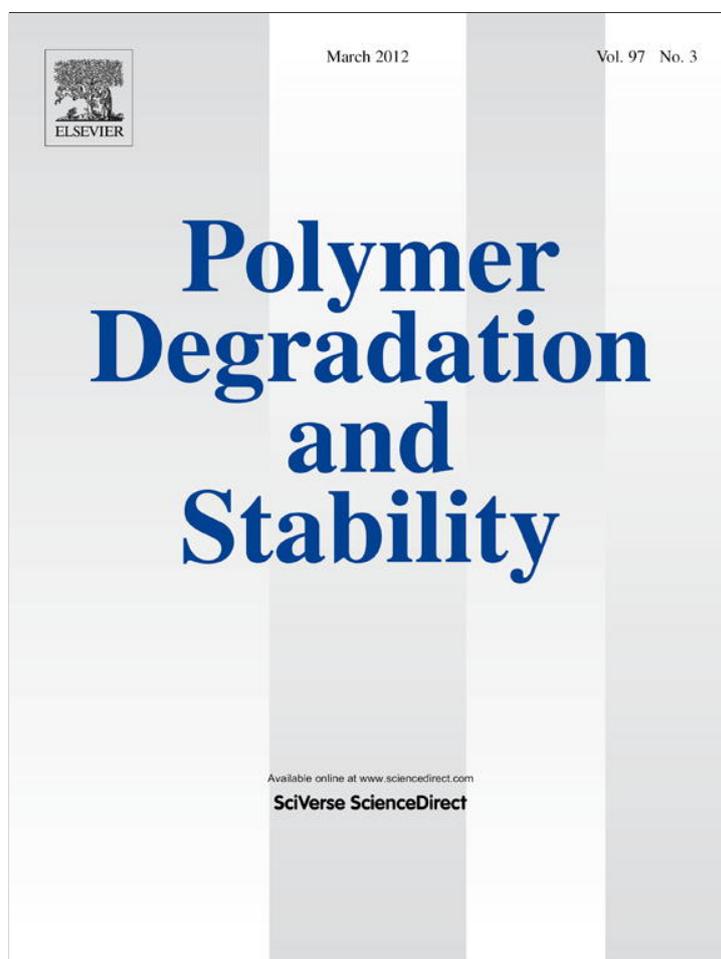


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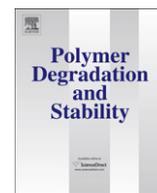
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Effects of reprocessing of oxobiodegradable and non-degradable polyethylene on the durability of recycled materials

Ignacy Jakubowicz*, Jonas Enebro

SP Technical Research Institute of Sweden, Chemistry and Materials Technology, Brinellgatan 4, SE-501 15 Borås, Sweden

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ABSTRACT

The use of plastics is steadily increasing in our daily lives, and plastics are the fastest-growing component of the waste stream. Although the efficiency of plastic recycling is increasing, plastics are often seen as a permanent environmental problem because of littering. The introduction of oxobiodegradable polyolefins (OBDs), containing prodegradant additives, is considered to be a way to reduce this problem by enabling the fast degradation of plastics in the environment. The prodegradant additives form radicals that attack the polymer chains, causing chain scissions and generation of low molecular mass oxidation products that can be consumed by microorganisms. There is, however, a concern that the prodegradant additives will present a problem if OBD materials end up in the conventional plastic recycling streams. The present study therefore highlights the impact of mixing OBD materials with conventional polyolefins to evaluate the impact on the remaining service life of the recyclates.

The study included the use of two different OBDs, mixed in different proportions (10% and 20%) in a conventional polyethylene. The remaining service life of the mixtures was evaluated by monitoring the reduction in tensile strain after exposure to thermo-oxidative degradation at 70 °C, compared with a pure polyethylene. The impact of stabilizer content in the mixtures was also evaluated together with the effect of mixing partially degraded OBDs into the recyclate.

