Kinetics of chlorine-induced polyethylene degradation in water pipes

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A B S T R A C T

The presence of chlorine in drinking water supplies in many countries creates the undesirable side effect of causing a relatively under investigated degree of polymer degradation in the polyethylene pipes used for transport. In order to predict pipe lifetimes and ensure safe water supplies, a kinetic model using data for the degradation rates of polyethylenes immersed in chlorine solutions, was developed. In order to replicate phenomena that normally occur very slowly at low concentrations of chlorine, accelerated ageing studies were necessary. These were carried out at high chlorine concentrations under well-defined experimental conditions (70, 400 and 4000 ppm). Results showed that, for the chlorine concentrations studied, a chain scission process associated with carbonyl formation is occurring. It was also shown that the rate of this degradation does not depend on the presence of stabilizer. A kinetic model, taking into account the chlorine concentration, is proposed in order to simulate the molar mass changes occurring. This will facilitate the prediction of the degree of polyethylene embrittlement and ultimately the lifetime.

1. Introduction

High density polyethylene (HDPE) is a semi-crystalline polymer widely used for the transport of drinking water supplies. In order to ensure good microbiological quality of the water being distributed it is necessary to add disinfectants such as chlorine dioxide ClO_2 or chlorine Cl_2 [1]. However, these disinfectants have the potential to initiate oxidation processes. Indeed, under specific operational conditions (chlorine concentration, pressure and temperature), long-term contact with water containing chlorine is known to lead to degradation effects such as polyethylene embrittlement [2]. Already several studies have confirmed that this embrittlement is driven by oxidation induced by chlorine [3]. This oxidation can be followed by measuring the carbonyl group content, antioxidant level and molar mass [4,5]. However, as pointed out by Welton et al. in their exhaustive review, none of the literature data available allows the influence of the chlorine concentration for a given pH solution at low temperatures to be identified. [6]. The aim of the current study is to investigate the impact of chlorine on the degradation kinetics. This will greatly facilitate the prediction of the degree of polyethylene embrittlement since it is this phenomenon that is directly linked to the drop in molar mass during contact with chlorine [7].

In order to accelerate the ageing, two approaches have previously been used [8]. The first consisted of increasing the temperature of the water containing the chlorine. However, there is some question about this particular approach since both the HClO and ClO^- species are unstable at high temperatures i.e., $T > 40\,^{\circ}C$ [6]. To avoid HClO and ClO^- species instability, a circulation loop was used to ensure a chlorine level constant with a replacement of the medium every 30 min [8]. The second approach consisted in increasing the chlorine concentration up to 4000 mg/l while keeping the immersion temperature close to room temperature ($\sim 20\,^{\circ}C$). In this study, the second method was used in order to build a degradation kinetic model that takes the chlorine concentration into account. Particular attention was paid to the role of the stabilizers with respect to the contact conditions under study.

In the accelerated ageing experiments designed to investigate the chlorine effects on HDPE both thin and thick samples were by immersed in the chlorine solutions at room temperature. To exhibit phenomena that occur very slowly at low concentrations, the accelerated ageing experiments were carried out at three different chlorine concentrations: 70, 400 and 4000 mg/l. As a first approach, the thin samples can be considered either as a simulation of the surface of the thicker samples or as the inner walls of the pipes in the absence of the stabilizer diffusion process. To explore the influence of the stabilizers, both stabilized and unstabilized polyethylene thin films were exposed to the same water/chlorine contact conditions (i.e., 400 and 4000 mg/l).

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2. Experimental

2.1. Materials

Two types of polyethylene were chosen in order to check the influence of the stabilizers on the chlorine-induced degradation process. The first is an unstabilized polyethylene and the second a stabilized (Irganox and Irgafos 168) polyethylene which includes carbon black. Density value was close to 0.935 and 0.943, respectively. Unstabilized polyethylene samples were compression moulded into films (100 μm) in order to avoid diffusion-controlled processes. Furthermore, in the case of the stabilized polyethylene two sample geometries were investigated: thin films (∼100 μm), flat thick samples (∼3.8 mm) as well as commercial pipes used for drinking water applications (∼4 mm). Thick samples were taken as being equivalent to samples which were cut from the commercial pipes or tubes. Whereas polyethylene films were obtained by compression moulding (2 min at 200 °C), the flat thick samples were cut out from injected moulded plates. The characteristics of the resulting samples with three geometries are reported in Table 1.

