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# DEGRADATION OF POLYETHYLENE PIPES BY WATER DISINFECTANTS

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## ABSTRACT

Polyethylene (PE) pipes are commonly used for the transport of drinking water under pressures of few bars. There is an abundant literature on the results of isobaric and isothermal ageing tests made in pure water. These results show that, at ambient temperature, in the pressure domain of practical interest, the pipes perish by brittle fracture with lifetimes exceeding 50 years. There were considerable research efforts, in the past half century, to optimize the polymer structure and processing conditions in order to improve the pipe durability. In the last decade, however, it was discovered that disinfectants, of which the effect was ignored in previous studies, attack the antioxidants and, presumably, shorten the pipe lifetime because PE can undergo an oxidative degradation. This deleterious effect is especially pronounced when chlorine dioxide is used as a disinfectant, but chlorine and bleach lead also to measurable effects.

The present chapter is aimed to answer the following question: Is it possible to build a kinetic model leading to a prediction of the time to failure for a given PE pipe, at given couple of temperature and pressure, for a given disinfectant in a given concentration in water?

Such an investigation must cover three very distinct domains which will constitute the three main sections of this chapter:

1. Chemical aspects: Mechanisms and kinetics of disinfectant-antioxidant and disinfectant-polymer reactions, role of oxygen, macromolecular processes (chain scission) having consequences on the mechanical behaviour;

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2. Transport phenomena: Penetration of disinfectants or their by-products in PE, loss by extraction and evaporation of antioxidants, couplings between these processes, composition and structure gradients resulting from diffusion controlled reactions;
  3. Mechanical aspects: Kinetic modelling of pipe fracture under pressure. Coupling with chemical degradation.

**Keywords:** Polyethylene pipe, water disinfectant, chemical degradation, kinetic modelling, lifetime prediction.

## INTRODUCTION

Polyethylene (PE) pipes are widely used for the transport of gas or drinking water. It was shown, more than 30 years ago, that pipes undergo a delayed failure, after a time  $t_F$  depending on the pressure  $p$  in the transported fluid, or better on the hoop stress  $\sigma$  in the pipe wall, this latter being linked to the pressure by:

$$\sigma = p \times \frac{D_{\text{out}} - L}{2L} \quad (1)$$

where  $D_{\text{out}}$  is the outer diameter and  $L$  the wall thickness.

In former studies, it was assumed that PE does not interact with the transport fluids and that failure results only from mechanical processes. Ageing tests were performed under static pressure, at constant temperature, using generally pure water. The practitioners chosen to present experimental data in  $\text{Log}(\sigma) = f(\text{Log}(t_F))$  plots. The shape of these latter is shown in Figure 1.

The plots put in evidence the existence of two distinct kinetic regimes of failure: At high stresses, approaching the tensile stress yield  $\sigma_Y$  (Truss, 1986), fracture is ductile and the slope  $\Delta\text{Log}(\sigma) / \Delta\text{Log}(t_F)$  is of the order of 0.03. At low stresses (corresponding to the pressure domain of practical interest), fracture is brittle and the slope  $\Delta\text{Log}(\sigma) / \Delta\text{Log}(t_F)$  is of the order of 0.3.

The mechanism of slow crack propagation raised up a considerable interest in the community of polymer mechanics in the 80's (Lustiger and Markham, 1983; Kausch, 1987; Truss, 1987 and 1988; Huang and Brown 1988; Lu and Brown, 1990 and 1991).

At the end of the 80's, most of the research workers were convinced that slow crack propagation is exclusively a problem of polymer mechanics. Stress concentrations at macroscopic (processing) or nanoscopic (crystalline lamellae) defects, tie-chain concentration, entanglement density in the amorphous phase and disentanglement rate under stress, were generally considered as the most important phenomena. At the same time, however, Gandek et al. (1989a and b) and latter Gedde and coll. (Karlsson et al., 1992; Smith et al., 1992; Gedde et al., 1994; Viebke et al., 1996 and 1997; Neway et al., 2001 and 2004; Lundback et al., 2006a and b) put in evidence antioxidant loss and thus, possible oxidation induced failure of PE. Attention was then focused on antioxidant concentration profiles and modelling of antioxidant loss kinetics. Two kinds of profiles were found (Figure 2).

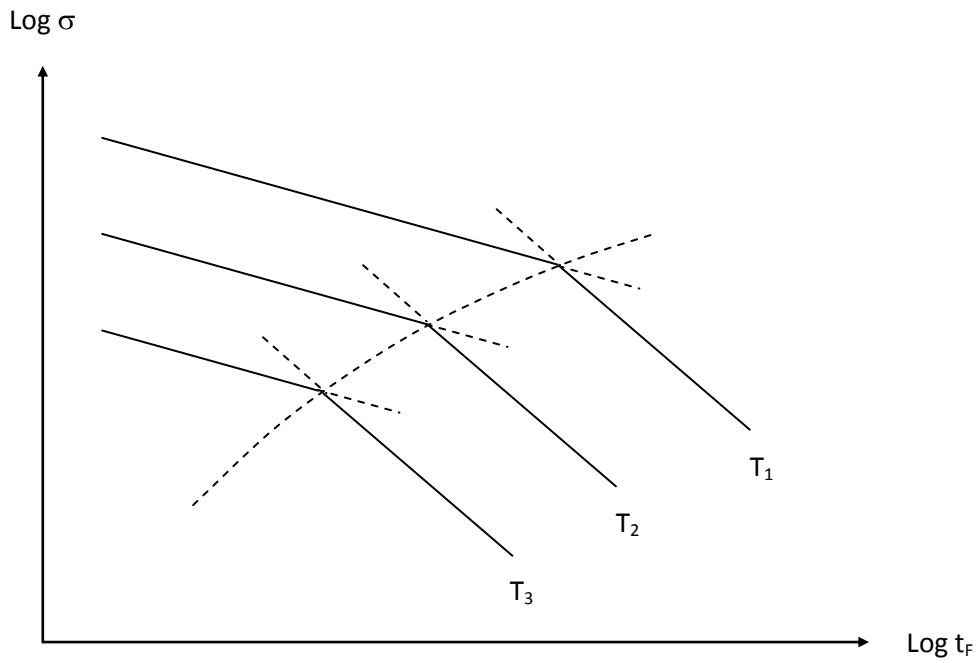


Figure 1. Shape of the plots  $\text{Log}(\sigma) = f(\text{Log}(t_F))$  at three temperatures  $T_1 < T_2 < T_3$  for PE pipes under pressure, in the absence of chemical interaction between PE and transported fluid

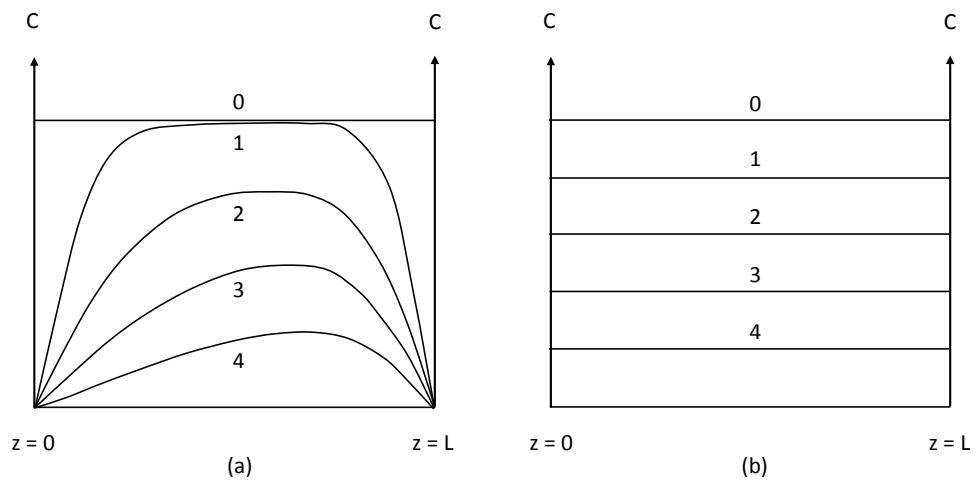


Figure 2. Schematic types of stabilizer concentration wall profiles for pipes aged in pure water. The stabilizer is lost by extraction by water at the water–polymer interface ( $z = 0$ ) and by evaporation at the polymer–air interface ( $z = L$ )

The loss of a stabilizer molecule initially located at the distance  $z$  of the surface can be described as the sequence of two processes: First diffusion towards the surface, second evaporation or water extraction at the surface.

Diffusion is characterized by the coefficient of diffusion  $D$ . Evaporation is characterized by a (thickness dependent) first-order rate constant  $\beta$  (see below). As it will be seen later, one can define a dimensionless parameter  $\Phi$ :

$$\Phi = \frac{\beta L^2}{D} \quad (2)$$

If  $\Phi \gg 1$ , diffusion is slower than evaporation or extraction, it governs loss kinetics and one obtains profiles of type (a). If  $\Phi \ll 1$ , diffusion is faster than evaporation/extraction, this latter governs loss kinetics and one obtains almost flat profiles of type (b).

Indeed, one can expect an intermediary behaviour when  $\Phi$  is of the order of unity and when the evaporation rate constant  $\beta_{ev}$  differs from the extraction one  $\beta_{ext}$ . In the case of phenols, it has been found that, generally,  $\beta_{ext} > \beta_{ev}$  (Lundback, 2006a and b; Colin et al., 2009b).

At the end of 80's, some authors suggested a possible effect of disinfectant on PE ageing (Tanaka et al., 1987; Henry and Garton, 1990), but detailed literature data on this topic appeared only one decade later (Bradley et al., 1997; Ifwarson and Aoyama, 1998; Gill et al. 1999; Hassinen et al., 2004; Dear and Mason, 2001 and 2006).

In the presence of disinfectants, the antioxidant concentration profiles take a more asymmetric shape (Figure 3). The profiles clearly show that a reactive species generated by the disinfectant or the disinfectant itself penetrates in the polymer and attacks the stabilizer. This process is obviously diffusion controlled since the depth of the superficial layer, in which the stabilizer is chemically consumed, is generally lower than the half thickness and rarely exceeds 1 mm.

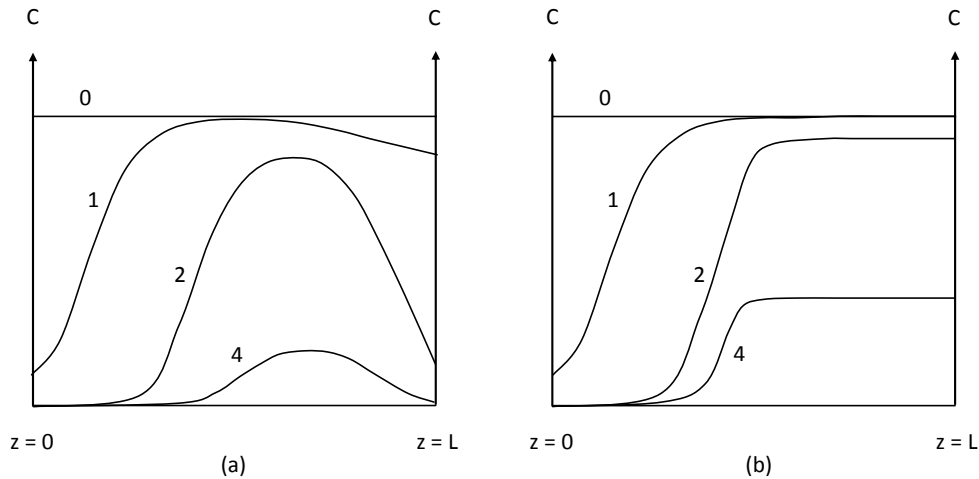


Figure 3. Stabilizer concentration profiles in the case of disinfected water. (a) Diffusion controlled loss, see, for instance, Hassinen et al. (2004). (b) Evaporation controlled loss, see for instance Colin et al. (2009a)

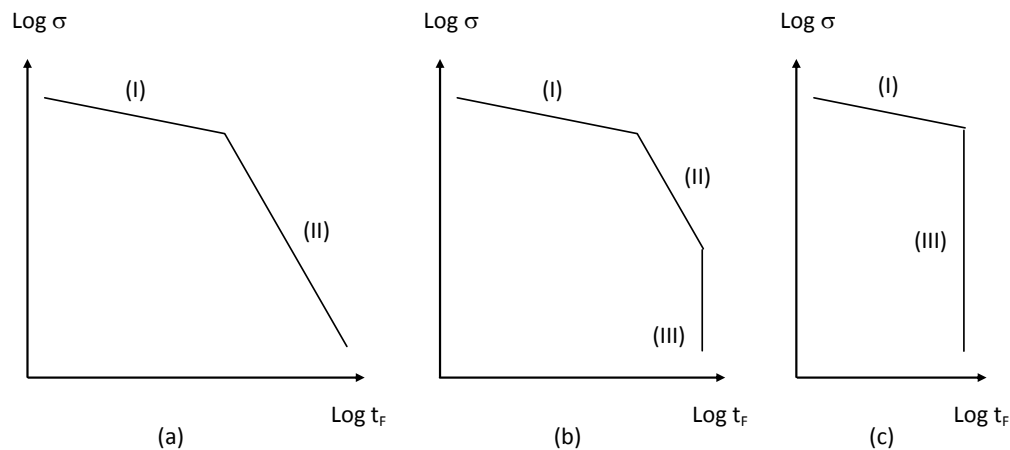


Figure 4. Shape of stress–lifetime plots. (a) In the absence of chemical degradation. (b) In the presence of slow chemical degradation. (c) In the presence of fast chemical degradation

In France, where chlorine dioxide is abundantly used, failures occurred especially in dog-days of 2003, on pipes aged, sometimes, of less than 10 years against 50 years expected. Indeed, a chemical attack accelerates pipe failure. Gedde and coll. (1994) have shown that it is responsible for a third kinetic regime of rupture (Figure 4).

