PROPOSAL

MULTI-CLIENT PROJECT
“OXO”

#2014/171/26510-B2

1. SUMMARY

In 2013, OWS performed a large desk research study for Plastics Europe on the benefits and challenges of bio- and oxo-degradable plastics. Besides a comprehensive overview of the available standards and certifications for both types of plastics, the report also discusses the available data in literature on the abiotic and biotic degradation of oxo-degradable plastics, verifying whether these match with the many claims which are today being made in the market.

The study revealed that at least three fundamental claims on oxo-degradable plastics can be questioned:

1. The molecular weight decrease, initiated in the presence of oxygen and accelerated by light and/or heat, is claimed by some to go on indefinitely, resulting, in the end, in low molecular weight readily biodegradable intermediates;
2. The time-temperature superposition principles used to extrapolate laboratory conditions to real-life conditions is claimed to be valid over a wide range of temperature; and
3. (Partial) biodegradation results are allocated to given (average) molecular weight values, while due to the Gaussian distribution of the molecular weight, results might possibly need to be allocated to the low(er) molecular mass 'parts'.

Further information on these claims can be found in Chapter 3 of this proposal. However, independent proof (or disproof) of these claims is today not (yet) available. Therefore, a logical next step would be to verify these claims by means of laboratory testing, hopefully resulting in a "once and for all" (independent) answer on whether oxo-degradable plastics are biodegradable or not.

Details on the proposed test program are discussed in Chapter 4 of this proposal. In a 1st phase, several oxo-degradable plastic products picked from the market and/or supplied by oxo-degradable plastic producers will be abiotically treated, after which the fragmented, residual parts will be used for further biodegradation testing in a 2nd phase. Besides this "top down" approach, also a "bottom up" approach will be included in which low molecular weight polyethylene will be synthesized, fractionated and tested for biodegradation (3rd phase).

This project will be performed in cooperation with IKT (Institut für Kunststofftechnik), the plastics technology institute at the University of Stuttgart. While IKT will be responsible for the material characterization (molecular weight and FT-IR analyses) and the synthesis and fractionation of low molecular weight polyethylene, OWS will be responsible for the abiotic degradation of the oxo-degradable samples as well as for the biodegradation testing (in soil).

The contribution per partner is estimated to vary from 10,000€ to 20,000€, depending on the number of interested parties. Interim results will be provided to participants on a regular basis. At the end of the project, participants will be granted 6 months of exclusivity. Afterwards, OWS and IKT intend to publish the results in a scientific journal. Participants will also be invited to become member of the steering committee.

Gent, Sep-05-2014

Bruno De Wilde
Lab Manager
OWS nv

2. INTRODUCTION

While (bio)degradable plastics were originally developed in order to solve specific problems related to agricultural films and to address the issue of separate collection and treatment of food waste, it is claimed that oxo-degradable plastics have been developed in order to provide a potential solution to littering issues. For such a solution to be viable, however, oxo-degradable plastics should not only fragment in the environment into small pieces which are no longer visible to the naked eye, but should also be entirely metabolized by bio-assimilation or conversion to CO_2 and H_2O, which is being claimed but for which solid independent proof (but also disproof) is missing.

As this is a very complex topic with various parameters such as raw materials, application sector and end-of-life questions, last year, Plastics Europe assigned to OWS a desk research study to compare the benefits and challenges of bio- and oxo-degradable plastics.

The study has been finalized in 2013 and an executive summary as well as the complete report is available through both Plastics Europe's website as well as OWS' website (see http://ows.be/lab-consulting-services/publications/).

Besides an overview of the available standards and certifications for both types of plastics, also a significant share of the report deals with the available data on the abiotic and biotic degradation of oxo-degradable plastics, verifying whether these match with the claims which are being made in the market.

The main results of the study are:

1. The majority of the biodegradable plastics meet the requirements of well-recognized standards of industrial composting;
2. Solid proof of biodegradation is available through certification by accredited laboratories and institutes for biodegradable plastics;
3. The very few positive biodegradation results obtained with oxo-degradable plastics were achieved in unrealistic testing environments and could not be repeated.
4. Oxo-degradable plastics do not meet the requirements of industrial and/or home compostability set out in various established standards;
5. In light of the above, the study recommends using the term *'thermo- or photo-fragmentable plastics'* instead of "oxo-degradable" plastics.

