Towards a Non Empirical Kinetic Model for the Lifetime Prediction of Polyethylene Pipes Transporting Drinking Water

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Summary: A kinetic model has been elaborated to predict the lifetime of polyethylene pipes transporting slightly pressurized (3–12 bars) drinking water disinfected by free radical reagents. This model is composed of three levels: i) A system of differential equations, derived from a mechanistic scheme for radical chain oxidation in the presence of free radical reagents, giving access to the spatial distribution (in the pipe wall) of oxidation products and stabilizer concentration; ii) Equations allowing to predict the profiles of average molar masses from the spatial distribution of chain scissions and crosslinking events; iii) An empirical creep equation and a failure criterion derived from regression curves obtained in pure water (without disinfectant). It is assumed that the chemical degradation modifies only the time to transition between ductile and brittle regimes of failure, and that this time is linked to the weight average molar mass according to the classical power law. By superimposing these three levels, it is possible to predict the time to failure under the coupled effects of pressure and chemical degradation. This model is successfully applied to the case of chlorine dioxide.

Keywords: chlorine dioxide; failure; kinetic modelling; oxidation; polyethylene

Introduction

It is well known that polyethylene (PE) pipes transporting slightly pressurized water undergo failure after a time t_F which is a decreasing function of pressure p and temperature T. Laboratory isothermal and isobaric experiments aimed to establish the dependence of t_F with T and p, are usually translated into (log σ–log t_F) regression plots, σ being the hoop stress. Starting from the observation that, in certain (σ, t_F) domains, these plots are quasi-linear, international standards propose to characterize the material by the equations of the corresponding straightlines [e.g. NFT 54091 (AFNOR)]. In the case of a PE generation anterior to the PE 80 one, three kinetic regimes corresponding to three distinct straightlines were put in evidence.[1–3] By watching the graph from the highest to the lowest stresses (i.e. from the shortest to the longest lifetimes), one can distinguish: The ductile regime (I) ($\mu = d(\log \sigma)/d(\log t_F) \approx 0.03$); The "physical" brittle regime (II) obtained in the absence of chemical degradation ($\mu \approx 0.3$); and the "chemical" brittle regime (III) involving a chemical degradation of the polymer ($\mu \gg 0.3$). The differences between regimes (II) and (III) can be established from molar mass measurements. Indeed, the molar mass distribution is not affected in regime (II), whereas it is shifted towards low values in regime (III). If the chemical degradation is fast enough, regime (III) can totally supplant regime (II) (Figure 1).

Water is non reactive with PE, but it contains generally two reactive species:

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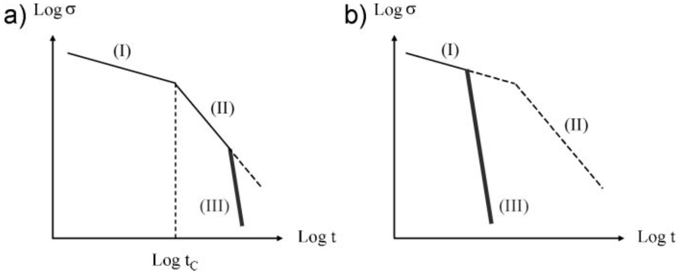

Figure 1.
Shape of regression plots with three regimes of failure. (a) Slow chemical degradation; (b) Fast chemical degradation.

oxygen and disinfectants. In current use conditions on water distribution networks (under 3–12 bars of water pressure, at 15 °C), but in the absence of disinfectant, the "chemical lifetime" is longer than the "physical aging lifetime" t_C and regime (II) becomes the predominant mode of failure. The time to failure t_F is higher than 50 years, that seems to satisfy entirely practitioners. In this case, various mechanical/physical approaches have been proposed for lifetime prediction.[4–6]

