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Biodegradation of plastics in the open (natural) environment.

The need to assess and characterise the biodegradation of plastics which are lost to the open environment, through littering (intentional or otherwise), commonly referred to as “fugitive” plastics, has been recognised for a long time, with the use of several established methods being successfully employed for this purpose for many years.

The conditions which plastics are exposed to in the open (natural) environment are complex and variable; temperature range, moisture levels, UV exposure, bioactivity levels of the terrestrial or marine environments. Consequently, unlike conditions found in synthetic environments such as industrial composting, it is impossible to standardise any single set of conditions which are representative of the open (natural) environment.

The biodegradation of plastics, in general, requires that the high molecular weight polymeric material be structurally and chemically altered to produce lower molecular weight carbonaceous molecules, which is typically achieved by the introduction of (additional) oxygen into the molecular structure. This oxidation is produced by one or more processes such as thermal/photo-oxidative degradation or hydrolysis reactions.

The resulting substances, structurally degraded and chemically altered from the original polymeric material, can then be used as a food source by bacteria etc., resulting in the biodegradation of the lower molecular weight materials.

Several standards, specifications or test guides have been developed to assess and characterise the biodegradation of plastics in the open (natural) environment. A detailed comparative summary of three of these documents, ASTM D6954-18, BSi 8472:2011 and PAS 9017:2020, is provided after the overview discussed below.

ASTM D6954-18: The (first) standard test guide, initially published in 2004, has been revised and developed several times since, most recently in 2018. This standard test guide recognises the variability of the conditions in the open environment by not imposing artificial time-frames on the various aspects of the biodegradation processes characterised in the laboratory testing environment.

Biodegradation of plastics in the open (natural) environment is characterised through a three-tier process (a system also used in all other national and international testing regimes, including BSi 8472:2011 and PAS 9017:2020, for biodegradation of plastics in the open (natural) environment).

Tier 1 involves the abiotic degradation of the plastic; various conditions of UV level, temperature and moisture conditions are permitted with the time to achieve certain parameters of reduction in M_w (<5000 Daltons) recorded, thus reflecting the variability of the exposure conditions fugitive plastic would encounter in the open environment, and are thus independent of sample thickness. Carbonyl Index and mechanical property measurements may be used to follow the degradation process.

The degraded material is subjected to a standard laboratory-based biodegradation process, Tier 2, which may be selected from various methods, representative of the different conditions found in the open environment. The methodologies of the standard biodegradation tests are utilised, with the time required to achieve specified minimum levels (60% or 90% dependant on polymer type) of biodegradation recorded.

The resulting biodegradation residues within the test inoculum are assessed for ecotoxicity to flora and fauna in Tier 3 through the use of international standards and methodologies. Additionally, there is a requirement for materials to comply with the heavy metal and toxic substance lists of the applicable jurisdictions.

BSi 8472:2011: This British Standard utilises a similar three-tier methodology as ASTM D6954-18.

Tier 1 abiotic degradation is assessed by the exposure of the plastic under standard conditions of UV and temperature, independent of sample thickness. The level of structural degradation is assessed through empirical “mechanical” testing methods with the exposure time required to meet the subjective, empirical requirements recorded.

The degraded material is assessed for biodegradation in Tier 2, using the standard methodology of BS EN ISO 17556 (soil environment), with the time required to achieve 50% (minimum) biodegradation recorded.

The residues within the test inoculum once 50% biodegradation has been achieved are assessed for ecotoxicity to flora in Tier 3, through the use of international standards and methodologies. However, there are no requirements for materials to be assessed for ecotoxicity to fauna or heavy metal and toxic substances.

PAS 9017:2020: This publicly available specification utilises a three-tier methodology to assess the biodegradation of, specifically, polyolefins in an open-air terrestrial environment.

Tier 1 involves the abiotic degradation of the polyolefin-based product under defined conditions of UV exposure level and temperature for specified times. The time of, and the exposure conditions, are dependent on the material thickness; counter-intuitive to the variable exposure conditions fugitive plastic would encounter in the open environment.

Molecular weight parameters determined; M_n <5000 Daltons, M_z <30,000 Daltons and M_w >90% reduction, with carbonyl index (methodology defined in PAS) >1, to be achieved within the specified time frames applicable to the different thicknesses of polyolefin samples.

Note: the methodology for determining carbonyl index defined in this PAS utilises the determination of the area under the curve between two sets of wave numbers which include characteristic peaks of typical polymer additives found in commercially available polymers, which may affect the validity of the carbonyl index measurement.