3. OVERVIEW CLAIMS

Oxo-degradable plastic producers claim that, due to exposure to light, oxygen and/or heat, the molecular weight of the oxo-degradable plastic drops below a certain ‘threshold value’ at which the plastics becomes biodegradable. Some standards refer to 5,000 Dalton, others to 10,000 Dalton.

Figure 1 shows a common profile of the molecular weight decrease over 90 days. The blue solid line is characterized by a fast decrease during the first days and is leveling off towards the end. The majority of the articles discussed in the literature study stopped the abiotic degradation phase after a period varying from 10 to 80 days. However, only a few obtained molecular weight values below 10,000 Dalton (see red line in Figure 1), respectively 5,000 Dalton. Yet, according to some oxo-degradable plastic producers, the molecular weight will decrease further over time and eventually reach a value (far) below 5,000 Dalton and lower (see blue dotted line in Figure 1).

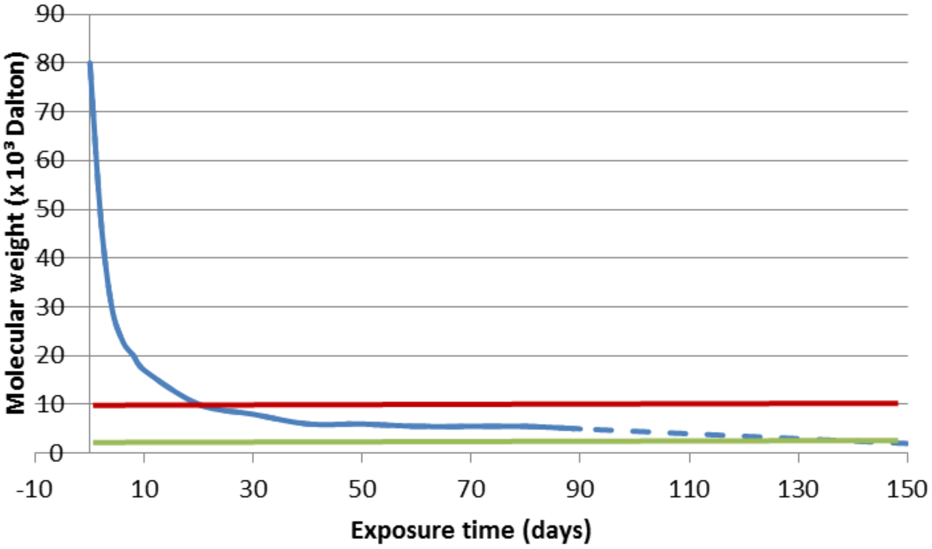

Figure 1.Molecular weight decrease of oxo-degradable plastics during abiotic pretreatment

It can be questioned whether the molecular weight decrease does indeed go on indefinitely, or at least until biodegradable residuals are formed. Furthermore, it can be questioned whether this ‘threshold value’ is product dependent, whether it has a value (much) lower than 5,000 Dalton (see green line in Figure 1) or whether it does not exist.

Also, even if molecular weight would continue to decrease over time, it might only happen under very specific conditions. The majority of the authors used temperatures ranging from 55°C to 70°C. In addition, these (very) high temperatures were also maintained for relatively long periods, ranging from 44 days (at 55°C) to 80 days (at 70°C). Time-temperature superposition principles, like the Arrhenius principle, have been used in the last years as a methodology to translate these accelerated conditions to real-life conditions. Obviously, these principles are based on the assumption that there is a linear correlation between molecular weight decrease rate and temperature over a wide range of temperature, and not only over a smaller partial range. Evidence of the decrease of molecular weight of oxo-degradable plastics at ambient temperature is not available.

Instead, data published by Jackubowicz (see Figure 2) and the US based laboratory Advanced Materials Center (see Figure 3) show that the rate of oxidation is temperature dependent and that at cooler temperatures decrease of molecular weight of oxo-degradable materials is slower and possibly also less.

