

KINETIC MODELLING OF PHENOL STABILISER EFFICIENCY IN POLYETHYLENE SUBMITTED TO NUCLEAR ENVIRONMENTS



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ABSTRACT

This work is aimed to build a non-empirical kinetic model for the lifetime prediction of electrical cable insulators exposed at low dose rates at room temperature in air, in nuclear plants. Previous studies have been devoted to the first stage of our approach, i.e. establish a kinetic model efficient for neat PE matrices whatever temperature and dose rates. This work deals with the second stage of our approach. It consists in proving that this approach is possible for stabilized matrices, in introducing the stabilisation reactions into the model and showing the performances of a first very simple model.

KEYWORDS

Lifetime prediction, kinetic modelling, polyethylene, phenolic antioxidants.

INTRODUCTION

1 – Typical approach for lifetime prediction

It has often been proposed that lifetime (denoted t_F) for insulating cables could be predicted by laws such as:

$$\text{Thermal ageing: } t_F = t_{F0} \cdot \exp\left(-\frac{E}{RT}\right) \quad [1]$$

$$\text{Radiochemical ageing: } t_F = t_{F0} \cdot I^{1/2} \cdot \exp\left(-\frac{E}{RT}\right) \quad [2]$$

T being the absolute temperature (K), I the dose rate (Gy s^{-1}). Nevertheless, it can be recalled that in case of thermal ageing (at low dose rates), such laws could be not well adapted because mechanisms significantly change with temperature. For example, true lifetime curve against reciprocal temperature is “down bended” whereas law 1 predicts a linear variation (Fig 1a) [1].

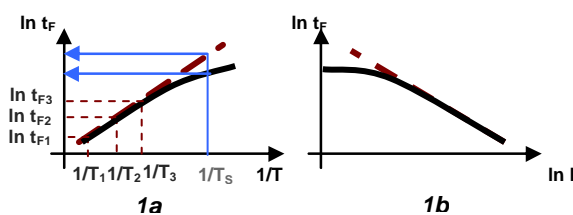
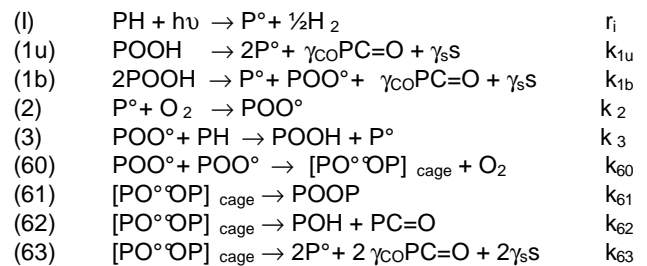


Figure 1: Methods for lifetime estimation from empirical laws (full lines) and shape of experimental lifetimes curves (dashed lines)

Law 2 is quite well adapted to accurately estimate lifetime at strong dose rates but at lower rates, it is now well established that lifetime is shortened by thermal oxidation processes (Fig 1b). Consequently, the aim of researches performed in our laboratory is to develop a non empirical tool for lifetime prediction being able to predict ageing kinetics whatever the mechanism (radio, thermal, or radio and thermal oxidation), this one being of course adapted to the material nature (chemical structure of polymer matrices and formulation).

2 – Lifetime prediction by kinetic modelling: case of pure PE radio-thermal oxidation

This approach is based on the mechanism of chemical (microscopic) structure changes:



In the classical frame of chemical kinetics, a system of differential equations is derived from this scheme:

$$\frac{d[\text{P}^\circ]}{dt} = r_i + 2k_{1u}[\text{POOH}] + k_{1b}[\text{POOH}]^2 - k_2[\text{P}^\circ][\text{O}_2] + k_3[\text{POO}^\circ][\text{PH}] + 2k_{63}[\text{PO}^\circ\text{OP}]_{\text{cage}} \quad [3]$$

$$\frac{d[\text{POO}^\circ]}{dt} = k_{1b}[\text{POOH}]^2 + k_2[\text{P}^\circ][\text{O}_2] - k_3[\text{POO}^\circ][\text{PH}] - 2k_{60}[\text{POO}^\circ]^2 \quad [4]$$

$$\frac{d[\text{POOH}]}{dt} = -k_{1u}[\text{POOH}] - 2k_{1b}[\text{POOH}]^2 + k_3[\text{POO}^\circ][\text{PH}] \quad [5]$$

$$\frac{d[\text{PO}^\circ\text{OP}]_{\text{cage}}}{dt} = k_{60}[\text{POO}^\circ]^2 - (k_{61} + k_{62} + k_{63})[\text{PO}^\circ\text{OP}]_{\text{cage}} \quad [6]$$

$$\frac{\partial[\text{O}_2]}{\partial t} = -k_2[\text{P}^\circ][\text{O}_2] + k_{60}[\text{POO}^\circ]^2 + D_{\text{O}_2} \cdot \frac{\partial^2[\text{O}_2]}{\partial x^2} \quad [7]$$

