# Accelerated Ageing of Polypropylene Stabilized by Phenolic Antioxidants Under High Oxygen Pressure

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Received 21 March 2008; accepted 23 May 2008
DOI 10.1002/app.28915
Published online 10 September 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Polypropylene (PP) samples stabilized by a hindered phenol (Irganox 1010) were submitted to thermal ageing at 80°C in air at atmospheric pressure or in pure oxygen at 5.0 MPa pressure. Both the polymer oxidation and the stabilizer consumption were monitored by Infrared spectrometry and thermal analysis. The stabilizer efficiency, as assessed by the ratio induction time/stabilizer concentration is almost constant at atmospheric pressure even when the stabilizer concentration is higher than its solubility limit in PP (0.4% or $24 \times 10^{-3}$ mol $L^{-1}$). In contrast, at high pressure, the efficiency decreases almost hyperbolically with the stabilizer concentration when this latter is higher than $6.0 \times 10^{-3}$ mol $L^{-1}$. The results indicate the existence of a direct phenol-oxygen reaction negligible at low oxygen pressure but significant at 5.0 MPa pressure. The reality of this reaction has been proved on the basis of a study of the thermal oxidation of a phenol solution in a nonoxidizable solvent. A kinetic model of PP oxidation in which stabilization involves three reactions has been proposed. It simulates correctly the effect of oxygen pressure and stabilizer concentration on carbonyl build-up and stabilizer consumption. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 3313–3321, 2008

**Key words:** polypropylene; phenolic antioxidant; thermal oxidation; oxygen pressure; kinetic modeling

## INTRODUCTION

Polypropylene (PP) geotextiles have been used in civil engineering for about 30 years. Applications range from soil reinforcement, the protection of geomembranes under pavements and in tunnels, etc., which are structures where the product is inaccessible. The required service life is often of the order of 100 years.[1–3] To be able to produce materials that can be assumed to meet such requirements, an accelerated ageing test is needed.

To assess PP geotextiles durability, a new accelerated test has recently been proposed.[4] It is performed at 80°C, a more moderate temperature than in usual tests (110°C),[5] under a high oxygen pressure with fibers plunged into a liquid alkaline media. We can reasonably assume that oxidative behavior and durability of geotextiles depends on the efficiency of the antioxidants. Consequently, it seems necessary to investigate the consequences of this exposure conditions on the degradation of various geotextiles by studying phenomena in an increasing complexity order.

In this context, we had first investigated on the simplest case, i.e., the effect of oxygen pressure on oxidation kinetics of a stabilizer free PP,[6,7] thus establishing the accelerating role of oxygen pressure on PP oxidation. In these previous articles, a kinetic model has been proposed to simulate oxygen pressure effect on the oxidation process. In this model, all parameters have a physical meaning and their values have been discussed.

Knowing antioxidants are always included in PP geotextiles, a specific effort is needed to take into account stabilizer effect during the new accelerated test using high oxygen pressure. In this article, we will follow the work of Shiono et al.,[8] Mueller and Jakob,[9] Vink and Fontijn,[10] and Li and Hsuan[11] by focusing on the effect of oxygen pressure on PP samples with various amount of Irganox 1010, which is a widely used phenolic antioxidant.

The stabilization of hydrocarbon polymers by phenolic antioxidants has been widely studied in the last 30 years.[12] All the authors agree with the fact that the primary stabilization process is the abstraction of the phenolic hydrogen by a peroxy radical. The resulting phenolic radical displays a low reactivity owing to its steric hindrance that explains at least partially, the stabilization effect since peroxy scavenging can be assimilated to an unimolecular termination.

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In fact, the phenoxy radical isomerizes very easily into a cyclohexadienyl radical which can participate to various processes among which scavenging of peroxy radicals increases the stabilizing power of the phenol.

It is also well-known by practitioners[13] that additives of relatively small size (molar mass typically lower than few kg $mol^{-1}$), tend to migrate out polymer matrices that limits their performance. Experimental data about their transport properties are available in the literature.[14]

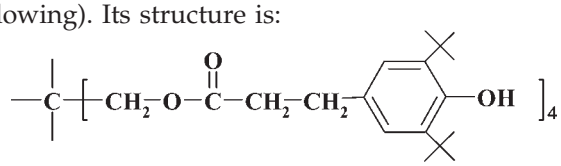
In the chosen modeling approach, diffusion-reaction coupling can be taken into account, provided that chemical (rate constants) and transport (solubility-diffusivity) parameters are determined separately. In the case of the relatively heavy Irganox 1010 molecule, it is easy to find accelerated ageing conditions in which physical loss by migration is negligible.

The aim of the present work is to determine the chemical parameters specific of the stabilization by Irganox 1010, to simulate the kinetics of PP thermal oxidation in the aforementioned accelerated ageing conditions.

## EXPERIMENTAL

### Materials

The used stabilizer was Irganox 1010, a commercial antioxidant supplied by Ciba SC (denoted AH in the following). Its structure is:



The PP is a metallocene grade supplied as 30 μm diameter manufactured fibers (Bidim Tencate). Microstructure (average molar mass, crystallinity) was detailed in a previous article.[15] The UV spectrum displays an absorption close to 280 nm, which is characteristic of a phenolic antioxidant stabilization.[16] The presence of a phosphite is not excluded since this stabilizer also absorbs in this wavelength region[17] and the combination of phenol and phosphite leads to a strong synergistic effect.[12,18]

Samples were prepared by a two-steps procedure adapted from previously published ones[19,20]:

1. *PP purification:* As received fibers (~ 2 g) were dissolved into refluxing 1,2-dicholorobenzene (200 mL). After 2 min at refluxing temperature (i.e., the solvent boiling point, close to 180°C), solution was hot filtered to eliminate impurities (carbon black, etc...). Methanol was dripped to selectively precipitate PP. The obtained PP pellets were washed with ethanol and dried.
2. *Incorporation of antioxidant in PP:* Necessary quantity of Irganox 1010 to obtain a given weight ratio was dissolved in THF. Solution was spilled on the pure PP pellets under $N_2$ flow to quickly evaporate the solvent. The stabilized pellets were pressed under 15 MPa at 180°C during 20 s. This duration was taken as low as possible to enable a good processing but limiting the phenol consumption. Thickness of obtained films was of the order of 70 μm, and can be considered as low enough to neglect oxidation thickness gradients due to the kinetic control by oxygen diffusion, so that we can consider the oxidation as homogeneous.

