# ARTICLE IN PRESS

# Analytical pyrolysis in the determination of the aging of polyethylene

Clemens Schwarzinger [a,*], Ingrid Hintersteiner [b], Bettina Schwarzinger [a],
Wolfgang Buchberger [b], Bernhard Moser [c]

[a] Institute for Chemical Technology of Organic Materials, Johannes Kepler University, Linz, Austria
[b] Institute for Analytical Chemistry, Johannes Kepler University, Linz, Austria
[c] Tiger Coatings GmbH, Wels, Austria

## ARTICLE INFO

## ABSTRACT

Polyethylene is nowadays used in many applications with lifetimes of several decades. To predict the lifetime artificial aging is widely used, but only little is known of the chemical change of the polymer chains itself. We have used different types of unstabilized polyethylene and aged them in water at elevated temperature and a high pressure of oxygen to accelerate the natural aging processes and analyzed the materials by Py-GC–MS, infrared spectroscopy and size exclusion chromatography. With pyrolysis 2-oxoalkanes and 2-oxoalkenes as well as carboxylic acids were identified as the degradation products. Thermally assisted hydrolysis and methylation was successfully applied to assess the degree of oxidation, especially targeting the more polar compounds. With this technique alkane dioic acids have been identified as valuable marker compounds for the oxidative degradation of polyethylene. The mechanism of formation of fatty acids in thermally assisted hydrolysis and methylation has been elucidated using two different alkanones. With size exclusion chromatography it could be shown that the oxidation occurs randomly along the polymer chain and that the final degradation products are in the range of a few thousand $g \, mol^{-1}$, irrespective of the original molar mass.

## 1. Introduction

Polyethylene (PE) is the most commonly used plastic, covering wide areas of application. Particularly for PE products with a shelf life in the order of several decades, such as pipes, degradation caused by different environmental conditions e.g., heat, humidity or UV irradiation can severely impact optical and physical properties.

In order to predict product lifetimes and to understand degradation processes of polymers, accelerated aging tests are commonly employed [1–7]. Thereby the polymer material is exposed to harsh environmental conditions such as elevated temperatures, intense UV irradiation, mechanical load or acidic, alkaline or corrosive surroundings [3]. Particularly a combination of high temperatures and oxygen atmosphere is reported in the literature to be the most commonly used acceleration condition [3].

Different techniques are available to monitor degradation processes, whereby physical properties, chemical changes but also a degradation of the polymer stabilizers can be investigated [4–11]. These include methods such as tensile testing, infrared (IR) spectroscopy, differential scanning calorimetry (DSC) or photoluminescence spectroscopy [7]. Size exclusion chromatography (SEC) and pyrolysis gas chromatography mass spectrometry (Py-GC–MS) are also reported as suitable methods for aging characterization of polymers [12]. Even though Py-GC–MS has been used in the analysis of polymers for decades [12,13], there is only a limited number of studies employing Py-GC–MS in life-time predictions and aging experiments of polyolefins [12–15].

Pyrolysis of virgin PE and PP usually results in a series of triplets of alkanes, α-alkenes and α,ω-alkadienes [16]. According to the literature, detecting changes in the polymer backbone is difficult except for severely degraded materials. Aging-induced oxidation, chain scission and crosslinking account only for relatively small changes in comparison to the intact polymer backbone. As a matter of fact, distinguishing between differences due to aging or to material inhomogeneity is problematic [12]. However, instead of backbone analysis also volatile compounds such as chain scission products or additives can be analyzed to determine the aging status [12]. FTIR analysis after natural exposure of HDPE revealed significant photo-oxidation resulting in changes in the carbonyl index and a decrease of the molecular weight distribution. With Py-GC–MS, only the above mentioned triplets, ranging from C14 to C29, and no additional oxidative species were detected, concluding that the oxidative groups are still connected to the polymer backbone [12]. Other aging studies of PE revealed that the relative intensities

of the respective triplets are dependent on the aging level of the polymer, showing higher intensities at lower carbon numbers for an advanced stage of aging [13].

Whereas previous studies focused on the analysis of volatiles, the present research investigates changes of the polymer backbone of two PE samples with different molar mass under harsh degradation conditions in order to extend the knowledge about aging processes of polyolefins. The current work presents the characterization of PE samples after several periods of accelerated aging in the presence of oxygen (60 bar) and water at an elevated temperature (125 °C) combining Py-GC–MS, THM-GC–MS, FTIR and SEC measurements. Several marker compounds for the tracking of the aging process could be identified, such as 2-oxo hydrocarbons in conventional pyrolysis and 2-oxo fatty acids or diacids in thermally assisted hydrolysis and methylation.

