

DEGRADATION OF POLYETHYLENE IN THE NATURAL ENVIRONMENT

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ABSTRACT

A plastic material is any of a wide range of synthetic or semi-synthetic organic solids that are mouldable. Plastics are typically organic polymers of high molecular mass, but they often contain other substances. It is a white, waxy polymer constituted of only carbon and hydrogen. The drastic rise in the use of non-biodegradable plastic materials during the past decades has not been accompanied by corresponding development procedure for the safe disposal or degradation of these polymers. This research paper is mainly evaluating the oxo-degradable response of a polyethylene film sample containing pro-degradant additive by means of successive accelerated UV and thermal ageing. The results of the successive accelerated UV and thermal ageing test demonstrate that the film sample containing the d₂w pro-degradant additive has undergone significant degradation. The film sample containing the additive demonstrates a large change in carbonyl optical density measurement at the conclusion of the test (Figure 1). These results are consistent with the film sample containing the pro-degradant additive being in an advanced state of degradation.

The sample containing additive reached a carbonyl optical density value of 0.0361 after 528 hours ageing (inclusive of 48 hours UV pre-ageing). This result is consistent with inclusion of additive promoting degradation in the film sample. This conclusion is confirmed by observation: at the end of the ageing tests the oxo-biodegradable film sample show signs of breakdown (Figure 1). The film containing the additive demonstrated no significant increase in carbonyl optical density measurement at the conclusion of the test (Figure 2). This result is consistent with the film sample having undergone no significant degradation. The absence of degradation of the film sample confirms that the polyethylene is intrinsically stable to thermal ageing. This is consistent with the product having a usable fit for purpose shelf-life in storage conditions away from prolonged exposure to UV light and at an average temperature not exceeding 30°C. These results are confirmed by observation. At the end of the test the sample remains intact.

KEYWORDS: Additives, Degradation, Plastics, Thermal Ageing, Ultra Violet

INTRODUCTION

Plastics were first invented in 1860, but have only been widely used in the last 30 years. The word plastic comes from the Greek word “plastikos”, which means ‘able to be moulded into different shapes’. Plastics are usually high-molecular-weight polymers that at some stage in their existence are capable of flow, but may also be brought into a non-fluid form in which they have sufficient toughness and strength to be useful in self-supporting applications. It is a white, waxy polymer constituted of only carbon and hydrogen. Polyethylene also known as polyethylene or polythene was the first of the polymers to be discovered. Plastics are synthetic organic polymers that exist for just over a century.

The material has become an essential part of modern everyday life due to its versatility and properties, such as low cost, adjustable transparency, light weight, strength and high durability. Plastics are made up of long chain molecules called polymers. Polymers are made when naturally occurring substances such as coal, natural gas and oil are transformed into other substances with completely different properties. These polymers can then be made into granules, powders and liquids, becoming the raw materials for plastic products. Polyethene is a plastic. It is a polymer produced by reacting oxygen and ethane, in this reaction the small ethane molecules attach together to form long chain polymer molecules. This process is known as addition polymerization. It can also be produced through radical polymerization, anionic addition polymerization, ion coordination polymerization or cationic addition polymerization.

Polyethene is manufactured by cracking/decomposing petroleum distillates into small, reactive ethane molecules that can be rearranged. Ethene molecules polymerize to long chains of Polyethene, chains that are kept close to each other by weak bonds to form a material, comparable with the fibers of a felt.

Biodegradation of Plastics

Biodegradation is the chemical dissolution of materials by bacteria or by other biological means. Recently biodegradable plastics are of great interest. Biodegradation takes place by the action of enzymes, chemical degradation with living organisms. This takes place in two steps. The first step is the fragmentation of the polymers into lower molecular mass species by means of abiotic reactions, like oxidation, photo degradation or hydrolysis, or biotic reactions, like degradations by microorganisms. This step is followed by the bio-assimilation of polymer fragments by the microorganisms and their mineralisation. Biodegradability depends not only on the origin of the polymer, also on its chemical structure and the environmental degrading conditions.

