

PEMBROKE MULCHING FILM TRIAL

West Orierton Farm, Pembrokeshire

1. Introduction.

The trial was arranged to demonstrate that Symphony's d₂w controlled-life plastic film can remain intact as a cover for a growing potato crop for the 10 week period required by the farmer, and that it will subsequently degrade.

The film is required to protect the plants in the early stages of growth and is designed to degrade rapidly once the plants are established, so that the film, contaminated with earth and vegetable matter, does not have to be removed and disposed of, and so that the film will instead degrade then biodegrade on and in the soil, leaving no harmful residues.

2. Materials.

The oxo-biodegradable additive and films for the trials were produced at Symphony's Telford experimental facility on 22nd May 2012.

Two oxo-biodegradable films were produced with Symphony's d₂w masterbatch:

1. DG12-05- a masterbatch based on a manganese catalyst
2. DG12-06- a masterbatch based on a cobalt catalyst.

The masterbatches were produced on a Rondol 24mm twin-screw laboratory compounder.

The masterbatches were incorporated at 1% w/w in a pre-blended polymer mixture of 75% LDPE (Total 1022FN24) and 25% LLDPE (Sabic 118W), and blown into film.

The film (with a nominal thickness of 35µm) was blown on a 20mm single screw Rondol laboratory extruder fitted with a 40mm diameter die. A lay-flat film ca. 130mm wide was produced and cut into a centre-fold sheet prior to opening out and winding onto a cardboard core. The final sheet width was ca. 260mm. The film was clear and un-pigmented, as requested by the farmer.

3. Outdoor exposure- field trial on site.

The films were not exposed to uv light before being laid on 27th July 2012 on the surface of the field used for growing potatoes in the presence of the farmer, Mr. Walter Simon, and of representatives of the Environment Agency Mr. Ged Davies, Mr. Brian Klass and Ms. Liane Bacon, and of Mr. Michael Stephen, a Director of Symphony Environmental Ltd. The samples were lifted by the farmer from the trial site in late September 2012 and returned to Symphony on 29th September.

Observation showed that the cobalt DG12-06 film had shown the greatest degree of degradation, and this was confirmed on laboratory examination of the returned film samples. The DG12-06 film sample was brittle (too weak to test mechanically) whilst the DG12-05 sample retained some elasticity.

The DG12-06 film had therefore performed as expected by the farmer.

Timescale can be adjusted by modifying the formulation of the d₂w additive.

4. Analysis of films from field trials.

The molecular-weight of the samples returned from West Orierton Farm was determined by high temperature Gel Permeation Chromatography (GPC). The results are tabulated below.

Table 1: Gel Permeation Chromatography analysis of film residues

Sample ref.	Mw	Mn	Intrinsic Viscosity
DG12-05 Unaged	125,100	19,400	1.07
DG12-05 Aged	153,900	17,800	0.93
DG12-06 Unaged	143,600	17,500	10.6
DG12-06 Aged	36,900	6,200	0.42

The molecular weight (Mw) of the DG12-06 film had therefore fallen by ca. 75%

The DG12-05 film did not show a reduction in molecular weight under the conditions in which it had been exposed, and the DG12-06 film was therefore better suited to this particular application.

5. Further outdoor exposure.

The materials returned from the Pembroke site were further exposed outdoors at a site in Telford, Shropshire, in order to observe any further reduction of the molecular weight through oxidation.

A frame was constructed to contain the two films so that they were exposed side by side. The exposure was started on 1st November 2012 (Figure 1). Plastic crop-protection netting (mesh size: 15mm x 20mm) was placed over the materials, to reduce losses due to the wind.