2.2. Contact conditions

Ageing solutions were prepared from a commercial solution of sodium hypochlorite (NaClO) concentrated at 36°Cl, i.e., 100 g mol^{-1}. After dilution in ultrapure water, the pH of the solutions were adjusted using HCl in order to reach a pH value close to 7. This value corresponds to the usual conditions observed in drinking water distribution systems.

Knowing that hypochlorite anions (ClO^-) and hypochlorous acid HClO are highly unstable at temperatures greater than 40 °C [5], all experiments were performed at room temperature. The three high chlorine concentrations were: 70, 400 and 4000 mg/l. Immersion times of 40, 15 and 5 weeks, respectively were used.

For the experiments carried out under the 400 and 4000 mg/l conditions, the samples were immersed in chlorine solutions in glass bottles. In addition, the ageing solutions were renewed three times per week to ensure that constant chlorine conditions during the long immersions, especially at these high concentrations, were maintained. Samples were obtained and periodically characterized: once a week for 4000 mg/l and once every three weeks for 400 mg/l solutions.

At 70 mg/l, it was necessary to employ a specific device to simulate the ageing process. Commercial HDPE pipes were exposed hydrodynamically with a dedicated pilot using the closed loop mode. With this device, chlorine concentration and pH was measured and adjusted in real time. Fresh water was added automatically [9].

2.3. Characterization methods

In order to characterize the chemical changes occurring in the unstabilized HDPE films, FTIR spectrophotometric measurements were made using the transmission mode of a Bruker IFS 28 spectrophotometer with a resolution of 4 cm^{-1}. The concentration of carbonyl groups (C=O) was determined using the Beer–Lambert law, from the absorbance value at 1712 cm^{-1} with a molar absorptivity of 300 l mol^{-1} cm^{-1}. FTIR measurements were carried out in ATR mode to characterize the stabilized films and thick samples surfaces and tube inner wall.

To follow any changes on a macromolecular scale, size exclusion chromatography (SEC) was found to be the most appropriated method. Indeed, molar mass distribution is susceptible to change during chlorine contact i.e., not only a molar mass drop is expected but also a decrease in the polydispersity index (PI). SEC measurements were only carried out on film samples where degradation was expected to be homogeneous throughout the whole thickness of the sample. For SEC measurements, the samples were dissolved in trichlorobenzene at 160 °C and stabilized with BHT as stabilizer. Samples were first filtered and then injected into a chromatograph equipped with a refractometer. It should be recalled here that, due to the extension of the MWD to very low masses, the precision of M_n values is limited. In contrast, M_w values are relatively precise which is why molar mass values are reported in terms of M_w.

Table 1
Geometry and characteristics of samples studied: crystallinity ratio (X_C), weight average molar mass (M_w), polydispersity index (PI), oxidation induction time (OIT), carbon black content.

	Geometry sample	X_C	M_w	I_p	OIT (at 190 °C)	carbon black content (%)
PE unstabilized	Film	45%	143 kg/mol	19,1	0	0%
PE stabilized	Film, thick, tube	55%	203 kg/mol	20,3	>20 min	2.2%

3. Results

3.1. Chemical modification

The FTIR results for the series of experiments in which the unstabilized films were immersed in 4000 mg/l solution are shown in Fig. 1. The spectra were recorded in transmission mode and the results clearly show that the main modification is linked to a carbonyl formation. A new strong band at an absorbance value of 1712 cm^{-1} is seen to increase with increasing contact time. Similar results were obtained in the series of experiments for samples immersed in 400 mg/l solution. This carbonyl appearance can be safely attributed to the occurrence of an oxidation process. These results strongly suggest that the chlorine solution leads to the formation of a species which initiates polyethylene oxidation. Indeed, it is also well known that thermal oxidation processes alone can also lead to carbonyl formation but at 20 °C they require much longer than the contact time periods in this study.