The results show that the incorporation of minor fractions of OBD materials in the existing recycling streams will not create a severe effect on the service life of the recyclates as long as the polymer mixture possesses a reasonable degree of stabilization.

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1. Introduction

Plastics play a very important role in our daily lives. Throughout the world the demand for plastics, particularly plastic packaging, bags, thin films, etc., continues to grow rapidly. As a consequence, the problem of plastic litter is growing as well. Plastic is the fastest-growing component of the waste stream and because most of the plastics are essentially not biodegradable, littered plastic becomes a permanent environmental problem [1]. To prevent this, a new generation of biodegradable plastics has emerged on the global market that is predicted to grow significantly. Simultaneously, education of consumers that the availability of biodegradable plastics is not an encouragement to litter is being conducted.

Polyolefins contain structural elements that are particularly susceptible to oxidative degradation reactions. In the process of polymerization, catalysts such as transition metals react and form

peroxy radicals ROO^\bullet that abstract hydrogen atoms from the polymer and form alkyl radicals. During melt processing, additional peroxy radicals are formed by reaction with oxygen at the high temperature and mechanical shear forces. No activation energy is required when alkyl radicals react with molecular oxygen. This means that the formation of peroxy radicals occurs at almost the same rate at any temperature. The rate-determining step in auto-oxidation is therefore abstraction of hydrogen (H) by a peroxy radical ROO^\bullet . The reaction involves the breaking of a C–H bond, which requires activation energy.

Polyolefins always contain stabilizers that are used to protect the polymer during melt processing. Stabilizers also contribute to the service lifetime of the finished article upon exposure to light and heat. Thermo-oxidative degradation is normally inhibited using suitable antioxidants (AO) such as phenolic AO, which act as H-donors. The result is formation of hydroperoxides. To avoid thermally or photo-induced formation of alkoxy and hydroxyl radicals from the decomposition of the hydroperoxides, so-called hydroperoxide decomposers are used, which are classified as secondary antioxidants. The stabilizers are continuously consumed

* Corresponding author. Tel.: +46 105165305; fax: +46 33103388.
E-mail address: ignacy.jakubowicz@sp.se (I. Jakubowicz).

during processing and usage. It should be noted that the products of the consumed stabilizers remain in the material. The main mechanisms of the oxidation reactions and stabilization are well known and have been described [2–4].

Oxobiodegradable polyolefins (OBDs) are materials that contain special additives called prodegradants that cause them to degrade by a free radical chain reaction involving oxygen from the atmosphere. The primary degradation products are hydroperoxides, which can either thermolyse or photolyse under the catalytic action of a prodegradant, 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 [5–7]. In addition to prodegradants, industrial materials contain also stabilizers that will be consumed in the first place before the oxidation will start. The time over which the oxidation process takes place depends thus on the type and concentration of stabilizers and prodegradants in the material and the amount of sunlight and/or heat to which the material is exposed. It can be emphasized that the mechanism of oxidation in polyolefins is essentially the same with or without prodegradants but the prodegradants significantly accelerate the oxidation.

Mechanical recycling, i.e., direct reprocessing of thermoplastics, is the most effective, economical and reliable method for recycling of plastics waste. However, mechanically recycled plastics have less desirable properties when compared with the same articles manufactured from virgin materials [8]. The quality of plastics intended for recycling is strongly dependent on their origin and history [9]. Furthermore, melt processing, which is used in plastics recycling, may induce oxidative and thermomechanical degradation of the polymer [10]. The result of the degradation processes is a modification of the molecular structure of the polymer and a subsequent deterioration of various properties. Therefore, appropriate recycling must take into account the oxidative damage introduced to a polymer during its lifetime. It is necessary to deal with processing and long-term stability of recyclates through appropriate deactivation of structures with prodegrading properties, especially peroxides and hydroperoxides. This is achieved by restabilization of recyclates. Restabilization has to take into account previous damage, subsequent application and residual stabilizer content. A balanced combination of suitable stabilizers and co-stabilizers contributes to processing stability and to service lifetime of a recyclate during its intended applications. The type and amount of required stabilizers depend on the reprocessing conditions as well as on the intended use of the recycled materials, which means that the consumed stabilizers often must be replaced.