Irganox 1010 weight ratios were converted into antioxidant groups concentration (denoted by [AH]) in amorphous phase by the formula:

$$[\mathrm{AH}] = f_{\mathrm{AH}} \frac{1}{1 - x_c} \times \frac{m_{\mathrm{AH}}/M_{\mathrm{AH}}}{m_{\mathrm{PP}}/d_{\mathrm{PP}}} \approx 6.0 \times x_{\mathrm{AH}}$$

with

$f_{\mathrm{AH}}$ being the antioxidant functionality defined as the number of phenol groups per antioxidant molecule, i.e., 4 for Irganox 1010. It is important to distinguish the concentration of phenolic groups which is the key quantity in chemical kinetics, from the concentration of antioxidant molecules which is the key quantity in transport processes.

$x_C$ being the crystallinity ratio of films of the order of 0.5.

$m_{\mathrm{AH}}$ and $m_{\mathrm{PP}}$ being the masses of Irganox 1010 and PP employed for making the sample.

$M_{\mathrm{AH}}$ being the molar mass of Irganox 1010 equal to 1176 g $mol^{-1}$.

$d_{\mathrm{PP}}$ being the density of PP (0.90 kg $L^{-1}$).

$x_{\mathrm{AH}}$ being the antioxidant weight ratio, in others words the concentration used by practitioners.

The following antioxidant concentrations were: 0, 0.003, 0.006, 0.012, 0.03, and 0.097 mol $L^{-1}$. The highest concentration is greatly higher than the concentration corresponding to limit of solubility value (0.4% corresponding to 0.024 mol $L^{-1}$). Even if it can be considered as unrealistic, we have used this sample to highlight physicochemical phenomenon occurring for Irganox 1010 and to observe them more easily with detection techniques such as Infrared spectrometry.

In case of exposure of Irganox 1010 solutions (2 g $L^{-1}$ that corresponds to $1.7 \times 10^{-3}$ mol $L^{-1}$) in a nonoxidizable solvent, we have employed 1,2-

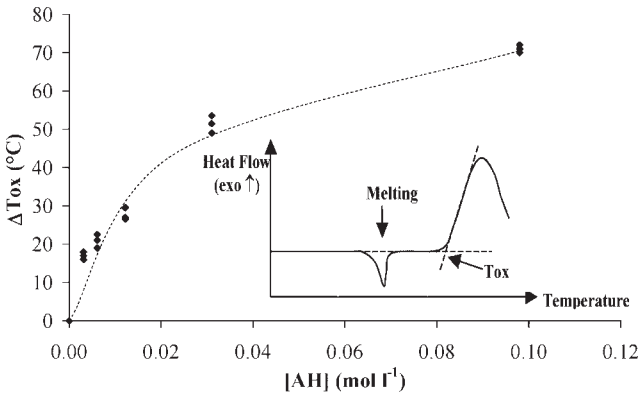



**Figure 1** Changes of ΔTox against Irganox 1010 concentration including schematization of determination method of degradation temperature under oxygen (Tox).

dichlorobenzene (analytic grade supplied by VWR). This concentration was under solubility limit but enough for satisfying detection by Infrared spectrometry.

### Exposure conditions

Samples were exposed in air under atmospheric pressure (0.02 MPa) and in pure oxygen at 5.0 MPa. The temperature was fixed at 80°C. The autoclaves were thermally equilibrated for 24 h prior to sample exposure.

### Samples characterization

#### Infrared analysis

FTIR spectrometry was used to characterize the extent of polymer oxidation and antioxidant consumption using a Nicolet Impact 410 spectrophotometer driven by Omnic 3.1 software. Measurements were made on spectra resulting from the accumulation of 32 runs, the resolution being 4 $cm^{-1}$. The carbonyl absorbances resulting from PP oxidation were converted to concentrations using Beer-Lambert's law with a molar absorptivity of 300 L $mol^{-1}$ $cm^{-1}$ at the peak maximum (1712 $cm^{-1}$). The ester (1745 $cm^{-1}$) and hydroxyl (3645 $cm^{-1}$) peaks were used to follow the antioxidant consumption.

#### Thermal analysis

The stabilizing efficiency of the antioxidant was characterized by measuring the temperature of degradation under oxygen (denoted by Tox). This is the temperature at which an exotherm appears when a sample is heated under oxygen at a constant rate of temperature increase (Fig. 1).

It was shown that this technique allows to evaluate residual stabilizer concentration.[21–24] Experiments were carried out on about 5 mg samples heated from 25 to 270°C at 10°C $min^{-1}$ rate under 50 mL $min^{-1}$ of pure oxygen, with a Netzsch apparatus. The thermogram shape and the graphical method for Tox determination are given in Figure 1, with the curve giving ΔTox against Irganox 1010 concentration [AH], ΔTox being defined by:

$$\Delta\text{Tox} = \text{Tox} - \text{Tox (additive free sample)}$$

with Tox (additive free sample) being equal to 186°C.

Later, this curve will be used as a calibration curve to estimate residual stabilizer concentration during oxidation.

## RESULTS

Experimental data of carbonyl build-up at 80°C gathered with kinetic modeling data (see in 'DISCUSSION' part for explanations about kinetic modeling) are shown in Figure 2 for ageing under 0.02 MPa $O_2$ pressure and Figure 3 for ageing under 5.0 MPa $O_2$ pressure.

The changes of experimental induction time (denoted by $t_{ind}$) as a function of antioxidant concentration and simulations by kinetic modeling are plotted in Figure 4.

The experimental results call for the following comments:

1. Under 0.02 MPa $O_2$ (atmospheric) pressure, experimental induction time (and so the stabilizing effect of the phenol under study) linearly increases with AH concentration, even above its solubility limit ($\sim 24 \times 10^{-3}$ mol $L^{-1}$ against $30 \times 10^{-3}$ mol $L^{-1}$ maximum concentration under study).