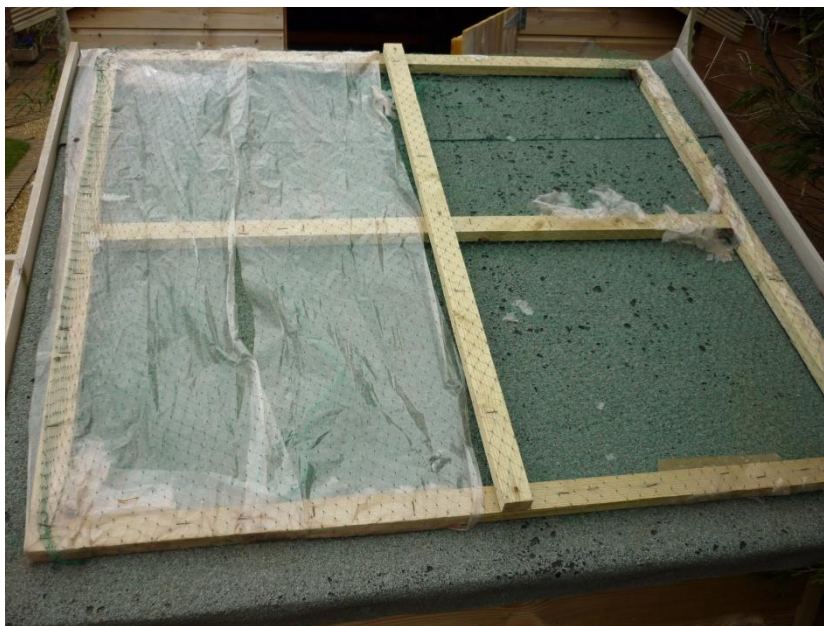
Figure 1: Exposure of films at Telford site- 1st November 2012.



Film DG12-05 is on the left of the central dividing bar and film DG12-06 is on the right.

After 4 further months of outdoor exposure, film DG12-06 had disintegrated, and film DG12-05 was still intact. Figure 2 shows the condition of the films on 1st March 2013.

Figure 2: films exposed at Telford site- 1st March 2013.



Film DG12-05 is on the left of the central dividing bar and film DG12-06 is on the right.

By August of 2013, Film DG12-05 had also disintegrated.

Figure 3 shows the condition of the films on 16th August 2013.

Figure 3: Exposure of films at Telford site- August 2013.



Film DG12-05 was on the left of the central dividing bar and film DG12-06 was on the right.

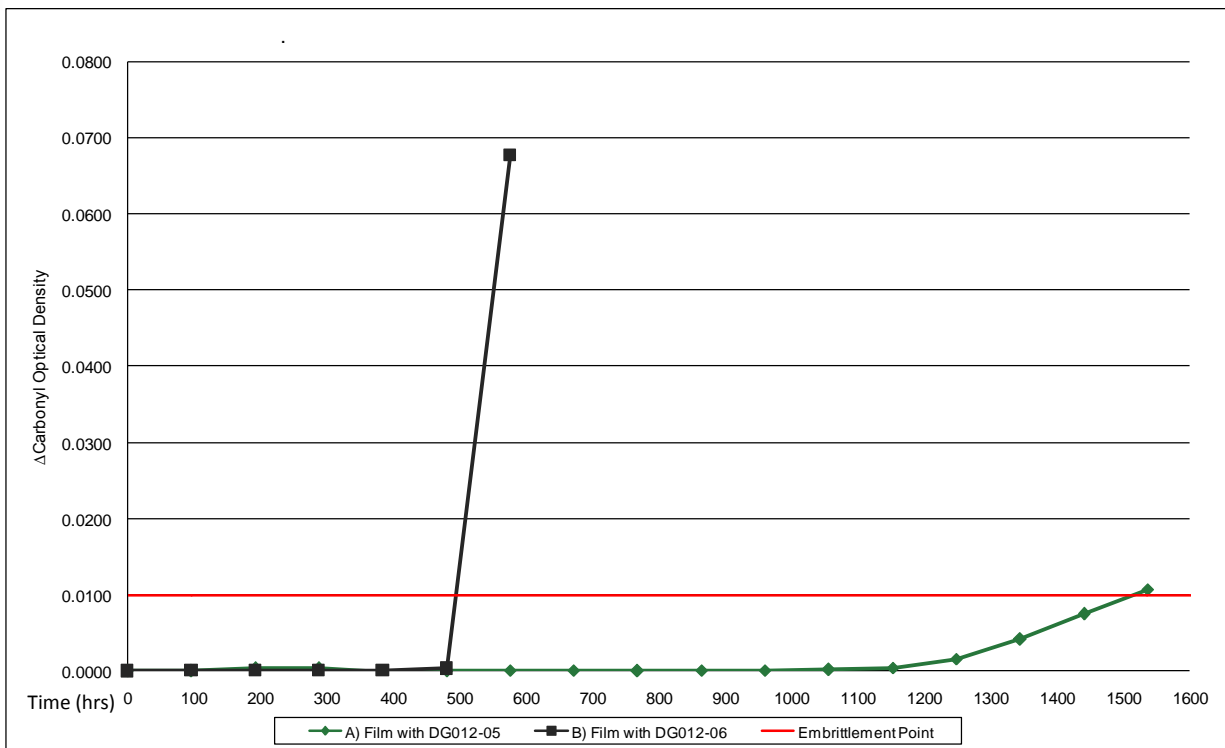
6. Laboratory evaluation of films.