Households are the biggest source of plastic waste; however, recycling household plastics presents a number of challenges related to collection, sorting and upgrading/restabilization. Besides these difficulties, many recyclers fear that the new biodegradable materials could compromise the quality of recycled plastics if they enter the recycling stream. In particular, they are concerned about OBDs [11], which are practically indistinguishable from the regular materials. The present study aims at elucidating possible effects on mechanical recycling of post-consumer OBDs that erroneously end up in a sorted municipal collection system. Consumption of all types of biodegradable plastics accounted for less than 1% of the global demand for plastics in 2009 [12]. Starch-based plastics, poly(lactic acid)s and polyhydroxyalkanoates, accounting for 90% of the global consumption of biodegradable plastics, have seen their capacity grow rapidly with an annual compound growth rate of 51%. Compared with this statistic the proportions of oxobiodegradable materials used in the present study to simulate unintentional incorporation were at least 100 times higher.

2. Experimental

2.1. Materials

All materials were prepared by SP Technical Research Institute of Sweden using a microcompounder (DSM Xplore 15) as 40 mm wide and 50 μm thick strips for testing. The reference material used was Borealis LDPE designated CA8200. One commercial OBD material was LDPE film containing a prodegradant system designated “P-Life”, which is based on a manganese salt and was kindly supplied by P-Life Japan Inc. The second commercial OBD material was LDPE film containing a prodegradant system supplied by Nor-X Industry AS. Nor-X supplies different grades of prodegradants depending on where and how the materials will be handled. According to Nor-X, the OBD material supplied for this investigation was mainly based on an iron salt and was the one with the highest thermo-oxidative degradation rate.

The OBD materials were mixed with the reference material in the proportions of 10% and 20%. The reference LDPE was used in its original form as unstabilised as well as stabilized with 1000 ppm Irganox 1010.

In addition to the mixtures of pristine OBD materials, mixtures with 10% pre-oxidized OBD materials ($\approx 30\%$ reduction in elongation at break) in stabilized LDPE were produced and evaluated by the same procedure.

2.2. Accelerated ageing

Thermo-oxidative degradation was performed on pre-cut test strips (10 mm wide) from each material in heating cabinets with low airflow at 70 ± 1 °C. After various periods, one set of the test samples (5–8 strips) was removed for testing of elongation at break and analysis by infrared spectroscopy.

2.3. FT-IR (Fourier Transform-Infrared Spectroscopy)

Carbonyl formation during heat ageing was monitored by FT-IR using a Nicolet 6700 FT-IR instrument (Thermo Scientific, Waltham, MA, US). The analyses were performed by collecting spectra (32 scans) from the films using a micro-ATR. The carbonyl index was calculated as the peak intensity ratio between the carbonyl peak at 1712 cm^{-1} (terminal ketones) and a reference peak at 1472 cm^{-1} ($-\text{CH}_2-$ groups). The carbonyl indexes were calculated as average values from at least two spectra from each sample.

2.4. DSC (Differential Scanning Calorimetry)

The DSC analyses for evaluating the oxidative induction time (isothermal OIT) were performed on a DSC 1 instrument (Mettler-Toledo GmbH, Schwerzenbach, Switzerland) equipped with a gas controller and sample robot. Small pieces of sample (≈ 5 mg) were subjected to a temperature programme based on ISO 11357-6 using an oxidative temperature of 205 °C.