The regime (III), in which failure is kinetically governed by the polymer chemical degradation, is represented by an almost vertical straightline. Depending on the degradation rate, it can appear after the physical ductile–brittle transition (b) or before (c).

There is a strong request from water suppliers and users for failure prediction models in which the input parameters would be the temperature  $T$ , water pressure  $p$ , disinfectant nature and concentration  $[\text{Dis}]$  and pipe geometry. The output quantities would be the time to failure, antioxidant concentration profile, and polymer degradation (ideally the polymer molar mass distribution) profile. Such models would necessarily be composed of three interconnected moduli: i) A “chemistry” modulus describing the antioxidant and polymer attacks by the disinfectant or its by-products and by oxygen. ii) A “transport” modulus describing the transport of the reactive species, i.e. disinfectant, oxygen and stabilizer through the pipe wall thickness. Here, transport equations must be coupled with chemical kinetic equations. iii) A “mechanical” modulus describing failure kinetics and taking into account degradation effects.

As it will be seen, various “scenarii”, based on different starting assumptions, are possible for each modulus. For instance, the following “scenario”, called “C1”, is often used for the “chemistry” modulus: As long as it is present, the antioxidant protects the polymer but this latter degrades rapidly just after the complete antioxidant disappearance. This scenario is based on the vast experience on PE thermal oxidation at temperatures typically higher than  $70^\circ\text{C}$  where it is well established that the end of the induction period coincides with the total disappearance of the antioxidant and that embrittlement occurs at the end of the induction period. This “scenario” is reasonably realistic in the case of exposure in hot, non disinfected water. At  $25^\circ\text{C}$ , however, the induction time for unstabilised PE thermal oxidation is about 20 years (Khelidj et al., 2006b), that suggests a long delay between the disappearance of antioxidants and the polymer embrittlement (no experimental data are available). Furthermore, water disinfectants can attack the polymer and induce an “extrinsic” initiation of

oxidation radical chains. This leads us to imagine a “scenario C2” in which there would be a part of the polymer degradation induced by the disinfectant, and more or less independent of the antioxidant presence.

One sees that antioxidant concentration profiles would be a key information in the frame of “scenario C1”, but would appear less important in the frame of “scenario C2”. Ideally, a model would include all the chemical events belonging to both scenarii, and the predominance of “scenario C1” or “scenario C2” would not be decided a priori, but determined by the model in function of exposure conditions, disinfectant nature and concentration, etc ...

A similar duality can be imagined for the “mechanical” modulus of the kinetic model. In “scenario M1”, cracks would initiate soon and the pipe lifetime would schematically corresponds to the time of (slow) crack propagation through the pipe wall. In this case, the polymer degradation at the crack tip would accelerate the crack propagation. Fracture mechanics would be the most pertinent tool to predict the pipe failure kinetics. An example of this type of treatment has been given by Piques and coll. (Hamouda, 2000).

In “scenario M2”, the pipe would undergo homogeneous creep under the water pressure, and failure would occur when a strain component reaches a critical value depending on the polymer chemical state. The crack propagation time would be considerably shorter than the crack initiation time. Classical (homogeneous) polymer mechanics would be then the most pertinent tool in lifetime modelling.

As it will be seen in the following sections, we have decided to elaborate a model based on a “chemistry” modulus including both “scenarii C1” and “C2” and a “mechanical” modulus based on “scenario M2”. In our approach, transport phenomena are directly incorporated into the chemical kinetic modulus, however it seemed to us interesting, for the seek of clarity, to treat them in a separate section. The text will be thus organized in three sections respectively devoted to: 1) Chemical aspects; 2) Transport aspects; 3) Mechanical aspects.

## CHEMICAL ASPECTS

### 1. Preliminary Remarks

#### *1.1. About the reactivity of disinfectants*

Disinfectants are aimed to destroy the organic substances present in water, essentially by oxidizing processes among which radical ones play often an important role. In the case of saturated substrates, radical attack proceeds mainly by hydrogen abstraction:



$Y^\circ \rightarrow$  decomposition and other reactions

where YH is the substrate and  $R^\circ$  a radical generated by the disinfectant.

The rate constant  $k_p$  of hydrogen abstraction is a decreasing function of the dissociation energy  $E_D$  of the YH bond. For instance, in the case where  $R^\circ$  would be a peroxy radical ( $PO_2^\circ$ ), one would have, at ambient temperature (Korcek et al., 1972):

**Table 1. Order of magnitude of Y–H bonds dissociation energy in organic substrates**

Broken Y–H bond	$E_D$ (kJ.mol <sup>-1</sup> )
Weakest bond in organic molecules with heteroatoms	335–376
Methynic CH in polypropylene	378
Methylenic CH in polyethylene	393
OH in phenols	335–355

$$\frac{d \text{Log}(k_p)}{d E_D} \approx -0.0478 \quad (3)$$

$k_p$  being in l.mol<sup>-1</sup>.s<sup>-1</sup> and  $E_D$  in kJ.mol<sup>-1</sup>.

The order of magnitude of  $E_D$  for various substrates is given in Table 1.

One sees that PE would be 4 to 1000 times less reactive than organic impurities, but its reactivity would be non negligible over long periods (dozens of years).

In the same way, one sees that phenols must be attacked at a rate about 1000 times higher than PE. The shape of antioxidant profiles in Figure 3 begins thus to be explained: disinfectants are highly aggressive towards phenolic antioxidants because these latter are highly reactive in radical processes.

### ***1.2. About the nature of reactive species***

The chemistry of disinfection in water media is relatively well known. Both radical and ionic species (for instance ClO<sup>-</sup> in the case of chlorine or bleach) can have a strong oxidizing power, but PE acts as a highly selective absorber, because ions are totally insoluble in this matrix. This characteristic was first discovered by Ravens (1960) in the frame of a study on poly(ethylene terephthalate) hydrolysis. PE is among the less polar polymers, its dipolar moment is zero, its dielectric permittivity is 2.3. Only poly(tetrafluoroethylene) is less polar. Ions are highly polar species totally insoluble in non polar polymers. Radicals, in contrast, are more or less soluble depending on their solubility parameters.

Many “scenarii” are thus possible:

- “Scenario T1”: The disinfectant is itself a radical which can migrate into PE. This is the case of chlorine dioxide (DOC).
- “Scenario T2”: The disinfectant generates radicals in the water phase and the radicals migrate into PE.
- “Scenario T3”: The disinfectant itself or a non dissociated molecule formed from the disinfectant in water phase migrates into PE and dissociates into radicals in the PE matrix.

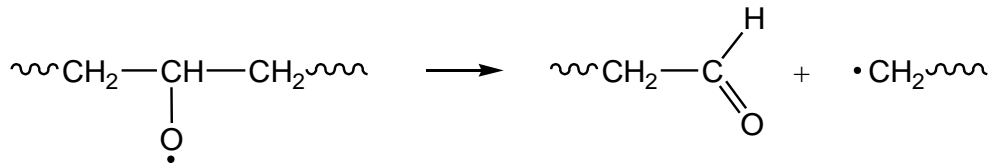
One can have prescience that the identification of reactive species and the determination of their concentration in PE is a challenging objective.



### 1.3. About the accelerating effect of disinfectant on mechanical failure

The fact that mechanical failure is accelerated in the presence of disinfectants is well established, at least in the case of chlorine dioxide (Colin et al., 2009b).

There is no other way, to explain this effect, than the occurrence of a chain scission process. As a matter of fact, at reasonably low conversion, only reactions leading to a change in chain dimensions can affect the mechanical behaviour. These reactions belong to two families: crosslinking or chain scission. Crosslinking would rather improve the resistance to cracking, therefore only chain scission can explain the observed effects. In PE, at ambient temperature, macro-radicals resulting from hydrogen abstraction can react only by coupling (i.e. crosslinking) or disproportionation (i.e. without chain scission), as well established by studies on radiolytic ageing (see, for instance, Schnabel, 1978). It seems that chain scissions (at ambient temperature) can only result from oxidation processes, more precisely from rearrangement of alkoxy radicals ( $\text{PO}^\circ$ ):



Alkoxy radicals can result from hydroperoxide uni or bimolecular decomposition or from non terminating bimolecular combinations of peroxy radicals. The global simplest mechanistic scheme could be the following:

Initiation	(Id)	$\text{R}^\circ + \text{PH}$	$\rightarrow \text{RH} + \text{P}^\circ$	( $k_{1d}$ )
Initiation	(Iu)	$\text{POOH}$	$\rightarrow \text{PO}^\circ + \text{HO}^\circ$	( $k_{1u}$ )
Initiation	(Ib)	$2\text{POOH}$	$\rightarrow \text{PO}^\circ + \text{PO}_2^\circ + \text{H}_2\text{O}$	( $k_{1b}$ )
Propagation	(II)	$\text{P}^\circ + \text{O}_2$	$\rightarrow \text{PO}_2^\circ$	( $k_2$ )
Propagation	(III)	$\text{PO}_2^\circ + \text{PH}$	$\rightarrow \text{POOH} + \text{P}^\circ$	( $k_3$ )
Termination	(IV)	$\text{P}^\circ + \text{P}^\circ$	$\rightarrow$ inactive products	( $k_4$ )
Termination	(V)	$\text{P}^\circ + \text{PO}_2^\circ$	$\rightarrow$ inact. prod.	( $k_5$ )
Cage formation	(VI-0)	$\text{PO}_2^\circ + \text{PO}_2^\circ$	$\rightarrow [\text{PO}^\circ \text{ } ^\circ\text{OP}]_{\text{cage}} + \text{O}_2$	( $k_{60}$ )
Termination	(VI-1)	$[\text{PO}^\circ \text{ } ^\circ\text{OP}]_{\text{cage}}$	$\rightarrow$ inact. prod.	( $k_{61}$ )
Cage escape	(VI-2)	$[\text{PO}^\circ \text{ } ^\circ\text{OP}]_{\text{cage}}$	$\rightarrow 2\text{PO}^\circ$	( $k_{62}$ )

where  $\text{R}^\circ$  is a radical coming from the disinfectant, PH is polyethylene.

The rate of chain scission would thus be given by:

$$\frac{dS}{dt} = \frac{1}{\rho} \left[ \gamma_S k_{1u} [\text{POOH}] + \gamma_S k_{1b} [\text{POOH}]^2 + 2\gamma_S k_{62} [\text{PO}^\circ \text{ } ^\circ\text{OP}]_{\text{cage}} \right] \quad (4)$$

where S is the number of chain scissions per mass unit and  $\rho$  is the polymer specific weight ( $\approx 940 \pm 20 \text{ kg.m}^{-3}$ ).  $\gamma_S$  is the yield of chain scission from alkoxy radicals.

S is obtained by integration of Equ. 4, when  $[\text{POOH}]$  and  $[\text{PO}^\circ \text{ } ^\circ\text{OP}]_{\text{cage}}$  are obtained by resolution of the set of differential equations derived from the above mechanistic scheme.

The weight average molar mass  $M_W$  of the polymer can be determined from  $S$  using the Saito's equations (1958a and b):

$$\frac{1}{M_n} - \frac{1}{M_{n0}} = S \quad (5)$$

$$\frac{1}{M_W} - \frac{1}{M_{W0}} = \frac{S}{2} \quad (6)$$

$M_W$  must be preferred to  $M_n$  because it carries, generally, less incertitude. The polymer toughness or the tensile ultimate elongation ( $\epsilon_R$ ) varies with  $M_W$  according to Figure 5.

