



## Accelerated aging of polyethylene materials at high oxygen pressure characterized by photoluminescence spectroscopy and established aging characterization methods



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### ARTICLE INFO

#### Article history:

Received 22 April 2014

Received in revised form

18 June 2014

Accepted 28 June 2014

Available online 5 July 2014

#### Keywords:

Polyethylene

PE-RT

High oxygen pressure

Photoluminescence spectroscopy

Aging

### ABSTRACT

Two commercial polyethylene grades were exposed to water at elevated temperatures and enhanced oxygen pressure. To characterize their aging behavior laser-induced photoluminescence spectroscopy was applied. Additionally, aging characterization was performed by established methods such as tensile testing, infrared (IR) spectroscopy, high performance liquid chromatography (HPLC), differential scanning calorimetry (DSC) and UV–VIS spectroscopy. During the initial stages of aging, the overall concentration of phenolic antioxidants as well as oxidation onset temperatures decreased exponentially. Simultaneously, significant discoloration due to the formation of conjugated degradation products from phenolic antioxidants (e.g., quinone methides) was detected. After the consumption of antioxidants, photoluminescence started to grow continuously presumably due to the formation of photoluminescent unsaturated carbonyls. In the final stages of aging, embrittlement of the materials as characterized by the degradation of mechanical properties (i.e., loss in ductility) coincided with rising carbonyl index values as well as an increase in crystallinity due to chemocrystallization. Between integrated photoluminescence intensity and carbonyl index, a linear correlation was established. In the induction period, the photoluminescence method exhibited a significantly higher sensitivity to reflect aging induced material changes.

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### 1. Introduction

The long-term thermooxidative stability of polyolefins is usually evaluated by time-consuming oven aging tests [1–3]. These tests rely on the fact that thermooxidative degradation is thermally driven and exhibits an Arrhenius type temperature dependence [4–6]. To provide sufficient acceleration, oven aging tests are sometimes carried out at temperatures close to the melting point of the materials. This leads to changes in the polymer morphology as well as in the oxidation chemistry compared to service-relevant temperatures [7–9]. Additionally, the effectiveness of antioxidants is significantly temperature dependent, and the physical loss

of antioxidants due to evaporation, migration or extraction is enhanced at higher temperatures [10–24]. Accelerated aging tests at lower temperatures would therefore be favorable, but require an environmental factor other than temperature to provide sufficient aging acceleration. Increasing the concentration of oxygen in the aging environment is one possibility [25–27]. Extensive work in terms of aging of polyolefinic materials at high oxygen pressure has been carried out in the field of geosynthetics and geomembranes in dry conditions as well as water immersion in air and pure oxygen at oxygen (partial) pressures up to 6.3 MPa [5,18,28–32,87]. It is well established that increasing the oxygen concentration significantly accelerates the aging of polyolefinic materials and that the rate of oxidation is dependent on the oxygen partial pressure [25,27,28,31]. Restrictions of the method exist due to possible direct reactions of oxygen with antioxidants [33]. Furthermore, the oxidation characteristics may change from limited by oxygen

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diffusion to rate controlled in an environment of excess oxygen supply [29]. Also, in contrast to antioxidants, the diffusion rate of oxygen into the polymer will significantly increase, so surface regions may oxidize faster as diffusion of antioxidants from the bulk to the surface may not be fast enough [1]. Finally, previous investigations showed that the relationship between rate of oxidation and oxygen partial pressure for polyolefins is not linear in the range from 0.2 MPa to 6.3 MPa [18,28–30,32]. As a consequence, accelerated aging tests at high oxygen pressure are mostly used for ranking materials, while lifetime predictions are limited in significance [34]. More research is needed to describe the aging behavior of polymeric materials at high oxygen pressure.

To characterize the thermo-oxidative behaviour of aged polymeric materials, established methods comprise spectroscopic characterization by infrared (IR) spectroscopy, thermal analysis by differential scanning calorimetry, chemical analysis by high performance liquid chromatography (HPLC) or mechanical characterization by tensile tests [1,2]. Among these, only IR spectroscopy is non-destructive and its sensitivity is mostly confined to the intense build-up of carbonyls in the final stages of aging associated with embrittlement. While the photoluminescence behavior of polymeric materials is largely depending on the aging state [35–40], no established photoluminescence method exists for polymer aging characterization, even though various reports in the literature suggest a link between the evolution of photoluminescence in polymers and oxidative degradation [35–48]. Regarding the relevant photoluminescent species,  $\alpha,\beta$ -unsaturated carbonyls mainly of the enone and dienone type, are widely recognized as the source of photoluminescence detected in polyolefins [36,41,45–48]. These species serve as initiating centres for oxidation [42,49], and their initial concentrations are related to the thermo-oxidative and photo-oxidative stabilities of the materials [42,49].