2.5. Tensile testing

The tensile strain at break was determined based on standard ISO 527-3:1995 Plastics – Determination of tensile properties – Part: 3 Test conditions for films and sheets. The machine used was a Zwick Z100 (Zwick GmbH & Co. KG, Ulm, Germany) equipped with a static load cell ± 100 N with force accuracy class 1 and elongation accuracy class A according to the standard ISO 5893. The initial grip-to-grip separation was 50 mm, the preload 0.1 N and the crosshead speed was set to 50 mm/min. Conditioning and testing were performed at standard atmospheric conditions (23 ± 2 °C and

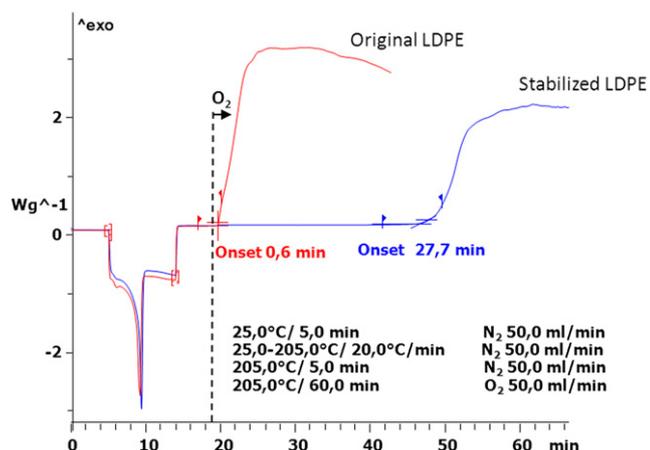


Fig. 1. OIT curves for the original (red) and stabilized (blue) LDPE at 205 °C. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

50 ± 10% RH). The test specimens were conditioned for at least 2 h prior to the testing.

3. Results and discussion

The service life of polyethylene is normally determined by its oxidative stability. Therefore, the main concern from plastics recyclers is that the presence of OBDs in a recycling stream will have an adverse effect on the quality and usability of the final product. Consequently, this concern was addressed in our study by determining the rate of thermo-oxidative degradation of the materials produced as a mixture of the reference LDPE and OBD materials. The kinetics of thermo-oxidative degradation were studied using both unstabilised and stabilized materials.

The degree of stabilization for the pure and stabilized LDPE was estimated by OIT measurements at 205 °C (Fig. 1) and revealed a substantial oxidative stability for the stabilized LDPE (OIT > 27 min) while the original LDPE showed no stabilization (OIT < 1 min).

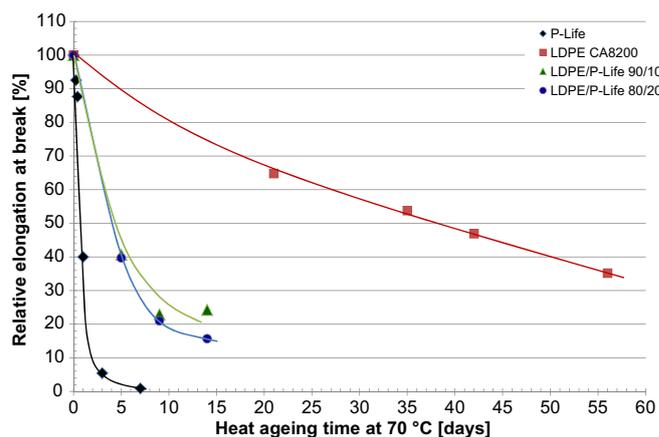


Fig. 2. Effect of heat ageing at 70 °C on unstabilised films with P-Life OBD.

An additional experiment using lower oxidation temperatures (190 °C) still generated an OIT lower than 1 min for the original LDPE, hence indicating that oxidation occurs immediately in an oxidative environment.

The rate of oxidation at 70 °C was determined by following changes in elongation at break as a function of exposure time. The results of the heat ageing tests using P-Life OBD are summarized in Figs. 2 and 3. It is seen that the unstabilised LDPE without any prodegradant starts to degrade immediately and after about 38 days at 70 °C the elongation at break is reduced to 50% of the original value. The corresponding value for the P-Life OBD is one day. When P-Life material is mixed with unstabilised LDPE, the 50% reduction of elongation at break is obtained after 3–4 days, which is most probably the result of prodegradant dilution.