One observes a relatively sharp ductile–brittle transition at:

$$M_W = M_F = (70 \pm 30) \text{ kg}\cdot\text{mol}^{-1} \quad (7)$$

Below this limit, the polymer becomes extremely brittle. In fact, the molar mass change is not directly responsible for embrittlement, the causal chain would be rather (Fayolle et al., 2008):

Polymer oxidation  $\rightarrow$   $\text{PO}^\circ$  radicals  $\rightarrow$  chain scissions  $\rightarrow$  chemocrystallisation  $\rightarrow$  decrease in interlamellar spacing  $l_a \rightarrow$  embrittlement

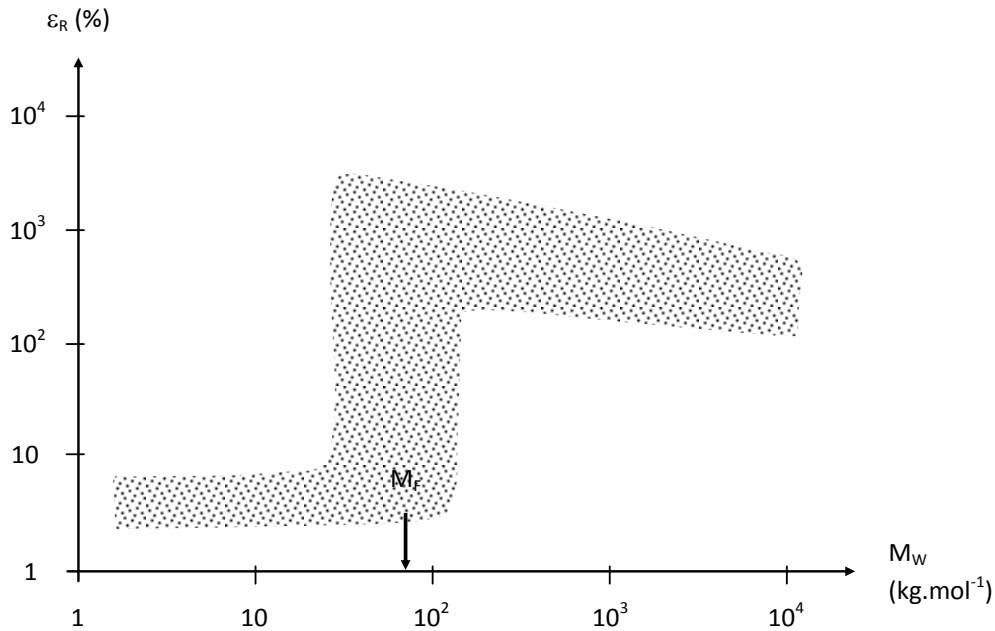


Figure 5. Schematic shape of the dependence of the ultimate elongation of PE measured in usual tensile testing conditions with the weight average molar mass

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The critical value of  $l_a$  would be close to 6 nm (Kennedy et al., 1994). Using extreme crystallisation conditions, these latter authors have seen that it is possible to obtain critical  $l_a$  values with polymers of molar mass significantly higher than  $100 \text{ kg}\cdot\text{mol}^{-1}$ . However, in the practical case of pipes used at ambient temperature, the critical  $l_a$  value corresponds to a critical  $M_w$  value of  $(70 \pm 30) \text{ kg}\cdot\text{mol}^{-1}$ .

#### ***1.4. About the role of antioxidants***

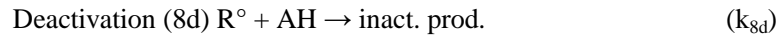
Phenolic antioxidants (AH) play their stabilizing role. It is widely recognized that the most important reaction is the hydrogen abstraction:



Phenoxy ( $\text{A}^\circ$ ) radicals can isomerise and their isomers can participate to various reactions among which terminations with  $\text{PO}_2^\circ$  radicals, but this latter reaction is extremely fast so that hydrogen abstraction is the rate controlling process, and one can write, in a first approach:



Radicals  $\text{R}^\circ$  coming from the disinfectant can, indeed, react with phenols:



Both reactions have to be added to the previous mechanistic scheme with an additional boundary condition:

$$[\text{AH}] = [\text{AH}]_0 \text{ at } t = 0.$$

One can expect small variations of the phenol reactivity with its structure. In a coarse grain study, these variations can be neglected, the stabilizers differ essentially one from another by their transport properties.

May antioxidants play a key role in polymer aging in the presence of disinfectants?

Disinfectants play (certainly in the case of chlorine dioxide, probably in the case of bleach) an “extrinsic” initiation role on polymer radical chain oxidation. It has been shown, experimentally through gamma irradiation experiments (Rivaton et al., 2006) and from kinetic modelling (Verdu et al., 2003), that phenolic antioxidants lose a part of their efficiency when “extrinsic” initiation occurs. As for irradiation (Khelidj et al., 2006a), one can expect a dependence of PE lifetime  $t_F$  with initiation rate by disinfectant  $r_i$  having the shape of Figure 6.

Very schematically, two kinetic regimes can be distinguished: Regime (I) where “extrinsic” initiation predominates over hydroperoxide decomposition, and regime (II) where “extrinsic” initiation is negligible relatively to initiation by hydroperoxide decomposition.

The stabilizer is expected to be efficient in regime (II), i.e. in thermal oxidation, but considerably less efficient in regime (I). This curve can be simulated with the above model using an arbitrarily endlife criterion, for instance  $M_F = 70 \text{ kg}\cdot\text{mol}^{-1}$ .

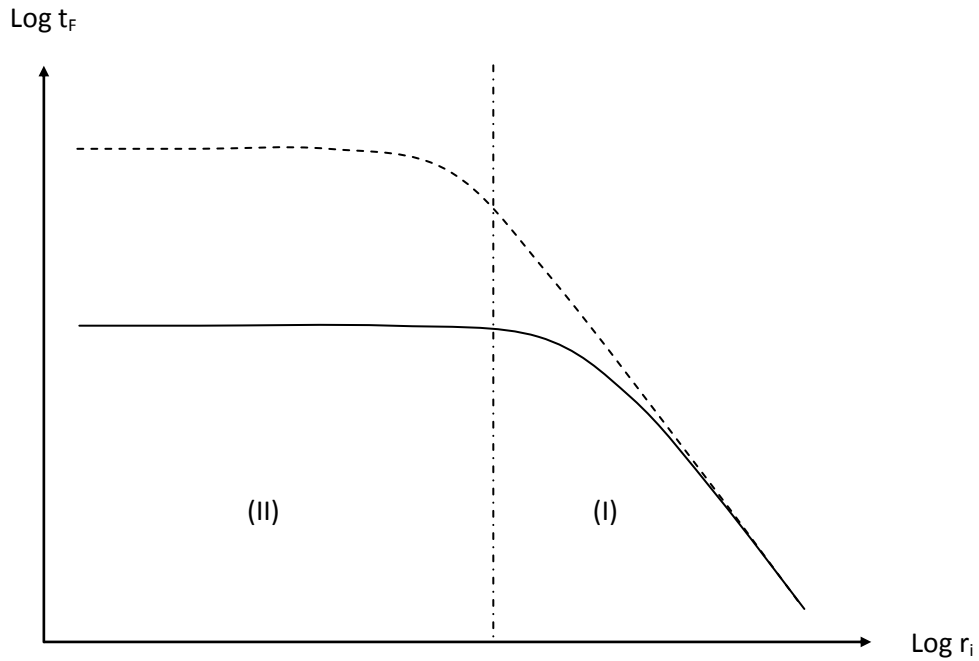


Figure 6. Expected shape of the curve  $\text{Log}(\text{lifetime}) = f(\text{Log}(\text{rate of "extrinsic" initiation}))$ . Full line = unstabilised polymer. Dashed line = stabilized polymer

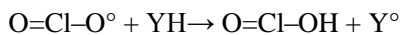
The problem, here, is to determine which regime predominates in pipe use conditions. The classical approach would consist in trying to accelerate aging by increasing the disinfectant concentration. One sees, here, that the concentration dependence of lifetime would be far from being linear, that discourages empirical modelling.

## 2. Chlorine Dioxide

The peculiarity of the chlorine dioxide (DOC) molecule is that it is a free radical in ground state:



It is moderately stable in aqueous media. DOC solutions must be regularly regenerated (every week) during long term ageing tests. As a free radical, it can abstract hydrogens to organic substrates:



Its non ionic character allows its dissolution in PE.

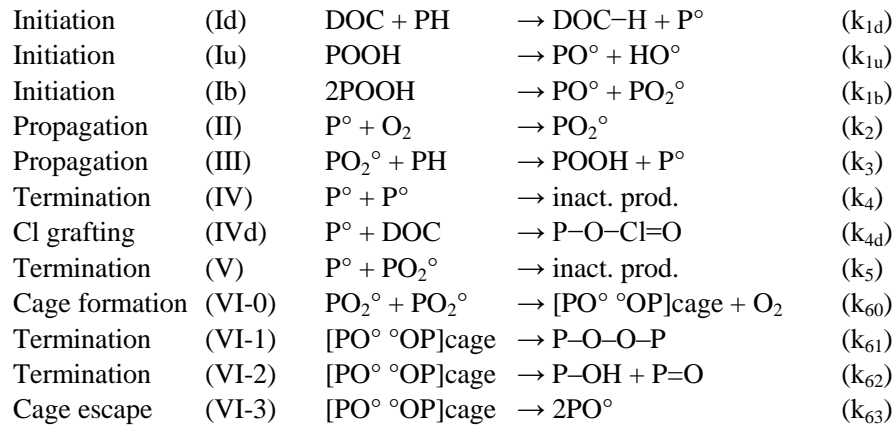
Experiments on unstabilised PE thin films immersed in oxygenated, highly concentrated (80–90 ppm) DOC solutions put in evidence the accelerating effect of chlorine dioxide on PE

oxidation (Colin et al., 2009a). The molar mass and ultimate elongation decrease and carbonyl and hydroxyl groups appear after exposure of 1300 hours at 40°C. Some chlorine remains grafted to the polymer (Figure 7).

These results call for the following observations:

- To give an idea of the accelerating effect of DOC, it can be recalled that the induction period of PE thermal oxidation in air at 40°C is of the order of 3.3 years (Colin et al., 2007).
- As previously observed, embrittlement occurs when  $M_w$  approaches a critical value of  $\approx 70 \text{ kg.mol}^{-1}$ . There is no difference, from this point of view, between aging in DOC solution and aging in air.
- At the embrittlement point, the number of chain scissions is  $S = 5.2 \times 10^{-3} \text{ mol.kg}^{-1}$  and the number of carbonyl is  $[C=O] = 1.2 \times 10^{-1} \text{ mol.kg}^{-1}$ . Only a relatively small number of oxidation events lead to chain scission.

The simplest mechanistic scheme able to simulate the observed behaviour would be thus the already established PE thermal oxidation scheme (Khelid et al., 2006b) to which two new elementary processes would be added: hydrogen abstraction to PE by DOC, to explain its accelerating effect on aging, and coupling of DOC with macro-radicals, to explain chlorine grafting (Colin et al., 2009a):



The boundary conditions for the resolution of the kinetic scheme would be:

- At  $t = 0$ :  $[P^\circ] = [PO_2^\circ] = 0$ ;  $[POOH] = [POOH]_0$ ;  $[PH] = 60 \text{ mol.l}^{-1}$ .
- At every  $t$ :  $[O_2] = [O_2]_E = 3.8 \times 10^{-4} \text{ mol.l}^{-1}$  (it is considered, here, that water is saturated by oxygen, but in the case of pipes, other boundary conditions can be chosen);

$[DOC] = [DOC]_E = 1.4 \times 10^{-3} \text{ mol.l}^{-1}$ , where  $[DOC]_E$  is the DOC concentration in PE, in equilibrium with the aqueous solution. It is thus assumed that, for the thin films under study, DOC consumption is not diffusion limited.

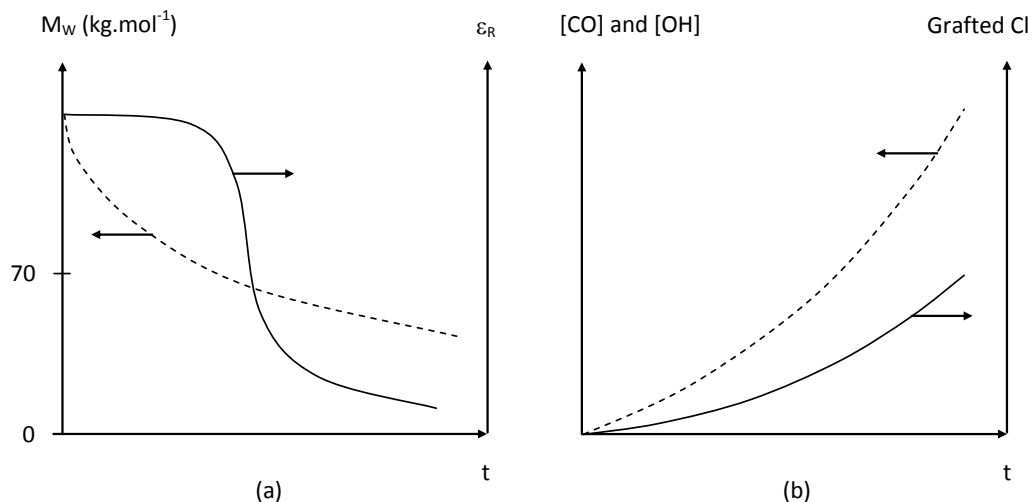


Figure 7. Shape of kinetic curves for ageing of PE thin films immersed in highly concentrated DOC solutions (80–90 ppm) at 40°C. (a) Weight average molar mass and ultimate elongation. (b) Carbonyl, hydroxyl and grafted chlorine concentrations

The homogeneity of the reaction can be proved from steric exclusion chromatographic data: It is observed that, during aging, the molar mass distribution sharpens, that is only compatible with the assumption of homogeneous random chain scission.

The 10 rate constants characteristic of PE thermal oxidation were already determined (Colin et al., 2004; Khelidj et al., 2006b). The rate constant of reactions involving DOC can be determined from experimental results using the kinetic model through an inverse approach. But the DOC concentration in PE ( $[\text{DOC}]_E$ ) must be determined independently, which is not easy owing to the low stability of DOC and the lack of experimental data.

A theoretical way for the determination of  $[\text{DOC}]_E$ , essentially based on the closeness of  $\text{ClO}_2$  and  $\text{SO}_2$  molecules, has been proposed by Colin et al. (2009a). Its description would be out of the scope of this chapter, we will only recall the relationship between  $[\text{DOC}]_E$  and the DOC concentration in water  $[\text{DOC}]_W$ :

$$[\text{DOC}]_E = \xi_{\text{DOC}} \times [\text{DOC}]_W \quad (8)$$

where  $\xi_{\text{DOC}} = 1.7 \times 10^{-5} \text{ mol}\cdot\text{l}^{-1}\cdot\text{ppm}^{-1}$  if  $[\text{DOC}]_E$  is expressed in  $\text{mol}\cdot\text{l}^{-1}$  and  $[\text{DOC}]_W$  in ppm.