Using the Beer–Lambert law, the carbonyl concentrations can be determined. Subsequently these are used to build up a carbonyl curve for the unstabilized films exposed at 400 and 4000 mg/l. These results are presented in Fig. 2 where the carbonyl curves are shown for both experimental contact conditions. Several conclusions can be drawn from the results shown in this figure. First, a slight induction period of about 4 weeks can be measured for the

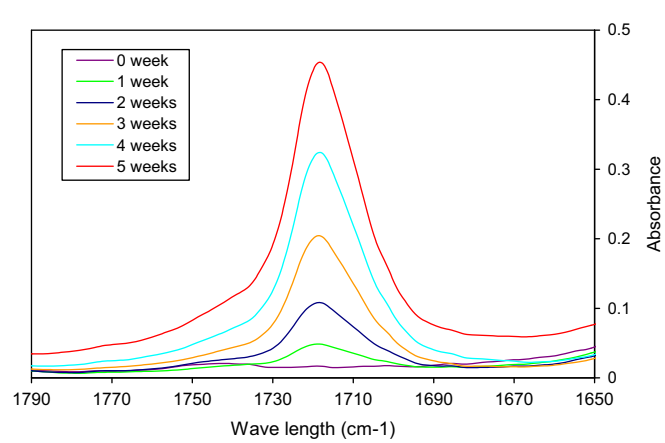

Fig. 1. FTIR spectra for unstabilized polyethylene aged in 4000 mg/l solution.

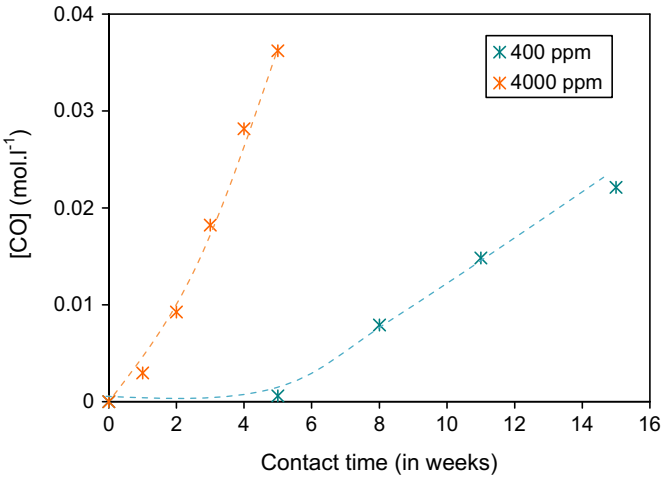

Fig. 2. Carbonyl curves from FTIR measurements for both concentrations (400 and 4000 mg/l solution) in transmission mode for unstabilized polyethylene film.

400 mg/l series whereas no induction period can be observed for the 4000 mg/l series. It is known that at 20 °C, the induction period for unstabilized polyethylene is longer than 16 weeks [10]. Hence it can be safely concluded that the presence of the chlorine strongly accelerated the polymer degradation process. The experimental results indicate that this acceleration is proportional to the chlorine concentration in the ageing solution. These conclusions are further confirmed by considering the results for the slope determined from the carbonyl curves. Indeed, this slope which corresponds to the oxidation rate (r_{CO} in Fig. 2) is also highly dependent on the chlorine concentration; a ratio close to 4 can be estimated for the r_{CO} values obtained from the 4000 mg/l and 400 mg/l solutions.

Since the carbonyl product is the main degradation side-product and its rate of formation is linked to the chlorine concentration, it can be safely concluded that degradation is due to an oxidation process in which the reactive species such as radicals are generated by the chlorine solution. This process is like an oxidation process where initiation is not only due to hydroperoxide decomposition but also due to the formation of new radicals.