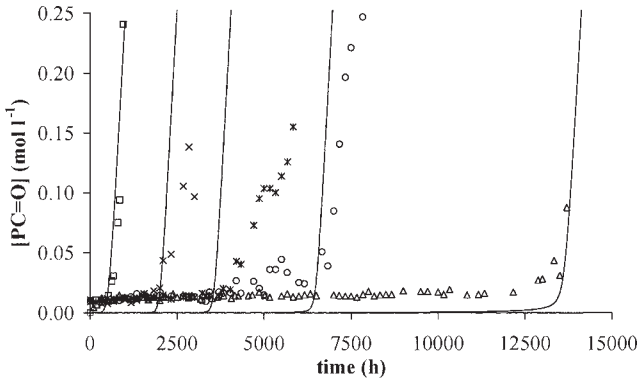



**Figure 2** Experimental carbonyl build up for additive free PP (□), and containing 0.003 (×), 0.006 (*), 0.012 (○) and 0.03 mol $L^{-1}$ (△) of Irganox 1010 for exposures under atmospheric pressure at 80°C and simulations by kinetic modeling for each stabilizer concentration with parameters given in Tables I, II and III (full lines).

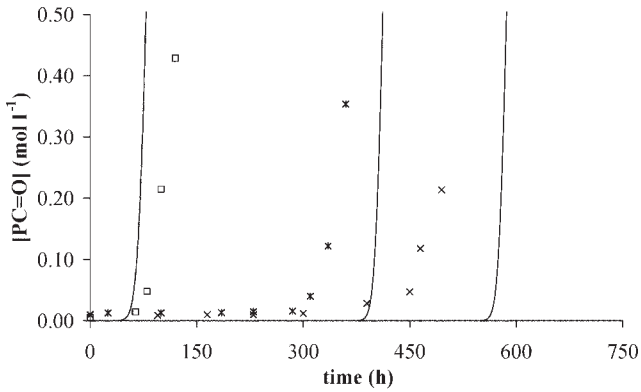



**Figure 3** Experimental carbonyl build up for additive free PP (□), and containing 0.003 (*), 0.006 (×) mol $L^{-1}$ of Irganox 1010 for exposures under 5.0 MPa of oxygen at 80°C and simulations by kinetic modeling for each stabilizer concentration with parameters given in Tables I, II and III (full lines).

2. Under high oxygen pressure, induction periods are considerably reduced compared to air. In this case, induction period duration remains almost constant for stabilizer concentration above $6.0 \times 10^{-3}$ mol $L^{-1}$.

Stabilizer concentration has been estimated from Tox measurements on samples exposed for various times under 0.02 MPa $O_2$ at 80°C. Results are plotted in Figure 5 (with simulations by kinetic model) for samples containing an initial concentration equal to $3.0 \times 10^{-3}$ and $6.0 \times 10^{-3}$ mol $L^{-1}$. From these results, one can observe that:

1. For both samples, one can check the total stabilizer disappearance at the end of induction period of carbonyl build-up.[25]
2. For the sample containing initially $3.0 \times 10^{-3}$ mol $L^{-1}$, concentration keeps nearly constant during the induction period (as estimated from carbonyl build-up) and then dramatically decreases. For the sample initially containing $6.0 \times 10^{-3}$ mol $L^{-1}$, curve also exhibits a strong drop for exposure time slightly lower than the induction period but is noticeably scattered especially during the earlier exposure period (that could be caused by the numerous experimental uncertainties).

To check an eventual effect of stabilizer loss by evaporation/diffusion, we have monitored the absorbance of the ester group at 1745 $cm^{-1}$ during thermal ageing. This group is expected to be unaffected by chemical changes occurring during stabilization events but it can, indeed, disappear by physical loss of stabilizer.[26]

The results [Fig. 6(a,b) the global trend being given by dashed lines] show clearly that for durations of the order of the induction period, the physical loss can be considered as negligible in the timescale under study, that is not very surprising considering the very low diffusivity and volatile loss of the Irganox 1010 molecule.[27]

However, significant changes are observed in the same time by following absorption at about 3650 $cm^{-1}$ corresponding to —OH bond [Fig. 7(a,b), the global trend being given by dashed lines]:

Under 0.02 MPa [Fig. 7(a)], —OH bond absorbance also decreases slightly, which suggests that chemical consumption is not significant in the considered time range.

Under 5.0 MPa $O_2$ [Fig. 7(b)], nearly all the hydroxyl bonds of phenol (FTIR measurements) and residual stabilizer (DSC measurements) disappeared during the earliest exposure period,

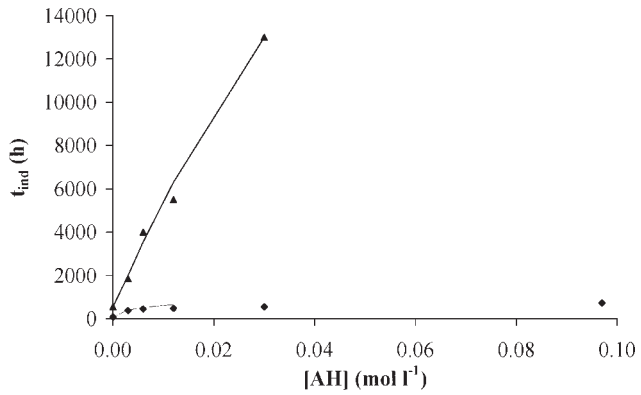



**Figure 4** Induction period as a function of phenolic antioxidant concentration for samples exposed at 80°C under atmospheric pressure (▲), 5.0 MPa $O_2$ (◆), and simulations by kinetic modeling for each stabilizer concentration with parameters given in Tables I, II and III (full lines).

