

Evaluation of degradability of biodegradable polyethylene (PE)

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Abstract

Thermo-oxidative degradation of polyethylene films, containing pro-oxidant has been studied at three temperatures that normally occurs during composting conditions. Beside temperature, oxygen content was also varied. After various periods of time the effects of thermo-oxidation were evaluated by measurements of molecular mass of the materials. It is shown that the temperature is the most important factor influencing rate of thermo-oxidative degradation of the materials while oxygen content is of negligible importance. The investigation has also shown that when the material is degraded into low molecular mass products the material is bioassimilated. The degree of bioassimilation in our case was about 60 % and still increasing, after 180 days.

Keywords: degradable polyethylene, thermo-oxidation, pro-oxidant, molecular weight, biodegradation, mineralisation, activation energy

1. Introduction

New environmental regulations and a growing concern for the environment has led to the development of different types of polymeric materials that are compatible with the environment. In particular, usage of biodegradable polymers has greatly increased in various applications. Synthetic polymers are normally not biodegradable until they are degraded into low molecular mass species that can be assimilated by microorganisms [1, 2]. It means that biodegradation must be preceded by an abiotic degradation that gives monomeric and oligomeric products. Hydro-biodegradable polymers such as polyesters and thermoplastic starch are degraded by abiotic hydrolysis. Polyolefins belonging to hydrophobic hydrocarbon polymers are resistant to hydrolysis and for this reason they cannot hydro-biodegrade.

Polyolefins, as commercial products are also resistant to oxidation and biodegradation due to the presence of antioxidants and stabilisers. However, they can be made oxo-biodegradable by the use of pro-oxidant additives [3, 4]. The most active pro-oxidants are those which are based on metal combinations capable of yielding two metal ions of similar stability and with oxidation number differing by one unit only e.g. Mn^{2+}/Mn^{3+} [4]. Thus, the material degrades by a free radical chain reaction involving oxygen from the atmosphere. The primary products are hydroperoxides, which can either thermolyse or photolyse under the catalytic action of a pro-oxidant leading to chain scission and the production of low molecular mass oxidation products such as carboxylic acids, alcohols, ketones and low molecular mass hydrocarbon waxes [5]. Peroxidation leads also to hydrophilic surface modification, which is favourable to micro-organisms [6], which can then bio-assimilate the low molecular mass oxidation products.

The purpose of this work was to evaluate the kinetics of the thermo-oxidative degradation of PE materials containing pro-oxidant. The rate of degradation depends on the type of polymer, type and amount of additives and temperature. It was also demonstrated previously [7] that degradation in compost of PE containing pro-oxidants could be very slow due to the low partial pressure of oxygen. The main goal of this work was to find a relationship between temperature, oxygen content and the time needed for the formation of biodegradable low molecular mass oxidation products. The rate of biodegradation of the oxidation products was also evaluated.

2. Experimental

2.1 Material

Two transparent films designated AF 10 and AF 20 were supplied by EKM Produktentwicklung. Both films were about 30 µm thick, based on polyethylene and contained Mn-stearat as the prooxidant. AF 20 contained twice as much prooxidant as AF 10.

2.2 Thermo-oxidative tests

The thermo-oxidation was performed at three temperatures within the temperature range that normally occurs during composting conditions namely 50, 60 and 70 °C. Beside temperature, oxygen content was also varied using air and mixtures of oxygen and nitrogen: one with 5 % oxygen and one with 10 % oxygen. After various periods the effects of thermo-oxidation were evaluated by measurements of the molecular mass of the materials using size exclusion chromatography (SEC).

The molecular mass was determined in Waters Alliance GPCV 2000 equipment using 1,2,4 - trichlorbenzene as the solvent at 135 °C, dissolving time 16 hours and a concentration of 1 g/l.

2.3 Mineralisation test in soil columns

In order to study the rate of biodegradability of oxidation products formed during thermo-oxidative degradation of PE, the PE films were thermo-oxidised in an oven at 70 °C for 4 weeks before use in the mineralisation test. These preaged materials were studied using the following test.