Where:

$$k_i = k_i(T)$$

$$r_i = \alpha I$$

$$[\text{O}_2] = s_{\text{O}_2} \times P_{\text{O}_2} \quad (s_{\text{O}_2} \text{ being the oxygen solubility in polymer})$$

In other words, instead of using environmental strains (T , I ,

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P_{O_2} ...) to assess lifetime value t_F by an empiric law such as Equations [1] or [2], we use these parameters as input data of the differential system. Its resolution (using mathematical software) gives output data of system:

- o Reactive species concentration: P° , POO° , $POOH$, $[PO^\circ OP]_{cage}$, PH , O_2 , as a function of time (in case of thin films), or time and depth (in case of thick samples).
- o Carbonyl species concentration, given by the equation:

$$\frac{d[CO]}{dt} = \gamma_{CO} k_{1u} [POOH] + \gamma_{CO} k_{1b} [POOH]^2 + \gamma_{CO} k_{62} [PO^\circ OP]_{cage} \quad [8]$$

- o The chain scissions rate is given by:

$$\frac{ds}{dt} = \gamma_S k_{1u} [POOH] + \gamma_S k_{1b} [POOH]^2 + 2\gamma_S k_{63} [PO^\circ OP]_{cage} \quad [9]$$

The changes of average molar mass (leading to mechanical properties lost) can be assessed by:

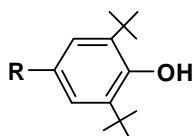
$$s(t) = \frac{1}{M_n(t)} - \frac{1}{M_n(0)} \quad [10]$$

Kinetic rate constants k_i and yields γ_{CO} and γ_S were previously estimated [2,3] and are usable without any restriction in a wide range of temperatures and dose rates. It was shown in many studies that this model could predict very reasonable values of lifetime whatever T and I values but only in case of pure PE.

APPLICATION TO STABILIZED MATERIALS

Lifetime prediction by kinetic modelling can be a very efficient tool because prediction is possible without performing lot of expensive and time-consuming laboratory tests. Nevertheless, the kinetic model (including kinetic parameter values) has to be adapted to the considered material. For example, a model established for PE is different to the one established for PP (concerning k_i values) or a copolymer (for structure of model). In the same way, the model obtained for a pure PE has to be completed in order to describe oxidation kinetics of stabilized PE matrices.

Kinetic modelling of stabilized polymers could seem a very difficult work, since there are a wide variety of stabilizer packages. The amount of work could be considerably diminished considering for example that the same model could be employed for all mixtures of PE with any stabilizers of a given family. In the present work, we will focus on this last assumption and try to demonstrate it in the case of antioxidants molecules from the family of 2,6 di-tertbutyl-phenol with various R- *para* substituents:



Our objective is not, of course, to solve completely the problem but at least to try to prove that kinetic modelling is a pertinent tool able to predict lifetime of stabilized polymers.

3.1 – Experimental observations

For PE samples only containing various amounts of stabilizers, experimental data cropped into literature are gathered on the same curve lifetime versus stabilizer amount $[AH]$, with:

$$[AH] = \frac{d}{M_{AH}} \times f_{AH} \times X_{AH} \quad [11]$$

- o $[AH]$ being the total phenolic function concentration
- o d being the polymer density
- o M_{AH} being the molar mass of the molecule
- o f_{AH} being its functionality (4 for Irganox 1010, 1 for Irganox 1076...)
- o X_{AH} being the weight ratio of antioxidant (what is “engineering” measure of additive amount)

Presented results were obtained for thin films (thickness lower than 500 μm) and for concentrations lower or on the order of the solubility limit [4]. In the chosen conditions, the timescale of antioxidant physical loss by evaporation/diffusion is noticeably longer than the time scale of antioxidant chemical consumption, so that it can be considered that here, what is compared is essentially the stabilizer chemical reactivity (reactivity with “oxidation active centres”).

