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Evaluation of Philips and Ziegler–Natta high-density polyethylene degradation during processing in an internal mixer using the chain scission and branching distribution function analysis

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Abstract

The oxidative and thermo-mechanical degradation of HDPE was studied during processing in an internal mixer under two conditions: totally and partially filled chambers, which provides lower and higher concentrations of oxygen, respectively. Two types of HDPEs, Phillips and Ziegler–Natta, having different levels of terminal vinyl unsaturations were analyzed. Materials were processed at 160, 200, and 240 °C. Standard rheograms using a partially filled chamber showed that the torque is much more unstable in comparison to a totally filled chamber which provides an environment depleted of oxygen. Carbonyl and transvinylene group concentrations increased, whereas vinyl group concentration decreased with temperature and oxygen availability. Average number of chain scission and branching (n_s) was calculated from MWD curves and its plotting versus functional groups' concentration showed that chain scission or branching takes place depending upon oxygen content and vinyl groups' consumption. Chain scission and branching distribution function (CSBDF) values showed that longer chains undergo chain scission easier than shorter ones due to their higher probability of entanglements. This yields macroradicals that react with the vinyl terminal unsaturations of other chains producing chain branching. Shorter chains are more mobile, not suffering scission but instead are used for grafting the macroradicals, increasing the molecular weight. Increase in the oxygen concentration, temperature, and vinyl end groups' content facilitates the thermo-mechanical degradation reducing the amount of both, longer chains via chain scission and shorter chains via chain branching, narrowing the polydispersity. Phillips HDPE produces a higher level of chain branching than the Ziegler–Natta's type at the same processing condition.

Keywords: Chain scission; Chain branching; HDPE; Internal mixer; Thermo-oxidative degradation; Average number of chain scission and branching CSBDF

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1. Introduction

The degradation of high-density polyethylene (HDPE) during processing is a subject of great interest not only for its scientific importance but also for technical reasons. The methods of HDPE polymerization give rise to differences in the structure of polymer chains, like differences in concentration and type of unsaturations, mainly vinyl, transvinylene, and vinylidene groups. This is an important aspect to be considered since the thermo-mechanical degradation mechanisms are affected by these unsaturations [1–3]. Temperature and shear stress strongly affect the kinetics and the mechanisms of HDPE degradation. The literature reports two predominant degradation mechanisms, which are dependent upon temperature and shear stress [4–6]: chain scission and chain branching, leading to a decrease and increase in the molecular weight (MW), respectively. A steady increase in the chain branching conversion will lead to crosslinking. Processing HDPE in a closed mixing chamber Földes et al. [7,8] verified that the concentration of carbonyl groups increases and unsaturated (mainly vinyl) groups

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decrease with the processing time. An increase in torque with time leads them to conclude that chain branching was present. Cruz and Zanin [9] compared the melt flow indexes (MFI) and data from cone-plate rheometry for stabilized and non-stabilized reprocessed HDPE and concluded that reprocessing without stabilization leads to an increase in molecular weight due to chain branching. Dontula and Campbell [10] observed the same effect when HDPE was processed in a twin-screw extruder, following differences in viscosity of the extruded material at different temperature profiles and feeding rates.

Oxygen available in the system and its concentration also have an important role in the thermo-mechanical degradation [11–16]. During processing, macromolecules undergo scission due to the action of temperature and shear stress, yielding macroradicals. If the concentration of oxygen is low, these macroradicals can react with each other, giving rise to branching and unsaturated groups, like vinyl and transvinylene groups [11,12]. On the other hand, if oxygen is present in high content, it easily reacts with those macroradicals, resulting in the propagation of degradation through formation of free radicals and unstable compounds that attack the polymer chains. The origin of the chain scission mechanism in polymers is due to the oxygen attacking the polymer chain yielding alkoxy and peroxy radicals. These radicals abstract a hydrogen atom from the chain, giving rise to β scission, leading to a decrease in molecular weight and formation of carbonyl end groups. The chain branching mechanism arises when alkyl macroradicals are added to vinyl groups, yielding in the final stages, cross-linked molecules [11,12]. Disproportionation of almost all of these radicals leads to the formation of transvinylene and vinylidene groups.