The mineralisation of the materials occurred in soil columns at an incubation temperature of 60 °C. The mineralisation was monitored by measuring the carbon dioxide produced. Precise amounts of the test materials were mixed with microbial activated soil, which itself contained very low amounts of easily degradable carbon compounds. Glass columns were filled by this mixture. The microorganisms in the soil utilized the organic component (test materials), thereby producing new biomass. The glass columns (containing the soil) were continuously aerated with oxygen. The gas at the outlets of the columns transported the carbon dioxide, produced by the microorganisms, out of the glass columns. The gas was then washed in an adsorbing solution. The carbon dioxide produced was trapped as sodium carbonate in a sodium hydroxide solution. Periodically an aliquot of the sodium hydroxide solution was taken and the carbonate content measured by titration. The carbon contents of the test materials were analysed before starting the mineralisation test. Once the carbon content of the test material was known, the theoretical amount of carbon dioxide that could be produced from that carbon could be estimated. The degree of mineralisation of the test materials was calculated from the carbon dioxide produced and plotted on a graph versus time of mineralisation.

3. Results and discussion

3.1 Thermo-oxidative degradation

Thermal oxidation was investigated in well-defined conditions prevailing in industrial composting units. Oxidation processes take advantage of the high temperatures (50–70 °C) but consideration was also given to a possible decrease in oxygen content in compost due to oxygen consumption by microorganisms. The results of the investigation show that the materials degrade quickly at all temperatures used. Temperature seems to be the most important factor. The average molecular weight (Mw) values of both materials dropped below 5000 after 2 weeks at 70 °C and after 8 weeks at 60 °C. Typical curves representing change of Mw as a function of oxidation time at various temperatures are

demonstrated in figure 1. Similar diagrams were constructed for both materials oxidised in air, in 10 % oxygen and in 5 % oxygen respectively.

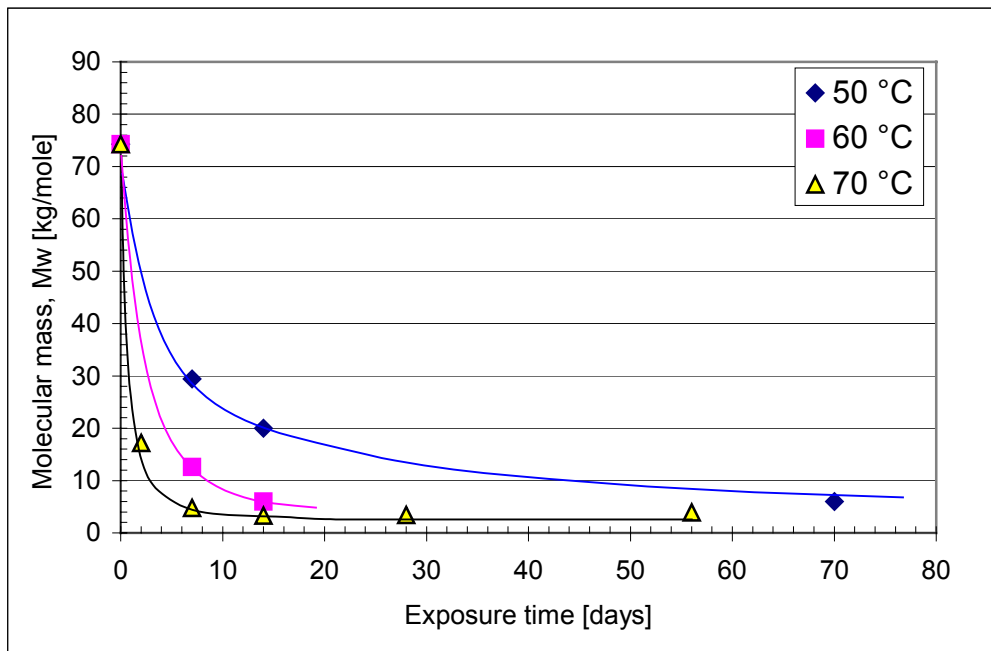


Figure 1. Change of molecular mass (Mw) of the AF 20 material with exposure time at various temperatures in air.

In the last few years, time-temperature superposition principles have been established as a methodology for materials lifetime predictions in accelerated ageing tests [8, 9]. These principles have been used here in order to facilitate the comparison of the test results between the materials with different pro-oxidant content and between different environments. For this reason, a superposition analysis has been done by shifting all data to 60 °C using empirically chosen multiplicative time factors. Figure 2 shows superposed results for the Mw of the material AF10 and Figure 3 shows corresponding results of the material AF 20.