The activation energies for PE rate constants have been determined elsewhere (Colin et al., 2004; Khelidj et al., 2006b). The activation energies for DOC reactions, determined from data obtained only at two temperatures (Colin et al., 2009a), are very rough data, which could be modified in the future if new experimental results are available. In the above form, the model is only valid for thin films or thin superficial layers of bulk specimens where DOC and oxygen concentrations are assumed to be constantly in equilibrium with the aqueous medium. Furthermore, eventual stabilizer reactions are not taken into account.

DOC–stabilizer reactions were studied only in industrial pipes exposed to accelerated or natural aging. The results, mainly antioxidant concentration profiles in wall thickness, will be presented in the section dedicated to “transport aspects”, but the data relative to reactivity can

be briefly summarized here: DOC reacts fastly with phenolic antioxidants and destroys them in a process which can be simulate by a single reaction:

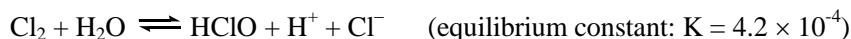


where A is the phenoxy moiety and H is the functional phenolic hydrogen.

DOC has been found 1900 times more reactive with the phenol than with PE, a reactivity ratio of the same order of magnitude as for  $\text{PO}_2^\circ$  radicals, which are 1200 times more reactive with phenols than with PE. Comparative studies showed that DOC reactivity is not very dependent of water pH or polyethylene type.

### 3. Bleach and Chlorine

The basic reaction is the dissociation of (di)chlorine in water:



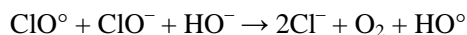
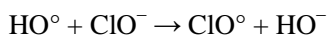
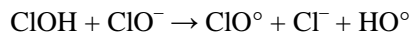
The chlorine solubility in water is relatively low (Durliat et al., 1997):

$$S_{\text{Cl}_2} \approx 10^{-6} \text{ mol.l}^{-1}.\text{Pa}^{-1}$$

CIOH is a weak acid:



The equilibria are shifted towards the left when acids are added, and towards the right when bases are added. Thus, in highly acid solutions ( $\text{pH} < 3$ ), chlorine is the major product. In basic solutions ( $\text{pH} > 7.5$ ), the hypochlorite ion  $\text{ClO}^-$  is the major product. In solutions of low acidity ( $3 < \text{pH} < 7.5$ ), CIOH is the major product, its maximum yield is obtained at  $\text{pH} = 5$ . These three species have a strong oxidizing power, but only two are able to react with PE:  $\text{Cl}_2$  and CIOH, since ions are insoluble in PE. According to Holst (1954), when CIOH and  $\text{ClO}^-$  coexist, they generate radicals in aqueous media:



We have thus the possibility to envisage “scenarii” of type “T2” where radicals  $\text{HO}^\circ$  and/or  $\text{ClO}^\circ$  would be formed in water and then, would migrate into PE. Several authors have envisaged this possibility, for instance Roesink (1989), Rouaix (2005) and Gaudichet-Maurin (2005). In the case where hydroxyl radicals  $\text{HO}^\circ$  would play the main role, one would expect the same results from hydrogen peroxide as from disinfectants. Fukutsa and Kokot (2001)

have obtained results effectively similar in a peculiar case where  $\text{ClO}^-$  was generated by electrolysis in the presence of bromine. Checking of this assumption in the case of PE–bleach systems will be achieved in the next months in our laboratory.

As recalled by Durliat et al. (1997),  $\text{ClOH}$  and  $\text{ClO}^-$  coexist only around a  $\text{pH} \approx 7.5 \pm 1.0$ . In their study of polysulfones aging, Rouaix (2005) and Gaudichet-Maurin (2005) find effectively a maximum degradation rate at  $\text{pH} = 8$ , that could be consistent with a “scenario” of “T2” type. It would remain, then, to determine the relative part of  $\text{ClO}^\circ$  and  $\text{HO}^\circ$  radicals in polymer degradation events.  $\text{HO}^\circ$  radicals are small, i.e. they have high diffusivities in PE, and they are extremely reactive, probably more than one million times more reactive than  $\text{PO}_2^\circ$  radicals (Denisov and Afanas'ev, 2005).  $\text{ClO}^\circ$  radicals are larger than  $\text{HO}^\circ$  ones, they are characterized by a slower diffusivity in PE but also, presumably, by a reactivity several orders of magnitude lower than  $\text{HO}^\circ$  ones. The depth  $L_R$  of penetration of a reactive species in a polymer can be estimated from a simple scaling law (Audouin et al., 1994):

$$L_R \approx \left( \frac{D}{K} \right)^{1/2} \quad (9)$$

where  $D$  is the diffusion coefficient and  $K$  the first-order constant for the consumption of the diffusing species by its reaction with the polymer.

It comes:

$$\frac{L_{R,\text{HO}^\circ}}{L_{R,\text{ClO}^\circ}} \approx \left( \frac{D_{\text{HO}^\circ} K_{\text{ClO}^\circ}}{D_{\text{ClO}^\circ} K_{\text{HO}^\circ}} \right)^{1/2} \quad (10)$$

The diffusion coefficients of these species are not known but, from comparisons with known values of current gases, for instance  $\text{H}_2$  and  $\text{CO}_2$  (Van Krevelen and Hoftyzer, 1976), one can assume that:

$$0.1 < \frac{D_{\text{HO}^\circ}}{D_{\text{ClO}^\circ}} < 1 \quad (11)$$

So that, presumably:

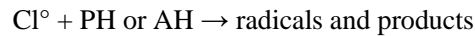
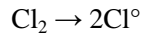
$$\frac{L_{R,\text{HO}^\circ}}{L_{R,\text{ClO}^\circ}} \approx 10^{-3} - 10^{-2} \quad (12)$$

$\text{HO}^\circ$  radicals are presumably scavenged in a micrometric or submicrometric superficial layer, whereas  $\text{ClO}^\circ$  can penetrate deeply in PE pipe walls. According to this analysis, in the frame of a “scenario T2”, at  $\text{pH}$  values of  $7.5 \pm 1.0$ , the main reactive species would be  $\text{ClO}^\circ$ .



One cannot exclude, however, cases where PE degradation would be maximum at  $\text{pH} < 7$ . In this case, the formation of  $\text{Cl}_2$  would be favoured and PE degradation would result from a “scenario T3”, i.e.:

Formation of  $\text{Cl}_2$  in the aqueous phase  $\rightarrow$  penetration of  $\text{Cl}_2$  into PE walls  $\rightarrow$  homolytic dissociation of  $\text{Cl}_2$  within the polymer matrix:



Thermal dissociation of  $\text{Cl}_2$  is very slow in dark, but eventually not enough to be negligible in large timescales. Dear and Mason (2001 and 2006) and Mittelman et al. (2008) consider, more or less explicitly, that chlorine is the reactive species, i.e. that its dissociation into  $\text{Cl}^\circ$  radicals is not a rate controlling process despite the fact that it is considerably slower than the reaction of  $\text{Cl}^\circ$  radicals with the substrate. Furthermore, Mittelman et al. (2008) assume that the rate of the chlorine–phenol reaction is the same as the rate of the water–phenol reaction, that seems to us a highly questionable assumption. To our opinion, the chemistry of chlorine or bleach in PE, in pipe use conditions, is far from being totally understood.

It will be necessary, in a next future, to establish unequivocally the nature of the reactive species, in order to determine the corresponding transport parameters, that is not obvious in the case of unstable species, and to determine elementary rate constants, that can be made with model systems simpler to manipulate.

Comparative data clearly show that chlorine or bleach are considerably less aggressive towards PE than chlorine dioxide, but we do not know, for the moment, the exact reason of this difference, which can be due to, at least, three causes:

- (a) A difference in reactivity of the radical species generated by the disinfectant;
- (b) A difference in solubility of the reactive species into PE matrix;
- (c) A difference in the generation rates of reactive species from the disinfectant.

## **TRANSPORT ASPECTS ANTIOXIDANT THICKNESS PROFILES**

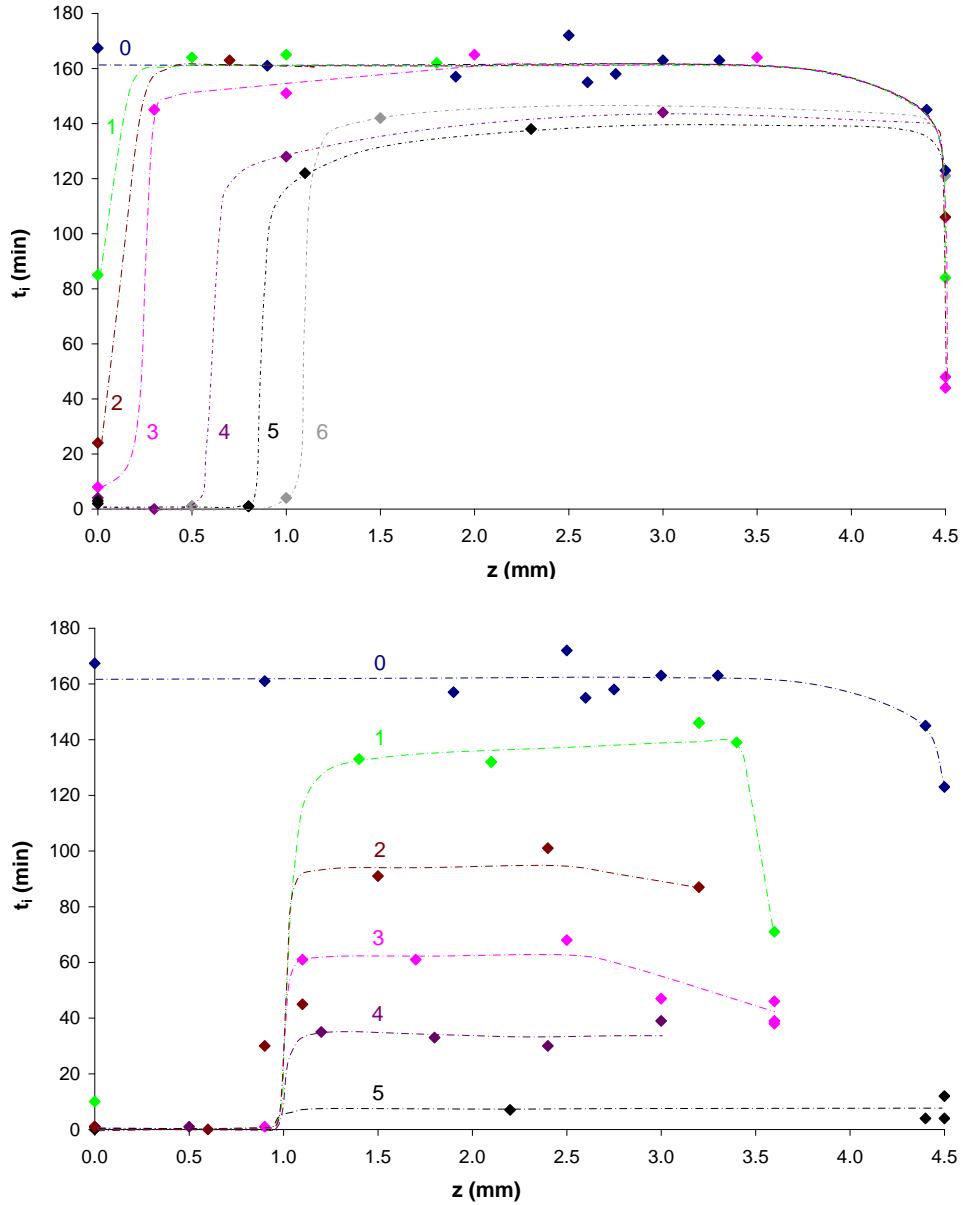
### **1. Induction Time Profiles**

Some induction time thickness profiles are shown in Figure 8 for DOC and in Figure 9 for bleach. The origin of abscissa corresponds to the water–polymer interface.

These results call for the following comments: Three regions of the pipe wall can be distinguished: The inner superficial layer (ISL), the core zone (CZ) and the outer superficial layer (OSL). All the profiles are initially flat except for a small decrease in the OSL, revealing some antioxidant loss by evaporation during processing. The initial antioxidant distribution can be considered homogeneous in ISL and CZ.

The initial induction time in these regions does not vary strongly from a manufacturer to another, it remains in the [140–175 min] interval at 190°C.