However, disinfectants, especially chlorine derivatives, are known to destroy organic compounds by free radical processes. It is true that PE presents a relatively high chemical stability, but zero radical reactivity would be surprising because radical reactions are never totally selective. Moreover, PE contains antioxidants, generally hindered phenols, which are very sensitive to radical processes.[7] Disinfectants are thus expected to shorten PE pipe lifetime, at least by accelerating the antioxidants consumption. This latter has been clearly put in evidence from experimentally established antioxidants concentration profiles. Antioxidants are consumed more rapidly in the presence than in the absence of disinfectant in water, at least in a superficial layer at the water–polymer interface.[8,9] The aim of the present article is to elaborate a non empirical kinetic model to try to answer the following questions: Is the disinfectant–PE reaction negligible or not? Which is the role of oxidation? Which is the embrittlement mechanism? How to predict the times to embrittlement and fracture?

The Kinetic Model

The kinetic model for lifetime prediction is composed of three levels.

i) The first "chemical" level is derived from the PE thermal oxidation mechanistic scheme established at low temperature,[10,11] but completed to take into account the main stabilization reactions by phenols antioxidants,[12] and the chemical attack of PE and these antioxidants by radicals coming from the disinfectant Y°.[13] This scheme can be summarized as follows:

where Q represents an cage paired alkoxyl radicals, and S and X the respective chain scissions and crosslinking events.

γ_S and γ_{CO} are the respective yields for chain scission and ketones formation, and

(1d)	$Y^{\circ} + PH$	$\rightarrow P^{\circ} + \text{inactive products}$	(k_{1d})
(1u)	$POOH$	$\rightarrow 2P^{\circ} + \gamma_S S + \gamma_{CO} P{=}O$	(k_{1u})
(1b)	$2POOH$	$\rightarrow P^{\circ} + PO_2^{\circ} + \gamma_S S + \gamma_{CO} P{=}O$	(k_{1b})
(2)	$P^{\circ} + O_2$	$\rightarrow PO_2^{\circ}$	(k_2)
(3)	$PO_2^{\circ} + PH$	$\rightarrow POOH + P^{\circ}$	(k_3)
(4)	$P^{\circ} + P^{\circ}$	$\rightarrow \text{in. prod.} + \gamma_4 X$	(k_4)
(4d)	$P^{\circ} + Y^{\circ}$	$\rightarrow \text{in. prod. } (P - Y)$	(k_{4d})
(5)	$P^{\circ} + PO_2^{\circ}$	$\rightarrow \text{in. prod.} + (1 - \gamma_5)\text{-}POOH + \gamma_5 X$	(k_5)
(60)	$PO_2^{\circ} + PO_2^{\circ}$	$\rightarrow Q + O_2$	(k_{60})
(61)	Q	$\rightarrow POOP + X$	(k_{61})
(62)	Q	$\rightarrow P{=}O + P\text{–}OH$	(k_{62})
(63)	Q	$\rightarrow 2P^{\circ} + 2\gamma_S S + 2\gamma_{CO} P{=}O$	(k_{63})
(7)	$PO_2^{\circ} + AH$	$\rightarrow POOH + \text{in. prod.}$	(k_7)
(8d)	$Y^{\circ} + AH$	$\rightarrow \text{in. prod.}$	(k_{8d})

γ_4 and γ_5 the yields for crosslinking events in the considered reactions.

This scheme leads to the following set of differential (non linear) equations:

$$\frac{d[P^\circ]}{dt} = k_{1d}[Y^\circ][PH] + 2k_{1u}[POOH] + k_{1b}[POOH]^2 - k_2[O_2][P^\circ] + k_3[PH][PO_2^\circ] - 2k_4[P^\circ]^2 - k_{4d}[P^\circ][Y^\circ] - k_5[P^\circ][PO_2^\circ] + 2k_{63}[Q] \quad (1)$$

$$\frac{d[PO_2^\circ]}{dt} = k_{1b}[POOH]^2 + k_2[O_2][P^\circ] - k_3[PH][PO_2^\circ] - k_5[P^\circ] \times [PO_2^\circ] - 2k_{60}[PO_2^\circ]^2 - n_{AH}\, k_7[PO_2^\circ][AH] \quad (2)$$

