



The effect of thermal and thermo-oxidative degradation conditions on rheological, chemical and thermal properties of HDPE



A.A. Cuadri^{*}, J.E. Martín-Alfonso

Departamento de Ingeniería Química, Centro de Investigación en Tecnología de Productos y Procesos Químicos (Pro²TecS), Campus de 'El Carmen', Universidad de Huelva, 21071, Huelva, Spain

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ABSTRACT

This research evaluates the effect that thermal and thermo-oxidative degradation conditions exert on the rheological, chemical and thermal properties of high-density polyethylene (HDPE). To that end, dynamic oscillatory rheology, solubility tests in xylene, TGA, DSC and FTIR were conducted on HDPE samples subjected to different degradation conditions: atmosphere (air or nitrogen), temperature (150, 175, 200, 225 or 250 °C) and time (10, 30 or 60 min). Thus, under nitrogen atmosphere, chain scission mechanism prevails over the formation of long chain branching/crosslinking phenomena, which is reflected in a decrease in complex viscosity ($|\eta^*|$) and an increase in crystallinity (χ_c). Interestingly, under air atmosphere, two rheological responses were observed: a) a well-developed rubbery region, at degradation temperatures of 225 and 250 °C and, b) a so-called second “plateau” in G' and G'' , for lower degradation temperatures. Solubility tests in xylene point out that the rubbery region is consequence of both branching phenomena and the presence of crosslinking; however, the second “plateau” should be solely ascribed to the increase in the branching mechanism. In this case, the decrease in χ_c is consequence of both increase in branching and formation of degradation products (accordingly supported by FTIR results). Finally, TGA results reveal that thermal and thermo-oxidative degradation shift the characteristic temperatures ($T_{5\%}$ and T_{max}) to lower values, compared to virgin HDPE.

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1. Introduction

Polyolefins are a class of polymers synthesized by addition reactions of unsaturated monomers (alkyl-ethylenes), of which high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE) and low-density polyethylene (LDPE) are good representatives. They differ structurally in the number and length of branches, whose presence tends to reduce the amount and size of crystals, as well as their melting and crystallization temperatures [1]. These commodity polymers are the most produced and consumed synthetic polymer worldwide with many applications in packaging films, healthcare, construction, automobile and agriculture [1,2].

Before being employed or during their reprocessing, polyolefins need undergo melt processing at different conditions, such as elevated temperature, the presence of oxygen, and/or mechanical stresses, giving rise to changes in chemical structure of

macromolecule which can considerably influence their liquid and solid-state properties [3]. Therefore, both thermal (i.e., polymer degradation only due to the effect of temperature, which was carried out here under nitrogen atmosphere) and thermo-oxidative degradation (i.e., degradation arises as a result of elevated temperatures and the presence of oxygen) [4] of these materials in melt state is vital to understand the structural properties relationship and their processability [2], even more when polyolefins are known to be sensitive to thermal oxidation due to the impurities generated during their manufacture at high temperatures [5]. Researchers suggested two competing mechanisms during thermal/thermo-oxidative degradation or reprocessing of HDPE, those are chain scission and side-chain branching [6–8]. Thus, starting from the scission of a macromolecule due to shear stress or temperature, free radicals may be formed. These free radicals may either recombine, react with oxygen or form secondary radicals by abstraction of a hydrogen atom, leading to the formation of long chain branching and different oxidation products (e.g., carboxylic acids, ketones, aldehydes or lactones) [4,5,9–11]. In addition to this, some suggested also presence of crosslinking [12,13].

^{*} Corresponding author.

E-mail address: antonio.cuadri@diq.uhu.es (A.A. Cuadri).

In order to detect and quantify the changes in chemical structure of polymer macromolecules, various analytical techniques, including differential scanning calorimetry [14,15], thermogravimetric analysis [16,17], scanning electron microscopy [18,19], Fourier transform infrared spectroscopy [11,20], gel permeation chromatography [16,21], nuclear magnetic resonance spectroscopy [20,22] and rheology [11,22–27], have been employed. Among them, dynamic oscillatory rheology of melted polymers, especially under low frequency, was found to be one of the most efficient techniques for detecting microstructural transformations due to chain scission and long chain branching/crosslinking, because different polymer chains could behave diagnostic viscoelastic response in long time regime due to the difference of relaxation rate [3,22,24,28]. In addition to that, dynamic oscillatory rheological measurements are conducted in the linear viscoelasticity (LVE) region, so its strain is too small to damage the structure of a polymer, in contrast with the large strains applied for the steady shear measurements [3,25].

Therefore, the objective of the present contribution is to investigate the effect that thermal and thermo-oxidative degradation conditions, which are the result of combining different atmosphere and degradation time/temperature, exert on the dynamic oscillatory rheology, chemical and thermal properties of HDPE. Thus, depending of the atmosphere used (nitrogen or air), dynamic oscillatory rheology and xylene-insoluble tests allow us to deduce which mechanism (chain scission, long chain branching or crosslinking) prevails over the other. Among other conditions, degradation temperature leads to degraded samples with significant changes in their rheological response. Finally, the chemical and thermal changes due to thermal and thermo-oxidative degradation was evaluated by thermogravimetric analysis, differential scanning calorimetry and Fourier transform infrared spectroscopy.