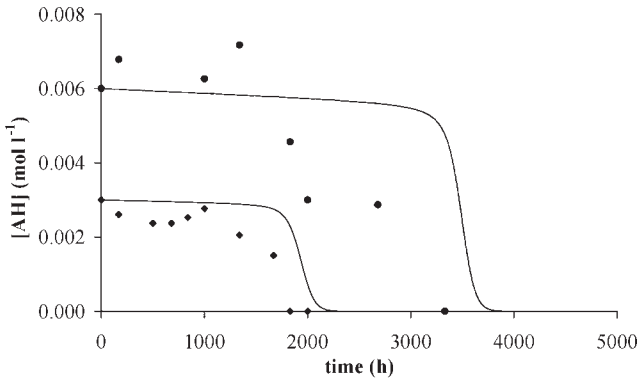



**Figure 5** Antioxidant consumption for films containing 0.003 (◆) at 0.006 mol $L^{-1}$ (●) Irganox 1010 for exposures under atmospheric pressure at 80°C and simulations by kinetic modeling for each stabilizer concentration with parameters given in Tables I, II and III (full lines).

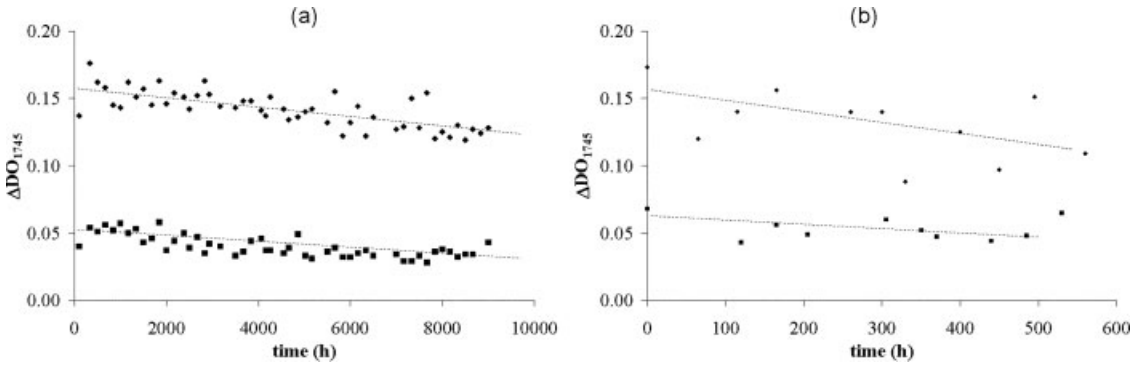



**Figure 6** Changes of absorptions at 1745 $cm^{-1}$ for PP samples containing 0.03 mol $L^{-1}$ (■) and 0.09 mol $L^{-1}$ (◆) of Irganox 1010 for exposures at 80°C under atmospheric pressure (a) and under 5.0 MPa $O_2$ (b).

i.e., less than 100 h [Fig. 7(b)]. We can note that oxidation induction time measurements made by Li and Hsuan for PP tape yarns stabilized with phenolic antioxidants and hindered amine stabilizers mix suggested similar results.[11]

These latter results clearly indicate that —OH groups of phenolic antioxidants are consumed but the backbone of molecule is not much modified. There is a wide consensus on the fact that AH reacts with $POO^{\bullet}$ radicals. There are therefore three possible origins for —OH groups disappearance:

Reaction with $POO^{\bullet}$: $r_1 = k_{S1}[POO^{\bullet}][AH]$
This term must tend toward 0 at $t = 0$ because we can assume that there are no $POO^{\bullet}$ radicals when the exposure begins.
Reaction with other species: $r_2 = k'[X][AH]$
Physical loss or exudation depending on temperature T [and negligible according to Fig. 6(a,b)]: $r_3(T)$

At $t = 0$, $[POO^{\bullet}]_0 \sim 0$ so that:

$$\left(\frac{d[AH]}{dt}\right)_{t=0} = r_2 + r_3$$

Since the rate of physical loss $r_3$ is independent of oxygen pressure, the difference for exposure under 0.02 MPa and 5.0 MPa oxygen pressure can be explained only by the second term $r_2$ that corresponds to reaction between AH and species able to react with phenol. By comparing Figure 7(a,b), the rate $r_2$ is a function of oxygen pressure. The consumption of phenols —OH groups presented in Figure 7(b) could be explained by a direct interaction between the hydroxyl group of the phenol molecule and oxygen. It led us to study the kinetic of the reaction:

$$O_2 + AH \rightarrow A^{\bullet} + {}^{\bullet}OOH$$

This reaction has already been proposed in the literature,[28,29] but its role has not, to our knowledge, been taken into account in kinetic treatments of oxidation.[30–32] To quantify the influence of such a process and if this reaction could take place in the absence of an oxidizable substrate (thus causing direct phenol disappearance), the following experiment has been made: a solution (2 g $L^{-1}$ corresponding to $1.7 \times 10^{-3}$

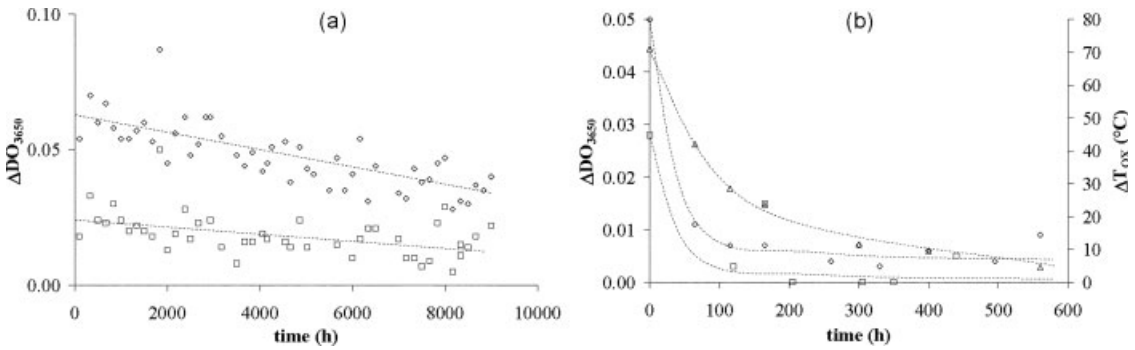



**Figure 7** Changes of absorptions at 3645 $cm^{-1}$ for PP samples containing 0.03 mol $L^{-1}$ (□) and 0.09 mol $L^{-1}$ (◇) of Irganox 1010 for exposures and changes of $\Delta T_{OX}$ for PP samples containing 0.09 mol $L^{-1}$ (△) at 80°C under atmospheric pressure and under 5.0 MPa $O_2$ (b).

