



# Kinetic modelling of phenols consumption during polyethylene thermal oxidation



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## ABSTRACT

Irganox 1010 stabilized PE was monitored by carbonyl build-up and DSC under oxygen. A scheme for PE stabilization by phenols was implemented and its kinetic parameters were calculated from experimental results. This model was validated from its ability to simulate kinetics curves for carbonyl build up, induction period changes with stabilizer concentration, and stabilizer depletion curve in thermal ageing. The use of OIT measurement for quantifying stabilizer is also discussed. Kinetic analysis showed that OIT is actually proportional to stabilizer concentration in virgin samples but this is not true for aged samples because of negative influence of oxidation unstable by-products. The model was also employed for discussing some scenarii proposed as explanation of heterogeneity observed during thermal oxidation of stabilized polyolefins.

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## 1. Introduction

Many studies illustrate the effect of stabilizer on polymer ageing. Most of them compare stabilizers molecules by their ability to increase time to embrittlement, or carbonyl induction period [1]. Studying the rate of stabilizer depletion would permit to determine the phenomena involved in stabilizer disappearance (chemical consumption, physical loss, etc.) and further to improve the choice of stabilizer. For that purpose, two approaches can be envisaged:

- Analytical methods: spectroscopic, chromatographic or thermal detection of stabilizer and its by-products [2,3]. The measurement of Oxidation Induction Time by DSC under oxygen is one of most popular methods because of its simplicity [4–6].
- Kinetics approach: proposal of a mechanistic scheme for stabilizer action, determination of kinetics parameters from experimental data and prediction of changes in antioxidant concentration.

Implementing the kinetic approach requires understanding the stabilizer physico-chemistry, which is very complex [7]:

- Stabilizer can be consumed by chemical reaction or lost by evaporation or extraction [8].
- Stabilizer is partially soluble [9–12]. In previous papers [13,14], we successfully simulated the behaviour of phosphites and sulphurs by supposing that stabilizer soluble part disappear by reaction and evaporation, and insoluble one works as a reservoir maintaining the amorphous phase at the saturation limit as long as it is not totally consumed:
- In thick samples, its efficiency depends on its rate of diffusion from the bulk to the surface. The physical parameters (rate of evaporation  $H$ , solubility limit  $[\text{Stab}]_{\text{sat}}$ , or diffusivity  $D$ , etc.) can be estimated for each polymer-stabilizer mixture:
- $D$  value for several antioxidants in polyolefins are available in several papers [15–18], and can be predicted by some models linking  $D$  with temperature and stabilizer molar mass [19].
- Values of parameter  $H$  for evaporation rate values are also given in literature [20]. Their value may be estimated from kinetics of stabilizer loss under nitrogen [14].
- Estimation of solubility limit of stabilizers (being relatively polar molecules) in polyolefins from a theoretical approach is relatively complex: as observed for example by Billingham [9,14], regular solution theory (which is

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derived from Flory Huggins approach) is shown to give a good basis for extrapolation of data but cannot predict solubilities. This is not surprising first because approach derived from Flory's theory cannot be when polar interactions exist between polymer and stabilizer, and also because of the semi-crystalline nature of polyolefins [21]. Hence, the solubility of a stabilizer in a polyolefin can only be estimated from reported experimental values together with some structure properties relationships [22].

It remains to estimate the kinetic constants for stabilizer chemical consumption. In the case of 2,6 di-tert-butylphenols, it was shown that the efficiency per phenol group does not differ strongly from a family member to another [23]. Rate constants of stabilization were thus calculated from a literature review of degradation of several PP + phenol mixtures. Their physical sense constituted a partial validation which needs to be confirmed regarding other criteria.

