BD Report

Evaluation of the Oxo-degradable characteristics of white HDPE net samples with and without 1% Reverte™ BD 92771 supplied by True Products Group Ltd t/a Holly International, care of Fist Plastika doo Beograd, Serbia

Report issue date: 25th February 2019
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Sample details:

Received supplied from: True Products Group Ltd t/a Holly International
Project Reference No.: BD 1962
Sample(s) received: 22/01/2019

Sample description:

Sample Number	Material Type	Sample Form	Thickness	Base Colour	Print	Reverte™ Grade	Reverte™ Batch No.	Addition Level (wt%)
14429	*HDPE*	*Net*	*~15 µm*	*White*	*No*	*BD92771*	*#16282*	*1%*
14430	*HDPE*	*Net*	*~15 µm*	*White*	*No*	*None*	*N/A*	*N/A*

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Date	15th May 2019	15th May 2019

The testing detailed in this report was performed wholly at:

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This report is applicable to the unique samples supplied to Wells Plastics Ltd by True Products Group Ltd t/a Holly International via our local distributor Fist Plastika doo Beograd, Serbia. It should be noted that the report does not guarantee that subsequent production batches manufactured by True Products Group Ltd t/a Holly International will contain Reverte™ oxo-biodegradable masterbatch manufactured by Wells Plastics Ltd at the correct dosage level.

Unless otherwise stated, the testing, analysis and reporting of the results of the evaluation reported here were performed in accordance with the referenced applicable methods (internal, national or international.)

Work Instructions used in this evaluation:
QWI82 Production of BD graph & test report
QWI85 Accepting a BD sample
QWI86 BD Sample preparation
QWI91 Operating FT-IR for analysis of BD samples
QWI92 Printing BD sample FT-IR scans
QWI93 Conducting UV degradation testing

Evaluation of the oxo-biodegradable characteristics of yellow, blue and red stripped PE bag samples supplied by True Products Group Ltd t/a Holly International, care of Fist Plastika doo Beograd, Serbia.

1. Background

True Products Group Ltd t/a Holly International is interested in evaluating Wells' "Reverte" oxo-biodegradable masterbatch for use in PE nets.

Reverte™ oxo-biodegradable masterbatch BD 92771 has been recommended for their application. This product contains a mixture of a metal ion pro-oxidant and a photoinitiated initial degradation inhibition package.

The grade utilised is polyethylene based and is generally suitable for inclusion in a broad range of polyethylenes including high density polyethylene (HDPE), low density polyethylene (LDPE) and linear low density polyethylene (LLDPE).

The formulation has been developed for a 1% addition to give thin section PE films maintained at 20^{o}C a controlled in-house shelf life of approximately 18 months, a further dwell time, normally around 2 to 6 months after photoinitiation and then a rapid breakdown of film properties resulting in acute embrittlement, normally after around 8 - 18 months. However, thicker section products, some stabiliser packages and specific polymer blends and pigmentation can significantly extend this embrittlement period and thinner sections, mineral fillers etc. can shorten it.

True Products Group Ltd t/a Holly International supplied two samples for evaluation of their oxo-biodegradable properties. The samples were both white nets detailed as being produced from HDPE. One of the nets measured ~15 µm in thickness and was submitted as containing 1% BD 92771. The other net also measured ~15 µm in thickness and was submitted as a control, understood to not contain any oxo-degradable additive. Sections were cut out of each sample and labelled with a description/internal testing number for identification. The samples were subjected to testing of their oxo-degradable properties in Wells Plastics' laboratory at their plant in Stone, Staffordshire, UK.

2. Samples as received / before testing

3. Method

The high molecular weight of commercial grades of polymers render them fundamentally hydrophobic and, therefore, very resistant to direct microbial attack. A reduction of the polymer chain length from its initial value of around 250,000 to a value between 4,000 and 10,000 increases its intrinsic microbial accessibility and enables subsequent biodigestion.

Reverte products initially catalyse the oxo-degradation of the polymer chains and then promote the growth of microbial colonies to expedite the second biodegradation stage. The initial chain scission (degradation) of the polymer chain causes a serial reduction in polymer molecular weight which ultimately results in acute embrittlement, micro-fragmentation and biodigestion.

