REPORT

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A+B degradability of LDPE film containing P-Life pro-degradant additive

(five appendixes)

Summary

"P-Life 15 µm " blown LDPE film was tested in accordance with SP´s certification rules SPCR 141 Appendix 4, which is in close agreement with ASTM D 6954: "Exposing and Testing Plastics that Degrade in the Environment by a Combination of Oxidation and Biodegradation".

Abiotic peroxidation of the material for the subsequent test of biodegradability was performed for 240 hours (10 days) at 65 °C. Test of biodegradability was performed in accordance with ISO 17556 "Plastics — Determination of the ultimate aerobic biodegradability in soil by measuring the oxygen demand in a respirometer or the amount of carbon dioxide evolved".

The result of the biodegradability test in the soil after 607 days was 79 % CO_2 emission and still increasing. The result of the eco-toxicity test was performed on the soil taken after the biodegradability test in accordance with SP method 4149 to ensure that the degradation products will not cause any negative effects on plants germination and growth.

The test results fulfill all the requirements stated in the SPCR 141, Appendix 4.

Background and aim

The commission included testing of the P-Life pro-degradant system used in a LDPE film for certification as oxo-biodegradable. The material was tested to prove degradability by a combination of **A**biotic and subsequent **B**iological degradation processes (A+B degradable) in accordance with SPCR 141 Appendix 4 , which is in accordance with ASTM D 6954: "Exposing and Testing Plastics that Degrade in the Environment by a Combination of Oxidation and Biodegradation".

The test procedure is used in three tiers for accelerating and measuring the loss in properties and molecular weight by thermal oxidation process (Tier 1), measuring ultimate biodegradation (Tier 2), and assessing ecological impact of the products from these processes (Tier 3). According to ASTM D 6954 an abiotic degradation test shall simulate or accelerate the degradation processes likely to occur in a chosen application and disposal environment. The abiotically degraded material is then examined for the ultimate biodegradability under optimal conditions in a simulated disposal environment.

Commission

This report contains results from the Tire 1 test: an abiotic test using Arrhenius type of approach and also summary of results from the Tire 2 and Tire 3 tests along with chemical characterization of the material for reference according to SPCR 141 Appendix 4, clause 3.

After various periods of exposure, the effects of thermo-oxidation were evaluated by measurements of elongation at break. An appropriate curve was then drown through the values obtained at elevated temperatures and extrapolation of the obtained short-time data was then used to predict performance at different service temperatures. Finally, an appropriate amount of the film was pre-oxidized at the temperature and period decided from the Arrhenius test, for the subsequent tests of biodegradability. The pre-aged material was characterized with regard to molecular weight by size exclusion chromatography (SEC). Biodegradability of the pre-aged material was followed using measurements of the amount carbon dioxide evolved. The soil from the biodegradability test was used for assessing ecological impact of the products from the degradation processes.

Material

The material was 15 µm thick blown film consisted of 99,7 % LDPE and 0,3 % P-Life prodegradant designated SMC 2522, produced in May 2008. The material was sent by the commissioner and arrived at SP on May 26th 2008. The material was kept in a storage space at 3-5 °C until the tests.

Tier 1. Abiotic degradability

Thermo-oxidative degradation was performed in heating cabinets with low, laminar air flow at three different temperatures viz. 55, 65 and 75 ± 1 °C. In addition to that, the material was also tested after exposure at 40 °C and after keeping in standard atmosphere (23 °C, 50 % RH). After various periods, one set of the test samples was removed for the measurements of elongation at break. At the end of the test GPC analysis was performed.

The Tire 1 tests were performed by Dr. Nazdaneh Yarahmadi.

Mechanical properties

Tensile tests were performed using Instron 5566 Universal Testing Machine equipped with an Instron Static Load Cell ± 100 N. The crosshead speed was set to 100 mm/min. Conditioning and testing was performed at standard atmosphere (23±2 °C and 50±10 % RH).

Molecular weight

GPC analysis was performed using following settings:
Equipment: Waters Alliance GPCV 2000
Solvent: 1,2,4-trichlorbensen at 135 °C, concentration: 1 g/l
Calibration: Polystyrene standard with universal calibration
Date: 080825 and 080918

Technician: Anders Mårtensson, CTH

Tier 2. Biodegradability

The ultimate biodegradability of the degraded material was examined under optimal conditions simulating soil environment at room temperature in accordance with ISO 17556. Method by analysis of evolved carbon dioxide was applied using Maihak S710 analyser equipped with Multor NDIR detector and measurements each 14 hours and 40 minutes. Through the

composting vessels carbon dioxide free air was flown at the rate of 300 ml/min. Three parallel composting vessels (6 l desiccators) were used for the test of oxidised material in the soil.