## 2. Experimental

### 2.1. Samples

Polyethylene with a molar mass of $M_w$ 64,000 g mol$^{-1}$ (sample 1) was synthesized with a Ziegler–Natta catalyst as described elsewhere [17]. Polyethylene with a molar mass of $M_w$ 460,000 g mol$^{-1}$ (sample 2) was obtained from Borealis, both polymers were not stabilized. The polymer powders were pressed in a mold at a temperature of 160 °C with 100 bar for 20 min to yield PE rods with a dimension of 10 × 8 mm and a length of 40–50 mm. 2-Dodecanone, 5-dodecanone and tetramethylammonium hydroxide were purchased from Sigma–Aldrich.

### 2.2. Artificial aging

The PE samples were placed in an autoclave filled with deionized water and pressurized with oxygen to 50 bar at room temperature (60 bar at 125 °C). The autoclave was then placed in an oil bath at 125 °C for up to 3 weeks. After reducing the pressure to ambient pressure the samples were removed from the autoclave, washed with water and dried in a vacuum oven at 40 °C.

### 2.3. Pyrolysis and GC/MS

Pyrolysis experiments were carried out with a CDS Pyroprobe 5250 heated filament pyrolyser (CDS Analytical Inc.), a Trace GC Ultra (Thermo Electron Corp.) equipped with a capillary column Restek RTX35 (30 m × 0.32 mm × 0.25 μm), and a quadrupole mass spectrometer MD 800 (Fisons Instruments). Pyrolysis was performed at 700 °C for 10 s with a heating rate of 20 °C ms$^{-1}$, the sample weight was between 100 and 300 μg. The pyrolyser interface was set at 300 °C and the injector at 280 °C. The GC column temperature conditions were as follows: initial temperature 50 °C, hold for 2 min, increase at 20 °C min$^{-1}$ to 300 °C, and hold this temperature for 10 min. Helium gas flow was set at 1.5 mL min$^{-1}$ and the slpit flow was 45 mL min$^{-1}$. Mass spectra were recorded under electron ionization at 70 eV electron energy in the range from m/z 15 to 400.

In thermally assisted hydrolysis and methylation (THM) experiments 3 μL of a saturated aqueous tetramethylammonium hydroxide (TMAH) solution were added to the sample and the pyrolysis was performed at 550 °C for 10 s.

### 2.4. SEC

For SEC measurements a SEC IR5 instrument from Polymer Char was employed. Separations were performed on 3 Agilent PLGel Olexis columns (300 × 7.5 mm) using 1,2,4-trichlorobenzene as solvent. Operating conditions of 150 °C for the columns oven, 160 °C

for the dissolution oven and a flow rate of 1 mL min$^{-1}$ were applied. Samples were dissolved at a concentration of 1 mg mL$^{-1}$, heptane was added as flow marker and 200 μL were injected. Mass calibration was done using polystyrene standards from 2430 to 2,000,000 g mol$^{-1}$.

### 2.5. FTIR

FTIR spectra were recorded on a Thermo Scientific iN10 MX microscope with an additional iZ10 unit capable of performing ATR (attenuated total reflectance) experiments. Spectra were recorded in the range of 400–4000 cm$^{-1}$ with a resolution of 4 cm$^{-1}$.

## 3. Results and discussion

In order to monitor the effects of oxygen diffusion into the polymer samples, the rods were cut in the middle and all analyses were performed on these newly formed positions. A first interesting result was that in all samples the formation of a darker colored core was visible, whereas the outer part of the polymer, which has been in direct contact with water and/or oxygen, remained white but showed surface cracks (Fig. 1). In some cases a thin layer of greenish material was found on the surface of the rods, which could be identified by FTIR as inorganic deposits from the dissolution of the steel autoclave.

### 3.1. FTIR

As a first nondestructive test ATR-FTIR spectra of the aged PE samples were recorded. Fig. 2a shows the spectra of sample 1 before aging, and after 9 days. Whereas the inner part is very similar to the original sample, with just one additional signal at 1700 cm$^{-1}$ indicating the formation of carbonyl moieties, the outer part shows not only a much stronger carbonyl band, but also signals below 1500 cm$^{-1}$ start to evolve. When the section between 2000 and 600 cm$^{-1}$ is compared to library spectra (Fig. 2b), a good agreement with succinic acid can be found and all signals can be explained by literature data [18].

### 3.2. Pyrolysis

Analytical pyrolysis of PE yields a series of triplets consisting of an alkane, α-alkene, and α,ω-alkadiene which are all separated by one CH$_2$-group (Fig. 3a). At a first glance the pyrograms of the aged samples look very similar, but upon close inspection several smaller signals can be found in between the triplets (Fig. 3b and c). These new peaks all show an intense m/z = 58 signal in their mass spectra, indicative of methyl ketones. When the pyrograms are displayed in selected ion mode with m/z = 58 (only the intensity of the 58 ion is displayed in the chromatogram) three new series of peaks can



**Fig. 1.** Picture of the new PE sample (top) and the aged sample (bottom left and right).