$$\frac{d[POOH]}{dt} = -k_{1u}[POOH] - 2k_{1b}[POOH]^2 + k_3[PH][PO_2^\circ] + (1-\gamma_2)k_5[P^\circ] \times [PO_2^\circ] \quad (3)$$

$$\frac{d[Q]}{dt} = k_{60}[PO_2^\circ]^2 - (k_{61} + k_{62} + k_{63})[Q] \quad (4)$$

$$\frac{d[PH]}{dt} = -k_{1d}[Y^\circ][PH] - (2+\gamma_S)k_{1u}[POOH] - (1+\gamma_S)k_{1b}[POOH]^2 - k_3[PH][PO_2^\circ] + 2\gamma_4 k_4[P^\circ]^2 + (3\gamma_5 - 1)k_5[P^\circ][PO_2^\circ] + 2k_{61}[Q] - 2(1+\gamma_S)k_{63}[Q] \quad (5)$$

$$\frac{d[O_2]}{dt} = D_{O2}\frac{\partial^2[O_2]}{\partial z^2} - k_2[O_2][P^\circ] + k_{60}[PO_2^\circ]^2 \quad (6)$$

$$\frac{d[Y^\circ]}{dt} = D_{Y^\circ}\frac{\partial^2[Y^\circ]}{\partial z^2} - k_{1d}[Y^\circ][PH] - k_{4d}[P^\circ][Y^\circ] - n_{AH}k_{8d}[Y^\circ] \times [AH] \quad (7)$$

$$\frac{d[AH]}{dt} = D_{AH}\frac{\partial^2[AH]}{\partial z^2} - n_{AH}k_{8d}[Y^\circ][AH] - n_{AH}k_7[PO_2^\circ][AH] \quad (8)$$

$$\frac{d[P=O]}{dt} = \gamma_{CO}k_{1u}[POOH] + \gamma_{CO}k_{1b}[POOH]^2 + k_{62}[Q] + 2\gamma_{CO}k_{63}[Q] \quad (9)$$

$$\frac{d[P-Y]}{dt} = k_{4d}[P^\circ][Y^\circ] \quad (10)$$

$$\frac{dS}{dt} = \gamma_S k_{1u}[POOH] + \gamma_S k_{1b}[POOH]^2 + 2\gamma_S k_{63}[Q] \quad (11)$$

$$\frac{dX}{dt} = \gamma_4 k_4[P^\circ]^2 + \gamma_5 k_5[P^\circ][PO_2^\circ] + k_{61}[Q] \quad (12)$$

where n_{AH} is the number of phenol groups per antioxidant molecule and D_{O2}, D_{Y° and D_{AH} are the respective diffusion coefficients of oxygen, antioxidant and disinfectant into the polymer.

z is the spatial co-ordinate in the pipe wall, the origin ($z = 0$) being taken at the water/polymer interface (at the internal pipe surface).

This system admits the following boundary conditions:

When $t = 0$, at any z in the pipe wall:

$[P^\circ] = [PO_2^\circ] = [Q] = 0$, $[POOH] = [POOH]_{t=0} = 10^{-2}\,mol \cdot l^{-1}$, $[PH] = [PH]_{t=0} = 60\,mol \cdot l^{-1}$, $[O_2] = [O_2]_{t=0} = 3.8 \times 10^{-4}\,mol \cdot l^{-1}$, $[AH] = [AH]_{t=0}$ and $[Y^\circ] = 0$.

When $t > 0$, at the water/polymer interface (at $z = 0$):

$[O_2] = [O_2]_{z=0} = 3.8 \times 10^{-4}\,\mathrm{mol \cdot l^{-1}}$, $D_{AH}\ \left(\partial^2[AH]_{z=0}/\partial z^2\right) = -\beta_{AH0}[AH]_{z=0}$ and $[Y^\circ] = [Y^\circ]_{z=0}$.