Cellulose (Merck, microcrystalline powder for thin layer chromatography, Avicel, 11,0 g, containing 44,4 % C) was used as positive reference material in three vessels. Three vessels were also used as blanks, containing the soil only but no test material.

Image: Grinded material that was used in the biodegradability tests

The Tire 2 tests were performed by Ms. Linda Eriksson and by Mrs. Catrin Lindblad

Soil environment

The soil environment was simulated using a mixture of the equal parts by volume of mature compost, plant soil and Vermiculite of concrete type. The test was in principle performed according to ISO 17556 at 23 ± 2 °C. Each vessel contained 1239 g of the soil mixture from which about two thirds was water (details about analyses are summarised in appendix 1).

Results – Tier 1

The results of the tensile tests as a function of exposure time at the test temperatures are presented in Figure 1. The exposure periods to achieve 100 % and 10 % absolute elongation at break respectively was read off in the diagram below. Readings of periods at 75, 65, 55 and 40 °C from Figure 1 to achieve elongation at break of 100 % and 10 % respectively were then used to draw appropriate curves using the equation below.

$$\ln t = (E/R)\cdot 1/T + B$$

A plot of **ln t** vs. **1/T** gave straight lines with the slope **E/R** which is known as Arrhenius plot (see Figure 2). The slope of the lines is a measure of the activation energy (E_a) for the degradation process.

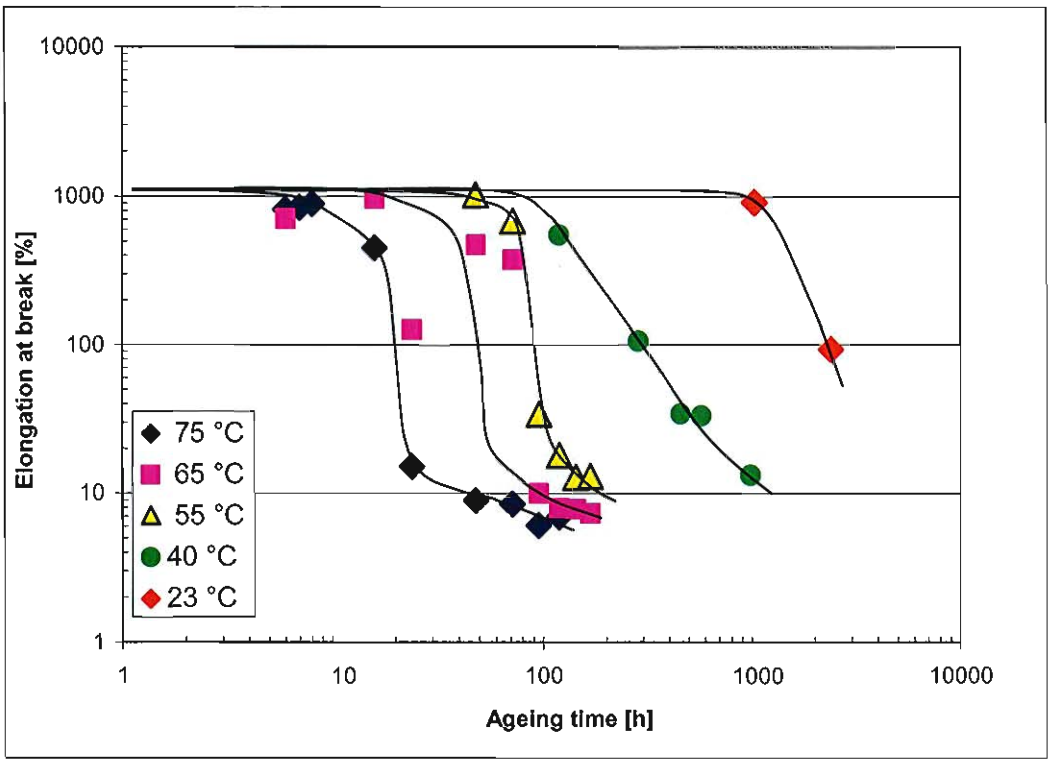

Figure 1. Elongation at break as a function of heat ageing time.