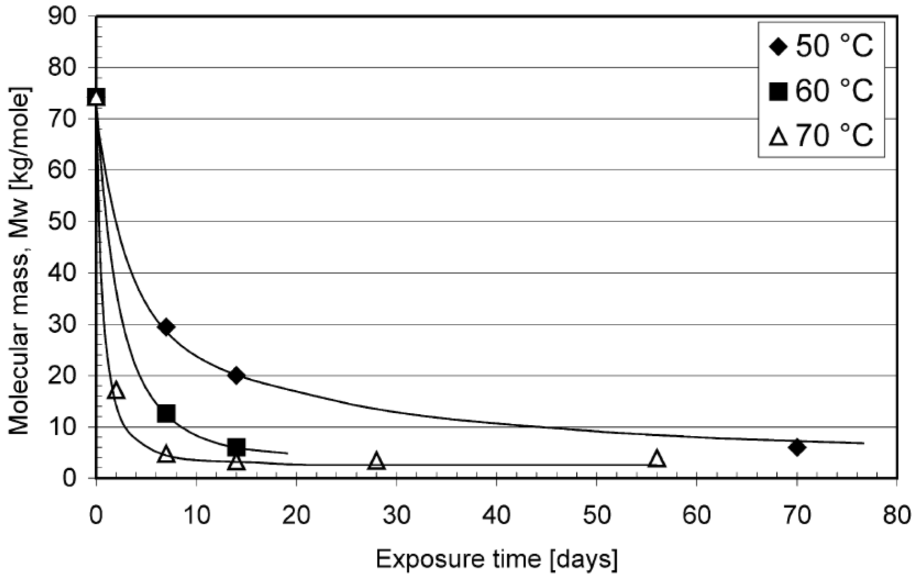

Figure 2. Molecular weight decrease of an oxo-degradable PE film at various temperatures (as reported by Jackubowicz, 2003)

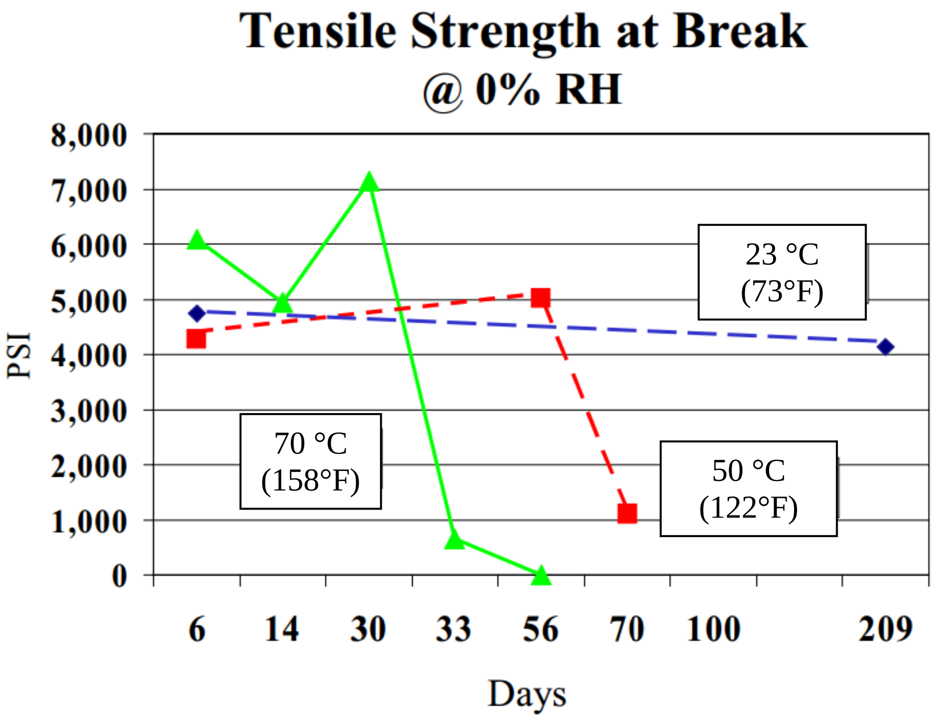

Figure 3. Loss of tensile strength at break of oxo-degradable products at various temperatures (as reported by AMC, Project #03P 1173)

As highlighted in the desk research study, numerous scientific articles are available on the biodegradation of oxo-degradable plastics, yet, only two articles showed a significant level of biodegradation (see Table 1).