When $t > 0$, at the air/polymer interface (at $z = L$):

$[O_2] = [O_2]_{z=0} = 3.8 \times 10^{-4}\,\mathrm{mol \cdot l^{-1}}$, $D_{AH}\ \left(\partial^2[AH]_{z=L}/\partial z^2\right) = -\beta_{AHL}[AH]_{z=L}$ and $\partial^2[Y^\circ]_{z=L}/\partial z^2 = 2\left([Y^\circ]_{z=(L-\Delta Z)} - [Y^\circ]_{z=L}\right)/\Delta z^2$ (even function).

β_{AH0} and β_{AHL} are the respective coefficients for antioxidant extraction/evaporation at the water/polymer (at the internal pipe surface) and air/polymer interfaces (at the external pipe surface).

The different transport and kinetic parameters: coefficients of diffusion D_i and antioxidant extraction/evaporation β_i, rate constants k_i and yields γ_i, have been determined step by step in previous studies dedicated to:

- Thermal oxidation of pure PE at moderate temperature (typically for $T < 80\,°C$);[10,11]
- Oxidation of pure and stabilized PE initiated by the chemical attack by chlorinated disinfectants in high concentration in water (up to 100 ppm) at low temperature (at 20 and 40 °C);[13–14]

Their values are recalled in Table 1.

This "stiff" system of differential equations has been numerically solved using the Rosenbrock's semi-implicit algorithm. Its resolution gives access to the spatial distribution in the pipe wall (against z) of the concentrations of the different chemical species involved in the mechanistic scheme (in particular, the numbers of chain scissions S and crosslinking events X), and its change against time of exposure (t).

ii) A second "physical" level constituted by the two Saito's equations:[15]

$$\frac{1}{M_n} - \frac{1}{M_{n0}} = S - X \tag{13}$$

$$\frac{1}{M_W} - \frac{1}{M_{W0}} = \frac{S}{2} - 2X \tag{14}$$

where M_{n0}, M_n, M_{W0} and M_W are respectively the number and weight average molar masses before and after ageing.

Table 1.
Arrhenius parameters and resulting values at 15 °C of kinetic parameters (rate constants, coefficients of diffusion and antioxidant extraction/evaporation, and yields) for kinetic modelling. Values of rate constants are expressed in $\mathrm{l \cdot mol^{-1} \cdot s^{-1}}$ or $\mathrm{s^{-1}}$, coefficients of diffusion in $\mathrm{m^2 \cdot s^{-1}}$ and antioxidant extraction/evaporation in $\mathrm{s^{-1}}$.

Parameter	Pre-exponential factor	Activation energy ($\mathrm{kJ \cdot mol^{-1}}$)	Value at 15 °C
k_{1d}	2.7×10^{-5}	0	2.7×10^{-5}
k_{1u}	8.0×10^{12}	140	3.4×10^{-13}
k_{1b}	2.8×10^{9}	105	2.6×10^{-10}
k_2	10^{8}	0	10^{8}
k_3	1.5×10^{10}	73	8.8×10^{-4}
k_4	8.0×10^{11}	0	8.0×10^{11}
k_{4d}	6.6×10^{9}	21.1	9.9×10^{5}
k_5	1.5×10^{12}	5.9	1.3×10^{11}
k_{60}	4.9×10^{19}	80	1.6×10^{5}
k_{61}	2.0×10^{6}	0	2.0×10^{6}
k_{62}	1.2×10^{6}	5	1.5×10^{5}
k_{63}	4.8×10^{9}	17.4	3.4×10^{6}
k_7	1.3×10^{9}	49.9	1.1
k_{8d}	5.0×10^{-2}	0	5.0×10^{-2}
D_{O2}	4.3×10^{-5}	35	1.9×10^{-11}
D_{ClO2}	2.0×10^{-11}	0	2.0×10^{-11}
D_{AH}	9.1×10^{4}	115.7	9.7×10^{-17}
β_{AH0}	1.9×10^{-9}	0	1.9×10^{-9}
β_{AHL}	1.0×10^{-10}	0	1.0×10^{-10}
γ_S	–	–	100%
γ_{CO}	–	–	61%
γ_4	–	–	50%
γ_5	–	–	0