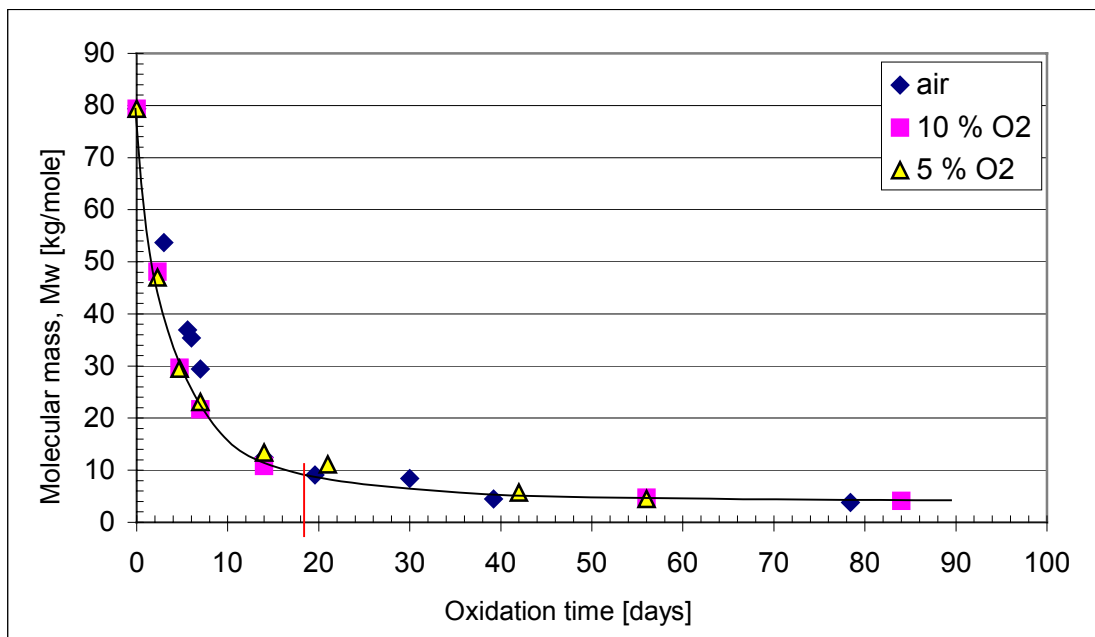


Figure 2. Effect of oxygen content on the rate of degradation of the AF 10 material. Superposition analysis by shifting data to 60 °C.

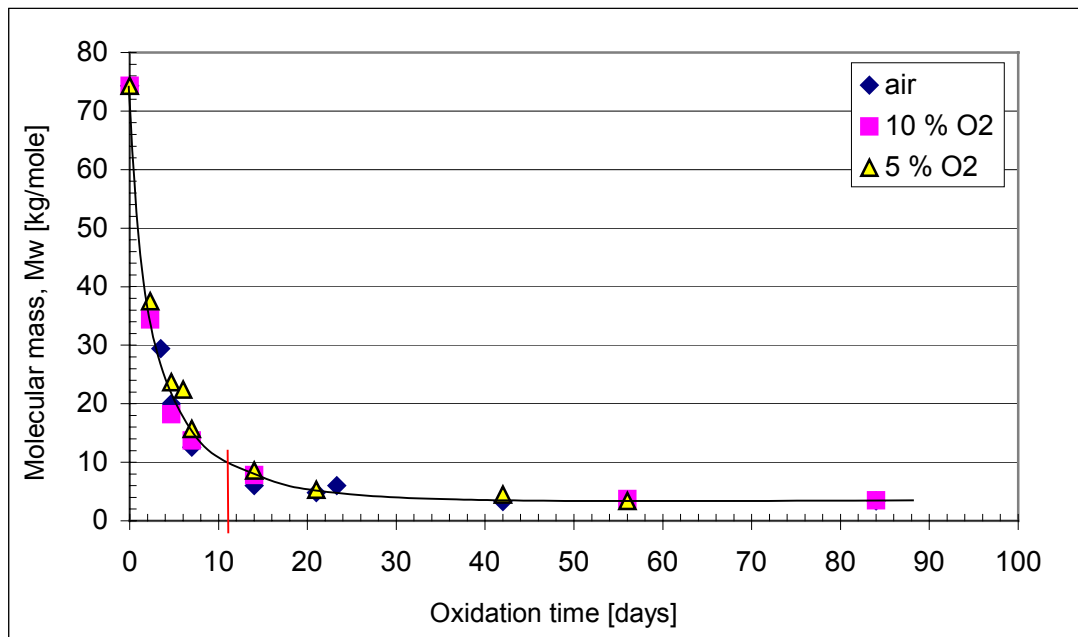


Figure 3. Effect of oxygen content on the rate of degradation of the AF 20 material. Superposition analysis by shifting data to 60 °C.