2. Material and methods

2.1. Material and sample preparation

The material used was a high-density polyethylene (HDPE), kindly supplied by Eslava Plásticos, S.A., with the following properties: $\rho_{23^\circ\text{C}} = 0.957 \text{ g cm}^{-3}$, MFI (190°C/2.16 kg) = 0.6, $M_w = 1.46 \cdot 10^5$, $M_n = 2.63 \cdot 10^4$ and $M_w/M_n = 5.57$.

HDPE disks about 1.5 mm in thickness and 25 mm in diameter were prepared by compression-moulding in a hot press. To that end, firstly, as-received HDPE pellets were subjected to 50 bar of pressure for 1 min, at 140 °C. Subsequently, the disks were allowed to cool down to room temperature. These conditions (50 bar, 140 °C, 1 min) were selected to diminish to the maximum a possible polymer degradation during the compression-moulding, since the objective of this stage was only to obtain disk-shaped specimens.

2.2. Thermal/thermo-oxidative degradation and characterization

Rheological measurements were carried out in a controlled-stress rheometer Physica MCR-301 (Anton Paar, Austria), using rough plate-and-plate geometry (25 mm diameter; 1 mm gap), and equipped with a CTD450 convection oven, which provides a gas flow of 1 L/min. Before starting with the rheological measurements, the thermal or thermo-oxidative degradation of HDPE were conducted on the rheometer itself, by using nitrogen or air, respectively, as gas. The procedure can be summarized as follows: a) a HDPE disk was placed on the lower plate and the convection oven was closed; b) the degradation conditions were selected, i.e., degradation temperature (150, 175, 200, 225 or 250 °C), degradation time (0, 10, 30 or 60 min) and atmosphere (nitrogen or air); c) the gap was adjusted to 1 mm and the remaining melted HDPE was

trimmed with the help of a metallic spatula; d) with the convection oven closed, a stress sweep test, at 1 rad/s, was performed to determine the LVE region; e) A fresh HDPE disk was again subjected to the same degradation conditions (i.e., the steps a), b) and c) were repeated) and an isothermal frequency sweep test, from 100 to 0.125 rad/s, under a stress value within the LVE region, was performed. Therefore, these tests were performed at the same conditions (temperature/atmosphere) as the degradation stage.

It is noteworthy that a waiting time of 30 s was used before performing the frequency ramp. This is because if, the degradation time is 0 min (i.e., when it is desired to measure the virgin HDPE sample), the samples need some time to melt.

In addition to rheological characterization, solubility tests in xylene, thermogravimetric (TGA) analysis, differential scanning calorimetric (DSC) tests and a chemical characterization by Fourier transform infrared spectroscopy (FTIR) were carried out on as-received HDPE and its corresponding degraded samples. These samples were directly taken from the rheometer when the degradation step is finished (i.e., after completing the step b).

TGA analysis were conducted in a TA Q-50 (TA Instrument, USA). Temperature sweeps (10°C/min; between 30 and 600 °C) were carried out on 5–10 mg samples placed on a Pt pan and under nitrogen gas flow of 100 mL/min. The temperature corresponding to a 5 wt % weight loss ($T_{5\%}$) and the temperature at which decomposition rate is maximum (T_{max}) were obtained from TGA curves.

DSC tests were performed with a TA Q-100 (TA Instruments, USA) using 5–10 mg samples sealed in hermetic aluminium pans. All tests were performed with a nitrogen gas flow rate of 50 mL/min. The samples were subjected to two heating steps, from 0 to 180 °C, and an intermediate cooling step, all them at the same rate of 10°C/min. The objective of the first heating step was to eliminate the heat history of the sample. Crystallization temperatures (T_c) and heat of the crystallization (ΔH_c), as well as melting temperatures (T_m) and heat of melting (ΔH_m), were recorded from the cooling step and the second heating sequence, respectively. Degree of crystallinity (χ_c) in each sample was calculated as follows:

$$\chi_c(\%) = \frac{\Delta H_m}{\Delta H_m^{100\%}} \cdot 100 \quad (1)$$

where ΔH_m is the integrated melting enthalpy from the second heating endothermic curve and $\Delta H_m^{100\%}$ is the theoretical melting enthalpy for HDPE with 100% of crystallinity. According to the literature [11], a theoretical enthalpy of 290 J/g was used for the melting enthalpy of HDPE with 100% of crystallinity.

FTIR spectra were recorded in a Jasco FT/IR 4200 spectrometer (Jasco Analytical Instrument, Japan), in a wavenumber range of 400–4000 cm^{-1} , at 4 cm^{-1} resolution in the absorbance mode.

Solubility tests were performed by extraction in Soxhlet assembly. A portion of 1.5 g of a specimen material was introduced into the cellulose Soxhlet extraction thimble and extracted by p-xylene for 24 h. Mentioned technique provides information on the crosslinked portion in the degraded HDPE samples.

In order to ensure accurate results, at least three replicates were conducted for every sample/test. Figures present the average values and the data were presented as mean \pm standard deviation (SD).

3. Results and discussion

3.1. Rheological properties

It is well known that the dynamic oscillatory measurements are very sensitive to the topological structure changes of melted polymers as a consequence of alterations in its molecular weight,

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