The factors, on which the mechanical nature of biodegradable materials depends on, are their chemical composition, production, storage and processing characteristics, their ageing and the application conditions². Degradable plastic is the one in which the degradation results from the action of naturally occurring microorganisms such as bacteria, fungi, and algae. Biodegradable plastics must biodegrade in specific environments such as soil, compost, or marine environments⁷. The biodegradable bags are made of polymers that degrade when exposed to sunlight, water or air⁷.

EXPERIMENTAL PROCEDURE

Successive Accelerated UV and Thermal Ageing

This method involves subjecting the substrate to 48 hours accelerated UV pre-ageing before accelerated thermal ageing and monitoring degradation via changes in the carbonyl optical density as determined by FT-IR (Fourier Transform Infra Red) spectroscopy.

Thermal Ageing

The method involves subjecting the substrate to accelerated thermal ageing and monitoring degradation via changes in the carbonyl optical density as determined by FT-IR (Fourier Transform Infra Red) spectroscopy.

TEST METHODOLOGY

Accelerated Fluorescent UV Ageing

The sample was placed in a sample holder, in which the film is sandwiched between two metal plates (35 x 90 mm) with four exposure windows, and exposed to ultraviolet radiation in a Q Panel QUV/se test apparatus fitted with UVA 340 lamps, in general accordance with ASTM D5208. A black panel temperature of 50°C was used in

conjunction with a humid environment. The irradiance of the lamps was 0.78 W/m²/nm. The test sample with the additive was withdrawn every 48 hours and its carbonyl optical density determined by FT-IR spectroscopy.

Accelerated Thermal Ageing

Thermal ageing of the sample was carried out in a Memmert UFE 600 fan assisted oven at a temperature of 70°C in general accordance with ASTM D5510 Procedure B: Forced Ventilation Oven. The test sample with the additive was withdrawn every 96 hours and its carbonyl optical density determined by FT-IR spectroscopy.

Carbonyl Optical Density Measurement

The carbonyl optical density ($\Delta 1713\text{ cm}^{-1}$) of the sample was determined by FT-IR spectroscopy in transmission mode using a Thermo Electron Nicolett FT-IR instrument.

The optical density is defined by the magnitude of the carbonyl peak at 1713 cm⁻¹ divided by the sample thickness. Four optical density measurements were taken at each time point and an average determined.

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 etc.) are reaction by-products of the oxidative degradation process and as such their accumulation is indicative of ongoing degradation.

XRF Spectroscopy

The anticipated presence of the pro-degradant additive in each sample was confirmed by energy-dispersive X-ray fluorescence (ED-XRF) spectroscopy using a Bruker S2 Ranger A20-X10 bench top spectrometer against reference samples produced by Symphony.

The XRF spectrum of each sample was determined in air over 120 s with 40.00 kV, 250 mA X-ray source and 500.0 µm aluminum filter. Samples of film were prepared in 38 mm diameter HDPE XRF sample cups and the total thickness made up to ~200 µm with 36 µm discs cut from the sample using a James Heal 230/10 sample cutter.

RESULTS

Successive Accelerated UV and Thermal Ageing

Table 1: Accelerated Successive UV and Thermal Ageing

Sample	Δ Carbonyl Optical Density						
	QUV Ageing		Thermal Ageing				
	0 Hrs	48Hrs	144 Hrs	240 Hrs	336 Hrs	432 Hrs	528 Hrs
L/LET/01) Film with additive	0.000	0.0001	0.0080	0.0144	0.0188	0.0266	0.0361