This degradation can be tracked by the measurement of critical physical properties, using test methods such as ASTM D3826 to measure properties such as elongation, but this method is somewhat flawed because as the degradation gets underway the test sample becomes too friable for physical testing.

However, because oxo-degradation causes the formation of a carbonyl group at the point of every scission, measurement of the onset and level of this carbonyl group development in the test product is a more accurate direct measure of its induced degradation by the metal ion pro-degradant system within the Reverte masterbatch. This carbonyl index, as it is directly proportional to the elongation at break, can be used to determine the elongation when the sample is too weak to be conventionally tested. The point of embrittlement in polyolefins is defined as the point at which the elongation at break is ≤ 5%.

Polyolefins are generally reduced to the embrittled state of ≤ 5% elongation when the carbonyl index is greater than approximately 0.1 to 0.6 depending on the type, grade, pigmentation and thickness of the product under consideration. Thicker sections, stabiliser packages and heavier pigmentations can give critical carbonyl indices far greater than the range given, but the actual critical carbonyl index is readily determined empirically during the testing procedure.

The samples were aged using a modified ASTM D 5208-01 (Cycle C) test method. The ageing cabinet utilised contained UV lamps to simulate gentle outdoor sunlight. The temperature of the cabinet was maintained at 50^{o}C according to the test method.

It should be noted that the level of UV exposure generated in the ageing cabinet is very low and should not be compared with the levels generated, for example, in QUV ageing experiments.

In effect, the UV exposure level is around 26kLy per year in the cabinet. To put this in perspective, to simulate a full year's outdoor exposure in the UK the samples would have to be in the cabinet for around 3 to 4 years, to match a year in mainland Europe they would have to be in the cabinet for around 4 to 5 years and a year in Florida USA would be simulated by 9 to 10 years in the cabinet.

The test pieces in this experiment only spent between 7 - 8 weeks in the cabinet, so we can see that the actual UV exposure was relatively low and that the acceleration of the ageing process should be largely attributed to the higher temperature (50^{o}C) following the photo-triggering stage of the breakdown reaction.

The test specimens were removed after fixed time periods and the carbonyl index determined by Infra-red analysis, using a modified ASTM D 5576 test method. In addition, each sample was empirically assessed for friability and state of embrittlement. The carbonyl index at the point at which the Reverte containing test piece was fully embrittled was noted and presented as 100% embrittlement. The remaining carbonyl indices were calculated as a percentage of this and presented as "Degree of Embrittlement".

Finally, Arrhenius principles were applied to the results obtained at 50^{o}C, transposing them into the real-time results that would be expected at 20^{o}C.