Tier 2 testing involves the assessment of the surface of undegraded material and the degraded material from Tier 1 for ecotoxicity to flora and fauna through the use of international standards and methodologies.

The degraded material is assessed for biodegradation in Tier 3, using the standard methodology of BS EN ISO 17556 or ASSTM D5988-18 (soil environment), with a maximum time of two years to achieve 90% (minimum) required.

There are no requirements for biodegradation residues to be assessed for ecotoxicity to flora or fauna, or for any material at any stage of the biodegradation process to be assessed for heavy metal and toxic substances.

In conclusion, from reviewing the testing performed in the biodegradation characterisation techniques detailed in these methodologies, it is clear that the analysis of molecular weight parameters (M_w, M_z & M_n) and FT-IR analysis (carbonyl index) utilised by ASTM D6954-18 and PAS 9017:2020 demonstrate the molecular structural changes that occur (molecular weight reduction) and chemical alteration of the plastic/polyolefin materials (carbonyl index growth), thus confirming that the abiotic degradation of the materials (characterised by these methods) do not generate microplastics.

ASTM D6954-18 is commonly referred to as the standard test guide to assess and characterise Oxo-Biodegradable Plastics. The extensive and obvious similarities between ASTM D6954-18 and PAS 9017:2020 demonstrate that these methodologies are different ways to assess and characterise the same types of materials.

Comparison of the requirements for ASTM D6954-18, BS 8472:2011 & PAS 9017:2020

	ASTM D6954-18	BS 8472:2011	PAS 9017:2020
Title	**Standard Guide for Exposing and testing Plastics that Degrade in the Environment by a Combination of Oxidation and Biodegradation.**	**Methods for the assessment of the oxo-biodegradation of plastics and of the phyto-toxicity of the residues in controlled laboratory conditions**	**Plastics – Biodegradation of polyolefins in an open-air terrestrial environment – Specification**

Overview	Standard guide evaluating the oxidative degradation and subsequent biodegradation of polymeric materials in a range of environments through a three-tier process: 1. Abiotic degradation 2. Biodegradation of abiotic degradation substances 3. Ecotoxicity of biodegradation residues	Standard evaluating the oxidative degradation and subsequent biodegradation of plastic materials and products in soil through a three-tier process: 1. Abiotic degradation 2. Biodegradation of abiotic degradation substances. 3. Phytotoxicity of biodegradation residues	Specification evaluating the oxidative degradation and subsequent biodegradation of plastic materials and products in a soil through a three-tier process: 1. Abiotic degradation 2. Ecotoxicity of abiotic degradation substances 3. Biodegradation

Tier 1	Accelerated ageing process in accordance with various standard conditions and apparatus as per ASTM D5208 / D5510 / D5071 Tested within a temperature range of 20°C-70°C.	Accelerated ageing by photo-oxidation and/or thermal oxidation: 1. Photo-oxidation in accordance with an exposure cycle in BS EN ISO 4892-3 2. Thermal oxidation in accordance with ASTM D5510-94(2001) Tested at range/single temp from ambient and temp at which chemical decomposition becomes significant.	Accelerated ageing of film and rigid samples: 1. Films – ASTM D4329-13/BS EN ISO 4892-1 /UV tubes providing 0.8W/m^2 / 60°C / 1hr UV – 23hr dark / 14 days exposure 2. Rigid – ASTM D2565-16 or BS EN ISO 4892-1 - Xenon-arc - 0.35W/m^2 - 340nm daylight filter / air temp. 60°C / back panel 70°C / 8hr UV – 16hr dark / 28 days exposure.
Requirements	Mw <5000Daltons EAB <5%	Embrittlement measured empirically by: a) Bending material on itself with material demonstrating brittle failure, or b) Rubbing between finger and thumb and assessing fragmentation characteristics	Molecular weight analysis as per ASTM D6474-20 or BS ISO 16014-4: a) Film: Mn <5,000 Daltons; Mz <30,000 Daltons; %Mw loss > 90%, before or at 14-day weathering period b) Rigid: Mn <5,000 Daltons; Mz <30,000 Daltons; %Mw loss > 90%, before or at 28-day weathering period
Recordable parameters	Polydispersity % gel fraction Time at temperature and environmental conditions to achieve requirement.	Exposure time to produce the requirements	Carbonyl index (redefined as per Annex D) >1 at end of 14day or 28day exposure for film and rigid samples respectively.