Table 1. Most promising biodegradation results for oxo-degradable plastics found in literature

Author(s)	**Abiotic degradation**	**Biotic degradation**	
		Compost	**Soil**
Jackubowicz et al.	10 days at 65°C	43% after 607 days	91% after 733 days
Chiellini & Corti	44 days at 55°C	49-63% after 600 days	28% after 430 days

The results shown in Table 1, however, need to be interpreted in the correct way. The results are valid for a given molecular weight value, obtained after intensive weathering of the oxo-degradable plastic. The molecular weight of a polymer follows a normal (or Gaussian) distribution (see Figure 4). Linear polymers, like polyethylene and polypropylene, always have a molecular weight distribution, representing the relationship between the number of moles of each polymer 'part' and the corresponding molar mass. The molecular weight usually reported is the average molecular mass (M_w, or the value corresponding to the top of the curve in Figure 4). Taking this into account, the percentages of biodegradation as shown in Table 1 may possibly need to be allocated to the low molecular mass 'parts' ($< M_n$, or the 'parts' appearing in the left side of the curve in Figure 4).

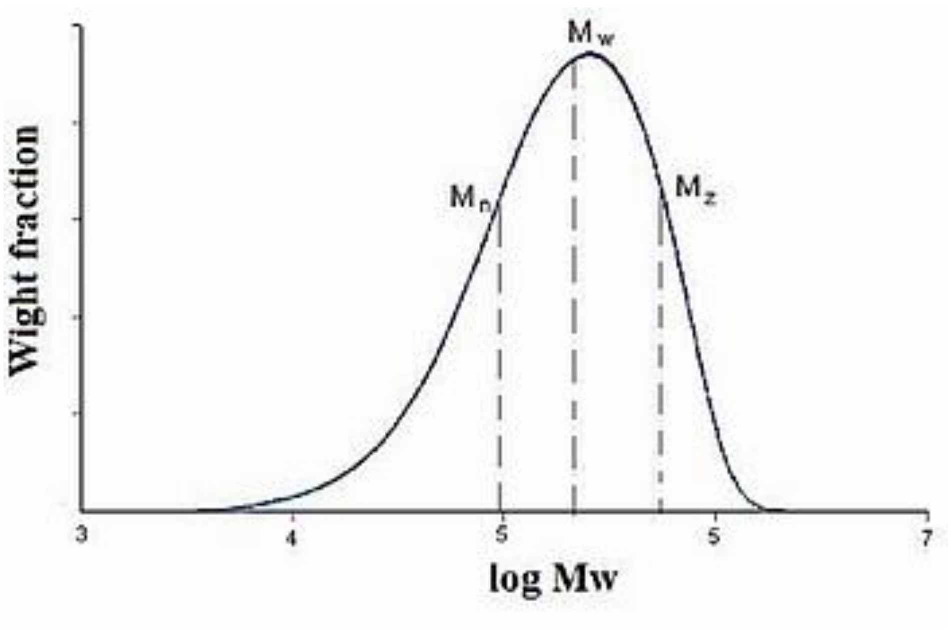

Figure 4. Molecular weight distribution of a polymer sample

Testing done by Chiellini et al. in 2007 proofs this reasoning. Chiellini tested the biodegradation of a thermally treated additivated LDPE sample by testing not only the complete sample, but also molecular weight extracts. The complete material showed a mean molecular weight of approximately 4,500 - 5,000 Dalton and only reached a biodegradation level of 12% after 100 days. Molecular weight extracts between 7,500 and 10,000 Dalton (right side of the Gauss curve) showed no significant biodegradation. Molecular weight extracts of 1,000 Dalton (left side of the Gauss curve) only showed 42-48% biodegradation. In other words, the 12% biodegradation obtained for the complete material can most probably be entirely allocated to the low molecular mass 'parts' of 1,000 Dalton.

From the above, it can be concluded that there are three fundamental basics of the oxo-degradable plastics technology which can at least be questioned:

1. The molecular weight decrease, initiated in the presence of oxygen and accelerated by light and/or heat, is claimed to go on indefinitely, resulting, in the end, in readily biodegradable intermediates;
2. The time-temperature superposition principles used to extrapolate laboratory conditions to real-life conditions is claimed to be valid over a wide range of temperature;
3. (Partial) biodegradation results are linked to the average molecular mass value of the oxidized polyolefin, but may probably need to be allocated to the low(er) molecular mass 'parts'.

4. MULTI-CLIENT PROJECT "OXO"

Independent proof or disproof of the above three basics is today not (yet) available. In this context, a logical next step could be to verify these claims by means of laboratory testing, resulting in, hopefully, a "once and for all" (independent) answer on whether oxo-degradable plastics are biodegradable or not.