The curves lifetime versus $[AH]$ are given in Figures 2, 3, 4 and 5. t_F is the time to reach an end-of-life criterion, as for example a given CO concentration, elongation at break or TIO (measured by DSC) value...

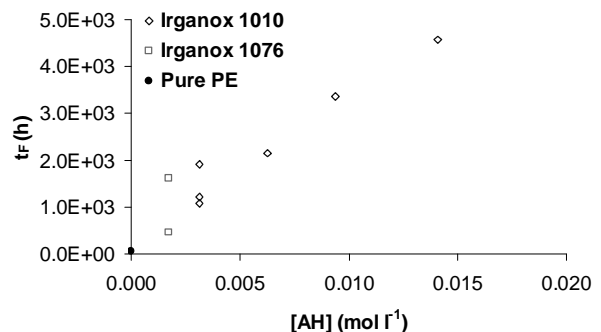


Figure 2: Induction period values of PE stabilized with various antioxidants for oxidations performed under air at 110°C ($I=0$) [5,6]

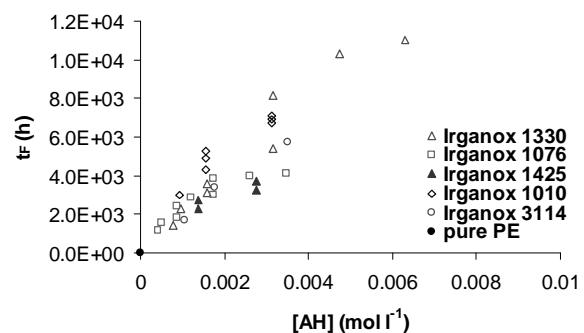


Figure 3: Induction period values of PE stabilized with various antioxidants for oxidations performed under air at 120°C ($I=0$) [7-9]

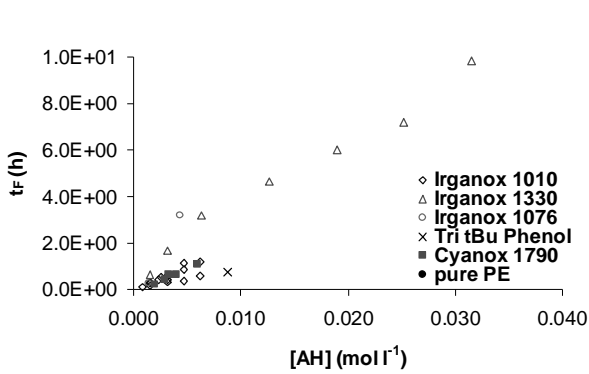


Figure 4: Induction period values of PE stabilized with various antioxidants for oxidations performed under air at 200°C (I=0) [8-13]

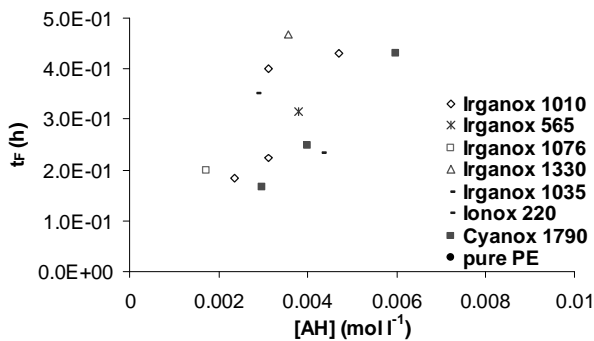


Figure 5: Induction period values of PE stabilized with various antioxidants for oxidations performed under air at 210°C (I=0) [12-14]

Whatever the temperature, induction period durations of course increase with the amount of stabilizers, with a basically linear trend. It is interesting to investigate for each kind of phenolic antioxidant molecule the slope of the straight lines “induction period-concentration of stabilizers”.

	$(t_{ind}-t_{ind0})/[AH]_0$ (s l mol ⁻¹)	
	average	std-dev
Irganox 1010	1.37 10 ⁹	0.37 10 ⁹
Irganox 1076	8.09 10 ⁸	0.17 10 ⁹

Table 1: Dependence of lifetime values with initial amount of di-tertbutyl-phenol functions [AH]₀ at 110°C

	$(t_{ind}-t_{ind0})/[AH]_0$ (s l mol ⁻¹)	
	average	std-dev
Irganox 1010	9.74 10 ⁹	1.84 10 ⁹
Irganox 1076	7.73 10 ⁹	2.16 10 ⁹
Irganox 1330	7.46 10 ⁹	1.16 10 ⁹
Irganox 1425	5.50 10 ⁹	1.23 10 ⁹
Irganox 3114	6.09 10 ⁹	0.63 10 ⁹