In this paper, we will try to complete this previous investigation by implementing the following approach:

1. Estimation stabilization constants from experimental data in the case of PE + Irganox 1010 chosen here as a model phenolic antioxidant (presumably non volatile and soluble enough for neglecting in a first approach physical effects of stabilisation and simplify the modelling).
2. Discuss on the ability of the model to simulate the shape of stabilizer residual concentration curve. We already obtained promising results in comparable studies for hydroperoxides decomposers [13,14] but it was in case of a major volatile loss so that it is not sure that the stabilizer depletion only due to chemical reaction is accurately simulated. Since Oxidation Induction Time measurement (by Chemiluminescence or DSC) is a commonly employed [4–6], we will try to discuss on the reliability of this method for determining the residual quantity of stabilizer in polymer after exposure.
3. Several papers report that oxidation of stabilized polymer is heterogeneous [24,25], due to local presence of impurities or inhomogeneous stabilizer repartition. The model will be here used as a comprehensive tool for testing the proposed scenario in literature.

## 2. Experimental

### 2.1. Materials

The PE powder (supplied by Borealis) was stabilizer free, as confirmed by the absence of any induction period in the control DSC isothermal thermograms at 200 °C. Compounded samples were prepared by pouring a solution of Irganox 1010 (CAS 98584-37-3) in dichloromethane onto the PE powder. The stabilizer concentration and the solution volume were adjusted in order to obtain the desired stabilizer concentration in the PE. After solvent evaporation at room temperature, thick films, about 100 µm, were compression moulded at 200 °C under 24 MPa pressure for 30 s using a laboratory press (Gibrite Instrument).

The initial stabilizer concentration in the PE amorphous phase was calculated using:

$$[AH] = \frac{1}{1 - x_C} \cdot \frac{\rho_{PE}}{M_{Stab}} \cdot x_{Stab} \cdot f_{Stab} \quad (1)$$

where is the  $x_C$  is the crystallinity ratio taken as equal to 0 in molten state and 0.5 in solid state,  $\rho_{PE}$  is the polymer density (935 g l<sup>-1</sup>),  $M_{Stab}$  is the stabilizer molar mass (g mol<sup>-1</sup>),  $x_{Stab}$  is the global stabilizer weight ratio in the polymer,  $f_{Stab}$  is the stabilizer functionality, i.e. the number of active groups per molecule (4 for Irganox 1010).

### 2.2. Characterization

#### 2.2.1. Infra Red spectrophotometry

FTIR spectra of the PE films were recorded in transmittance mode using a Bruker IFS 28 spectrophotometer by averaging 32 scans at 4 cm<sup>-1</sup> resolution. The absorbance of carbonyl compounds resulting from PE oxidation were converted into concentration using the molar absorptivity of 300 l mol<sup>-1</sup> cm<sup>-1</sup> for the peak at 1715 cm<sup>-1</sup> [26].

#### 2.2.2. Determination of the stabilizer concentration using OIT measurements

Samples were analysed using the standard DSC under oxygen (OIT) at 200 °C using a Q10 apparatus (TA Instruments). OIT temperature measurement triggers:

- Sensitivity, with the detection of the onset [27].
- Analysis time [27].
- Additive volatilization, as observed by comparing OIT values for PE + Irganox 1010 or PE + Irganox 1076 at 190 °C for instance.

Here,  $T = 200$  °C was chosen a good compromise.

The polymer samples (systematically ca 5 mg giving a ca. 100 µm sample thickness expected to minimize the DLO effect) were first heated under nitrogen to 200 °C followed by a 5 min isothermal segment before switching to oxygen and then monitoring the time to the exotherm (denoted by OIT<sub>200</sub>). This measure is currently used for determining both initial and residual stabilizer activities and its limits will be discussed in the present paper. Fig. 1 depicts the shape of isothermal segment under oxygen for pristine samples of PE with and without stabilizer.

### 2.3. Thermal ageing

Ageing of polyethylene films was carried out in air at 110 °C and 120 °C in ventilated ovens.

## 3. Results

### 3.1. Oxidation at molten state

DSC-OIT curves for PE with several amounts of Irganox 1010 are given in Fig. 1. They call for the following comments:

- ① Identically to what is very well documented in literature, OIT increases here linearly with stabilizer amount [15,27–36].

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