Both figures show that superposed results at 60 °C from different environments fit the same curves. This means that the oxygen content (at least between 5 and 20 %) has no significant influence on the rate of degradation of the PE films. On the other hand, when comparing figure 2 and 3 it is clear that the content of prooxidant is important. The oxidation time at 60 °C, required for the material AF 10 to achieve the molecular mass of 10000, was about 18 days. Doubling of the pro-oxidant content (AF 20 material) resulted in reduction of the corresponding time to about 11 days.

Using the experimental data obtained as exemplified in figure 1 the times to achieve Mw of 10000 at different temperatures were determined. The natural logarithms of these times were plotted versus $1/T$ according to the Arrhenius equation. The result is shown in figure 4.

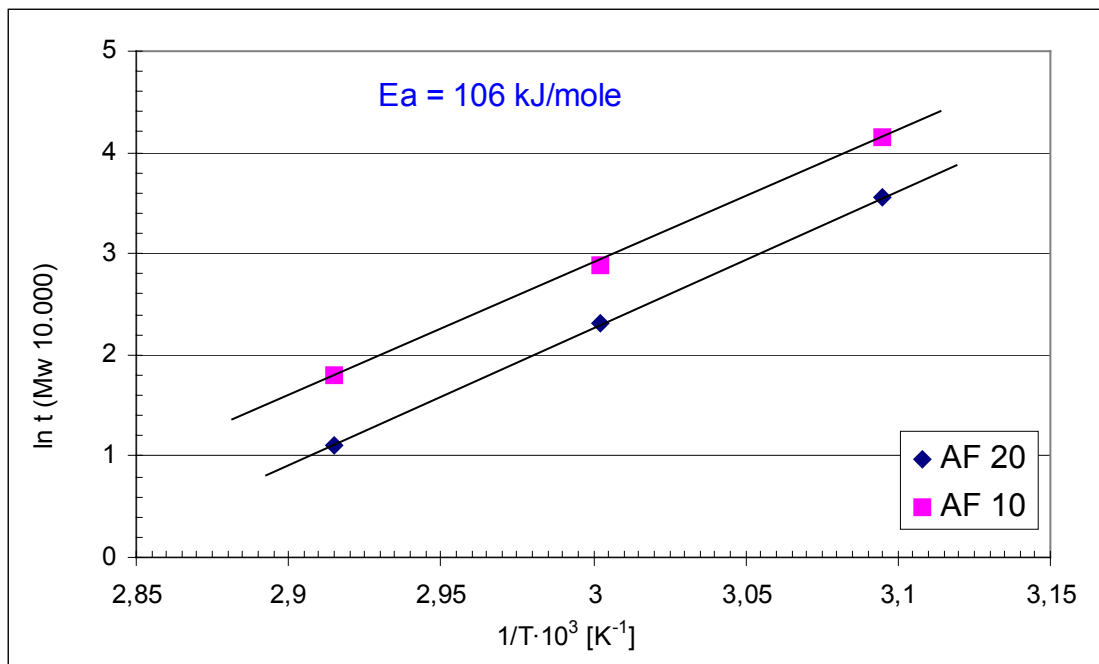


Figure 4. Arrhenius plot

From the slope of the lines in figure 4 the activation energy was calculated giving the value of 106 kJ/mole. If we calculate lifetime for the materials define as time to achieve 10000 in molecular weight and if we assume 25 °C as in-use temperature then, using the determined activation energy we will find that it will take about 4,5 years for the material AF 10 and about 2,5 years for the material AF 20 to reach this limit.

3.2 Mineralisation/biodegradation

The materials AF 10 and AF 20 were preaged in an oven at 70 °C in air for 4 weeks in order to produce oxidation products by thermo-oxidative degradation of PE. The reason was to study the rate of biodegradability of low molecular mass oxidation products that were available for bio-assimilation. The mineralization of the materials was examined in microbial activated soil at the constant incubation temperature of 60 °C. The degree of mineralisation was calculated from the carbon dioxide produced as a percentage of the theoretical amount of carbon dioxide that could be produced and plotted on a graph versus time of mineralisation (see figure 5).