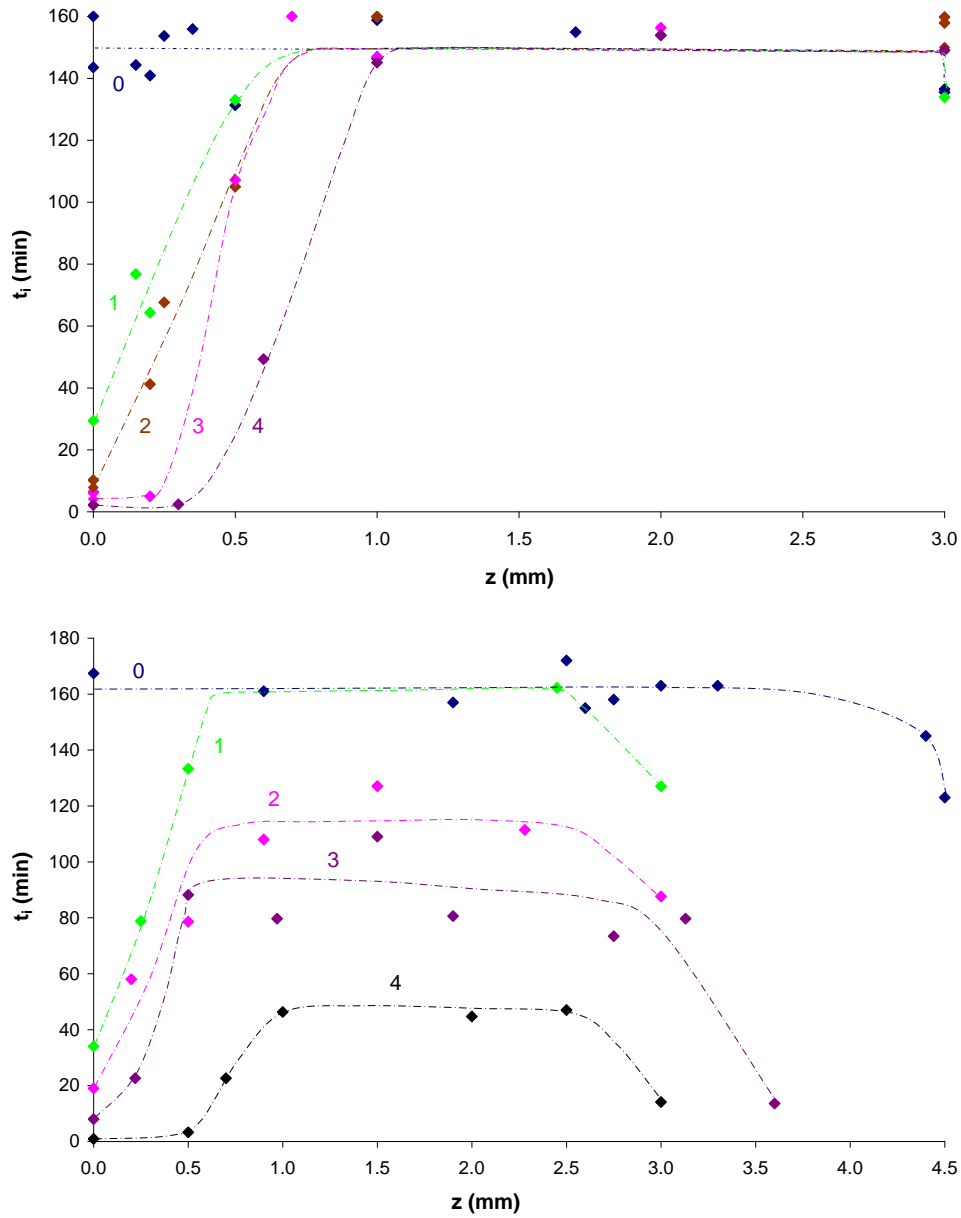
During exposure in the presence of disinfectants, the induction time decreases more fastly in the ISL than in other pipe zones, showing that there is a reactive species coming from the disinfectant (RSD) which destroys the stabilizer and that this attack is kinetically limited by the RSD diffusion.



Top: Accelerated ageing in highly concentrated (2.5–70 ppm) DOC solutions at 40°C. Ageing conditions are: 0 hours (0); 23 h in 2.5 ppm (1); 7 h in 11.5 ppm (2); 23 h in 10.1 ppm (3); 240 h in 31.8 ppm (4); 1 224 h in 66.8 ppm (5); 2 376 h in 68.5 ppm (6).

Bottom: Natural ageing in various sites of the south of France. Pipe ages are: 0 h (0); 5.5 years (1); 8 years (2); 9 years (3); 12 years (4); 18 years (5).

Figure 8. Induction time thickness profiles for pipes aged in the presence of chlorine dioxide



Top: Accelerated ageing in highly concentrated (4 ppm) bleach solutions at 40°C. Exposure times are: 0 h (0); 1 320 h (1); 2 136 h (2); 4 800 h (3); 8 760 h (4).

Bottom: Natural ageing in various sites in France. Pipe ages are: 0 hours (0); 5 years (1); 9 years (2); 12 years (3); 18 years (4).

Figure 9. Induction time thickness profiles for pipes aged in the presence of bleach

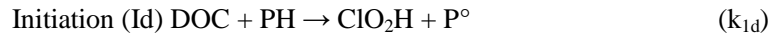
This interpretation is clearly confirmed by the results of exposures in non disinfected water (Figure 10).

In the case of accelerated aging, very little changes are observed. In the case of natural aging, however, there is a general decrease of  $t_i$  slightly faster in the ISL than in the other zones. It is clear that in CZ and OSL, there is a physical loss of antioxidant, but this phenomenon is too slow to be observed in the timescale of accelerated aging tests. The faster

decrease in ISL can be explained by the fact that antioxidant extraction by water is faster than evaporation as already observed by Lundback et al. (2006a and b), but not necessarily generalizable to all stabilizer formulae.

Two important additional remarks can be made:

- (a) *About the ISL depth:* In the case of DOC (and perhaps, also, in the case of bleach, but the results are not so clear), the separation between ISL and CZ is sharp, i.e. the front of DOC attack is abrupt and its depth *tends towards an asymptotic value of about 1 mm independent of exposure conditions*, i.e. identical for accelerated and natural aging. This result would be unexplainable if DOC was consumed only by reaction with the stabilizer because, in this case, the boundary of ISL would be continuously shifted towards the right until the complete disappearance of the stabilizer. The only possible explanation (Colin et al. 2009b) is that DOC is also consumed by its reaction with PE:



This is a second-order reaction, but at low conversions (i.e.  $[\text{PH}] \approx [\text{PH}]_0$ ), it behaves as a pseudo-first-order reaction:

$$\frac{d[\text{DOC}]}{dt} = -k_{1d}[\text{PH}][\text{DOC}] \approx -K [\text{DOC}] \quad (13)$$

where  $K = k_{1d}[\text{PH}]_0 \approx \text{constant}$ .

According to a simplified theory of diffusion controlled reactions, the depth  $L_R$  of reagent penetration in the case of first-order process is given by Equ. 9. Since, here, accelerated aging tests have been made at temperatures close to the ambient temperature,  $D$  and  $K$  values are not very different from natural ageing ones, and the depth of ISL must be almost the same, as experimentally observed.

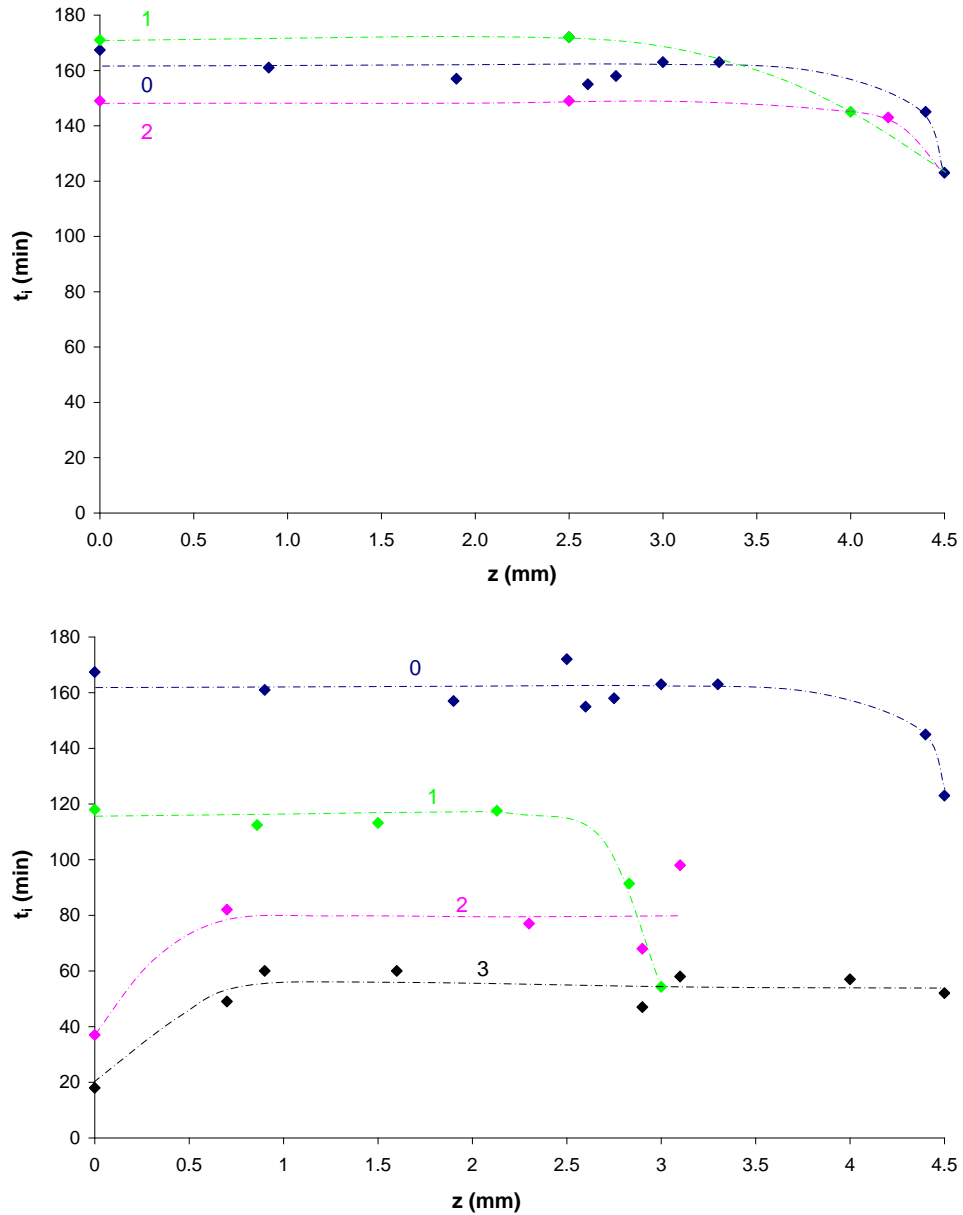
- (b) *About the flatness of profiles:* As mentioned in the introduction, antioxidant profiles remain flat during aging (in the regions not reached by the RSD, indeed) when the rate controlling physical process is evaporation or extraction by water or both. In such cases, the pertinent boundary condition at the sample surface is:

$$\left( \frac{d[\text{RSD}]}{dt} \right)_{z=0 \text{ or } L} = D \left( \frac{\partial^2 [\text{RSD}]}{\partial z^2} \right)_{z=0 \text{ or } L} - \beta_{0 \text{ or } L} [\text{RSD}]_{z=0 \text{ or } L} \quad (14)$$

$\beta$  has the dimension of a first-order rate constant with the following physical meaning for evaporation (the same reasoning can be made for extraction by water): If pure antioxidant evaporates at a rate  $r_0$  (in  $\text{mol.m}^{-2}.\text{s}^{-1}$ ), it is assumed that, in a polymer containing an antioxidant in concentration  $[A]$ , the evaporation rate would be:

$$r = r_0 \frac{[A]}{[A]_S} = h_V [A] \quad (15)$$

where  $[A]_S$  is the antioxidant concentration at saturation and  $h_V$  ( $\text{m}\cdot\text{s}^{-1}$ ) is a characteristic of antioxidant.



Top: Accelerated ageing at 40°C. Exposure times are: 0 h (0); 624 h (1); 2 376 h (2).

Bottom: Natural ageing in various sites in France. Pipe ages are: 0 hours (0); 7 years (1); 13 years (2); 15.5 years (3).

Figure 10. Induction time thickness profiles for pipes aged in non disinfected water

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For a sample of thickness  $L$ , the change in concentration is thus given by:

$$\frac{d[A]}{dt} = -\frac{r}{L} = -\beta[A] \quad (16)$$

where  $\beta = \frac{h_v}{L}$  is a first-order rate constant ( $s^{-1}$ ).

The time constant for this process would be:

$$\tau_v = \beta^{-1} \quad (17)$$

The time constant for antioxidant diffusion is:

$$\tau_D = \frac{L^2}{D} \quad (18)$$

One can thus define a dimensionless ratio (Crank, 1975; Calvert and Billingham, 1979 and 1980):

$$\Phi = \frac{\tau_D}{\tau_v} = \frac{\beta L^2}{D} \quad (19)$$

Then, if  $\Phi \gg 1$ , evaporation is faster than diffusion. The stabilizer concentration is close to zero in the superficial layers and increases regularly towards the CZ. On the contrary, if  $\Phi \ll 1$ , evaporation is slower than diffusion and controls antioxidant loss kinetics. Diffusion is fast enough to homogenize the antioxidant distribution at every time, the profile is flat.

Here, apparently, we are always in the case where  $\Phi \ll 1$  at ambient temperature, for wall thicknesses such as:  $3 \text{ mm} \leq L \leq 5 \text{ mm}$ . But, we do not exclude to observe the diffusion controlled regime for higher wall thicknesses and/or higher temperatures or for other stabilizers.

## 2. Degradation Profiles

A carbonyl concentration thickness profile superimposed to the corresponding induction time thickness profile, in the case of accelerated aging in a highly concentrated DOC (66.5 ppm) solution at  $40^\circ\text{C}$ , is shown in Figure 11.