The principal goal of these functions is to generate, at any time t, the molar mass profile in the pipe wall.

iii) In order to predict the pipes lifetime, it is necessary to interface the kinetic model with a third "mechanical" level, in which are coupled the creep and chemical degradation effects. This last stage is derived from the regression plots obtained in pure water (without disinfectant) and from the three following assumptions.

- The material is characterised, in its brittle regime (II), by the following empirical creep law:

$$\dot{\varepsilon} = k\, e_T\, \sigma\, t^{-a} \tag{15}$$

where the "strain" rate $\dot{\varepsilon}$ is considered as the progress parameter of the process responsible for the failure, and e_T is an Arrhenius function describing the temperature dependence of the material creep:

$$e_T = \exp - \frac{H_e}{RT} \tag{16}$$

a is an exponent expressing the self-retardated character of the polymer creep: $a \approx 0.7$.

k is a constant.

The integration of this equation leads to the "strain" expression:

$$\varepsilon = \int_0^t \dot{\varepsilon}\, dt = \frac{k\, e_T}{1-a} \sigma\, t^{1-\alpha} \tag{17}$$

So that:

$$t = \left[\frac{\varepsilon}{k} \frac{(1-\alpha)}{e_T}\right]^{-\frac{1}{1-a}} \sigma^{-\frac{1}{1-a}} \tag{18}$$

- The material is also characterized by an endlife criterion:

$$\varepsilon = \varepsilon_F \tag{19}$$

that leads to the following lifetime expression:

$$t_F = \left[\frac{\varepsilon_F}{k} \frac{(1-a)}{e_T}\right]^{-\frac{1}{1-a}} \sigma^{-\frac{1}{1-a}} \tag{20}$$

which can be also written such as:

$$\mathrm{Log}\, t_F = \mathrm{Log}\, t_{F0} - \frac{1}{1-a} \log \sigma \tag{21}$$

where $\mathrm{Log}\ t_{F0} = \frac{1}{1-a} \mathrm{Log}\left[\frac{\varepsilon_F}{k} \frac{(1-a)}{e_T}\right]$

Thus, the apparent activation energy of t_F is given by:

$$H = \frac{1}{1-a} H_e \tag{22}$$

with $H \approx 85{,}5\, \mathrm{kJ \cdot mol^{-1}}$ [1]

However, Equation (21) must also describe the shape of experimental results obtained in regime (II) in the absence of any chemical degradation:

$$\mathrm{Log}\, t_F = \mathrm{Log}\, t_d - b \log \sigma \tag{23}$$

with $\mathrm{Log}\ t_d \approx 27.9$ and $b \approx 27$

After some adequate transformations, one obtains finally:

$$\mathrm{Log}\, t_F = \mathrm{Log}\, t_d + m\, \mathrm{Log}\, t_C - \frac{1}{1-a} \mathrm{Log}\, \sigma \tag{24}$$

where t_C is the abscissa of the intersection point between the straightlines describing regimes (I) and (II) in Figure 1, and $m \approx 0.95$

- The transition from ductile to brittle regime is attributed to chain disentanglement in the amorphous phase. The corresponding time t_C is thus a decreasing function of the molar mass M_W, this function being chosen so that it describes the results available on the effect of molar mass on the regression plots. α could be in principle determined from experiments on pipes differing by their molar mass distribution in the absence of chemical degradation. At the present time, it can be reasonably assumed that:

$$t_C \propto M_W^a \tag{25}$$

with $\alpha = 3.4$.