4. Results

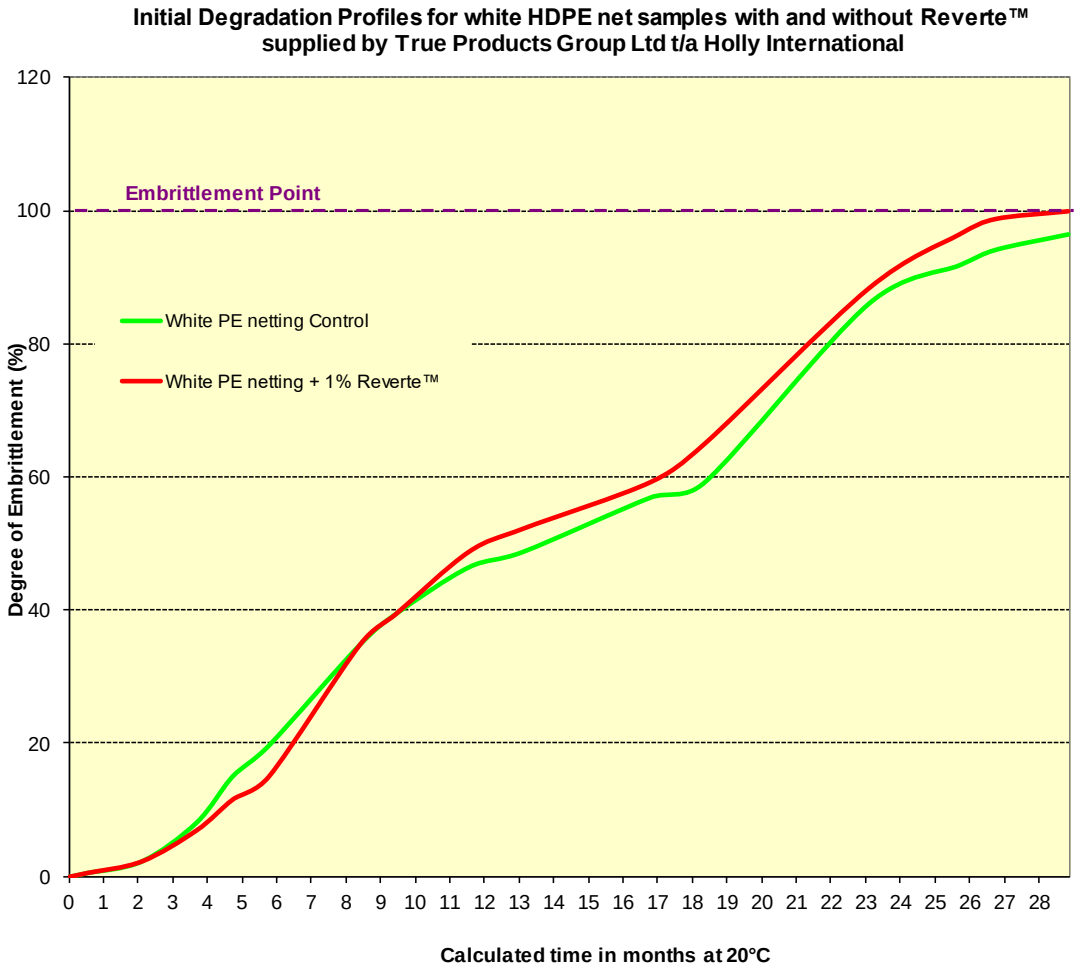
4.1 Degree of Embrittlement

	Degree of Embrittlement (%)							
Accelerated Ageing Time (hours at 50°C)	**0**	**24**	**96**	**168**	**216**	**264**	**384**	**432**
Calculated Time (months at 20°C)	**0.0**	**0.5**	**2.1**	**3.7**	**4.7**	**5.8**	**8.4**	**9.4**
White PE netting Control	0.0	1.2	2.3	8.1	15.1	19.8	34.9	39.5
White PE netting + 1% Reverte™	0.0	0.6	2.3	7.0	11.6	15.1	34.9	39.5

	Degree of Embrittlement (%)							
Accelerated Ageing Time (hours at 50°C)	**528**	**600**	**768**	**840**	**1056**	**1176**	**1224**	**1320**
Calculated Time (months at 20°C)	**11.5**	**13.1**	**16.8**	**18.4**	**23.1**	**25.7**	**26.8**	**28.9**
White PE netting Control	46.5	48.8	57.0	59.3	86.0	91.9	94.2	96.5
White PE netting + 1% Reverte™	48.8	52.3	59.3	65.1	88.4	96.5	98.8	100.0

Photographs of the test pieces after their accelerated ageing periods may be found in Appendix 1.

4.2 Graph of results



5. Discussion of Results

It is always difficult to precisely quantify results obtained in terms of real-time degradation due to the vagaries of natural conditions. However, the Arrhenius principles that we have applied to the accelerated ageing results enable us to present the results that would be expected from ageing in a real environment at a constant temperature of 20^{o}C in sunlight.

The white HDPE net sample containing Reverte demonstrated an enhanced degradation profile. Due to measuring difficulties that are discussed in more detail in the conclusion the “dwell time” was difficult to determine from the graph however from the FT-IR traces it could be seen up to of 216 accelerated ageing hours (calculated to around 4.7 months at 20^{o}C) no induced degradation was evident as a measurable carbonyl peak. This was followed by a steady degradation in physical properties with the sample reaching 100% embrittlement after ~1281 accelerated ageing hours (equivalent to around 28 months at 20^{o}C).