The carbonyl concentration decreases pseudo-exponentially with depth and vanishes at about  $600 \mu\text{m}$  depth, whereas the antioxidant is destroyed until about  $1 \text{ mm}$  depth. These results call for two important remarks which can be generalized to other aging conditions:

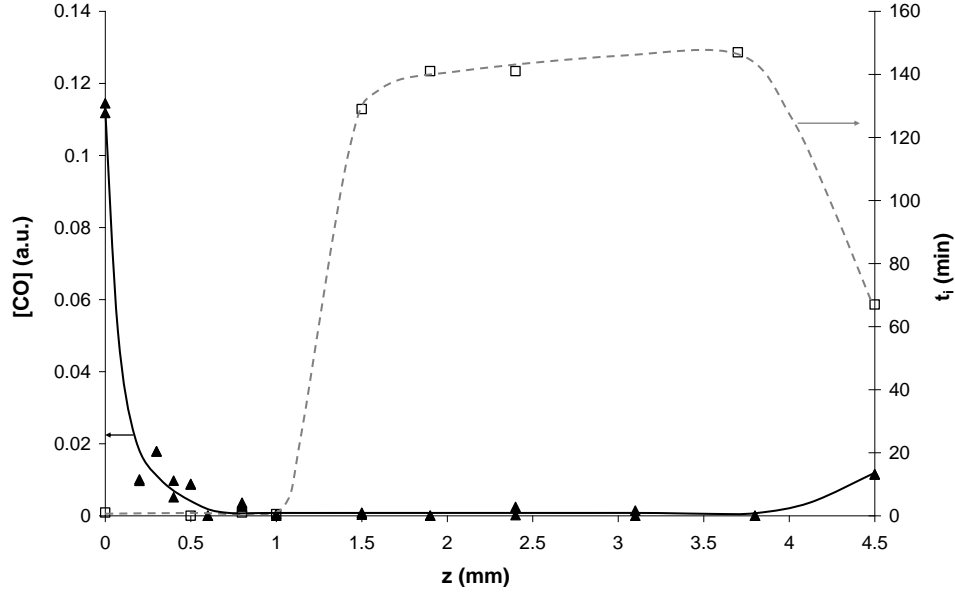


Figure 11. Carbonyl concentration and induction time thickness profiles obtained after exposure in DOC (66.5 ppm) solution at 40°C for 2376 hours

- Oxidation is diffusion limited and obviously initiated by RSD, otherwise the profile would be symmetrical.
- The oxidation area is sharper than the antioxidant attack area, both phenomena are not simply interrelated. Since we suppose that oxidation is the cause of embrittlement, it can be concluded that the relationship between the antioxidant profile and the pipe lifetime, if such a relationship exists, must be very complex.

### 3. Incorporation of Diffusion Terms into the Kinetic Model

The case of chlorine dioxide (DOC) (Colin et al. 2009a) will be taken as an example, but the principle remains the same for other mechanisms. Here, three molecular (e.g. mobile) reactive species have to be taken into account: chlorine dioxide (DOC), antioxidant (AH) and oxygen ( $O_2$ ). Their concentration changes are governed by differential equations derived from the mechanistic model. A diffusion term will be added to each of these equations (Colin et al., 2009c). These equations are:

$$\text{For oxygen: } \frac{d[O_2]}{dt} = D_{O_2} \frac{\partial^2 [O_2]}{\partial z^2} - k_2 [P^\circ] [O_2] + k_{60} [PO_2^\circ]^2 \quad (19)$$

$$\text{For stabilizer: } \frac{d[AH]}{dt} = D_{AH} \frac{\partial^2 [AH]}{\partial z^2} - k_7 [PO_2^\circ] [AH] - k_{8d} [DOC] [AH] \quad (20)$$

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$$\text{For DOC: } \frac{d[\text{DOC}]}{dt} = D_{\text{DOC}} \frac{\partial^2 [\text{DOC}]}{\partial z^2} - k_{1d} [\text{DOC}] [\text{PH}] - k_{4d} [\text{P}^\circ] [\text{DOC}] - k_{8d} [\text{DOC}] [\text{AH}] \quad (21)$$

where  $D_{\text{O}_2}$ ,  $D_{\text{AH}}$  and  $D_{\text{DOC}}$  are respectively the diffusion coefficients of oxygen, antioxidant and chlorine dioxide in PE.

With the four other differential equations describing the concentration changes of  $[\text{PO}^\circ]$ ,  $[\text{OP}]_{\text{cage}}$ ,  $\text{P}^\circ$ ,  $\text{PO}_2^\circ$  and  $\text{POOH}$ , these equations constitute the nucleus of the kinetic model. This system of 7 equations can be resolved in time  $t$  and space  $z$ , using a finite difference (Colin et al., 2009c) or a finite element method (Olivier et al., 2009) with pertinent boundary conditions. The resolution gives the concentration value of every reactive species at any time and any depth in the wall thickness. Using Eqs 4–6, it is then possible to determine the weight average molar mass  $M_w$  at every time, every depth, which is the key information to build the “mechanical” modulus of the model.

## MECHANICAL ASPECTS

### 1. Strategy of Model Elaboration

As mentioned in introduction, we chosen the “scenario M2” to predict the pipe failure, although at this state of our knowledge, “scenario M1” cannot be definitively rejected. “Scenario M2” can be schematized by Figure 12.

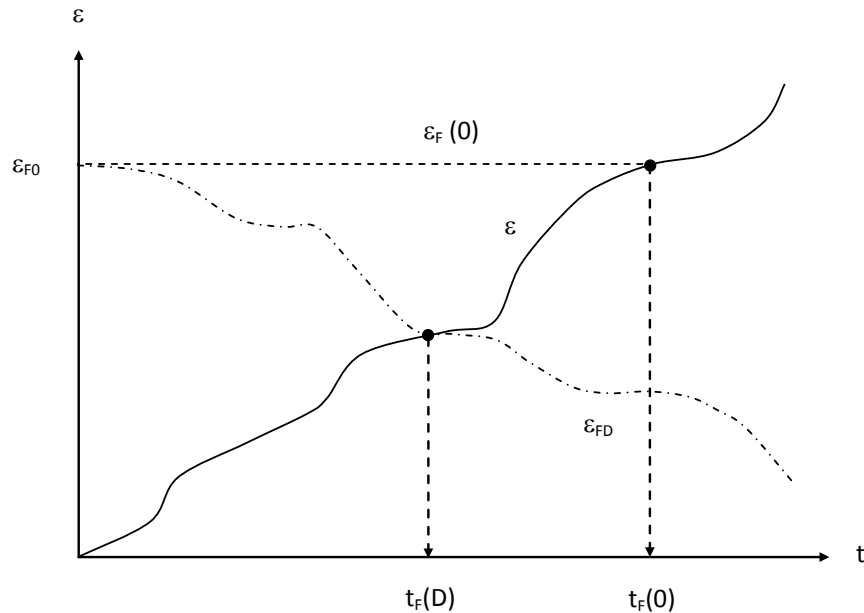


Figure 12. Schematization of “scenario M2” for pipe failure (see text)



Under a hoop stress  $\sigma$ , the pipe undergoes creep. Under this creep, the polymer can eventually reach a critical deformation state where cracks initiate and then, propagate catastrophically owing to accelerating effects of stress concentrations. The mechanisms of PE failure under static stress are now relatively well understood (see for instance Galeski, 2005; Plummer, 2005), but not at the point where they could be translated into equations able to be used in a kinetic model. Here, it will be assumed that there is an unspecified strain component  $\varepsilon$  (whole macroscopic strain? Anelastic macroscopic strain? Strain localized in the amorphous interlamellar region? etc ...) and that failure occurs when this strain component reaches a critical value:  $\varepsilon = \varepsilon_F$ . In a first approach, it is assumed that the creep kinetic law:  $\varepsilon = f(\sigma, T, t)$  is independent of polymer degradation. As a matter of fact, in the conversion range of interest, degradation modifies only the large scale structure of macromolecules, but does not modify significantly the molecular motions responsible for viscoelasticity, except in the final phase where chain reptation (De Gennes, 1971) becomes important. In contrast, the failure criterion  $\varepsilon_F$  depends on polymer structure, especially of molar mass  $M_W$ , through a dependence having presumably the shape of Figure 5. Two cases have then to be distinguished:

- In the absence of disinfectant, there is no change of molecular weight, the failure criterion remains constant:  $\varepsilon_F = \varepsilon_F(0)$ , and fracture occurs at time  $t_F = t_F(0)$ .
- In the presence of disinfectant, there is a molecular weight decrease and then, a decrease of the failure criterion:  $\varepsilon_F = \varepsilon_F(D)$ . Fracture occurs thus at time  $t_F(D) < t_F(0)$ .

Schematically: The chemical model predicts the change in molar mass:  $M_W = g(t)$ . We need in addition:

- A kinetic law for creep:  $\varepsilon = f(t)$ ;
- A relationship linking the fracture criterion  $\varepsilon_F$  to  $M_W$ .

The lifetime would be then given by:

$$t_F = f^{-1}(\varepsilon_F) \quad (22)$$

where  $f^{-1}$  is the reciprocal function of  $f$ .

In practice, temperature and eventually stress undergo fluctuations, for instance seasonal variations of temperature. These fluctuations can be eventually taken into account in the model if we start from rate expressions:  $\dot{\varepsilon} = \dot{f}(t)$

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## 2. Kinetic Model for Creep

The creep rate depends essentially on three variables: the stress  $\sigma$ , the temperature  $T$  and the time  $t$ .  $\dot{\varepsilon}$  increases with  $\sigma$  and  $T$  and decreases with  $t$ . The temperature effect can be represented, at least in a first approach, by Arrhenius law:

$$\dot{\varepsilon} \propto e_T \quad (23)$$

where

$$e_T = \exp - \frac{H}{RT} \quad (24)$$

The effect of stress and time is determined by viscoelastic deformation mechanisms and can take complex mathematical forms (Ferry, 1980). Here, it has been chosen to take an extremely simple form, but with a constraint: Applying a constant failure criterion, one must obtain results consistent with literature data according which, in the absence of polymer degradation:

$$\sigma = A t_F^{-b} \quad (25)$$

where  $A$  is temperature dependent and  $b \approx 0.3$ .

The simplest kinetic creep law fulfilling the above conditions would be:

$$\dot{\varepsilon} = k e_T \sigma t^{-a} \quad (26)$$

where  $k$  and  $a$  are constants.

The integration gives:

$$\varepsilon = \int_0^t \dot{\varepsilon} dt = \frac{1}{1-a} k e_T \sigma t^{1-a} \quad (27)$$

Failure occurs at  $t = t_F$  such as:

$$\varepsilon_F = \frac{1}{1-a} k e_T \sigma t_F^{1-a} \quad (28)$$

This equation is equivalent to Equ. 25:

$$\text{Log } \sigma = \text{Log } A - b \text{ Log } t_F \quad (29)$$

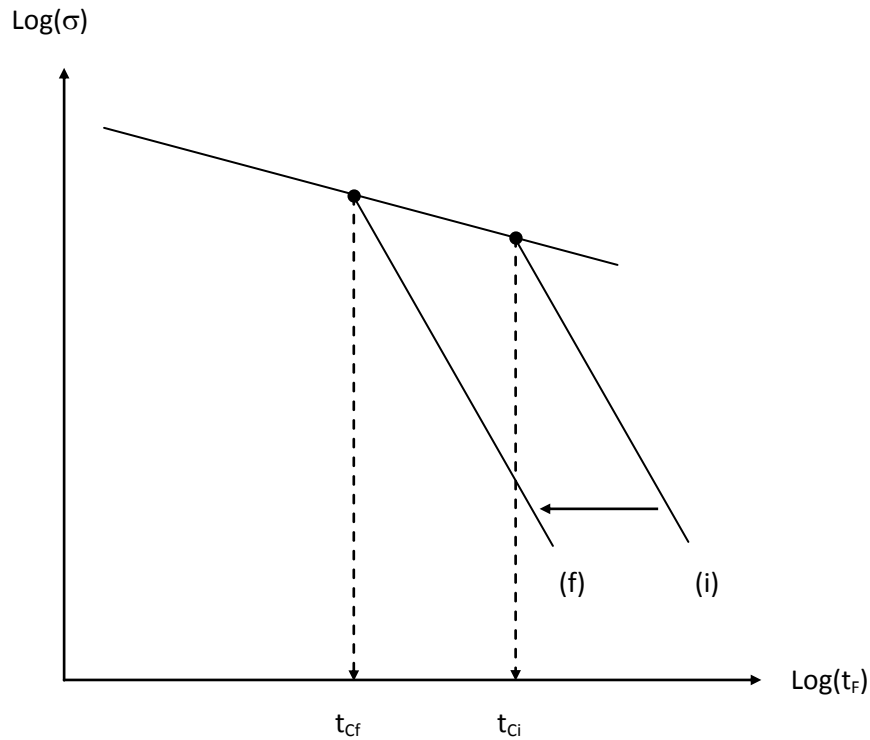


Figure 13. Presumed stress–lifetime logarithmic plot for a virgin (i) and degraded (f) pipe.

$$A = \frac{\varepsilon_F}{k} \frac{(1-a)}{e_T} \quad (30)$$

where

At this state of our knowledge,  $k$ , i.e. also  $A$ , is an adjustable parameter. Equ. 26 could thus predict the observed behaviour (in the absence of disinfectants) provided that  $b = (1 - a) \approx 0.3$  i.e.  $a \approx 0.7$ .

According to the chosen assumption,  $b$  is a characteristic of the creep mechanism, which remains unchanged during polymer degradation. In other words, the stress–lifetime graph (Figure 1) for a polymer before (i) and after (f) degradation would have the shape of Figure 13.