Table 2: Dependence of lifetime values with initial amount of di-tertbutyl-phenol functions [AH]₀ at 120°C

	$(t_{ind}-t_{ind0})/[AH]_0$ (s l mol ⁻¹)	
	average	std-dev
Irganox 1010	5.63 10 ⁵	1.74 10 ⁵
Irganox 1076	1.64 10 ⁶	1.41 10 ⁶
Irganox 1330	1.39 10 ⁶	0.34 10 ⁵
Tri tBu phenol	2.94 10 ⁵	-
Cyanox 1790	5.62 10 ⁵	1.30 10 ⁵

Table 3: Dependence of lifetime values with initial amount of di-tertbutyl-phenol functions [AH]₀ at 200°C

	$(t_{ind}-t_{ind0})/[AH]_0$ (s l mol ⁻¹)	
	average	std-dev
Irganox 1010	3.23 10 ⁵	0.91 10 ⁵
Cyanox 1790	2.20 10 ⁵	0.32 10 ⁵

Table 4: Dependence of lifetime values with initial amount of di-tertbutyl-phenol functions [AH]₀ at 210°C

For the four temperatures under investigation, it is obvious that the slopes of straight lines are really close for one stabilizer to another, and only depend on temperature. One could object that standard deviations are not negligible (they are in the most cases lower or on the order of 25% of the averages), but in our mind, it is not surprising given the diversity of data sources, samples differing by their processing, thickness, analysis method sensitivity.

These results clearly suggests the existence of a quasi-universal behaviour for hindered phenolic antioxidants similarly as an universal one was also established in case of “pure” PE [15]. Consequently, the embrittlement due to radio-thermal oxidation kinetics can be predicted by a single model, that we will try to elaborate in the following of the paper.

3.2 – Proposal of kinetic modelling

It is well established that phenolic antioxidants react by giving hydrogen atom to peroxy radical POO°[9]:



To take into account stabilization phenomena, model (1u)...(63) is completed with equation (S1). It involves modifying two differential equations:

$$\frac{d[POO^\circ]}{dt} = k_{1b}[POOH]^2 + k_2[P^\circ][O_2] - k_3[POO^\circ][PH] - 2k_{60}[POO^\circ]^2 - k_{s1}[POO^\circ][AH] \quad [12]$$

$$\frac{d[POOH]}{dt} = -k_{1u}[POOH] - k_{1b}[POOH]^2 + k_3[POO^\circ][PH] + k_{s1}[POO^\circ][AH] \quad [13]$$

Supplementary equation describing stabilizer consumption is also added:

$$\frac{\partial[AH]}{\partial t} = -k_{s1}[POO^\circ][AH] + \frac{\partial^2[AH]}{\partial x^2} \quad [14]$$

In thin films (typically such as samples whose results are presented in Figures 2, 3, 4, 5), one can neglect in a first approximation the gradient of stabilizer concentration in

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thickness. Last equation becomes:

$$\frac{\partial[AH]}{\partial t} = -k_{S1}[POO^\bullet][AH] \quad [15]$$

Let's precise that kinetic rate constant $k_{1u} \dots k_{63}$ values that were previously determined [2,3] are still valid: the model is completed but its core layer (1u)...(63) keeps unchanged. That way, we want to highlight the matter that the model we build draws on capitalizable data.

In the following, the kinetic model (1u)...(63)(S1) in case of low thicknesses (*i.e.* using equation [15] instead of [14]) will be performed and its results will be compared with the previously reported experimental trends in order to evaluate its reliability.

3.3 – Performances of this kinetic modelling

Thermal oxidation

Can this model simulate the oxidation kinetics (or at least its main features) of a phenolic antioxidant stabilized PE?

