

## Polyethylene loss of ductility during oxidation: Effect of initial molar mass distribution



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### ABSTRACT

This paper reports a study of thermal oxidation induced embrittlement in several polyethylene grades differing mainly by the broadness of the molar mass distribution (ranging for lower than 3 to more than 30). Thermal oxidation was monitored at macromolecular scale (Gel Permeation Chromatography, Differential Scanning Calorimetry) and macroscopic scale (tensile tests). As expected, the samples undergo predominant chain scission and plastic deformation is suppressed below a critical molar mass value ( $M'_C$ ). Even though this latter was previously reported to be independent of the initial weight average molar mass, it is shown here that it depends on initial polydispersity index. Samples were also shown to undergo chemicrystallization, i.e. that segments released by chain scissions migrate into the crystalline phase with a yield increasing with initial polydispersity index. Finally, the main novelty of this work is to evidence that the previously proposed end-of-life criteria at macromolecular level linked to loss of ductility (critical molar mass, crystallization yield) depend on the initial polydispersity index.

### 1. Introduction

Polyethylene (PE) mechanical, thermal and rheological properties allow it to be used in a large range of application areas (packaging, automotive ...). Organometallic catalysts were developed to produce PE with well-defined structures (average molecular mass, crystallization degree, etc ...) [1,2]. Oxidation mechanisms [3], kinetics [4] and the subsequent loss of ductility, often so called embrittlement (even if this term is rather linked to the loss of toughness instead of ultimate elongation) [5] are well documented in literature together with the detrimental role of metallic polymerization catalysts on oxidative stability [6].

Polymers with excellent mechanical properties are needed to overcome environmental stresses. In order to reach higher mechanical properties for specific applications, PE with high molecular weight had been commercialized [7,8]. The main drawback of high molecular weight PE's is their high melt viscosity which limits their processability. Some novel polymerization technologies have been developed to produce bimodal grades of polyethylene, i.e. made of two major chain length populations leading thus to a higher polydispersity index. The presence of high molecular weight chain induces improved mechanical properties and low molecular weight fraction makes process easier.

To the best of our knowledge, there is no information in literature about the degradation of bimodal PE's, about the effect of polydispersity

on the oxidation induced loss of ductility and about the possible consequences of the presence of the two chain length populations on the end-of-life criteria. In these previous studies [5,9], it has been proposed that plastic deformation is suppressed when the weight average molar mass becomes lower a critical value, the critical molar mass ( $M'_C$ ) whatever the initial molar mass value ( $M_{W0}$ ). For the PE family, it has been witnessed that the  $M'_C$  value associated to the ductile–brittle transition is spread over the 40–100 kg mol<sup>-1</sup> molar mass interval. However, in this approach, the influence of initial value for the polydispersity index (PDI<sub>0</sub>) and/or the initial molar mass value  $M_{W0}$  on  $M'_C$  has not been taken into account.

The aim of this paper is hence to study the homogeneous thermal oxidation of lowly and highly polydispersed PE's and to focus on the macromolecular and mechanical changes. For that purpose, five PE grades were selected based on supplier data sheet, with a MFI value acceptable for extrusion and varying polydispersity index (assuming that high dispersity leads to high weight average molecular weight).

### 2. Materials and methods

#### 2.1. Materials

The samples are listed in Table 1 with their designation, initial macromolecular and mechanical properties (measured as detailed in

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**Table 1**  
Sample designation and initials macromolecular and mechanical properties experimentally determined.

Sample Name	Nature of catalyst <sup>a</sup>	PDI <sub>0</sub>	M <sub>n,0</sub> (GPC) (kg mol <sup>-1</sup> )	M <sub>w,0</sub> (GPC) (kg mol <sup>-1</sup> )	M <sub>w,0</sub> (rheo.) (kg mol <sup>-1</sup> )	ε <sub>R0</sub> (%)	χ <sub>C0</sub> (%)	Vinyl index (A <sub>910</sub> /A <sub>2017</sub> )	Branching index (A <sub>1360</sub> /A <sub>1450</sub> )
PE <sub>2,9</sub>	m	2.9	27.0	81.0	75.6	909 ± 182	53.0	0.08	3.20
PE <sub>3,4</sub>	m	3.4	39.0	133.0	130.4	869 ± 25	65.7	0.07	4.91
PE <sub>5,1</sub>	m	5.1	29.5	149.0	158.0	682.8 ± 13	43.5	0.05	2.13
PE <sub>14,5</sub>	ZN	14.5	16.0	283.0	249.1	488.2 ± 10	56.6	0.23	3.99
PE <sub>33,0</sub>	Phillipps	33.0	14.0	463.5	321.5	526.0 ± 41	47.8	1.93	2.69

<sup>a</sup> m = metallocene catalyst; ZN = Ziegler-Natta catalyst; Phillipps = Phillipps catalyst.

the following). The five PE grades investigated here differ by nature of polymerization catalysts, initials number and weight average molar mass (M<sub>n,0</sub>, M<sub>w,0</sub>), initial polydispersity index (PDI<sub>0</sub>) and crystallinity ratio (Table 1). MWD measurements were performed by GPC during the oxidation process. Some rheological experiments were also performed to measure the Newtonian viscosity in molten state (200 °C) to confirm M<sub>w,0</sub> values. As it is shown in Table 1, a good correlation was witnessed between the M<sub>w,0</sub> values obtained by GPC and ones obtained by the rheological way. Vinyl index were measured by FTIR from the 910 cm<sup>-1</sup> absorbance. The presence of short chain branching was estimated from the ratio of absorbances at 1370 to 1450 cm<sup>-1</sup> (NB: It was chosen to consider the whole area of the absorbance in a first approach since there are actually several maxima for the absorbance centered at 1370 cm<sup>-1</sup> [10]).