A similar investigation was conducted using P-Life OBD but mixed with the stabilized LDPE. The elongation at break of the reference LDPE stabilized with 1000 ppm Irganox 1010 decreased to 50% after 224 days of heat ageing at 70 °C. Almost the same result was obtained with the mixture of stabilized LDPE and 10% P-Life material. When 20% P-Life OBD was used, the time to 50% reduction of elongation at break was reduced to 67 days. It must be emphasized

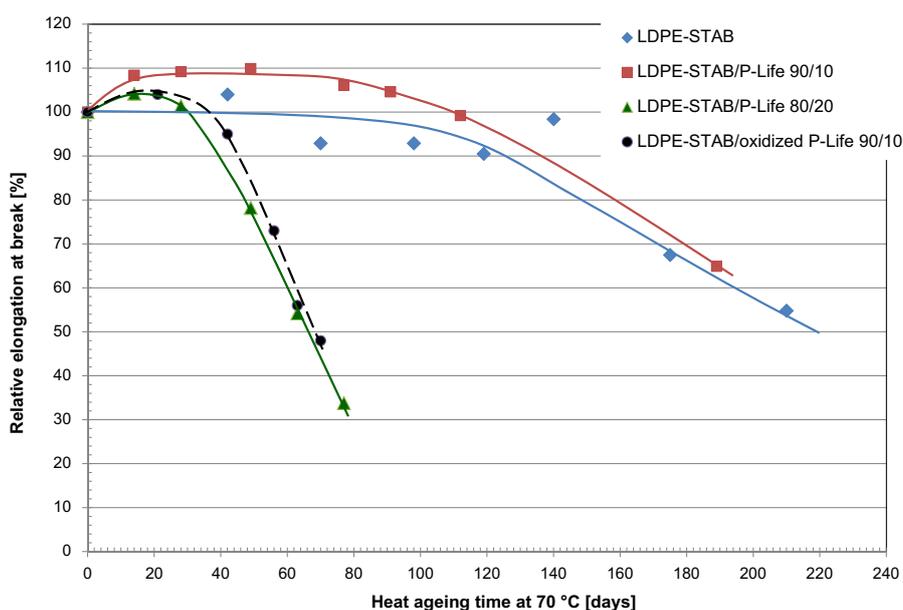


Fig. 3. Effect of heat ageing at 70 °C on stabilized films with P-Life.

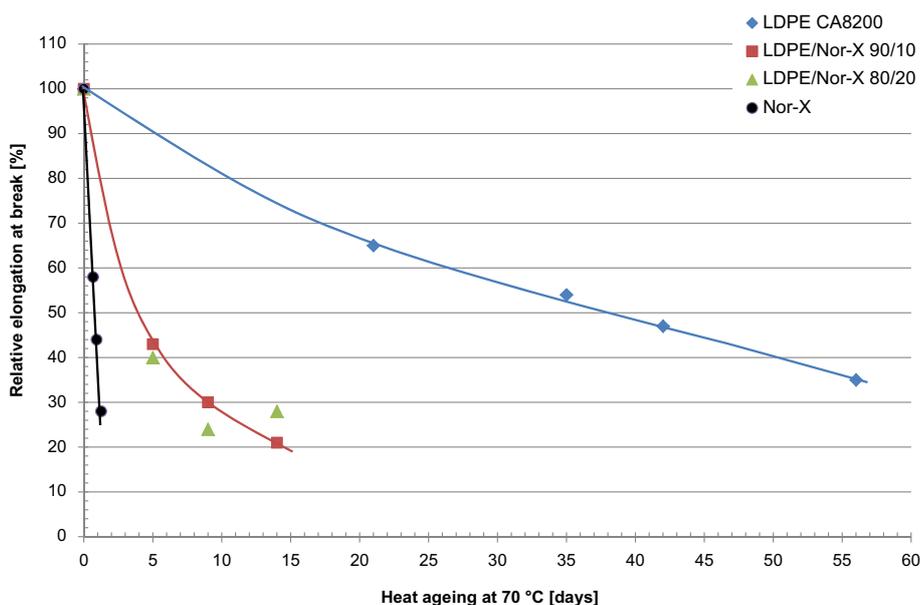


Fig. 4. Effect of heat ageing at 70 °C on unstabilised films with Nor-X OBD.

that the reduction in the lifetime is not only due to the addition of the OBD material but also to the fact that the content of stabilizer is reduced by 20% when 20% of an unstabilised material is added.

