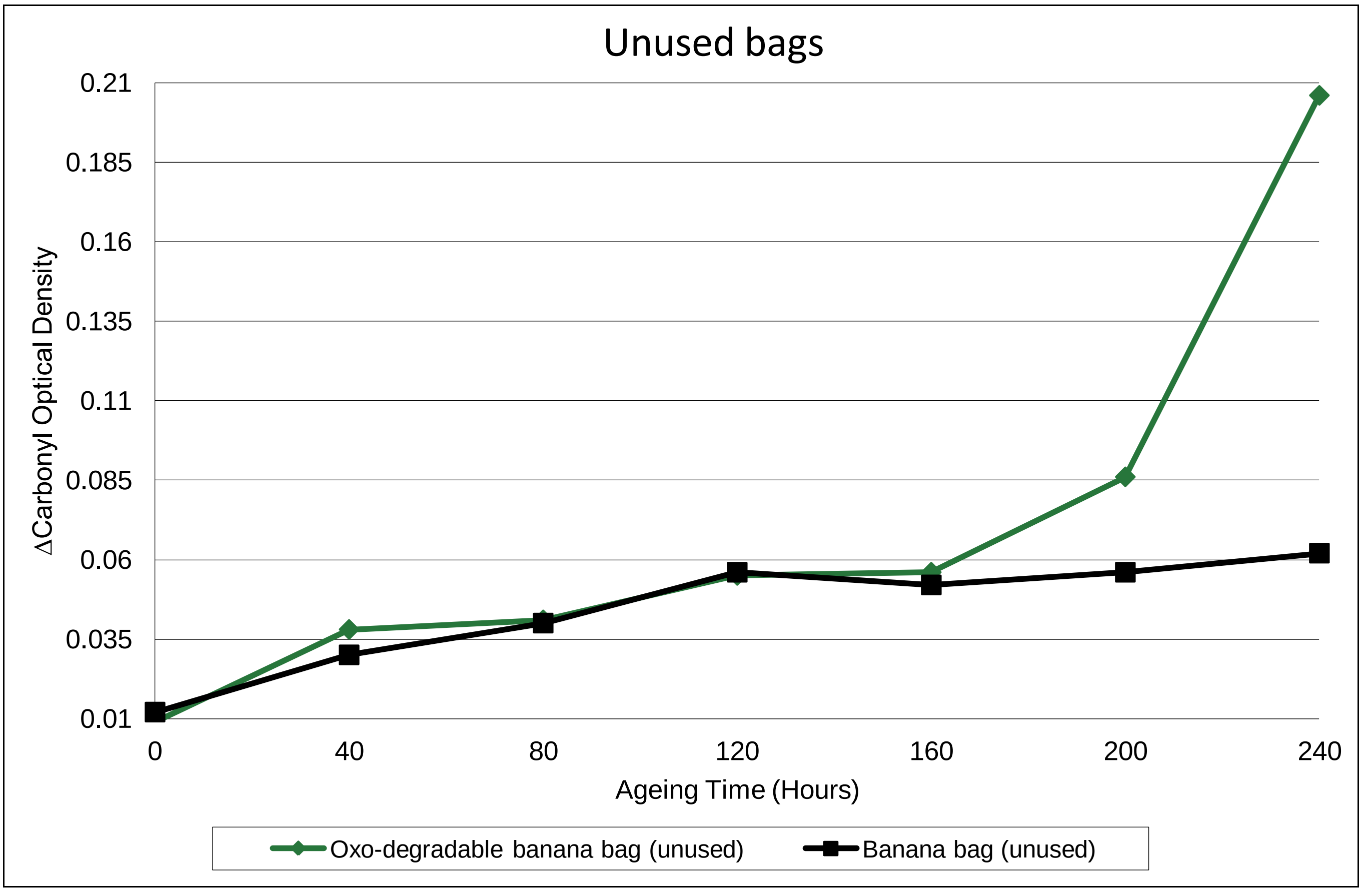
Tensile Strength for Clear Bags:

	Week 1 (10^3 psi)	After 15 Weeks (10^3 psi)	% Reduction
Non-degradable sample	3.71	2.35	36.7
Degradable sample	3.43	1.89	44.9

- WIBDECO, June 2008 (internal study), Used and unused banana bags

Sample description	Carbonyl Optical density						
	0 Hrs	40 Hrs	80 Hrs	120 Hrs	160 Hrs	200 Hrs	240 Hrs
Oxo-degradable banana bag (used)	0.013	0.019	0.044	0.049	0.079	-	-
Banana bag (used)	0.014	0.017	0.039	0.033	0.035	-	-
Oxo-degradable banana bag (unused)	0.009	0.038	0.041	0.055	0.056	0.086	0.206
Banana bag (unused)	0.012	0.03	0.04	0.056	0.052	0.056	0.062


Used bags
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
ΔCarbonyl Optical Density
0
40
80
120
160
Ageing Time (Hours)
Oxo-degradable banana bag (used)
Banana bag (used)


Unused bags
0.21
0.185
0.16
0.135
0.11
0.085
0.06
0.035
0.01
ΔCarbonyl Optical Density
0
40
80
120
160
200
240
Ageing Time (Hours)
Oxo-degradable banana bag (unused)
Banana bag (unused)

4. Symphony's Commitment to develop such applications

- Technical Infrastructure

    - R & D Centre

Symphony has its own research and development laboratories and test facilities in the UK which are the home to a team of scientific technicians with many years experience in the field.

Symphony is committed to developing new plastic technology solutions whilst improving on current products by working closely with, current and prospective customers, universities, independent laboratories and other specialist scientific centres in the UK, abroad and overseas. These include Rapra - UK, SP Technical Research Institute of Sweden, OWS - Belgium, Applus - Spain, Pyxis - UK, Imperial College - UK, Michigan State University – USA, University of Pisa – Italy, etc.

Symphony continues to make substantial investments into State-of-Art, latest analytical equipment, used for New Product Development, Quality Control of all products produced with d_2w as well as Investigative Research.

Laboratory scale manufacturing equipment allows Symphony to carry out trials of new additives and replicate finished products within their own facilities.

Symphony has also invested into the development of portable equipment capable of maintaining the reputation of the technology by allowing for easy detection of counterfeit products.

    - Services

Symphony provides support to customers around the world. We have technical support capabilities available across all time-zones and at short notice, and we will shortly be opening a laboratory in Mexico. Below is a list of services Symphony provides.

Accelerated degradation testing:	Standard procedure for all new products produced with d_2w but also available upon request for any product required.
Additive content confirmation:	Standard procedure for all new products produced with d_2w but also available upon request for any product required.
Finished Product Analysis:	In depth analysis into product makeup (FT-IR, XRF, Reverse engineering, GPC). Available upon request for any product required.
Troubleshooting issues:	Investigation into production issues primarily related to the addition of d_2w but also available for general manufacturing complications.

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Primary review: Radu Baciu P. Eng

Technical Executive   Technical Manager