6.1 Thermal aging.

Thermal ageing of unexposed samples of both films was carried out in a Memmert UFE 600 fan-assisted oven at a temperature of 70°C in accordance with ASTM D5510 Procedure B. Samples of the films were withdrawn every 96 hours and their carbonyl optical density (COD) determined by FT-IR spectroscopy. The COD is a technique for monitoring degradation which charts the accumulation of carbonyl break-down compounds in the polymer structure.

The results were that the film with cobalt additive (DG12-06) demonstrated the quickest thermal response (Figure 4), and that both films are likely to have storage lives of at least 12 months if stored at temperatures not exceeding 30C in the dark.

Figure 4: Thermal ageing response of films DG12-05 and DG12-06.



6.2 Combined UV aging and thermal aging.

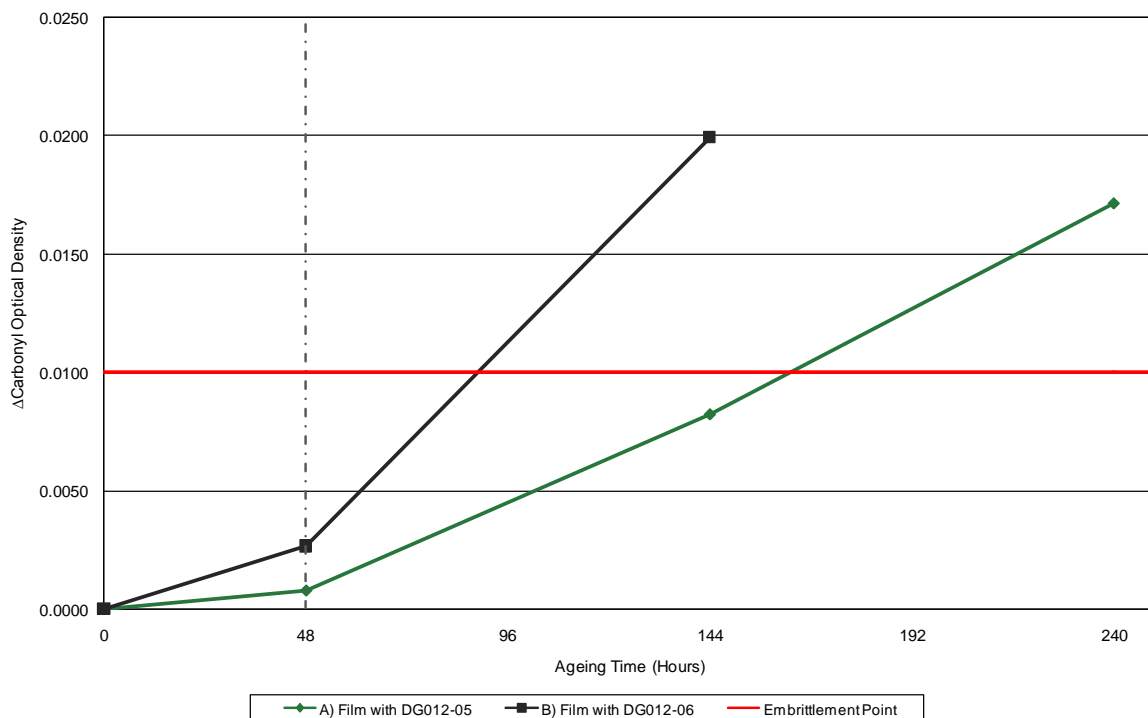
This test was performed to simulate the effect of short periods of UV exposure on the degradation behaviour of the films and therefore to model the behaviour of the film if it becomes occluded from sunlight. The samples were exposed to 48 hours of UV aging prior to being thermally-aged in the dark in an oven at 70C in accordance with the ASTM test method outlined above.