The activation energy E_a was calculated using equation: E_a = slope × R, where slope is calculated from the Figure 2 and R is the gas constant.

E_a was calculated to be **66,6** kJ/mol

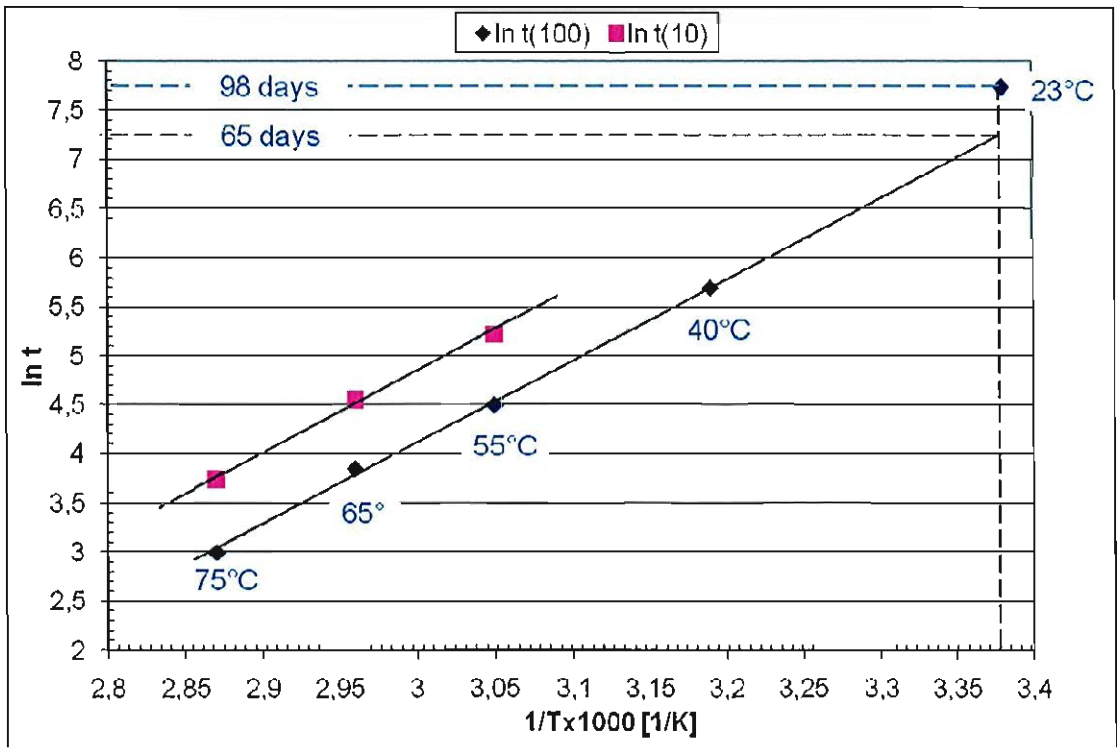

Figure 2. Arrhenius diagram.

Extrapolation of the obtained short-time data can then be used to predict performance at different service temperatures and disposal environments. Following equation can be used to calculate an expected lifetime:

$t_w = t_e \cdot \exp[E_a/R \cdot (1/T_w - 1/T_e)]$

where t_w is the calculated lifetime,

t_e is the lifetime at elevated temperature,

T_w and T_e are "in use" and elevated temperature respectively and
E_a is the activation energy, which was determined to be 66,6 kJ/mol

If we calculate lifetime for the material defined as a period to achieve 100 % in elongation at break and if we assume 23 °C as the in-use temperature then, using the determined activation energy we will find that it will take about 65 days for the material to reach this limit. The same result is received if we use the diagram in Figure 2 and extrapolate the blue curve to the temperature of 23 °C. However, in the real time test at 23 °C, the limit of 100 % in elongation at break was reached after about 98 days. This result indicates that there is a significant divergence from the Arrhenius relationship at temperatures below 40 °C for the material investigated.

A corresponding calculation of lifetime using 10 % in elongation at break as the criterion gives the lifetime of about 110 days at 23 °C. But, taking into consideration the divergence from the Arrhenius relationship this lifetime should probably be corrected to about 170 days.