Samples were studied as 15 μm thick films in order to avoid the complications linked to the so called Diffusion Limited Oxidation [11,12]. Films were obtained by blown-film extrusion with a single screw extruder (25 mm diameter, 20D) at 30 rpm, under a temperature profile between 200 and 240 °C, a 50 mm diameter blown die, 0.8 die gap and an air cooling device.

In order to focus only on the influence of microstructure on PE thermal oxidation and not on stabilizers initially introduced, films were purified by refluxing about 300 mg of PE films in a dichloromethane (VWR reference 23354.326) solution (250 mL) during 24 h. The total extraction of stabilizer was checked from the disappearance of Oxygen Induction Time value measured at 200 °C.

## 2.2. Exposure conditions

Films were aged at 100 °C in ventilated ovens (SCS), this temperature being chosen as a compromise between a high oxidation rate and an oxidation in a solid state i.e. below the onset of the melting peak.

## 2.3. Characterization

### 2.3.1. Gel permeation chromatography (GPC)

GPC analyses were performed using an Agilent HT 220 system equipped with a refractive index (RI) detector in 1,2,4-trichlorobenzene (TCB) stabilized with 0.0125% BHT at 135 °C as mobile phase with two PLgel Olexis columns (Agilent Technology) as stationary phase. PE films were dissolved in TCB (about 3 g L<sup>-1</sup>). The elution method consisted in an isocratic step at 1 mL min<sup>-1</sup> flow of TCB for 30 min at 135 °C. The calibration was done with polystyrene (PS) standards. Molar masses were then estimated using the universal calibration with  $K = 12,1 \times 10^5 \text{ dg L}^{-1}$  and  $\alpha = 0,707$  for PS, and  $K = 40,6 \times 10^5$  and  $\alpha = 0,725$  for PE [13].

GPC chromatograms shown in Fig. 1 for the polymers before exposure allow for the number and weight average molecular weight (M<sub>n</sub> and M<sub>w</sub>) and polydispersity index (PDI) assessment. Samples PDI range from 2.7 to 33.0. As expected, the narrower distributions (or lowest PDI<sub>0</sub>) correspond to materials made from metallocene catalysts [14].

### 2.3.2. Differential scanning calorimetry (DSC)

Analyses were performed using a Q1000 (TA Instruments)

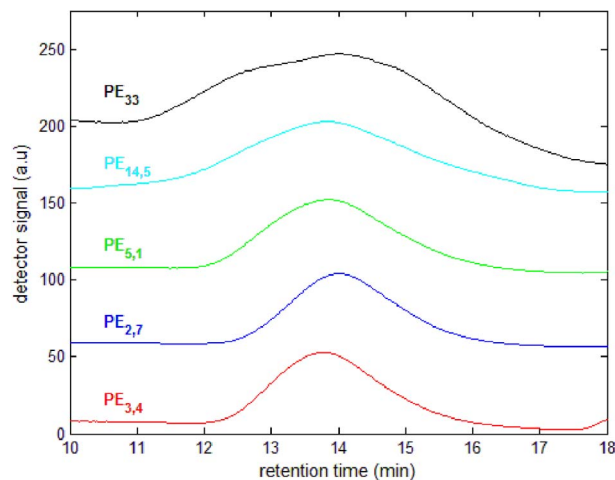


Fig. 1. GPC chromatograms of initial PE samples.

calibrated with indium standard. About 5 mg samples sealed in standard aluminum pans were heated from -50 to 200 °C at a 10 °C min<sup>-1</sup> ramp under N<sub>2</sub> flow (50 mL min<sup>-1</sup>). The percent crystallinity was classical assessed from:

$$x_c = \frac{\Delta H_m}{\Delta H_{m100}} \quad (1)$$

where  $\Delta H_m$  and  $\Delta H_{m100}$  are respectively the melting enthalpy of the investigated sample and the melting enthalpy for an ideally 100% crystalline PE sample, which is equal to 288 J g<sup>-1</sup> [15].

### 2.3.3. Tensile tests

Tensile tests were carried out at room temperature on Instron<sup>®</sup> 1301 machine equipped with a 1 kN cell load; the cross-head speed was 1 mm min<sup>-1</sup> on samples with dimensions according to standard ISO527-2 (1BB). As a result, nominal strain rate was 8.3 10<sup>-3</sup> s<sup>-1</sup>. Only nominal strain at break values (ε<sub>R</sub>) was reported with varying ageing times since it was shown that strain at break is the most relevant parameter to monitor the residual ductility as a function of ageing duration for these highly ductile polymers [16]. At least 5 measurements were done for each sample.

## 3. Results

### 3.1. Mechanical properties changes

Fig. 2 displays the changes of strain at break of sample with exposure time. All samples exhibit a similar behavior: first an induction period followed by a sudden decrease of strain at break. The time to ultimate properties loss can be defined as the onset of strain at break decrease. Its duration is undoubtedly related to the content in residual double bonds, short chain branching, in link with the nature of metallic catalysts [6] and unstable groups generated from the processing stage [17]. However, this will not be discussed here in the sake of conciseness

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