Since t_C and t_d have the same activation energy H, the lifetime in regime (III) can be written:

$$\mathrm{Log}\, t_F = A_0 + \frac{H}{2.3\, RT}(1+m) + \alpha\, m\, \mathrm{Log} M_w - \frac{1}{1-a} \mathrm{Log}\, \sigma \tag{26}$$

where A_0 is a coefficient containing all the pre-factors.

The different kinetic parameters of this law have been determined in the brittle regime (II) of the regression plots. As an example, for PE generations anterior to the PE80 one at 15 °C, their values are given in Table 2.

Then, Equation 1 to 14 plus Equation 26 constitute the general model for lifetime

Table 2.
Values of the kinetic parameters used for lifetime prediction 15 °C.

Parameter	A_o	$\frac{H}{2.3\,RT}(1+m)$	α m	$\frac{1}{1-a}$
Value	−29.7	30.2	3.2	3.3

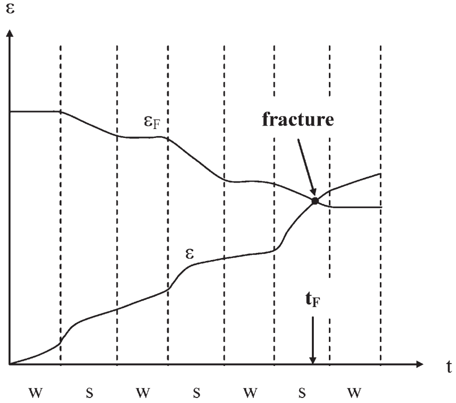

Figure 2.
Schematization of a pipe story. (w) winter. (s) summer.

prediction of PE pipes transporting drinking pressurized water disinfected (but also non disinfected) by free radical reagents. The two first levels (the ''chemical'' and the ''physical'' levels) calculate, at any time t, the value of M_W in an elementary sublayer situated at an arbitrarily depth, for instance 100 μm,[16] in the internal pipes wall. The value of M_W is then injected in the ''mechanical'' level which calculates, at any time t, the values of the ''strain'' ε and the endlife criterion ε_F. The failure is reached when ε equals ε_F, as shown in Figure 2.

Application to Chloride Dioxide (DOC)

There are several ways to check the validity of the kinetic model. As an example, one can calculate the profiles in the pipe wall of:

- Antioxidants concentration (determined by differential calorimetry, assuming that the oxidation induction time (OIT) is directly proportional to the remaining antioxidants concentration[17,18]);
- Carbonyl groups build-up (determined by IR spectrophotometry);
- Chlorine grafted to polymer (determined by elemental analysis);
- Weight average molar masses (determined by rheometry in molten state);

One can also determine the lifetimes of pipes naturally aged in the drinking water distribution networks.

Of course, the predictions are as good as the input data of the kinetic model are. In practice, the main unknown parameters are:

- The initial composition (exact nature and concentration of antioxidants) and structural state (cristallinity) of the PE under consideration;

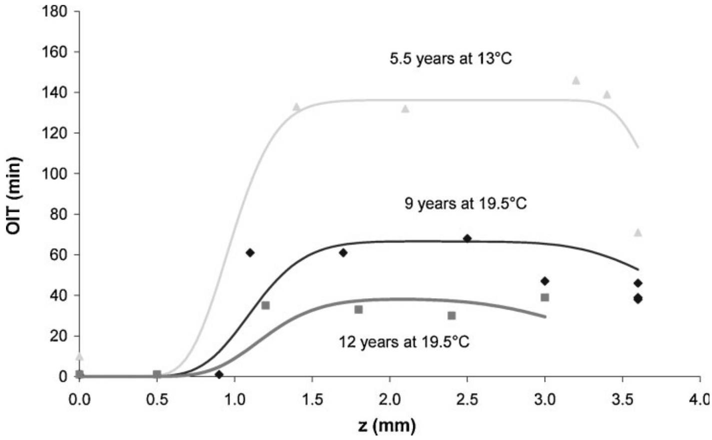

Figure 3.
Examples of simulations of oxidation induction time profiles (continuous lines). Comparison to experimental ones determined by differential calorimetry at 190 °C in pure oxygen on pipes naturally aged in the presence of DOC in the south of France during the 1970–2005's period (points).