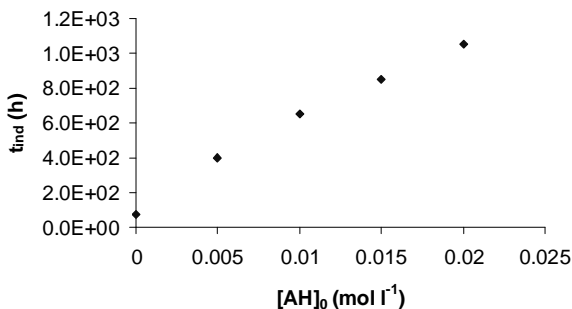


Figure 6: Variations of induction period duration (simulated by model at 110°C under air, $l = 0$) with initial amount of di-tertbutyl-phenol functions $[AH]_0$ ($k_{S1} = 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$)

To answer to this crucial question, we have plotted variations of induction period t_{ind} (given by CO build-up obtained from model simulation – see Equation [7]) against initial concentration of phenol function $[AH]_0$ (Figure 6) and k_{S1} (Figure 7). Both curves call for the following comments:

- t_{ind} increases with $[AH]_0$ (Figure 6). This result is not surprising but the experimentally observed quasi linear variation is well simulated by model curves, which can not be a simple coincidence and constitutes a good argument in favour of the proposed model.

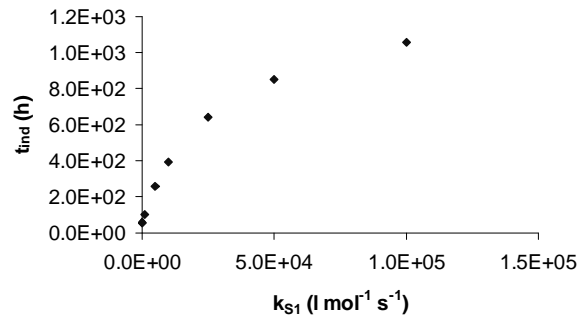


Figure 7: Variations of induction period duration (simulated by model at 110°C under air, $l = 0$) with k_{S1} value ($[AH]_0 = 0.005 \text{ mol l}^{-1}$)

- Figure 7 shows that induction period at 110°C of a PE stabilized with 0.005 mol l^{-1} of phenol (experimentally on the order of 1000 h) can be simulated with rate constant k_{S1} ranging from 5×10^3 to $10^4 \text{ l mol}^{-1} \text{ s}^{-1}$ *i.e.* differing by less than one decade. Consequently, kinetic rate constants of (S1) reaction would be on the same order of magnitude for a given family of stabilizer. Studies on e.g. Irganox 1010 would lead to assess k_{S1} (Irganox 1010). This value would be very close (ratio is less than one decade) to the one for others hindered phenols.

Radio oxidation

After having built a model able to acceptably simulate the thermo-oxidative ageing of stabilized materials (at very low dose rate), we have focused on the case of radio-thermal (medium dose rates) and radio ageing (high dose rates). To this purpose, we have compared CO build-up (that is an output data of the model given by Equation [8]) for additive free PE or PE containing 5 mmol l^{-1} of antioxidant. Oxidations were simulated and compared for ageing at 110°C under air with samples submitted to various dose rates (ranging for 10^2 to $10^{-15} \text{ Gy s}^{-1}$). Let's recall that l is a data entry of our model to simulate radiation effect (see Equation [3]). The results are given on Figures 8 and 9:

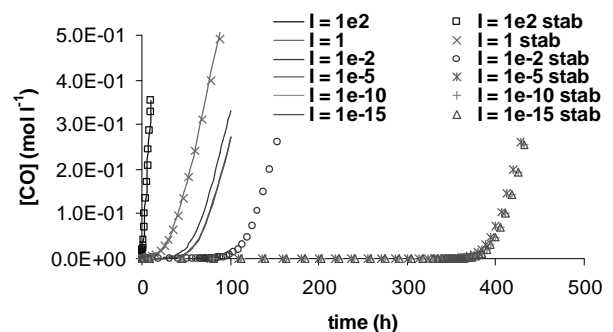


Figure 8: Variations of induction period duration simulated by model at 110°C under air for ageing under various dose rates (full lines : $[AH]_0 = 0$ - □, ×, ◇, *, +, △ : $[AH]_0 = 0.005 \text{ mol l}^{-1}$, $k_{S1} = 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$)

At enhanced dose rates (typically corresponding to a "pure" radiochemical ageing), curves for ageing of stabilized and non-stabilized polymers are quasi-undistinguishable. At very low dose rates (under $10^{-5} \text{ Gy s}^{-1}$), curves of stabilized polymer are significantly shifted to the long lifetime durations.