From the Figure 1 it was decided to perform pre-ageing of the material for the subsequent test of biodegradability for 240 hours (10 days) at 65 °C. The molecular weight of the new and the pre-aged material are given in the table below. Some gels can dissolve on further oxidative degradation and become available for ultimate biodegradation. However, ASTM D 6954 states that the gel content should not be higher than 10 %.

Table 1. Results of GPC analyses

	Unaged	After 7 days at 65 °C	After 10 days at 65 °C
Mw	131500	23000	8800
Mn	18300	2500	1700
Gel contents (%)	0	-	Will be given later

Results – Tier 2

The carbon content in the pre-aged test material was 79 %. The accumulated amount of CO_2 expressed as the percentage of the maximum theoretical value is presented in the Figure 3.

The biodegradability test was conducted during the period 18th September 2008 until July 2010.

The result of the biodegradability test after 607 days in soil at 23 °C was 79 % of the maximum theoretical value and still increasing. Details about analyses are summarised in appendix 1 and 2.

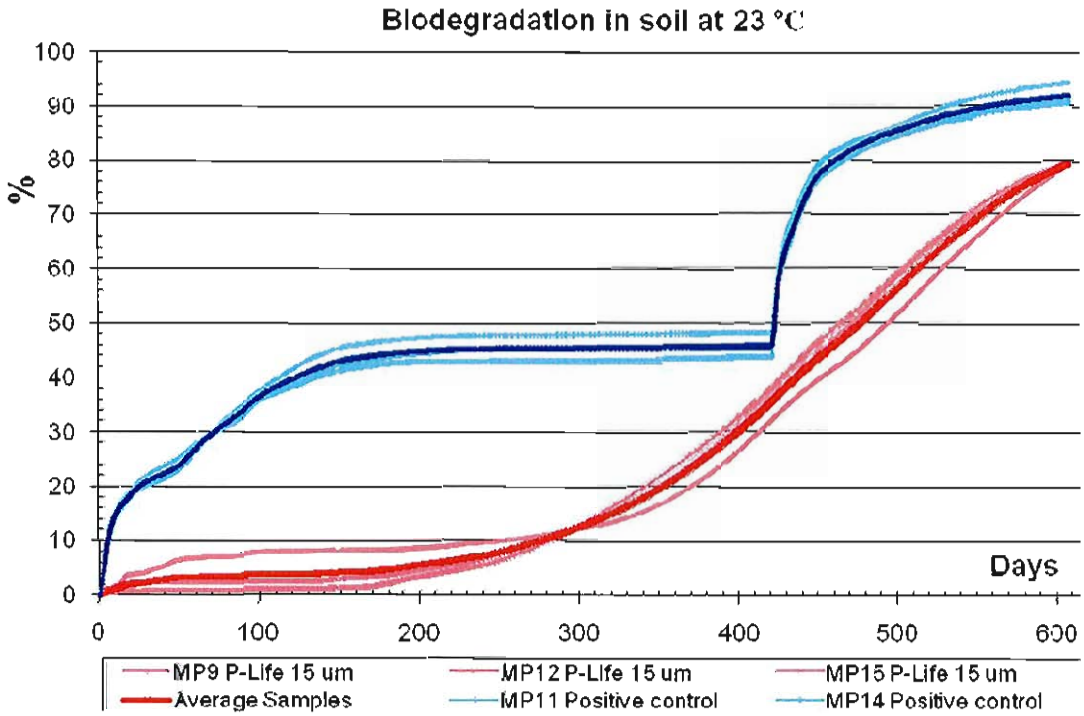

Figure 3. Amount of CO_2 expressed as percentage of the maximum theoretical value

Results – Tier 3

The full report from the screening eco-toxicity test using higher plants is presented in the report P804363 D, dated 9th July 2010.

The germination and growth test was performed on soil from three biodegradation tests viz.
Test soil: consisted of soil mix and the residues from the biodegradability test of the test material after 623 days.
Blank: soil mix only, after 623 days.
Positive reference: soil mix and the residues from the biodegradability test of the reference material (Avicel) after 623 days.
The tests were performed in triplicate using three different plants viz. mung bean, radish and oat. 15 seeds were planted in every single test.

Table 2. Results of germination

Plant	Soil	Number of seeds	% of the blank
Mung bean	Blank	75	100
	Positive ref	84	112
	Test soil	91	121
Radish	Blank	73	100
	Positive ref	84	115
	Test soil	75	103
Oat	Blank	53*	100
	Positive ref	69	130
	Test soil	80	151

* According to OECD 208 at least 70 % of the seeds in the blank must germinate to mark the test as valid.