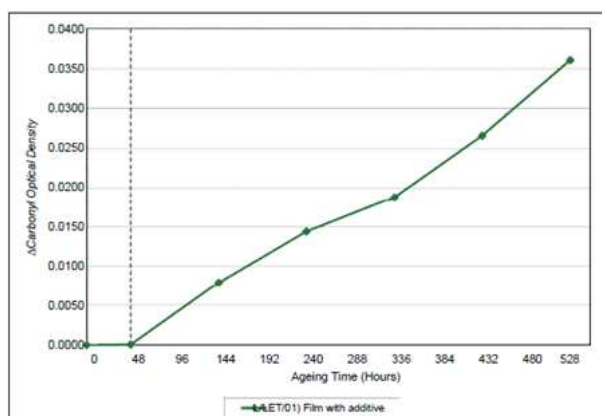


Figure 1: Successive Accelerated UV and Thermal Ageing

Accelerated Thermal Ageing

Table 2: Accelerated Thermal Ageing

Sample	Δ Carbonyl Optical Density						
	0 Hrs	96 Hrs	192 Hrs	288 Hrs	384 Hrs	480 Hrs	576 Hrs
L/LET/01)Film with additive	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

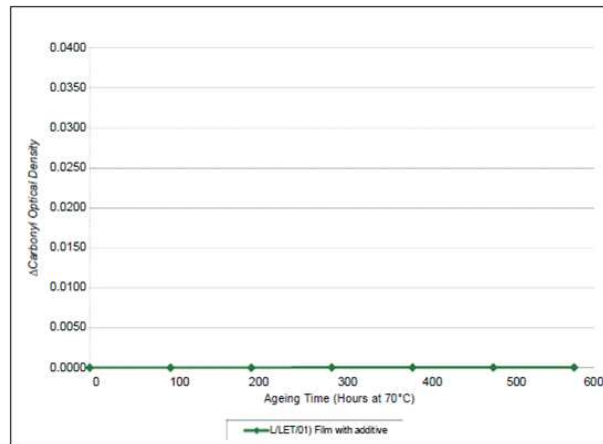


Figure 2: Accelerated Thermal Ageing

DISCUSSIONS

Degradation - Successive Accelerated UV and Thermal Ageing

The results of the successive accelerated UV and thermal ageing test demonstrate that the film sample containing the pro-degradant additive has undergone significant degradation.

The film sample containing the additive demonstrates a large change in carbonyl optical density measurement at the conclusion of the test (Figure 1). These results are consistent with the film sample containing the pro-degradant additive being in an advanced state of degradation.

The sample containing d_2w reached a carbonyl optical density value of 0.0361 after 528 hours ageing (inclusive of 48 hours UV pre-ageing). This result is consistent with inclusion of d_2w promoting degradation in the film sample.

This conclusion is confirmed by observation: at the end of the ageing tests the oxo-biodegradable film sample show signs of breakdown.

Shelf life – Accelerated Thermal Ageing

The film containing the additive demonstrated no significant increase in carbonyl optical density measurement at the conclusion of the test (Figure 2). This result is consistent with the film sample having undergone no significant degradation. The absence of degradation of the film sample confirms that the polyethylene is intrinsically stable to thermal ageing. This is consistent with the product having a useable fit for purpose shelf-life in storage conditions away from prolonged exposure to UV light and at an average temperature not exceeding 30°C.

These results are confirmed by observation. At the end of the test the sample remains intact.

CONCLUSIONS

Plastics wastes accumulate in the environment are posing an ever increasing ecological threat. The most problematic plastic in this regard is probably polyethylene, which is one of the most inert synthetic polymers and being

resistant to microbial attack. It is evident for the degradation of polythene films in the natural environment is slow and therefore, poses a serious environmental concern. A new generation of environmental friendly polyethylene containing a minimum of 9% starch and pro-oxidant additives are highly recommended for use since their degradation in natural environment is much faster¹³.

Hence it is proved that the usage of plastics is safer as it can be degraded in the soil. The results are confirmed by the weight, tensile strength and decrease in viscosity in some cases, molecular weight distribution, and fragility. The HDPE plastics are showing resistance to soil conditions than LDPE. This research is useful for the evaluation of the oxo-degradable response of a polyethylene film sample containing pro-degradant additive by means of successive accelerated UV and thermal ageing.

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