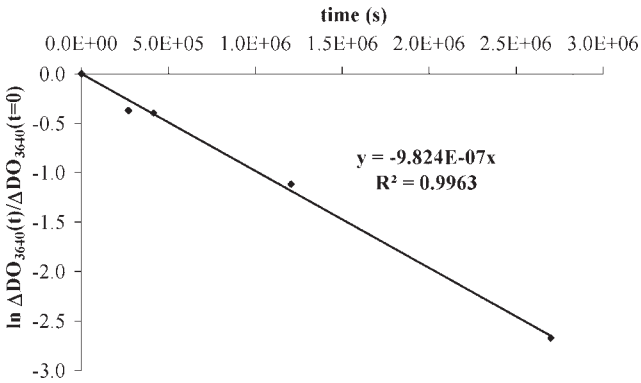



**Figure 8** Kinetic of Irganox 1010 consumption by oxygen in 1,2-dichlorobenzene under 5.0 MPa of oxygen at 80°C.

mol $L^{-1}$) of Irganox 1010 in 1,2-dichlorobenzene as an inert media was exposed under 5.0 MPa $O_2$ pressure at 80°C and the phenol consumption was monitored by IR spectrometry, using —OH absorbance band situated at 3640 $cm^{-1}$ in 1,2 dichlorobenzene.

The observed phenolic —OH groups consumption obeys pseudo first order kinetics with a rate constant: $\kappa = 9.8 \times 10^{-7}\ s^{-1}$ (Fig. 8). Here, it can be reasonably assumed that the temperature under investigation, there is no oxidation of the solvent, so that phenol is consumed only by direct reaction with oxygen. Consequently, this result has to be taken into account in the kinetic scheme of Irganox 1010 stabilized PP.

## DISCUSSION

### Elaboration of the kinetic scheme

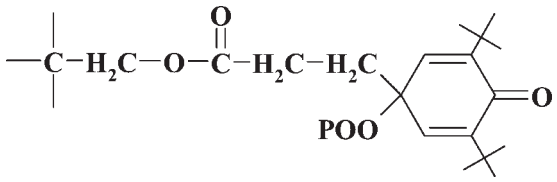
It has been recently shown[6,7] that PP oxidation kinetics can be adequately modeled by a kinetic scheme, derived from the standard mechanistic scheme, in which the predominating initiation event is the hydroperoxide decomposition. Let's recall that reactions 1u and 1b are balance equations that were completely described in a previously published article.[33] The corresponding rate constant values at 80°C, given in Tables I and II, were determined by an inverse method based on the best fitting of experimental results.[34] This model remains valid for a relatively wide temperature interval (at least 50–130°C, as it has been shown in our previous work,[35] for any oxygen pressure lower than 5.0 MPa, in the case of unstabilized PP.

$$\text{(1u)}\quad POOH \rightarrow 2P^{\bullet} + PC{=}O \qquad k_{1u}$$
$$\text{(1b)}\quad POOH + POOH \rightarrow P^{\bullet} + POO^{\bullet} + PC{=}O \qquad k_{1b}$$
$$\text{(2)}\quad P^{\bullet} + O_2 \rightarrow POO^{\bullet} \qquad k_2$$
$$\text{(3)}\quad POO^{\bullet} + PH \rightarrow POOH + P^{\bullet} \qquad k_3$$
$$\text{(4)}\quad P^{\bullet} + P^{\bullet} \rightarrow \text{inactive products} \qquad k_4$$
$$\text{(5)}\quad P^{\bullet} + POO^{\bullet} \rightarrow \text{inactive products} \qquad k_5$$
$$\text{(6)}\quad POO^{\bullet} + POO^{\bullet} \rightarrow \text{inactive products} + O_2 \qquad k_6$$

There is a wide number of publications dealing with stabilization mechanisms with phenolic compounds.[36–43] One can consider that they converge toward the hypothesis that every phenol group could scavenge two peroxy radicals by the following two steps process:

$$\text{(S1)}\quad POO^{\bullet} + AH \rightarrow POOH + A^{\bullet} \qquad k_{S1}$$
$$\text{(S2)}\quad POO^{\bullet} + A^{\bullet} \rightarrow \text{inactive products} \qquad k_{S2}$$

Because of 2,6 tertbutyl hindrance, the inactive compound produced by reaction S2 is probably a cyclohexadienone:




This is, obviously, a simplified view of the stabilization process. Indeed, the radical involved in the second process is not the phenoxy radical ($A^{\bullet}$) resulting from the first reaction, but rather another radical resulting from fast isomerization of the former. Moreover, many secondary processes (for instance dimerization, polymerization, oxidation, etc... of $A^{\bullet}$) have been put in evidence.[12,36] For example, $A^{\bullet} + A^{\bullet}$ is often quoted by authors,[25,44] but this reaction is limited in the case of a hindered 4-substituent,[41] which is precisely the case for Irganox 1010. On the contrary, reaction between $A^{\bullet}$ and

**TABLE I**
**Rate Constants Used for the Kinetic Modeling Simulation (Determined in Previous Study)**

| $k_{1u}$ ($s^{-1}$) | $k_{1b}$ ($L\ mol^{-1}\ S^{-1}$) | $k_2$ ($L\ mol^{-1}\ S^{-1}$) | $k_3$ ($L\ mol^{-1}\ S^{-1}$) | $k_4$ ($L\ mol^{-1}\ S^{-1}$) | $k_5$ ($L\ mol^{-1}\ S^{-1}$) | $k_6$ ($L\ mol^{-1}\ S^{-1}$) |
|---|---|---|---|---|---|---|
| $1.3 \times 10^{-8}$ | $5.0 \times 10^{-6}$ | $1.2 \times 10^{7}$ | $6.3 \times 10^{-2}$ | $5.0 \times 10^{10}$ | $4.0 \times 10^{9}$ | $1.2 \times 10^{4}$ |

**TABLE II**
**Materials Parameters Used for Kinetic Modeling Simulation**

| $[POOH]_0$ (mol $L^{-1}$) | $[PH]_0$ (mol $L^{-1}$) | $S_{O2}$ (mol $L^{-1}$ $Pa^{-1}$) |
|---|---|---|
| $1 \times 10^{-4}$ | 24 | $1.4 \times 10^{-8}$ |

$POO^\bullet$ should be the main pathway owing to its high rate.[45] In the same way, the peroxide generated by the reaction $POO^\bullet + A^\bullet$ is expected to be unstable at low temperature but we assume that the initiation by its thermolysis is negligible at 80°C compared with POOH initiation by reactions (1u) and (1b).