Comments	The molecular weight distribution of the abiotically degraded material when the Mw requirements are achieved results in a solid material with negligible mechanical integrity. The permitted conditions are independent on test material form (polymer type/thickness) and reflect the variability encountered by plastics which end up in the natural environment. The characteristics of the degraded material are definitive measurements.	The molecular weight distribution of the abiotically degraded material when the Mw requirements are achieved results in a solid material with negligible mechanical integrity. The permitted conditions are independent on test material form (polymer type/thickness) and reflect the variability encountered by plastics which end up in the natural environment. The characteristics of the degraded material are subjective rather than definitive measurements.	The molecular weight distribution of the abiotically degraded material when the Mw requirements are achieved results in a solid material with negligible mechanical integrity. The permitted conditions are independent of polymer type but dependant on test material thickness, thus not representative of conditions fugitive plastics encounter in the natural environment. The characteristics of the degraded material are definitive measurements. The accelerated ageing conditions for films are reported to be specifically equivalent to 4 months outdoor exposure under South Florida conditions. No such correlation is provided for rigid samples. Carbonyl Index defined spectral areas cover the wavenumbers of characteristic peaks of commonly used (and included by polymer manufacturers) anti-oxidant compounds and therefore cannot be considered an accurate measurement of carbonyl index.

Tier 2	Biodegradation may be assessed in various environments representative of the different conditions fugitive plastics may be exposed to in nature – aquatic, soil, tropical (compost-like) using the methodology of relevant and appropriate ASTM and ISO test standards. Heavy metal content of the material resulting from, Tier 1, abiotic degradation and material from, Tier 2, biodegradation assessed for heavy metal and toxic substance content.	Biodegradation assessed under soil using methodology of BS EN ISO 17556.	Ecotoxicity testing: a) Surface of test sample prior to weathering as per OECD 202 [N1] b) Eco-toxicity of material from Tier 1 weathering process to be assessed by: i. OECD 222 [N4] (earthworm) ii. OECD 208 [N2] (plant) iii. OECD 211 [N3] (Daphnia)
Requirements	Heavy metals/toxic substances before and after biodegradation testing must meet the requirements of national/ international list. Degree of biodegradation: a) Single polymers –60% absolute biodegradation of the organic carbon / Gel content <10% b) Block copolymers etc - 90% absolute biodegradation of the organic carbon	Minimum of 50% absolute biodegradation of the organic carbon (sample of material for phyto-toxicity testing to be taken once this point has been reached – biodegradation testing may continue after this point).	Surface ecotoxicity prior to weathering:- meet all requirements of OECD 202 [N1] Material generated in Tier 1 weathering process to meet all requirements of: OECD 222 [N4] (earthworm) OECD 208 [N2] (plant OECD 211 [N3] (Daphnia)
Recordable parameters	The time profile of carbon dioxide evolution is recorded and the time to reach the appropriate thresholds are noted	The time profile of carbon dioxide evolution is recorded and the time to reach the appropriate thresholds are noted	Eco-toxicity test results for material generated in Tier 1 weathering process

Comments	Timeframe to reach required biodegradation levels is not defined, reflecting non-standard natural environmental conditions.	Timeframe to reach required biodegradation levels is not defined, reflecting non-standard natural environmental conditions No requirement to assess heavy metal and toxic substances content.	Surface ecotoxicity testing is for demonstration only and is not reportable. No requirement to assess heavy metal and toxic substances content.

Tier 3	Eco-toxicity of material generated in Tier 1 weathering process to be assessed by: OECD 207 (earthworm) OECD 208 (plant) ASTM E1440 (aquatic)	Phyto-toxicity of material taken at or soon after 50% degree of biodegradation achieved, in accordance with OECD 208 (plant)	Biodegradation assessed under soil using methodology of ASTM D5988-18 or BS EN ISO 17556.
Requirements	Material generated in Tier 2 biodegradation testing process to meet all requirements of: OECD 207 (earthworm) OECD 208 (plant germination and growth) ASTM E1440 (aquatic)	Material generated in Tier 2 biodegradation testing process to meet all requirements of OECD 208 (plant germination and growth)	Degree of biodegradation - 90% or greater of the organic carbon in material generated in Tier 1 when compared to the positive control or in the absolute. Maximum testing time - 2 years.
Recordable parameters	Eco-toxicity test results for material generated in Tier 2 biodegradation testing.	Eco-toxicity test results for material generated in Tier 2 biodegradation testing	Time to achieve defined requirements
Comments	No requirement to determine ecotoxicity on the material produced in the abiotic degradation process	No requirement for ecotoxicity testing of fauna and aquatic species.	Timeframe to achieve biodegradation levels is restricted and therefore not representative of the variability of the conditions found in the natural environment.