From the carbonyl peak measured on the FT-IR traces it appears that the white HDPE net sample supplied as a control also achieved a high degree of embrittlement, reaching 96% embrittlement at the point that the Reverte containing sample was 100% embrittled. However as is discussed in the conclusion this result is not support by the physical samples with the Reverte sample fragmenting readily at the end of the test period while the control sample is still intact and still fully flexible.

Finally, it should be noted that even when a control film may have degraded through normal UV/oxidative attack, this doesn’t mean that the chain scission will continue in a uniform and controlled manner until the chains are short enough for microbial digestion.

This is what the use of Reverte additive does and it is this which speeds up and facilitates the ultimate biodegradation of the plastic following the initial oxo-breakdown.

It should be re-stated that these are idealised real-time projections based on accurate accelerated laboratory ageing and, as previously stated, natural climatic conditions of sunlight, soil temperature etc do vary. These extrapolated results have, therefore, been prepared in good faith, but any potential user would have to carry out his own empirical observations to ensure that the product was fit for his purpose in the precise ageing regime employed.

6. Conclusions

1. The addition of Reverte masterbatch to the white PE net sample submitted by True Products Group Ltd t/a Holly International has been shown to be effective in introducing an oxo-biodegradable characteristic, resulting in a controlled progression to full embrittlement.

2. The control PE net sample also showed a high degree of carbonyl growth in the FT-IR traces, however this is not reflected in the physical states of the samples after testing.

3. As seen in the photographs in Appendix 1 after 1320 hrs exposure the net containing Reverte is completely embrittled and breaks into fragments easily. In contrast after the same exposure period the control net is still intact and not embrittled at all, it can be bent repeatedly without snapping.

4. The FTIR test method is particularly suited to film samples.

5. The form of the sample lead to potentially misleading results via our standard analytical method.

6. The physical testing showed a distinct oxo-degradable effect not seen in the control sample.

7. We can therefore conclude that the Reverte containing sample showed a physical effect commensurate with the addition of Reverte at the correct level but this could not be determined using our standard analytical techniques.

8. The length of time taken for the Reverte containing net to reach 100% embrittlement was surprising long considering the large exposure area of a net. This strongly suggests that the net contains stabilisers of some form.

END OF REPORT

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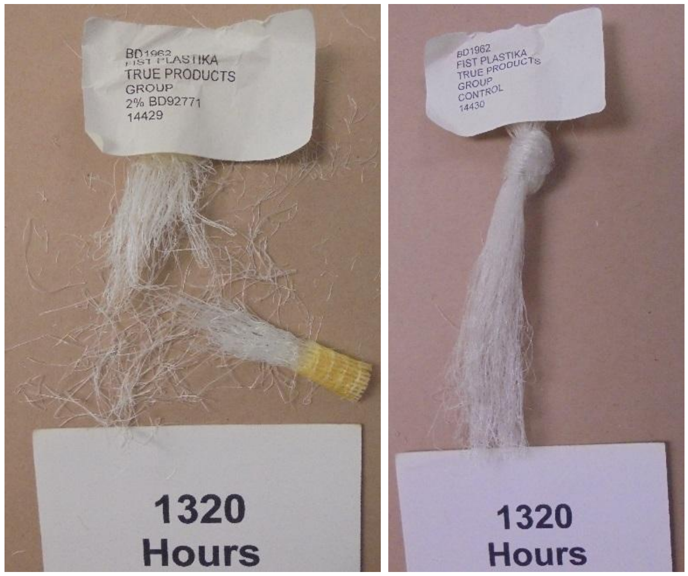
Appendix I

Photographs of the samples after ageing



Following the ageing period of 1320 accelerated ageing hours (calculated to around 28.9 months at 20oC); the white HDPE net sample containing Reverte can be seen to have lost its significant physical properties, is exhibiting extreme friability and breaking up when handled.

In contrast after the same ageing period the white HDPE net submitted as a control can be seen to be still intact and to have retained the majority of its physical properties.

These observations are commensurate with the measurements taken and contained within the body of this report.

END OF APPENDIX*