The above reactions are to be considered as balance reactions which will likely be decomposed into several elementary steps in the future. However, we will first, in a coarse grain study, assume that phenolic antioxidants stabilize polymers by reactions (S1) and (S2).

To take into account the results of our study of direct phenol-oxygen interaction, a new reaction must be added. $O_2$ molecule, as a diradical, can abstract hydrogen. However, only very labile hydrogens can be attacked due to its low reactivity. In the case of a (reactive) molecule substrate, the following reaction could be proposed:

$$AH + O_2 \rightarrow A^\bullet + HOO^\bullet$$
$$HOO^\bullet + PH \rightarrow HOOH + P^\bullet$$

The balance equation could be ascribed:

$$\text{(O2)} \quad AH + O_2 \rightarrow A^\bullet + POO^\bullet \qquad k_{O2}$$

Global kinetics is governed by the slowest step: $AH + O_2 \rightarrow A^\bullet + HOO^\bullet$.

In a first approach, it can be written:

$$-\frac{d[AH]}{dt} = k_{O2}[O_2][AH]$$

In attempts to estimate $k_{O2}$ independently of PP data, an experiment based on a model system constituted by a well oxygenated Irganox 1010 solution in orthodichlorobenzene was performed. In the conditions under study, the solvent can be considered inert.

Since the oxygen concentration can be considered constant here, one expects a pseudo first order behavior:

$$-\frac{d[AH]}{dt} = \kappa[AH]$$

where $\kappa = k_{O2} \times [O_2]$.

Indeed, the first order plot of the Irganox consumption showed in Figure 8 exhibits a linear behavior with $\kappa \sim 10^{-6}\ s^{-1}$ at 80°C.

Considering that $O_2$ transport properties in orthodichlorobenzene are not very far from benzene ones and that the $O_2$ solubility coefficient at 80°C is $S_{O2} = 10^{-2}$ mol $L^{-1}$ $MPa^{-1}$,[46] one can assess $k_{O2}$ value at 80°C with:

$$k_{O2} = \frac{\kappa}{S_{O2} \times P_{O2}} = 2.0 \times 10^{-5}\, L\, mol^{-1} \times s^{-1}$$

where $p_{O2}$ is oxygen pressure equal to 5 MPa.

This value of $k_{O2}$ is the same order of magnitude as the ones reported in the extensive review by Denisov and Afanas'ev[44] determined by using a semi-empirical model. $k_{O2}$ values will be also determined by an inverse method from our experimental results by using the kinetic model. The resulting value will be kept only if it is of the same order of magnitude as the above ones.

Finally, the mechanistic scheme relative to the oxidation of stabilized polymer could be composed of 10 elementary equations (1u) through (6), and eq. (S1)(S2)(O2). From the scheme, a system of seven differential equations constituting the kinetic model can be derived:

$$\frac{d[POO^\bullet]}{dt} = k_{1b}[POOH]^2 + k_2[P^\bullet][O_2] - k_3[POO^\bullet][PH] - k_5[P^\bullet][POO^\bullet] - 2k_6[POO^\bullet]^2 - k_{S1}[AH][POO^\bullet] - k_{S2}[A^\bullet][POO^\bullet] + k_{O2}[AH][O_2] \quad (1)$$

$$\frac{d[POOH]}{dt} = -k_{1u}[POOH] - 2k_{1b}[POOH]^2 + k_3[POO^\bullet][PH] + k_{S1}[POO^\bullet][AH] \quad (2)$$

$$\frac{\partial[O_2]}{\partial t} = D_{O2}\frac{\partial^2[O_2]}{\partial x^2} - k_2[P^\bullet][O_2] + k_6[POO^\bullet]^2 - k_{O2}[AH][O_2] \quad (3)$$

$$\frac{d[P^\bullet]}{dt} = 2k_{1u}[POOH] + k_{1b}[POOH]^2 - k_2[P^\bullet][O_2] + k_3[POO^\bullet][PH] - 2k_4[P^\bullet]^2 - k_5[P^\bullet][POO^\bullet] \quad (4)$$

$$\frac{d[PH]}{dt} = -k_{1u}[POOH] - k_3[POO^\bullet][PH] \quad (5)$$

$$\frac{\partial[AH]}{\partial t} = -k_{S1}[AH][POO^\bullet] - k_{O2}[AH][O_2] \quad (6)$$

$$\frac{\partial[A^\bullet]}{\partial t} = +k_{S1}[AH][POO^\bullet] - k_{S2}[POO^\bullet][A^\bullet] + k_{O2}[AH][O_2] \quad (7)$$

**TABLE III**
**Rate Constants Determined for Antioxidant Reactions (see Text)**

| $k_{S1}$ ($L$ mol$^{-1}$ S$^{-1}$) | $k_{S2}$ ($L$ mol$^{-1}$ S$^{-1}$) | $k_{O2}$ ($L$ mol$^{-1}$ S$^{-1}$) |
|---|---|---|
| 8 | $1.0 \times 10^5$ | $5.0 \times 10^{-5}$ |

Here, concentrations are given in amorphous phase of PP.

At every time, in superficial layers: $[O_2] = S_{O2} \times P_{O2}$, where $S_{O2}$ is the oxygen solubility coefficient in PP and $P_{O2}$ is the external oxygen pressure.