It is known that the initial oxidation rate of PE as well as the decomposition rate of hydroperoxides is increased by the increased carbonyl content of the starting material [13]. This was also the case when 10% of the pre-oxidized P-Life material was processed with the stabilized LDPE. The time to 50% reduction of elongation at break was reduced in this case to 68 days.

The results of the heat ageing tests using Nor-X OBD are summarized in Figs. 4 and 5. In the unstabilised LDPE the 50% reduction of elongation at break was obtained after 3–4 days using 10% and 20% OBD, which is almost the same result as with P-Life and is attributed to the prodegradant dilution.

Heat ageing of the mixtures of stabilized LDPE with 10% and 20% Nor-X OBD resulted in 77 and 41 days' ageing time, respectively,

until 50% reduction of elongation at break (Fig. 5). Upon mixing with 10% of the pre-oxidized Nor-X OBD, this ageing time was reduced to 15 days.

Prediction of service life of a material is important to avoid premature failure in the subsequent application. The following equation was used to calculate the service life of the materials investigated:

$$t_w = t_e \cdot \exp[E_a/R \cdot (1/T_w - 1/T_e)],$$

where t_w is the calculated lifetime, t_e is the lifetime at the elevated temperature, T_w and T_e are the “in use” and elevated temperatures, respectively, which were 23 °C and 70 °C in our case, E_a is the activation energy, which was assumed to be 80 kJ/mol (conservative assumption), R is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$).

The following service lives were calculated for the materials based on stabilized LDPE:

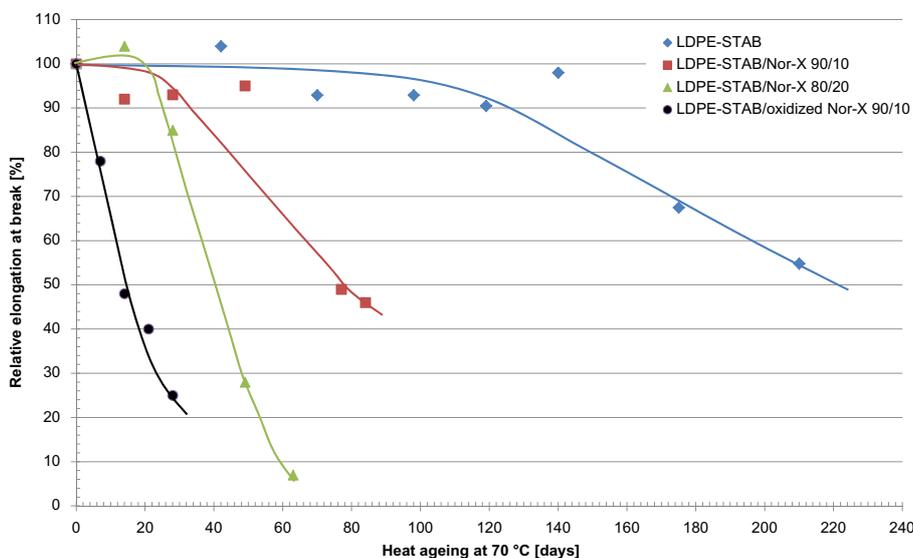


Fig. 5. Effect of heat ageing at 70 °C on stabilized films with Nor-X OBD.