The parameters that promote degradation always give rise to changes in the molecular weight and in its distribution curve. Thus, size exclusion chromatography (SEC) appears in the literature as a helpful tool to perform these observations [17–20]. David et al. [21] proposed a way to quantify the extent of degradation calculating the average number of chain scissions (n_s) from the ratio of initial (reference, i. e., non-degraded) and final (degraded) number average molecular weight ($\overline{M}_{n(0)}$ and $\overline{M}_{n(f)}$, respectively), according to Eq. (1).

$$n_s = \frac{\overline{M}_{n(0)}}{\overline{M}_{n(f)}} - 1 \qquad (1)$$

Recently [22,23] we have proposed a method to calculate the number of chain scission and branching events for the whole range of the molecular weight distribution (MWD) curve, extending the calculations for each molecular weight fraction, represented by Eq. (2).

$$N_s = \frac{MW_{i(0)}}{MW_{i(f)}} - 1 \qquad (2)$$

where N_s is the number of chain scissions or branching curve, $MW_{i(0)}$ is a particular value in the initial (reference) MWD curve and $MW_{i(f)}$ represents its corresponding value in the final (degraded) MWD curve. The way this correspondence takes place follows two methods, discussed elsewhere: the intensity [22] and concentration [23] methods. This latter method sets the correspondence between initial and final molecular weights at the same concentration fraction of polymer chains in the MWD curve. From that it is possible to obtain information whether the scission or branching rate is affected or not by the initial length of the chain, taking the non-processed polymer as reference. We proposed the name Chain Scission and Branching Distribution Function, or CSBDF [6], for this type of curve. The CSBDF value is related to the average number of chain scission per chains (N_s) as:

$$\mathrm{CSBDF} = \log(N_s + 1) = \log\left(MW_{i(0)}\right) - \log\left(MW_{i(f)}\right) \qquad (3)$$

Fig. 1 presents an example of the possible shapes of CSBDF, which sets the type of degradation: linear with no slope when the degradation is random (independent of the initial molecular weight); linear with non-zero slope when dependent on initial molecular weight, and a situation that is a combination of both. We draw attention to the values higher than zero, which mean chain scission, and values lower than zero, meaning chain branching.

In this work we have studied the influence of processing parameters and HDPE type during its processing in an internal mixer, analyzing the oxidative thermo-mechanical degradation of HDPE through rheogram curves, FTIR, MWD curves, and the newly proposed CSBDF analysis. The effect of oxygen concentration in the degradative process is assessed using two different chamber fill factors: 70 and 100%. In order to analyze the influence of different levels of vinyl terminal chain groups in the degradation two HDPEs obtained from different catalytic systems were used: Phillips and Ziegler–Natta. The effect of changes in processing temperature was also verified.

2. Experimental

2.1. Materials

Phillips and Ziegler–Natta HDPEs were provided by BRASKEM S.A., having a MFI of 0.54 and 0.36 g/10 min (190 °C, 2.16 kg, ASTM-D1238), respectively, and density of 0.96 g/cm^3. Both resins were initially used in powder form in which no additive or stabilizer was added, obtained directly from the reactor.

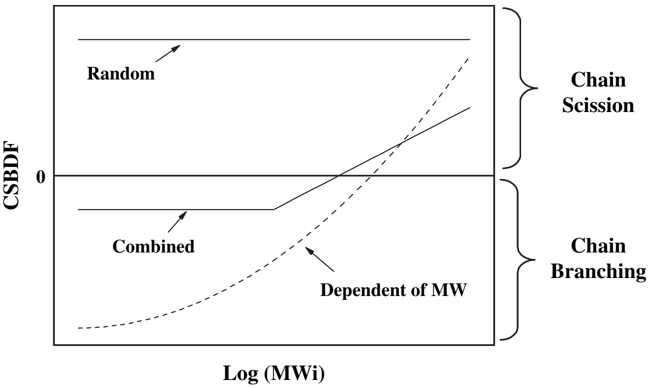

Fig. 1. Diagram of random, dependent of MW, and combined CSBDF curve.