Assuming that the initial hydroperoxide amount is not too modified by the phenolic antioxidant presence, the initial ($t = 0$) boundaries conditions are:

$$[P^\bullet] = [POO^\bullet] = 0$$
$$[POOH] = [POOH]_0 = 10^{-4} \text{ mol } L^{-1}$$
$$[PH] = [PH]_0 = 24 \text{ mol } L^{-1}$$

Let's recall that the model could be modified to take into account the reaction-diffusion coupling as well for $O_2$ as for AH and its molecular key products.

All the previously determined parameters are given in Tables I and II (compared with original articles, we have done slight modifications on some values to optimize the fit). $k_{S1}$, $k_{S2}$ and $k_{O2}$ will be determined by using an inverse approach[6,7,47] consisting to solve the system of eqs. (1)–(7) with a given set of parameters, to compare the kinetic curves generated by the model to experimental ones, and to modify the parameter values to minimize the difference between theoretical and experimental curves. Commercial software, Matlab, is used for these calculations.

### Comparison between kinetic modeling and experimental results

Experimental kinetic curves for carbonyl build-up were compared with those obtained by kinetic modeling. It was assumed that carbonyls (PC=O) are mainly formed in hydroperoxide decomposition events, so that [PC=O] is calculated by integrating the following equation, knowing that [POOH] as a function of time is obtained by solving the previous differential equation system:

$$\frac{d[PC=O]}{dt} = (1 - x_C)(\gamma_{1u} k_{1u}[POOH] + \gamma_{1b} k_{1b}[POOH]^2)$$

where: $\gamma_{1u}$ and $\gamma_{1b}$ are yields of carbonyl formation per initiation event. We suppose, in a fist approach, that alkoxy radicals PO$^\bullet$ mainly react by β-scission so that $\gamma_{1u}$ and $\gamma_{1b}$ are taken equal to 1.

[PC=O] = 0 at $t = 0$.

[POOH]($t$) is directly calculated by solving the set of differential equations (see above).

The best set of values obtained by this procedure was: $k_{S1} = 8$ L mol$^{-1}$ s$^{-1}$, $k_{S2} = 10^5$ L mol$^{-1}$ s$^{-1}$, $k_{O2} = 5.0 \times 10^{-5}$ L mol$^{-1}$ s$^{-1}$ (Table III). On can notice that $k_{O2}$ value is in a very good agreement with preceding ones (see part 1 of this discussion).

The curves for carbonyl build-up and stabilizer consumption generated by the model, using these rate constants values (together with the values of Tables I and II), are shown in Figures 2, 3, and 5.

All the model predictions are in acceptable agreement (see Figs. 2, 3, 4, and 5) with experimental curves, considering the complexity of the mechanistic scheme and the diversity of error sources. Indeed, the model cannot be applied to stabilizer concentration higher than its solubility limit, which is the case here for 0.03 and 0.097 mol L$^{-1}$ concentrations.

## CONCLUSIONS

Unstabilized and hindered phenol (Irganox 1010) stabilized PP samples were submitted to thermal ageing at 80°C, in air (0.02 MPa $O_2$) or in pure oxygen (5.0 MPa $O_2$) pressure according to the standard EN ISO 13438. The polymer oxidation (carbonyl build-up) and the stabilizer consumption (ester and phenol groups) were monitored by IR spectrometry and thermal analysis under oxygen.

In air, the stabilizer efficiency, as characterized by the ratio (induction time/antioxidant concentration) is almost constant up to concentration of $30 \times 10^{-3}$ mol L$^{-1}$ i.e., above the solubility limit of the stabilizer in PP. Under high oxygen pressure the stabilizer efficiency decreases almost hyperbolically at concentrations above $6.0 \times 10^{-3}$ mol L$^{-1}$.

A kinetic model based on previously obtained results on unstabilized PP has been proposed using first the classical hypothesis of a two steps stabilization mechanism:

$$POO^\bullet + AH \rightarrow POOH + A^\bullet \qquad k_{S1}$$
$$POO^\bullet + A^\bullet \rightarrow \text{inactive products} \qquad k_{S2}$$

This model gave acceptable results in the case of exposure at low pressure (air at atmospheric pressure) but overestimated considerably the induction period durations in the case of high oxygen pressure. To take into account this latter result, it was hypothesized that oxygen reacts directly with phenol

$$AH + O_2 \rightarrow A^{\bullet} + POO^{\bullet} \qquad k_{O2}$$

The reality of this reaction was proved by a study of the phenol consumption, under high oxygen pressure, in solution in a nonoxidizable solvent: 1,2-dichlorobenzene. Finally, the kinetic model (seven differential equations) derived from a mechanistic scheme incorporating the three above processes, simulates adequately the kinetic curves of carbonyl build-up as well in air at atmospheric pressure as in high oxygen pressure. The rate constant values giving the best fitting: $k_{S1} = 8$ L mol$^{-1}$ s$^{-1}$, $k_{S2} = 10^5$ L mol$^{-1}$ s$^{-1}$, and $k_{O2} = 5.0 \times 10^{-5}$ L mol$^{-1}$ s$^{-1}$ are physically realistic.

It is interesting to stress that phenol consumption processes are qualitatively different in air at atmospheric pressure and under high oxygen pressure because a direct oxygen-phenol reaction is negligible in the former case and important in the second one. In the classical approach of accelerated ageing, this difference would lead to reject high pressure testing because it is not a "good simulation" of natural ageing. In our approach, this is not an obstacle because the difference is taken into account in the model.

Authors especially want to thank MM. Mougin and Flaconneche (Institut Français du Petrole) for having kindly supplied thermodynamical data on oxygen solubility into organic solvents.