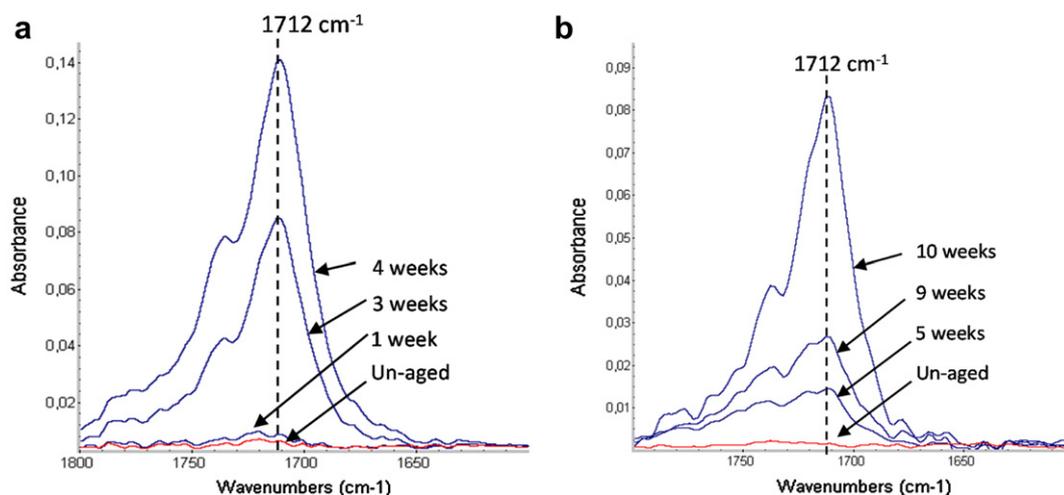


Fig. 6. FT-IR spectra in the carbonyl region for samples: “Nor-X (oxidized) 10% in stabilized LDPE” (a) and “P-Life (oxidized) 10% in stabilized LDPE” (b) after exposure at 70 °C for different periods. The intensity of the reference peak at 1472 cm⁻¹ is used as the reference.

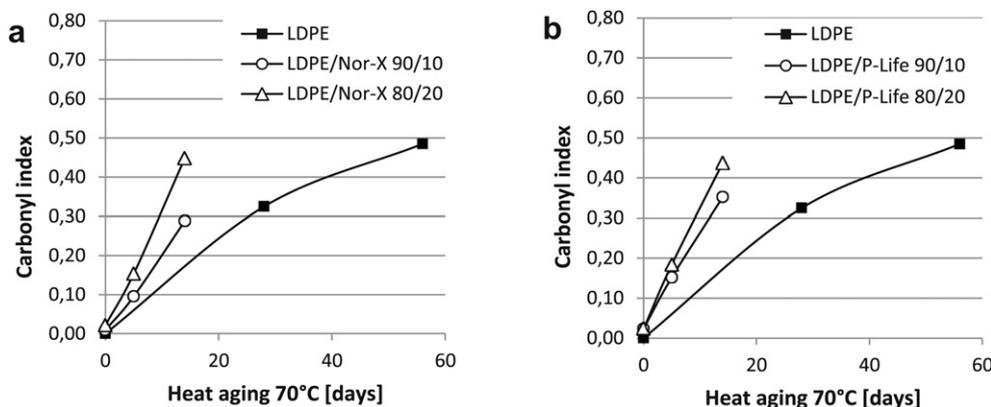


Fig. 7. Carbonyl index for mixtures (10% and 20%) of Nor-X OBD (a) and P-Life OBD (b) in unstabilised LDPE.

10% P-Life: >50 years, 20% P-Life: >15 years, 10% pre-oxidized P-Life: 16 years, 10% Nor-X: 18 years, 20% Nor-X: ≈ 10 years, 10% pre-oxidized Nor-X: 3.5 years.

The oxidation processes of the materials were also studied by FT-IR by monitoring the carbonyl index, i.e., the peak intensity ratio between the terminal ketone at 1712 cm⁻¹ and the LDPE reference

peak (at 1472 cm⁻¹, -CH₂- groups). Fig. 6 displays the increase in absorption in the carbonyl region for mixtures of pre-oxidized OBD (10%) in stabilized LDPE.