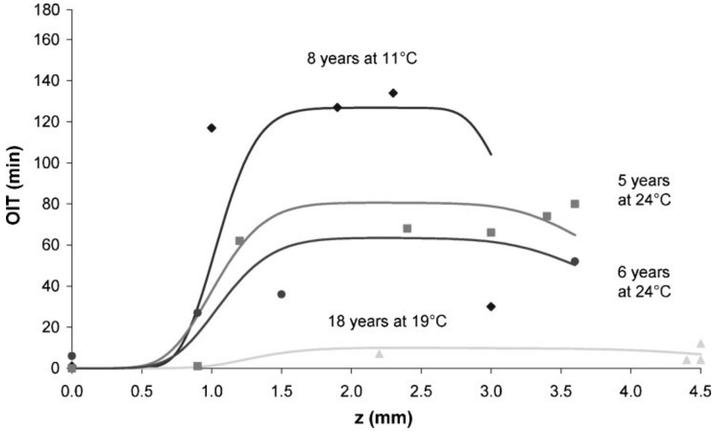

Figure 4.
Examples of simulations of oxidation induction time profiles (continuous lines). Comparison to experimental ones determined by differential calorimetry at 190 °C in pure oxygen on pipes naturally aged in the presence of DOC the south of France during the 1970–2005's period (points).

- The exposure conditions of the pipes (concentration of disinfectant in water, water temperature and pressure, water oxygenation, and their respective seasonal fluctuations) in the drinking water distribution network.

This model has been successfully applied to chlorine dioxide (DOC).

In general, the water temperature and the DOC concentration range respectively between 9 °C and 24 °C and 0.1 ppm and 0.3 ppm (milligram per litre of water) from one site (of drinking water network) to another. For the sake of simplicity, in a first approach, the simulations have been made for the average values of 15 °C and 0.15 ppm in water (i.e. for a concentration of DOC of $[Y^\circ]_{z=0} = 2.3 \times 10^{-6}\,\mathrm{mol \cdot l^{-1}}$ in PE). The lifetimes have been calculated for a virtual pipe of 40 mm diameter and 4.5 mm thickness, made in a PE generation anterior to the PE 80 one, having an initial average molar mass of $M_W = 150\,\mathrm{kg \cdot mol^{-1}}$, and containing an initial Irganox 1010

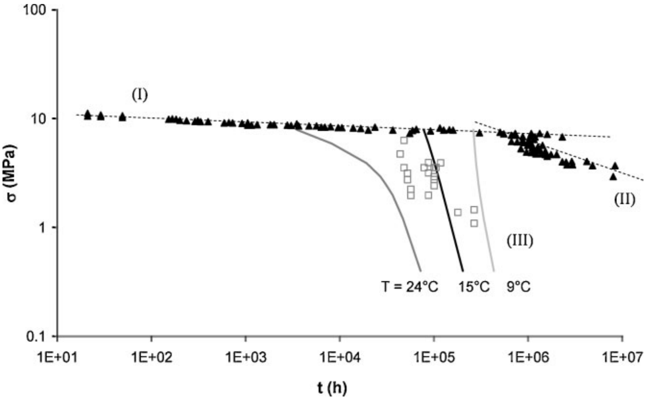

Figure 5.
Simulation of regime (III) at three different water temperatures (continuous lines). Comparison to lifetimes of pipes naturally aged in the presence of DOC in the south of France during the 1970–2005's period (□). The regression plot in pure water (without disinfectant) at 15 °C (▲) has been determined from experimental results reported in reference [1].

($n_{AH} = 4$) concentration equals to its equilibrium value ($[AH]_{t=0} = 1.8 \times 10^{-5} \, mol \cdot l^{-1}$).