Schematically, there is no significant change in behaviour in ductile regime, but degradation, i.e. molar mass decrease, induces a translation of the straightline characterizing brittle regime towards short time.

### 3. Failure Criterion

If, as assumed, a decrease in molar mass induces a translation of the “brittle regime” straightline in Figure 13, this means that the prefactor  $A$  in Equ. 25 or  $k$  in Equ. 28 must depend on molar mass. This dependence can be understood on the following physical basis:

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In the amorphous phase of PE, the macromolecules are entangled and behave as a physical network able to resist to cavitation under service stresses. However, at ambient temperature, i.e. relatively far above its glass transition temperature ( $\approx -40^\circ\text{C}$ ), the amorphous phase is “stirred” by molecular motions of various types among which reptation (De Gennes, 1971). PE chains can disentangle by reptation, but the characteristic time of disentanglement  $t_{\text{dis}}$  increases rapidly with the chain length, typically:

$$t_{\text{dis}} \propto M_{\text{w}}^3 \quad (31)$$

Indeed, if a polymer is continuously loaded for a time longer than the disentanglement characteristic time, it behaves as a non entangled polymer with practically no resistance to cavitation and failure. The transition time  $t_{\text{c}}$  between ductile (I) and brittle (II) regimes is thus expected to be a sharply increasing function of molar mass, i.e. a rapidly decreasing function of the number of chain scissions.

Colin et al. (2009b) decided to represent the influence of molar mass by a power law, that leads to the following equation:

$$\text{Log } t_{\text{F}} = A_0 + \frac{B}{T} + C \text{ Log } M_{\text{w}} - \frac{1}{1-a} \text{ Log } \sigma \quad (32)$$

For the PE under investigation, at  $15^\circ\text{C}$ , the parameter values were:

$$A_0 = -29.7; B/T = 30.2; C = 3.2; \text{ and } 1/(1-a) = 3.3.$$

We can now understand why the slope  $\Delta \text{Log}(\sigma) / \Delta \text{Log}(t_{\text{F}})$  in Figure 4 is almost vertical in regime (III), as illustrated in Figure 14.

Let us consider a PE sample having an initial molar mass  $M_{\text{w}0}$ . In the absence of disinfectant, at the stress  $\sigma$ , it would undergo failure at point A at time  $t_{\text{F}0}$ . After a certain time of ageing, its molar mass would decrease and take the value  $M_{\text{w}}$ . The straightline of regime (II) would be translated towards the left and failure would occur in the point B for the stress  $\sigma$ , the time to failure being  $t_{\text{F}1}$ . Let us now consider the behaviour at a stress  $(\sigma - \Delta\sigma)$ . For a molar mass  $M_{\text{w}}$ , fracture would occur at the point C, corresponding to the lifetime  $t'_{\text{F}1}$ . However, during the excess of lifetime relatively to  $t_{\text{F}1}$ , degradation continues and the molar mass becomes  $(M_{\text{w}} - \Delta M_{\text{w}})$ , that corresponds to a new translation of the straightline of regime (II) towards the left and thus, to a rupture at the point D corresponding to a lifetime  $t_{\text{F}2}$  such as:  $t_{\text{F}1} < t_{\text{F}2} < t'_{\text{F}1}$ . One sees that locally, the slope of the curve  $\text{Log}(\sigma) = f(\text{Log}(t_{\text{F}}))$  is expected to be higher than the slope of the straightline of regime (II). The slope ratio depends, indeed, on the polymer degradation rate. If this ratio is high enough, the curve in regime (III) will appear almost vertical and practically undistinguishable from a straightline, although it is not probably a straightline.

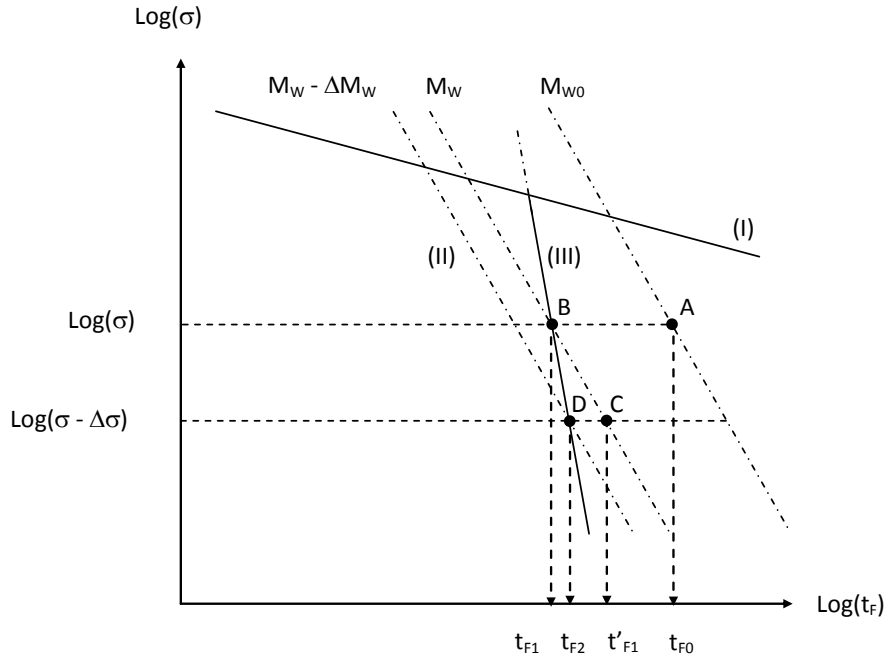


Figure 14. Quasi verticality of the graph  $\Delta \text{Log}(\sigma) / \Delta \text{Log}(t_F)$  in regime (III) (see text)

#### 4. Integration of the “Mechanical Modulus” into the Lifetime Prediction Model

According to the chosen assumptions, creep is expected to be homogeneous in the whole pipe wall thickness. However, embrittlement due to polymer degradation is localized, as seen in previous sections, in a relatively thin superficial layer. Cracks initiate and propagate easily in the degraded layer when the molar mass is lower than  $\approx 70 \text{ kg}\cdot\text{mol}^{-1}$ . The problem is now to determine if cracks will stop at the degraded/non degraded interface or if they will cross this latter and lead to the pipe failure.

From a simple application of Equ. 1, one sees that, since cracks reduce the wall thickness, they increase the stress. By derivation, one would obtain:

$$\frac{d\sigma}{\sigma} = -\frac{dL}{L} \frac{D_{\text{out}} + 2L}{D_{\text{out}} - L} \approx -\frac{\Delta L}{L} \left( 1 + \frac{3L}{D_{\text{out}}} \right) \quad (33)$$

According to the bases of fracture mechanics (Griffith, 1920), there is a critical defect size (i.e. here a critical depth of degraded layer) beyond which cracks propagate in the sample core and induce fracture. This concept has been refined later (Rolland et al., 1982; Schoolenberg, 1988). In the case of PE radiochemical oxidation, Audouin and Verdu (1991) have put in evidence (from tensile tests) the existence of a critical thickness of the oxidized layer, of the order of  $200 \mu\text{m}$ , beyond which thick samples become brittle.

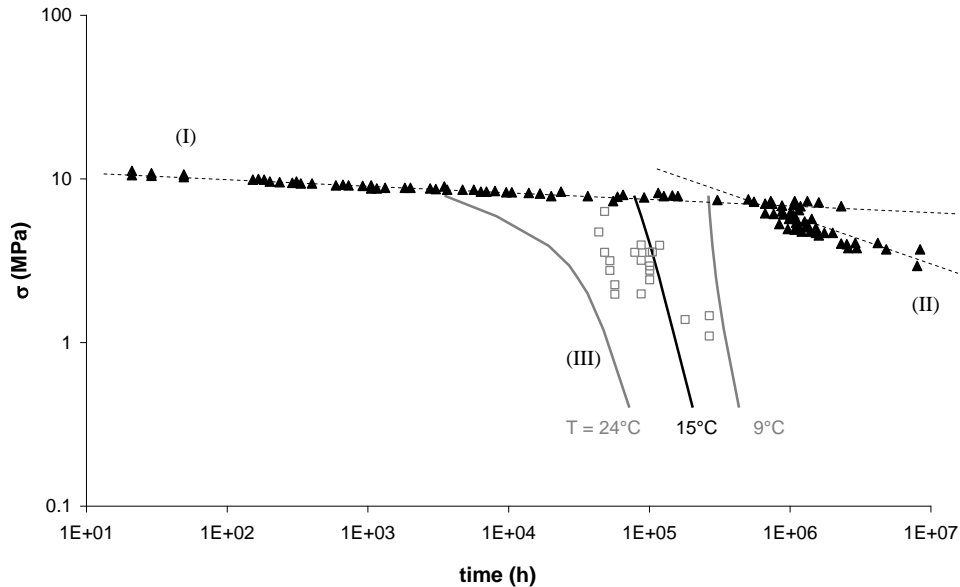


Figure 15. Stress–lifetime logarithmic plot. Closed symbols: Curve obtained from Lu and Brown (1990) results extrapolated at 15°C for a non disinfected water; Open symbols: Experimental results obtained on pipes naturally aged in a French network of drinking water disinfected by chlorine dioxide (south of France); Dashed line: Model prediction for a non disinfected water; Full lines: Model prediction for disinfected water at 9, 15 and 24°C

Rigorously speaking, it would be necessary, in the case under study, to establish the kinetics of crack propagation in a material characterized by a toughness gradient in the superficial layer. In a first approach, we will propose a simpler approach which can be summarized as follows: A critical depth  $L_C$  would be of the order of 100  $\mu\text{m}$ . It is considered that, when the molar mass reaches a value of  $\approx 70 \text{ kg}\cdot\text{mol}^{-1}$  at this depth, cracks propagate into the wall core and pipe failure occurs.

Lifetime was calculated on this basis, in the case of DOC disinfectant. The results are shown in Figure 15.

## CONCLUSIONS

In the normal use conditions for water transport in polyethylene pipes, brittle failure must occur after a finite time, but in the case of pure water, this latter must exceed 50 years, that is economically acceptable. Disinfectants such as chlorine, bleach or chlorine dioxide can induce polymer degradation through oxidative processes, and reduce lifetime at eventually unacceptable values. This problem has raised up a relatively abundant scientific and technical literature since the beginning of 80's.

It is now clear that any kinetic model aimed to predict the pipe lifetime must involve elements coming from three distinct disciplines:

- (i) Radical chemistry in polymer matrix and its kinetic modelling to explain the role of disinfectant nature and concentration on polymer degradation;

- (ii) Transport phenomena (coupled with chemistry) to explain the depth distribution of reactive species into the wall thickness;
- (iii) Mechanical failure processes and their coupling with polymer degradation.

Concerning first chemical aspects, it seems that PE can perish only by chain scission and that this latter can result only from oxidation. Most of the authors involved in this research have considered more or less implicitly that antioxidants play a key role in this process, that leads to give a key importance to antioxidant thickness profiles. In the model proposed here, the role of antioxidants would have an importance varying in the opposite way as the aggressivity of disinfectants. Antioxidants would play a determining role in pure water, practically no role in the case of DOC disinfected water, and probably an intermediary role in bleach or chlorine disinfected water. To our opinion, chemical mechanisms are reasonably well elucidated in the case of DOC, but open questions remain in the case of chlorine or bleach.

Concerning transport aspects, the main obstacle is, no doubt, to determine the basic parameters, i.e. solubility and diffusivity coefficients of species characterized by a relatively low solubility, a relative instability, and a reactivity with the matrix and its antioxidants. The knowledge of these quantities is absolutely needed for the model elaboration.

Concerning mechanical aspects, it is obvious that the assumptions made here are strong oversimplifications, but it seems to us that the strategy of modelling is pertinent and open to more sophisticated approaches, as well for creep kinetics as for failure mechanisms, and the influence of degradation on these latter. It seems important to keep in mind that the model, whatever the chosen scheme, must predict the stress–lifetime relationship observed in the absence of disinfectants for which a considerable set of experimental data is available.

## REFERENCES

- [1] Audouin, L. & Verdu, J. (1991). “Change in mechanical properties of low-density polyethylene during radiochemical aging”, in *Radiation Effects on Polymers*, édité par R.L. Clough & S.W. Shalaby, ACS Symposium Series, 475, American Chemical Society, Washington D.C., 473-484.
- [2] Audouin, L., Langlois, V., Verdu, J. & De Bruijn, J. C. M. (1994). Role of oxygen diffusion in polymer ageing: kinetic and mechanical aspects, *Journal of Materials Science*, 29(3), 569-583.
- [3] Billingham N. C. & Calvert, P. D. (1980). The physical chemistry of oxidation and stabilization of polyolefins, in *Development in Polymer Stabilization*, vol. 3, G. Scott ed., Applied Science Publishers, London, Chap., 5, 139-190.
- [4] Bradley S. W. & Bradley, W. L. (1997). The effect of chlorine on the long-term durability of crosslinked polyethylene pipe, in *Proceedings of the 10<sup>th</sup> International Conference on Deformation, Yield and Fracture of Polymers*, Cambridge, UK, 114-117, April 7-10,.
- [5] Brown, N., Donofrio, J. & et Lu, X. (1987). The transition between ductile and slow-crack-growth failure in polyethylene, *Polymer*, 28(8), 1326-1330.