As seen in Fig. 6, the shapes of the absorbance peaks in the carbonyl region are similar for both samples, indicating a similar oxidation process despite their different prodegradant systems.

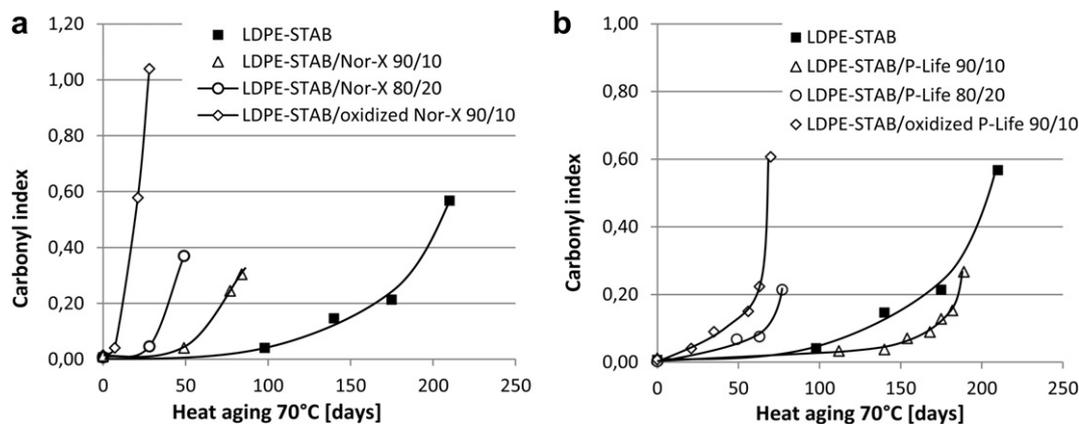


Fig. 8. Carbonyl index for oxidized and pristine mixtures of Nor-X (a) and P-Life (b) in stabilized LDPE.

The carbonyl index for aged mixtures (10% and 20%) of Nor-X and P-Life in unstabilised LDPE displays a steady increase over time (Fig. 7(a, b)). Similar behaviour is observed for the unstabilised LDPE material. It is also seen that the materials containing higher contents of OBD materials (e.g., 20%) display the fastest increase in carbonyl index.

The corresponding curves for the mixture with stabilized LDPE (Fig. 8(a, b)) show a different behaviour as the carbonyl index remains low at shorter exposure times and then increases rapidly. This behaviour could be attributed to the presence of stabilization in these systems where the stabilizer keeps the carbonyl formation low. Upon consumption of the stabilizer, the samples undergo rapid oxidation. Similar to the unstabilised samples, the time until oxidation occurs is related to the content of OBD material in the mixture. When examining the mixtures of pre-oxidized OBD materials, it is seen that these materials display a shorter oxidation period compared with the mixtures containing pristine OBD materials. This could be due to the OBD portion of these materials having been partially oxidized prior to the mixing and therefore being more susceptible to further oxidation upon consumption of the stabilizer.

4. Conclusions

Based on the results obtained in this study, it is concluded that the stabilizer content is a crucial factor for the thermo-oxidative stability of plastic mixtures containing OBD materials. It was also shown that partially oxidized OBD materials had an increased impact on the stability of the mixture compared with mixtures containing pristine OBD materials. This result was evident as it is well known that it is impossible to “heal” already badly damaged polyolefins [14]. Furthermore, a lower content of OBD materials prolongs the thermo-oxidative stability of the mixture, plausibly because of prodegradant dilution. The results show that all mixtures of OBDs in the stabilized LDPE displayed estimated service lives of at least 10 years despite having significantly higher contents of OBDs than may be experienced in real life. Even the addition of a substantial amount of oxidized materials gave an estimated lifetime of more than three years. It is therefore concluded that the incorporation of minor fractions of OBD materials in the existing

recycling streams will not present a severe effect on the stability of the recyclates, as long as the polymer mixture possesses a reasonable degree of stabilization.

Acknowledgements

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