For the UV exposure stage the samples were placed in a holder, so that the film was held between two metal plates (35 x 90 mm) containing four oval exposure windows, and exposed to ultraviolet radiation in a Q Panel QUV/se test apparatus

fitted with UVA 340 lamps, in accordance with ASTM D5208. A black panel temperature of 50°C was used, with a humid environment. The irradiance of the lamps was 0.78 W/m²/nm.

The results confirmed that the cobalt-based film, DG12-06, showed the most rapid degradation under lab conditions as well as in the field, but both samples show continuing oxidative degradation once the sunlight stimulus is removed - a positive feature of oxo-biodegradable technology.

Figure 5: Combined exposure response of films DG12-05 and DG12-06.



7. Further molecular-weight determination of DG 12-06.

The molecular weight of the DG12-06 film was measured after the three months of additional ageing, and an un-aged DG12-06 film was also evaluated as a reference. The results (Table 2) show a further reduction in molecular weight (Mw) of some 46% over that achieved when the film was first tested. The overall molecular weight reduction compared to the pre-exposed film was therefore ca. 86%.

Table 2: Gel Permeation Chromatography analysis of film DG12-06 after further outdoor ageing.

Sample ref.	Mw	Mn	Intrinsic Viscosity
DG12-06 Unaged	141,00	17,700	1.03
DG12-06 further aged at Telford	20,000	3,600	0.31

8. Elemental analysis of the film.

The DG12-06 film was tested for any hazardous elements, including heavy metals, which could be carried by rainwater into the soil or into the ground-water or watercourses. The criteria are as prescribed in European Standard EN 13432:2000 see Table 3

Mercury was investigated by the direct mercury-analysis technique. Fluorine was determined by ion chromatography after bomb-combustion.

All other elements were determined by Inductively-Coupled Plasma-Mass Spectroscopy (ICP-MS) following sample digestion in nitric acid. The results, tabulated below, demonstrate that all restricted elements were found to be below the limits prescribed by EN 13432:2000.

Table3: Elemental Analysis of Film DG12-06

Element	Concentration (mg/kg) of dry substance	EN13432 Limit (mg/kg)
Zinc	10	150
Copper	<2	50
Nickel	6	25
Cadmium	<0.2	0.5
Lead	1	50
Mercury	<0.4	0.5
Chromium	<10	50
Molybdenum	0.8	1
Selenium	<0.4	0.75
Arsenic	<2	5
Fluorine	<50	100

9. Conclusion

The study has demonstrated that the oxo-biodegradable film DG12-06 had an operational life suitable for the farmer's requirement to protect the emerging potato crop.

At the end of its operational life abiotic degradation of the film occurred rapidly and the film experienced significant reduction in molecular weight. At the end of this abiotic process the material could no longer be considered to be a plastic, and had suffered molecular changes in composition that allow it to biodegrade to nothing more than water, CO₂ and humus.

Analysis of the film has confirmed that it does not contain heavy metals nor any other restricted elements.

Biodegradation of abiotically-degraded polymer material has been studied in depth at the Technical Research Institute of Sweden and the Swedish University of Agricultural Sciences. A peer-reviewed report of the work was published in Vol 96 of the journal of Polymer Degradation & Stability (2011) at pages 919-928, which shows 91% biodegradation in a soil environment within 24 months.

The commercial benefit of using d₂w plastic film is that the farmer will no longer have to pay to have acres of contaminated plastic removed from his farm. The environmental benefit will be that heavy vehicles will no longer have to drive around the country lanes collecting contaminated plastic, consuming fossil fuels, emitting pollutants, and occupying road space.