The test program can be divided in 3 separate phases:

- Phase I: Abiotic treatment (reduction of molecular weight)
- Phase II: Biotic treatment ("top down" approach)
- Phase III: Biotic treatment ("bottom up" approach)

In the "top down" approach, biodegradation testing will be performed on the oxo-degradable plastics which were abiotically treated in Phase I, so after molecular weight reduction. In the "bottom up" approach, however, biodegradation testing will be performed on synthesized low molecular weight polymers instead.

4.1 Phase I

In a first phase, 8 oxo-degradable plastics will be abiotically treated in line with ASTM D5208. This test is an accelerated process of the oxidation of the material and represents Tier 1 testing of ASTM D 6954, UAE.S 5009, BS 8472 and other standards and guidelines on oxo-degradable plastics.

The degree of oxidation is measured by the loss of molecular weight and intermediate results can be obtained after each run of 300 hours (or about 12.5 days), which is indicative for an exposure of 6 ± 3 months in a Western-European climate.

More specifically, we suggest monitoring the molecular weight decrease of 3 oxo-degradable plastics in detail, with one measurement per sample every 12.5 days. For the additional 5 oxo-degradable samples, we would only include a start- and end-point analysis. Oxo-degradable plastic samples will be sourced directly from the market or supplied directly by oxo-degradable plastic producers.

Looking at the most common applications for oxo-degradable plastics, we suggest testing a thin oxo-degradable plastic film or bag with a thickness of 20-30µm, a thick(er) oxo-degradable plastic film or bag with a thickness of 80-100µm and a three-dimensional oxo-degradable plastic product (like a bottle) in detail. For the 5 additional oxo-degradable plastics, for which only molecular weight will be determined at start and end, we suggest to see what is available in the market. As oxo-degradable additives are mostly used in polyethylene, we will, if possible, collect and test only additivated polyethylene samples. Identification of the polymer will be done by means of FT-IR.

For the duration of the weathering test we suggest to opt for 75 days, which should be indicative for an exposure of approximately 36 ± 18 months in a Western-European climate. Looking at the available data in literature, the maximum duration found is 80 days. As such, 'optimal' pretreatment conditions are foreseen, avoiding any possible discussion on the duration of abiotic degradation.

Unlike the (highly) elevated temperatures which are often referred to in literature, we suggest to use the following test cycle: 20 hours UVA at 50°C + 4 hours condensation at 40°C. The higher temperatures mentioned in literature, going up to 70-80°C, are in our opinion not representative. Furthermore, as there is no proof that the time-temperature superposition principle is applicable over a broad range of temperature and as temperature clearly has an effect on the molecular weight reduction rate, we prefer running the test at 40-50°C, which is still (well) above ambient temperature. In addition, this test cycle is also prescribed by ASTM D6954, UAE.S 5009 and BS 8472.

For the 3 oxo-degradable plastics tested in detail, a graph will be presented showing the molecular weight decrease over time. Based on these results, we will be able to determine whether the molecular weight decrease does indeed go on indefinitely or reaches a plateau after a certain exposure time. In case of the latter, also the molecular weight level at which the graph levels out will be determined and compared with the 'threshold levels' set in the various guidelines and standards (i.e. 10,000 Dalton and 5,000 Dalton).

The collection and weathering of the oxo-degradable plastics will be performed by OWS, while the molecular weight analyses will be performed by IKT.

4.2 Phase II

While Phase I focuses solely on the molecular weight decrease during the abiotic degradation of oxo-degradable plastics, Phase II will focus on the biodegradation after weathering ("top down" approach).

At the end of Phase I, all remaining material of the 3 oxo-degradable plastics which have been tested in detail will be collected and used for subsequent biodegradation testing. Following the extensive oxidation phase of 75 days, the molecular weight of these oxo-degradable plastics should have been reduced significantly, yielding in intermediates which should have the highest chance on positive biodegradation results.

Despite the fact that industrial composting can be considered as the most aggressive environment, we suggest performing the biodegradation tests in soil. The oxo-degradable plastics industry clearly states that oxo-degradable plastics are not marketed for composting and that the most likely disposal routes are recycling (not in the scope of this study), soil surface exposure (through littering and the use of mulching films) and landfilling. Due to presence of oxygen and active fungi, soil can be considered more aggressive when compared to landfill. Biodegradation testing in soil can as such be considered as the most 'optimal' conditions and should result in the highest chance on positive results (avoiding as such any discussion on the chosen environment).