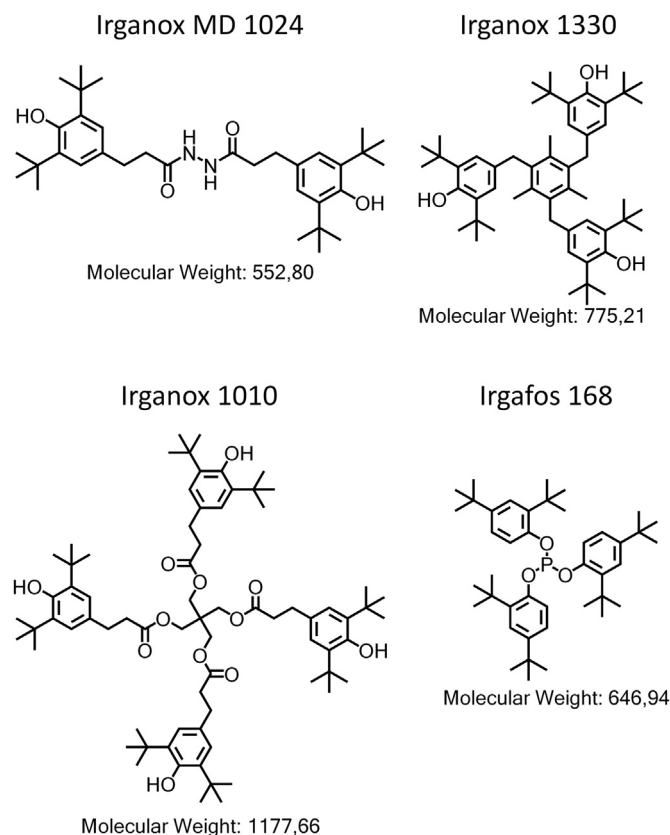
The main objective of this paper is to investigate the aging behavior of two commercial polyethylene grades for liners of hot water storage applications at enhanced oxygen pressure. Due to the fact that the maximum service temperature is up to 95 °C, aging tests were carried out in water at 95 °C. Aging characterization was performed by a photoluminescence technique using laser-induced photoluminescence spectroscopy. Complementarily to photoluminescence spectroscopy, the aging behavior was investigated by established characterization methods such as infrared (IR) spectroscopy, high performance liquid chromatography (HPLC), differential scanning calorimetry (DSC) and tensile testing.

## 2. Materials and methods

### 2.1. Materials

Two commercial PE-RT (RT: raised temperature resistance [50,51]) grades by two different manufacturers designated PE1 and PE2 (see Table 1) suitable for hot water applications were chosen for the investigations. PE-RT grades are PE-materials containing short chain branches introduced by copolymerizing ethylene with  $\alpha$ -olefins such as hexene or octene, which gives superior mechanical long-term behavior compared to conventional PE100

grades at elevated temperatures (above 70 °C). The degrees of crystallinity as detected by differential scanning calorimetry are around 48% for PE1 and 52% for PE2. The stabilization packages of the unaged materials as analyzed by HPLC are comprised of the sterically hindered phenolic antioxidants Irganox MD 1024, Irganox 1330 and Irganox 1010 as well as the phosphite Irgafos 168 (see Fig. 1). Sterically hindered phenolic antioxidants serve as processing and long-term heat stabilizers in polyolefins, while phosphites are used for process stabilization only [2]. Irganox MD 1024 serves as a metal deactivator for applications in contact with copper [2], though its sterically hindered phenolic groups are also able to provide stabilization against thermooxidation. The amounts of stabilizers are slightly differing for the two commercial PE grades (Table 1). Interestingly, the concentration of Irganox 1010 of 0.10 mass % in PE2 is 5 times higher than in PE1. Apparently, Irganox 1010 only serves as a processing stabilizer in PE1, while its higher concentration in PE2 presumably indicates its intended function for long-term heat and processing stabilization. As PE-RT type materials are primarily used in applications with water contact, this clearly is interesting, since Irganox 1010 contains ester moieties making it prone to hydrolysis [15]. The products of hydrolysis are of a lower molecular mass and of a higher polarity than Irganox 1010 and are therefore readily leached out by a water environment [15]. Hence, in applications with water contact the stabilizing efficiency of Irganox 1010 is worse than for Irganox 1330 [15,52], which is also used in the stabilizing systems of both PE1 and PE2. Irganox 1330 does not contain ester groups and is therefore suitable to act as a long-term heat stabilizer in applications with water contact [15]. Since the solubility of phenolic antioxidants in polyolefins is limited [53], the total concentration in phenolic stabilizers is below 0.5 mass %.



**Table 1**  
Stabilization packages of the materials PE1 and PE2.

PE grade	[mass %]			
	Irganox MD 1024	Irganox 1330	Irganox 1010	Irgafos 168
PE1	0.10	0.22	0.02	0.09
PE2	0.13	0.17	0.10	0.01

**Fig. 1.** Structural formulas of antioxidants Irganox MD 1024, Irganox 1330, Irganox 1010 and Irgafos 168 used in stabilizer packages of PE1 and PE2.

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