- [6] Calvert, P. D. & Billingham, N. C. (1979). Loss of additives from polymers: A theoretical model, *Journal of Applied Polymer Science*, 24(2), 357-370.
- [7] Colin, X., Audouin, L. & Verdu, J. (2004). Determination of thermal oxidation rate constants by an inverse method. Application to polyethylene, *Polymer Degradation and Stability*, 86, 309-321.
- [8] Colin, X., Monchy-Leroy, C., Audouin, L. & Verdu, J. (2007). Lifetime prediction of polyethylene in nuclear plants, *Nuclear Instruments and Methods in Physics Research Section, B265(1)*, 251-255.
- [9] Colin, X., Audouin, L., Verdu, J., Rozental-Evesque, M., Rabaud, B., Martin, F. & Bourguine, F. (2009a). Aging of polyethylene pipes transporting drinking water disinfected by chlorine dioxide. I-Chemical aspects, *Polymer Engineering and Science*, 49(7), 1429-1437.
- [10] Colin, X., Audouin, L., Verdu, J., Rozental-Evesque, M., Rabaud, B., Martin, F. & Bourguine, F. (2009b). Aging of polyethylene pipes transporting drinking water disinfected by chlorine dioxide. II-Lifetime prediction, *Polymer Engineering and Science* 49(8), 1642-1652.
- [11] Colin, X., Audouin, L. & Verdu, J. (2009c). Towards a non empirical kinetic model for the lifetime prediction of polyethylene pipes transporting drinking water, *Macromolecular Symposia*, 286, 81-86.
- [12] Crank, J. (1975). *"The Mathematics of Diffusion"*, 2<sup>nd</sup> edition, Oxford University Press, Oxford.
- [13] Dear, J. P. & Mason, N. S. (2001). The effects of chlorine depletion of antioxidants in polyethylene, *Polymers and Polymer Composites*, 9(1), 1-13.
- [14] Dear, J. P., & Mason, N. S. (2006). Effect of chlorine on polyethylene pipes in water distribution network, *Proceedings of IMechE 220, Part L: Journal of Materials: Design and Applications*, 97-111.
- [15] De Gennes, P. G. (1971). Reptation of a polymer chain in the presence of fixed obstacles, *Journal Chemical Physics*, 55, 572-579.
- [16] Denisov, E. T. & Afanas'ev, I. B. (2005). "Oxidation and antioxidants in organic chemistry and biology", Taylor and Francis, Boca Raton, Florida.
- [17] Durliat, G. (1997). L'eau de javel : Sa chimie et son action biochimique, *Bulletin de l'Union des Physiciens*, 91(792), 451-471 (Mars).
- [18] Fayolle, B., Richaud, E., Colin, X. & Verdu, J. (2008). Review: Degradation-induced embrittlement in semi-crystalline polymers having their amorphous phase in rubbery state, *Journal of Materials Science*, 43, 6999-7012.
- [19] Ferry, J. D. (1980). *"Viscoelastic properties of polymers"*, 3<sup>rd</sup> edition, John Wiley, New York.
- [20] Fukatsu, K. & Kokot, S. (2001). Degradation of poly(ethylene oxide) by electro-generated active species in aqueous halide medium, *Polymer Degradation and Stability*, 72(2), 353-359.
- [21] Galeski, A. (2005). "Strength and toughness of crystalline polymer systems", in *Mechanical properties of polymers based on nanostructure and morphology*, G.H. Michler and F.-J. Balta Calleja eds, CRC Taylor and Francis, Boca Raton, Chap. 5, 159-211.



- [22] Gandek, T. P., Hatton, T. A. & Reid, R. C. (1989a). Batch extraction with reaction. Phenolic antioxidant migration from polyolefins to water. I: Theory, *Industrial and Engineering Chemistry Research*, 28(7), 1030-1036.
- [23] Gandek, T. P., Hatton, T. A. & Reid, R. C. (1989b). Batch extraction with reaction. Phenolic antioxidant migration from polyolefins to water. II: Experimental results and discussion, *Industrial and Engineering Chemistry Research*, 28(7), 1036-1045.
- [24] Gaudichet-Maurin, E. (2005). "Characterization and ageing of a water ultrafiltration membrane", *PhD Thesis*, ENSAM (ARTS ET METIERS ParisTech), Paris, France.
- [25] Gedde, U. W., Viebke, J., Leijstrom, H. & Ifwarson, M. (1994). Long-term properties of hot-water polyolefin pipes: a review, *Polymer Engineering and Science*, 34(24), 1773-1787.
- [26] Gill, T. S., Knapp, R. J., Bradley, S. W. & Bradley, W. L. (1999). Long-term durability of crosslinked polyethylene tubing used in chlorinated hot water systems, *Proceedings of Plastic Pipes X* 28(6), Goteborg, Sweden, 309-313.
- [27] Griffith, A. A. (1920). The phenomena of rupture and flow in solids, *Philosophical Transactions of the Royal Society (Londres)* A221, 163-197.
- [28] Hamouda, H. B. H. (2000). "Endommagement et fissuration en fluage de polyéthylènes extrudés Approche locale- Approche globale", *PhD Thesis*, Ecole des Mines, Paris.
- [29] Hassinen, J., Lundback, M., Ifwarson, M. & Gedde, U. W. (2004). Deterioration of polyethylene pipes exposed to chlorinated water, *Polymer Degradation and Stability* 84(2), 261-267.
- [30] Henry, J. L. & Garton, A. (1990). Oxidation of polyethylene in water and aqueous salts, *Journal of Polymer Science: Part A: Polymer Chemistry Edition* 28, 945-948.
- [31] Holst, G. (1954). The chemistry of bleaching and oxidizing agents, *Chemical Reviews*, 54(1), 169-174.
- [32] Huang, Y. L. & Brown, N. (1991). Dependence of slow crack growth in polyethylene on butyl branch density: morphology and theory, *Journal of Polymer Science: Polymer Physics Edition*, 29(1), 129-137.
- [33] Ifwarson, M. & Aoyama, K. (1998). Results and experiences from tests on polyolefin pipes exposed to chlorinated water *Proceedings of the Plastic Pipes X Conference*, Gothenburg, 691-701.
- [34] Karlsson, K., Smith, G. D. & Gedde, U. W. (1992). Molecular structure, morphology, and antioxidant consumption in medium density polyethylene pipes in hot-water applications, *Polymer Engineering and Science*, 32(10), 649-657.
- [35] Kausch, H. H. (1987). "Polymer Fracture", 2<sup>nd</sup> edition, Springer Verlag, Berlin.
- [36] Kennedy, M. A., Peacock, A. J. & Mandelkern, L. (1994). Tensile properties of crystalline polymers: linear polyethylene, *Macromolecules*, 27(19), 5297-5310.
- [37] Khelidj, N., Colin, X., Audouin, L., Verdu, J., Monchy-Leroy, C. & Prunier, V. (2006a). Oxidation of polyethylene under irradiation at low temperature and low dose rate. Part I- The case of "pure" radiochemical initiation, *Polymer Degradation and Stability*, 91(7), 1593-1597.
- [38] Khelidj, N., Colin, X., Audouin, L., Verdu, J., Monchy-Leroy, C. & Prunier, V. (2006b). Oxidation of polyethylene under irradiation at low temperature and low dose rate. Part II- Low temperature thermal oxidation, *Polymer Degradation and Stability*, 91(7), 1598-1605.

- 
- [39] Korcek, S., Chenier, J. H. B., Howard, J. A. & Ingold, K. U. (1972). Absolute rate constants for hydrocarbon autoxidation. XXI. Activation energies for propagation and the correlation of propagation rate constants with carbon-hydrogen bond strengths, *Canadian Journal of Chemistry*, 50(14), 2285-2297.
- [40] Lu, Y., & Brown, N. (1990). The ductile-brittle transition in a polyethylene copolymer, *Journal of Material Science*, 25(1A), 29-34.
- [41] Lu, X., Qian, R. & Brown, N. (1991). Discontinuous crack growth in polyethylene under a constant load, *Journal of Materials Science*, 26(4), 917-924.
- [42] Lundback, M., Strandberg, C., Albertsson, A. C., Hedenqvist, M. S. & Gedde, U. W. (2006a). Loss of stability by migration and chemical reaction of Santonox R in branched polyethylene under anaerobic and aerobic conditions, *Polymer Degradation and Stability* 91(5), 1071-1078.
- [43] Lundback, M., Hedenqvist, M. S., Mattozzi, A. & Gedde, U. W. (2006b). Migration of phenolic antioxidants from linear and branched polyethylene, *Polymer Degradation and Stability*, 91(7), 1571-1580.
- [44] Lustiger, A. & Markham, R. L. (1983). Importance of tie molecules in preventing polyethylene fracture under long-term loading conditions, *Polymer*, 24(12), 1647-1654.
- [45] Mittelman, G., Davidson, J. H., Mantell, S. C. & Su, Y. (2008). Prediction of polymer tube life for solar hot water systems: A model of antioxidant loss, *Solar Energy*, 82(5), 452-461.
- [46] Neway, B., Hedenqvist, M. G. & Gedde, U. W. (2001). Free volume and transport properties of heterogeneous poly(ethylene-co-octene)s, *Polymer*, 42(12), 5307-5319.
- [47] Neway, B., Westberg, A., Mattozzi, A., Hedenqvist, M. G., Giacinti Baschetti, M., Mattot, V. B. F. & Gedde, U. W. (2004). Free volume and transport properties of homogeneous poly(ethylene-co-octene)s, *Polymer*, 45, 3913-3922.
- [48] Olivier, L., Baudet, C., Bertheau, D., Grandidier, J. C. & Lafarie-Frenot, M. C. (2009). Development of experimental, theoretical and numerical tools for studying thermo-oxidation of CFRP composites. *Composites: Part A: Applied Science and Manufacturing*, 40, 1008-1016.
- [49] Plummer, C. J. G., (2005). Microdeformation and fracture in semicrystalline polymers, in *Mechanical Properties of Polymers Based on Nanostructure and Morphology*, G.H. Michler and F.-J. Balta Calleja eds, Taylor and Francis, Boca Raton, Chap. 6, pp. 215-244.
- [50] Ravens, D. A. S. (1960). The Chemical reactivity of poly(ethylene terephthalate). Heterogeneous hydrolysis by hydrochloric acid, *Polymer*, 1, 375-383.
- [51] Rivaton, A., Cambon, S. & Gardette, J. L. (2006). Radiochemical ageing of ethylene-propylene-diene elastomers. 4. Evaluation of some anti-oxidants, *Polymer Degradation and Stability*, 91(1), 136-143.
- [52] Roesink, H. D. W. (1989). "Microfiltration, membrane development and module design", PhD thesis, University of Twente, The Netherlands.
- [53] Rolland, L., Thompson, K., Mostovoy, L. & Broutman, L. J. (1982). "Fracture mechanics approach to surface embrittlement in ductile polymers", *Proceedings of International Conference on Deformation, Yield and Fracture of Polymers*, Cambridge, 1-11.
- [54] Rouaix, S. (2005). "Characterisation and study of ageing of an ultrafiltration membrane", PhD thesis, University Paul Sabatier, Toulouse, France.

- [55] Saito, O. (1958a). On the effects of high energy radiation to polymers, *Journal of the Physical Society of Japan*, 13(2), 198-206.
- [56] Saito, O. (1958b). On the effects of high energy radiation to polymers, *Journal of the Physical Society of Japan*, 13(12), 1451-1464.
- [57] Schnabel, W. (1978). "Degradation by high energy radiation", in *Aspects of Polymer Degradation and Stabilisation*, H.H.G Jellinek ed., Elsevier, New York, Chap.4, 149-190.
- [58] Schoolenberg, G. E. (1988). A fracture mechanics approach to the effects of UV-degradation on polypropylene, *Journal of Materials Science*, 23(5), 1580-1590.
- [59] Smith, G. D., Karlsson, K. & Gedde, U. W. (1992). Modeling of antioxidant loss from polyolefins in hot-water applications. I: Model and application to medium density polyethylene pipes, *Polymer Engineering and Science*, 32, 658-667.
- [60] Tanaka, A., Akiyama, S. & Komukai, S. (1987). *Tokyo Gas Company ltd report*, 567.
- [61] Truss, R. W. (1986). Ensuring satisfactory service life of UPVC pressure pipe under static load, *Materials Forum*, 9, 45-52.
- [62] Truss, R. W. (1987). Temperature derating of unplasticised polyvinyl chloride (UPVC) pressure pipe, *Plastics and Rubber Processing and Applications*, 7(1), 51-56.
- [63] Truss, R. W. (1988). Lifetime predictions for UPVC pipes subjected to combined mean and oscillating pressures, *Plastics and Rubber Processing and Applications*, 10(1), 1-9.
- [64] Van Krevelen, D. W. & Hoftyzer, P. J. (1976). "*Properties of Polymers. Their Estimation and Correlation with Chemical Structure*", 3<sup>rd</sup> edition, Elsevier. Amsterdam, Chap. 18, 413,.
- [65] Verdu, J., Audouin, L. & Rychly, J. (2003). Synergism between polymer antioxidants – Kinetic modelling, *Polymer Degradation and Stability*, 79(3), 503-509.
- [66] Viebke, J., Hedenqvist, M. & Gedde, U. W. (1996). Antioxidant efficiency loss by precipitation and diffusion to surrounding media in polyethylene hot-water pipes, *Polymer Engineering and Science*, 36(24), 2896-2904.
- [67] Viebke, J. & Gedde, U. W. (1997). Antioxidant diffusion in polyethylene hot-water pipes, *Polymer Engineering and Science*, 37(5), 896-911.