Looking at literature, the longest test duration for biodegradation testing in soil is 733 days or 2 years (Jackubowicz). Therefore, we suggest running the biodegradation tests also for 2 years.

The outcome of Phase II will allow us to conclude whether the selected oxo-degradable plastic samples are (completely) biodegradable or not. ‘Optimal’ conditions are assured through a (very) long abiotic degradation phase and a relatively aggressive environment in which biodegradation can take place. The oxo-degradable plastics industry claims that oxo-degradable plastics are ‘slow degraders’, just like natural materials. In this context, we intend to include also 3 natural materials like oak leaves, wood fibers, straw or flax fibers and test these in parallel with the oxo-degradable plastic samples.

Finally, and in case partial biodegradation is being measured, we will use size exclusion chromatography (SEC) to determine the molecular weight distribution of the weathered sample(s) to see if the percentage of biodegradation can be linked to a certain percentage of low molecular weight fractions. See also Chapter 4.3 on Phase III for more details on the SEC technique.

Phase II will be performed solely by OWS.

4.3 Phase III

The sample used for biodegradation testing in Phase II are those samples which have been weathered in Phase I and which should have reached their lowest molecular weight value possible at the end of the 75 days of oxidation (“top down approach”). However, we cannot be sure whether the molecular weight values obtained at the end of the abiotic degradation phase lay above or below the so called ‘threshold value’ at which a polyolefin ‘becomes’ biodegradable.

While Phases I and II focus on the degradation of existing oxo-degradable plastics collected in the marketplace, Phase III will focus on the biodegradation of especially synthesized (and later on fractionated) low molecular weight polyethylene (“bottom up” approach).

At first, a medium molecular weight polyethylene sample will be synthesized. As it is, because of practical limitations, not easy to synthesize (very) low molecular weight polyethylene, the medium molecular weight polyethylene sample will in a second stage be fractionated into (very) low molecular weight parts by means of size exclusion chromatography (SEC).

The principle of SEC is shown in Figure 5. Molecules of different sizes travel different path lengths within the column. Smaller chain lengths can easily enter the pores of the porous beads in the column and therefore stay a longer time in these pores than larger polymer chains. This results in different elution volumes. Larger molecules with higher molecular weights are eluted first from the column followed by smaller molecules with lower molecular weights.

SEC can also be used to enrich and clean polymer samples after synthesis. As explained above, each polymer, including also polyethylene, is characterized by a molecular weight distribution where M_w represents the average molecular weight (see Figure 1). In order to avoid testing a polyethylene sample with a relatively large molecular weight distribution, which would make it impossible to link the percentage biodegradation to a given molecular weight value, the fractionated samples will be 'cleaned'. By injecting the small molecular weight fractions a second, a third and possibly also a fourth time into the SEC apparatus, the molecular weight distribution can be reduced significantly, resulting in a relatively 'pure' polyethylene sample with a fixed molecular weight. To achieve this, the selection of the right pore size distribution is very important to ensure proper separation.

Using the above discussed technique, polyethylene samples with a molecular weight of 500 Dalton, 1,000 Dalton and 2,000 Dalton will be produced and tested for biodegradation in soil. Similar to Phase II, biodegradation will be tested for a period of 2 years.