## References


1. Koerner, R. M.; Soong T. Y.; Koerner G. R.; Gontar A. Geotext Geomembranes 2001, 19, 413.
2. Mengjia Li M.; Hsuan, Y. G. Geotext Geomembr 2004, 22, 511.
3. Greenwood, J. H.; Friday, A. In proceedings of 8th International Conference on Geosynthetics 2006, ed.; Milpress: Rotterdam, Vol. 4, pp 1539–1542.
4. International standard PrEN ISO 13438, Geotextile and Geotextile related products: screening test method for determining the resistance to oxidation at elevated oxygen pressure; European Committee for Standardization: Brussels, 2002.
5. International standard ENV ISO 13438, Geotextile and geotextile-related products-Screening test method for determining the resistance to oxidation; European Committee for Standardization: Brussels, 1998.
6. Richaud, E.; Farcas, F.; Bartoloméo, P.; Fayolle, B.; Audouin, L.; Verdu, J. Polym Deg Stab 2006, 91, 398.
7. Richaud, E.; Farcas, F.; Fayolle, B.; Audouin, L.; Verdu, J. Polym Deg Stab 2007, 92, 118.
8. Shiono, T.; Niki, E.; Kamiya, Y. J Appl Polym Sci 1977, 21, 1635.
9. Mueller, W.; Jakob, I. Polym Degrad Stab 2003, 79, 161.
10. Vink, P.; Fontijn, H. F. N. Geotext Geomembr 2000, 18, 333.
11. Hsuan, Y. G.; Li, M. Geotext Geomembr 2005, 23, 55.
12. Schwartzenbach, K.; Gilg, B.; Müller, D.; Knobloch, G.; Pauquet, J. R.; Rota-Graziosi, P.; Schmitter, A.; Zingg, J. In Plastic Additives Handbook, 5th ed.; Zweifel, H., Ed.; Hanser Publisher: Munich, 2001; Chapter 1.
13. Tocháček, J. Polym Degrad Stab 2004, 86, 385.
14. Billingham, N. C. In Plastic Additives Handbook, 5th ed.; Zweifel, H., Ed.; Hanser Publisher: Munich, 2001; Chapter 20.
15. Fayolle, B.; Richaud, E.; Verdu, J.; Farcas, F. J Mater Sci 2008, 43, 1026.
16. Ferrara, G.; Bertoldo, M.; Scoponi, M.; Ciardelli, F. Polym Degrad Stab 2001, 73, 411.
17. Garrido-López, Á.; Sancet, I.; Montaño, P.; González, R.; Tena, M. T. J Chromotogr A 2007, 1175, 154.
18. Verdu, J.; Rychly, J; Audouin, L. Polym Degrad Stab 2003, 79, 503.
19. Aymes-Chodur, C.; Betz, N.; Legendre, B.; Yagoubi, N. Polym Degrad Stab 2006, 91, 649.
20. Faulkner, D. L. J Appl Polym Sci 1986, 31, 2129.
21. Abdel-Aziz, M. M.; Basfar, A. A. Nucl Instr Methods Phys Res B 2001, 185, 346.
22. Rudnik, E.; Szczucinska, A.; Gwardiak, H.; Szulc, A.; Winiarska, A. Therm Act 2001, 370, 135.
23. Gregorová, A.; Cibulková, Z.; Košíková, B.; Šimon, P. Polym Degrad Stab 2005, 89, 553.
24. Astruc, A.; Bartoloméo, P.; Fayolle, B.; Audouin, L.; Verdu, J. Polym Test 2004, 23, 919.
25. Pospíšil, J; Horák, Z.; Pilař, J.; Billingham, N. C.; Zweifel, H.; Nešpůrek, S. Polym Degrad Stab 2003, 82, 145.
26. Blumberg, M.; Boss, C. R.; Chien, J. C. W. J Appl Polym Sci 1965, 9, 3837.
27. Calvert, P. D.; Billingham, N. C. J Appl Polym Sci 1979, 24, 357.
28. Kolesnikova, N. N.; Tyuleneva, N. K.; Shlyapnikov, Y. A. Polym Degrad Stab 1993, 39, 305.
29. Tyuleneva, N. K.; Shlyapnikov, Y. A. Polym Degrad Stab 1995, 47, 257.
30. Zeynalov, E. B.; Allen N. S. Polym Degrad Stab 2004, 85, 847.
31. Zeynalov, E. B.; Allen, N. S. Polym Degrad Stab 2006, 91, 3390.
32. Boersma, A. Polym Degrad Stab 2006, 91, 472.
33. Audouin, L.; Gueguen, A.; Tcharkhtchi A.; Verdu, J. J Polym Sci Part A: Polym Chem 1995, 33, 921.
34. Fayolle, B.; Verdu, J.; Bastard, M.; Piccoz, D. J Appl Polym Sci 2008, 107, 1783.
35. Richaud, E. Ph.D Thesis. ENSAM. Paris, 2006.
36. Pospíšil, J. Polym Degrad Stab 1993, 40, 217.
37. Mallégol, J.; Carlsson, D. J.; Deschênes, L. Polym Degrad Stab 2001, 73, 259.
38. Pospíšil, J. Polym Degrad Stab 1993, 39, 103.
39. Pospíšil, J. In Developments in Polymer Stabilization-I; Scott, G., Ed.; Applied Polymer Sciences Publishers: London; 1979, Chapter 1.
40. Pospíšil, J.; Nešpůrek, S.; Zweifel, H. Polym Degrad Stab 1996, 54, 15.
41. Zweifel, H. In Polymer Durability—Degradation, Stabilization and Lifetime prediction; Clough, R. L., Billingham, N. C., Gillen K. T., Eds.; American Chem Society, 1996; pp 375–396.
42. Rivaton, A.; Cambon, S.; Gardette, J. L. Polym Degrad Stab 2006, 91, 136.
43. Hloušková, Z.; Lustoň, J.; Szöcs, F. J Appl Polym Sci 1993, 48, 1843.
44. Denisov, E. T.; Afanas'ev, I. B. In Oxidation and Antioxidants in Organic Chemistry and Biology; Taylor and Francis, CRC Press, 2005; Chapter 14, pp 465–489.
45. Denisov, E. T.; Afanas'ev, I. B. In Oxidation and Antioxidants in Organic Chemistry and Biology; Taylor and Francis, CRC Press 2005; Chapter 15, pp 491–561.
46. Private communication from Drs Flaconneche and Mougin, IFP, Reuil Malmaison, France.
47. Colin, X.; Audouin, L.; Verdu, J. Polym Degrad Stab 2004, 86, 309.