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The effect of antioxidants on the different ageing modes is visible on Figure 9:

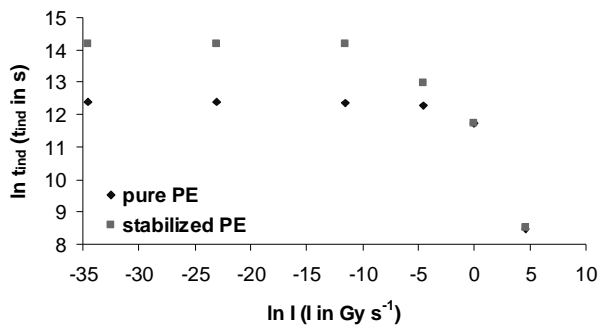


Figure 9: Variations of induction period duration simulated by model at 110°C under air for ageing under various dose rates, (♦ : pure PE, ■ : [AH]₀ = 0.005 mol l⁻¹, k_{S1} = 10⁴ l mol⁻¹ s⁻¹)

This curve illustrates the matter that antioxidants are effective in case of thermochemical ageing (low dose rates) but not in case of radiochemical ageing (high dose rates), which recently was reported by Gardette and coll. [16].

3.4 – Possible improvements of this kinetic modelling

Reactions of A° radical

Of course, such a model could be completed to take into account reactions occurring with A° radicals.

A° can react by many pathways, for example with O₂ to give an AOO° radical, with another A°, or with POO° radical, what leads to an inactive form. In a first simplified approach, we could assume that the main reaction is:



This represents the advantage to be in good agreement with the experimentally observed balance on phenolic antioxidant consumed and POO° trapped (on the order of 2). In this case, Equation [12] is modified:

$$\frac{d[POO^\circ]}{dt} = k_{1b}[POOH]^2 + k_2[P^\circ][O_2] - k_3[POO^\circ][PH] - 2k_{60}[POO^\circ]^2 - k_{S1}[POO^\circ][AH] - k_{S2}[POO^\circ][A^\circ] \quad [16]$$

And another equation is added to the differential system since, A° can be considered as a reactive specie:

$$\frac{d[A^\circ]}{dt} = k_{S1}[POO^\circ][AH] - k_{S2}[POO^\circ][A^\circ] \quad [17]$$

Physical phenomena: diffusion and solubility

For thick samples, diffusion has also to be taken into account, but this step is much easier to achieve, because it just consists in using Equation [14] instead of Equation [15] the diffusion coefficient being well known thanks to numerous studies [17]. In the same way, it is also certainly necessary to take into account limit of solubility, because a stabilizer mixed at a much higher concentration than solubility limit could exsudate more than stabilize and display therefore a lower efficiency than expected. This parameter is also well known

for many common phenolic antioxidants [4]. This step will therefore essentially consist in programming a mathematical function in kinetic model giving true concentration as a function of mixed concentration.

CONCLUSIONS

Predicting lifetime of stabilized polymers remains a crucial issue for any industrial applications. In this work, we have first recalled limits of empirical methods. Then we have presented a non empirical model, but only valid for additive free PE. We have then strived to demonstrate a quasi-universal chemical behaviour of phenolic antioxidants, which constitutes for us the major argument in favour of using kinetic modelling to predict stabilized PE lifetime. Consequently, the “pure PE” model has been completed on the basis of well established stabilization mechanism. The completed model is able to evaluate the main trends of oxidation of stabilized PE lifetime whatever the temperature and dose rate: influence of concentration and of dose rate for example. It also confirms the quasi-universal chemical behaviour of phenolic antioxidants by considerations about kinetic rate constant k_{S1} value. This one takes the same order of magnitude for the considered family of stabilizers under investigation. Consequently, a study on one molecule with a precise assessment of rate constants would be a good point of start for assessment of rate constants k_{S1} of the other compounds of the family. It opens the way to perform a non empirical, easy and cost-saving lifetime prediction of all the family of binary systems phenols-PE.

Acknowledgments

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PH: Polymer substrate (generic reactive specie)
P°: Alkyl radical
POO°: Peroxy radical
POOH: Hydroperoxyde
O₂: Oxygen
AH: 2,6 di-tertbutyl-phenol function (generic phenolic antioxidant)
A°: phenoxy radical (derivate of AH)
T: Temperature
I: Dose rate
P_{O₂}: Oxygen partial pressure
[M]: Concentration of M specie
s_M: Solubility of M specie into amorphous phase of polymer
D_M: Diffusion coefficient of M specie
k_i: Kinetic rate constant of i reaction
t_{ind}: Induction period (time to reach a given CO value)
t_F: Lifetime (time to reach an end-of-life criterion)

GLOSSARY

PE: Polyethylene