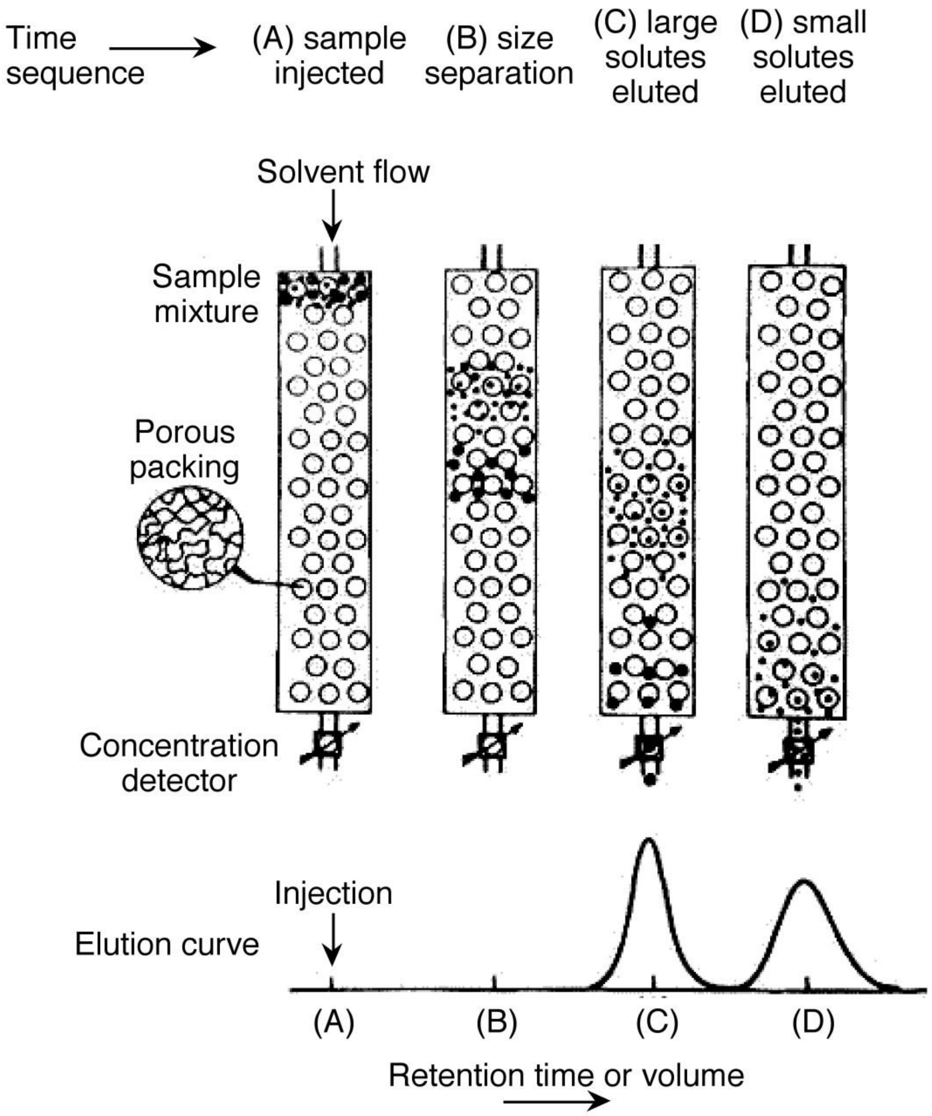

Figure 5. Principle of size exclusion chromatography (SEC)

The synthesis and fractionation of the polyethylene samples as well as the molecular weight analyses will be performed by IKT, while the biodegradation tests will be performed by OWS.

4.4 Overview

An overview of the project, including the number of samples foreseen per phase as well as the test duration, is shown below in Table 2.

Table 2. Overview of the project

Phase I: Abiotic degradation	
Set-up	
Number of samples with Mw analysis each 12.5 days	3
Number of samples with Mw analysis only at start and end	5
Testing period (days)	75
Phase II: Biodegradation of abiotically treated samples	
Set-up	
Number of samples	6
Testing period (months)	24
Phase III: Biodegradation of synthesized low molecular weight samples	
Set-up	
Number of samples	3
Testing period (months)	24

5. COSTS

The total price for this project is estimated to be around 125,000 €. Yet, depending on the number of participants, the project could be modified to need and possibilities.

Throughout the project, interim results will be provided on a regular basis. These intermediate results will be send to all project partners, providing as such the opportunity to follow the project from close-by. On a regular basis, the results will be discussed by the steering committee which consists of the different project partners. If necessary and upon agreement by the steering committee, the test program may be modified during execution.

At the end of each phase, a report will be published and distributed amongst the project partners. At the end of the study, a final report will be written, combining the results obtained in each phase. Compared to the intermediate reports, which will 'only' show the obtained results, the final report will also contain a chapter on discussions in which the three above mentioned claims will be compared with the results obtained throughout the study.

The project partners will be granted 6 months of exclusivity. During that period, neither OWS nor IKT will make the report publically available, unless otherwise agreed upon. After 6 months, OWS and IKT intend to publish the results in a scientific journal.