Examples of simulations are given in Figure 3,4 and 5. In each case, one observes a satisfying agreement between theory and experiment.

Conclusion

A kinetic model has been built for the lifetime prediction of PE pipes transporting slightly pressurized (between 3 and 12 bars) drinking water disinfected by l disinfectants which are free radical reagents. This model simulates satisfyingly the degradation profiles (oxidation induction time, antioxidants and oxidation products concentration, average molar masses, etc ...), and via an empirical law, the ''strain'' in the pipe wall. The failure occurs when the ''strain'' ε reaches a critical value ε_F depending of the weight average molar mass M_W in an elementary sublayer situated at a depth of 100 μm in the internal pipe wall.

Although more rigorous checking tests remain to be accomplished yet, it appears clearly that the kinetic model predicts the good order of magnitude of lifetimes in the case of a water treatment by chlorine dioxide.

[1] Y. Lu, N. Brown, *J. Mater. Sci.* **1990**, 25(1A), 29.

[2] C. J. G. Plummer, in: *Mechanical Properties of Polymers Based on Nanostructure and Morphology*, G. H. Michler, F. J. Balta Calleja, eds., CRC Press, New-York Chap. 6, **2005**, p. 216.

[3] J. Viebke, E. Elble, M. Ifwarson, U. W. Gedde, *Polym. Eng. Sci.* **1994**, *34*(17), 1354.

[4] H. Leijstrom, M. Ifwarson, Proceedings of *Plastic Pipes Conferences X*, Gothenburg, Cdrom, **1998**, p. 703.

[5] C. Munier, E. Gaillard-Devaux, A. Tcharkhtchi, J. Verdu, *J. Mater. Sci.* **2002**, *37*(19), 4159.

[6] N. Brown, J. Donofrio, X. Lu, *Polymer* **1987**, *28*(8), 1326.

[7] L. Reich, S. S. Stivala, *Autooxidation of Hydrocarbons and Polyolefins*, Marcel Dekker Inc., New-York **1969**, p. 141 and p. 151.

[8] J. P. Dear, N. S. Mason, *Polym. Polym. Comp.* **2001**, *9*(1), 1.

[9] J. Hassinen, M. Lundback, M. Ifwarson, U. W. Gedde, *Polym. Deg. Stab.* **2000**, *84*(2), 261.

[10] N. Khelidj, X. Colin, L. Audouin, J. Verdu, C. Monchy-Leroy, V. Prunier, *Polym. Deg. Stab.* **2006**, *91*(7), 1593.

[11] X. Colin, C. Monchy-Leroy, L. Audouin, J. Verdu, *Nucl. Instr. Meth. Phys. Res. B* **2007**, *265*(1), 251.

[12] M. Coquillat, J. Verdu, X. Colin, L. Audouin, M. Celina, *Polym. Deg. Stab.* **2008**, *93*, 1689.

[13] X. Colin, L. Audouin, J. Verdu, M. Rozental-Evesque, F. Martin, F. Bourgine, Proceedings of *Plastic Pipes XIII*, Washington DC, United States, CDrom, 2nd-5th Oct. **2006**.

[14] X. Colin, L. Audouin, J. Verdu, M. Rozental-Evesque, B. Rabaud, F. Martin, F. Bourgine, *Polym. Eng. Sci.*, in press.

[15] O. Saito, *J. Phys. Soc. (Japan)* **1958**, *13*(2), 198 and *13*(12), 1451.

[16] L. Audouin, J. Verdu, in *Radiation Effects on Polymers*, R. L. Clough and S. W. Shalaby, ACS Symposium Series, vol. 475, American Chemical Society, Washington D.C., **1991**, p. 473.

[17] J. B. Howard, *Polym. Eng. Sci.* **1973**, *13*(6), 429.

[18] J. Viebke, U. W. Gedde, *Polym. Eng. Sci.* **1997**, *37*(5), 896.