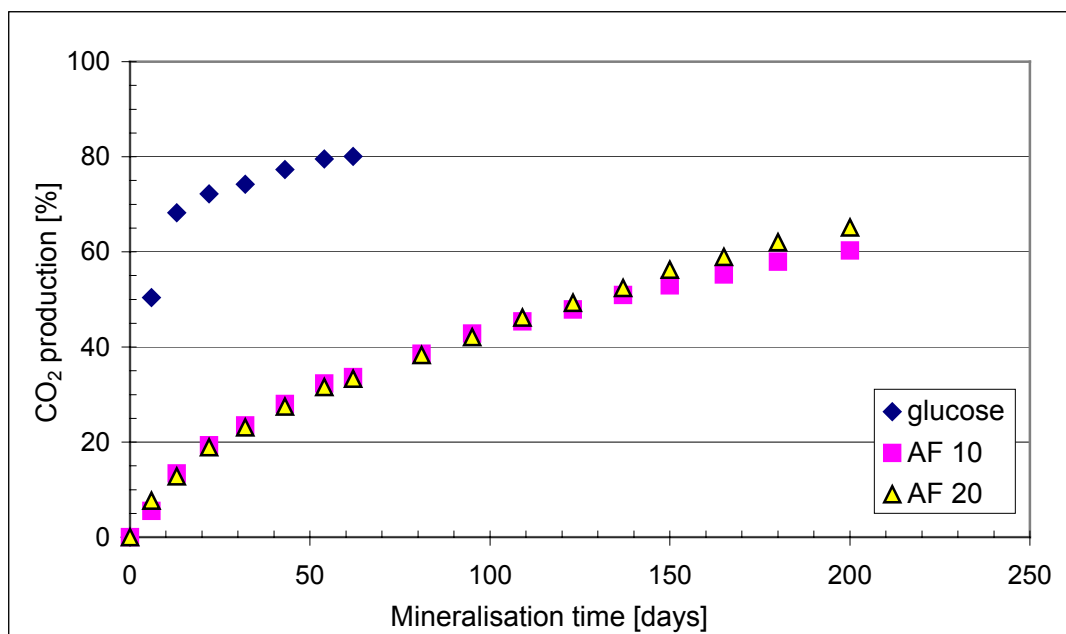


Figure 5. Mineralisation of the oxidised AF 10 and AF 20 materials in soil columns at 60 °C monitored by measurements of the produced CO₂.

It is demonstrated in figure 5 that when the materials are degraded to low molecular mass oxidation products the bioassimilation starts at once. The degree of mineralization after 180 days of incubation was 57,9 % and 62 % for AF 10 and AF 20 respectively. After 200 days of incubation the degree of mineralization of AF 10 was 60,3 % and of AF 20 was 65,1 %. The mineralization of AF 10 is a little bit slower which indicates that some additional oxidation takes place during the mineralisation period. It is important to point out that the results as demonstrated in figure 5, indicate that after this incubation period the mineralization of both materials was continuing. Therefore, it can be predicted that both materials can eventually be nearly completely mineralised to carbon dioxide.

4. Conclusions

In most cases plastic materials should manage a predetermined service life before physical degradation commences. There should be no significant changes in the physical and mechanical properties of the material during its service life. However after the material has served its primary purpose, rapid biodegradation and disintegration should occur. Thus, all biodegradable polymers are in a delicate balance between the achievement of useful technological performance and a rapid and effective biodegradability. This investigation can be regarded as a model for prediction of the behaviour of oxo-biodegradable materials where both service life and mineralisation time can be determined.

It is shown that temperature is the most important factor influencing the rate of thermo-oxidative degradation of the materials while oxygen content has negligible importance in the rate of oxidation at least in the range between 5 and 20 % oxygen. By measuring the rate of thermo-oxidative degradation at various temperatures the activation energy was determined to be 106 kJ/mole for both materials. This value was used for calculation of service life under indoor conditions.

This investigation has also shown that when the material is degraded to low molecular mass products the material is bioassimilated. The degree of bioassimilation in our case was about 60 % after 180 days and was still increasing.

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