Table 3. Results of dry biomass measurements

Plant	Soil	Dry biomass (g)	% of the blank
Mung bean	Blank	39,5	100
	Positive ref	42,2	107
	Test soil	45,1	114
Radish	Blank	28,6	100
	Positive ref	31,5	110
	Test soil	25,6	90
Oat	Blank	34,4	100
	Positive ref	42,9	125
	Test soil	32,2	94

Conclusion

The test material fulfils all the requirements stated in SPCR 141 appendix 4:

elements are below the high limit values according to EN 13432
Tier 1 – loss of mechanical strength occurs after 10 days at 65 °C and Mw is below 10000.
Tier 2 – biodegradability is > 60 % after 607 days in soil and still increasing
Tier 3 – germination and biomass is ≥90 % for all plants compared to controls.

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Technical specification for the biodegradability test in soil

Table 1. Results of analyses of the soil

Analysis	Mature compost	Plan soil	Vermiculite	Soil
pH	7,8	6,9	-	7,5
Dry content [weight-%]*	44,2	57,8	-	35,1
C, [weight-%]*	7,4	12,7	-	5,7
H, [weight-%]*	6,9	6,0	-	7,9
N, [weight-%]*	0,6	0,33	-	0,29
C/N-quotient*	12,3	38,5	-	19,7
C, dry sample [weight-%]	16,8	22,0	-	16,3
H, dry sample [weight-%]	1,6	2,3	-	2,0
N, dry sample [weight-%]	1,3	0,57	-	0,81
Volatile matter, 550 °C [weight-%]	19,8	24,6	-	17,0
Dry matter/vessel [g]	152	160	135	447**

* the material condition as received
** the total weight including water was 1239 g

Table 2. Points of measuring and the sample weights at the beginning of the test

Point of measuring	Total weight including vessel [kg]	Sample	Sample weight [g]
9	4,5650	P-Life 15 µm; A	12,035
10	4,5735	Blank control; A	-
11	4,5395	Positive control; A	14,523
12	4,5945	P-Life 15 µm; B	12,020
13	4,5430	Blank control; B	-
14	4,5285	Positive control; B	14,543
15	4,5430	P-Life 15 µm; C	12,040
16	4,5300	Blank control; C	-
17	4,4750	Positive control; C	14,445

Details about analyses and results of the biodegradability test after 180 and 607 days in soil at 23 °C.

Table 1: Total weight of the vessels after 180 days of the test and pH after 180 and 607 days

Sample	Total weight after 180 days [kg]	pH after 180 days	pH after 607 days
P-Life 15 µm; A	4,4935	6,6	7,9
P-Life 15 µm; B	4,5220	7,4	7,6
P-Life 15 µm; C	4,4695	7,6	7,7
Mean value: P-Life 15 µm	-	**7,2**	**7,7**
Positive control; A	4,4675	7,3	7,4
Positive control; B	4,4570	7,3	7,5
Positive control; C	4,4020	7,5	7,6
Mean value: Positive control	-	**7,4**	**7,5**
Blank; A	4,5010	6,8	7,3
Blank; B	4,4735	7,3	7,3
Blank; C	4,4600	7,5	7,4
Mean value; Blank	-	**7,2**	**7,4**

Table 2: Calculated and measured amount of carbon dioxide
Biodegradbility = (measured – blank)/theoretical

Sample	Theoretical max CO_2 [g] after		Measured CO_2 [g] after		Biodegradability [%] after	
	180 days	607 days	180 days	607 days	180 days	607 days
P-Life 15 µm; A	34,86		39,64	85,68	9	79
P-Life 15 µm; B	34,82		37,48	85,09	4	79
P-Life 15 µm; C	34,88		37,07	84,99	2	79
Mean value: P-Life	**34,85**		**38,18**	**85,25**	**5**	**79**
Positive control; A	23,64	46,74	57,57	100,54	87	90
Positive control; B	23,68	49,01	57,96	100,69	88	91
Positive control; C	23,52	46,84	58,94	102,34	93	94
Mean value: Positive control	**23,61**	**47,53**	**58,17**	**101,19**	**89**	**92**
Blank; A			36,24	56,02		
Blank; B			40,19	63,44		
Blank; C			34,77	55,47		
Mean value; Blank			**37,07**	**58,31**		

* Total amount including the contribution from the compost