3.2. Surface chemistry modification

In order to follow the oxidation, Fourier Transform Infra Red Attenuated Total Resonance (FTIR-ATR) proved the analytical technique of choice. It provides rapid analysis, is easy to use and requires minimal sample preparation, all of which are important requisites for industrial applications. Measurements were carried out on both unstabilized and stabilized polyethylene under the same conditions as previously described in part 3.1. It should be noted that the stabilized polyethylene was aged in two different forms: thin films and thick samples. This was necessary in order to investigate any eventual influence of the thickness on the degradation process at the sample surface. As can be observed from the data shown in Fig. 3, the carbonyl index is found to increase independently of the sample type. In other words, neither the influence of the stabilizers or the sample thickness have been found to affect the results data for the chlorine concentrations studied. By comparing films of unstabilized and stabilized polyethylene only, the impact of the stabilizers can be safely considered to be negligible for the chlorine concentration range in this study. Indeed, all the phenolic stabilizers are consumed from the very beginning of the immersion time period and hence the oxidation rate is mainly governed by the chlorine concentration. Where the influence of the thickness of the samples is concerned, the similar behaviour observed for both the films and the thick samples can be explained by the fact that the surface oxidation is not controlled by diffusion of the stabilizer from the centre of the sample to the surface.

As seen in Fig. 4, the carbonyl curves obtained for the stabilized polyethylene thick samples are plotted as a function of the contact time using a log scale for the three chlorine concentrations 70, 400 and 4000 mg/l. The results indicate that the carbonyl curves are proportional to the chlorine concentrations. As a result, the oxidation rate corresponding to the slope of the curve (r_{CO}) can be correlated with the chlorine concentrations using the following relationship: $r_{CO} = C \exp [\text{Chlorine}]$. This relationship is consistent with the fact that oxidation is mainly initiated by chlorine within the concentration range studied.

3.3. Molar mass changes

Since the experimental evidence confirms that chemical changes are occurring, one can expect that carbonyl formation is associated with a chain scission event. To check this hypothesis, molar mass measurements were performed on both unstabilized and stabilized polyethylene films. According to Fig. 5a, b, a weight average molar mass (M_w) drop was detected for the two conditions of chlorine solution contact, 400 and 4000 mg/l at 20 °C. It is noticeable that this decrease is observed from the very beginning of the immersion irrespective of the chlorine concentrations and the nature of the polyethylene (stabilizer present or not). After 5 weeks for samples kept under the 4000 mg/l conditions, the M_w values reached a value

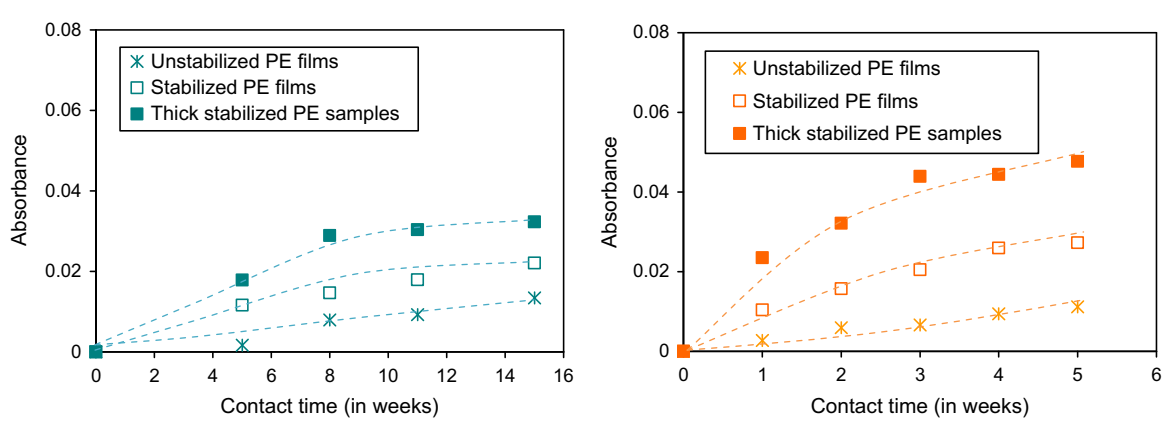

Fig. 3. Carbonyl curve data from FTIR-ATR measurements for both immersions (400 and 4000 mg/l solution), for films (unstabilized and stabilized PE) and thick samples (stabilized PE).

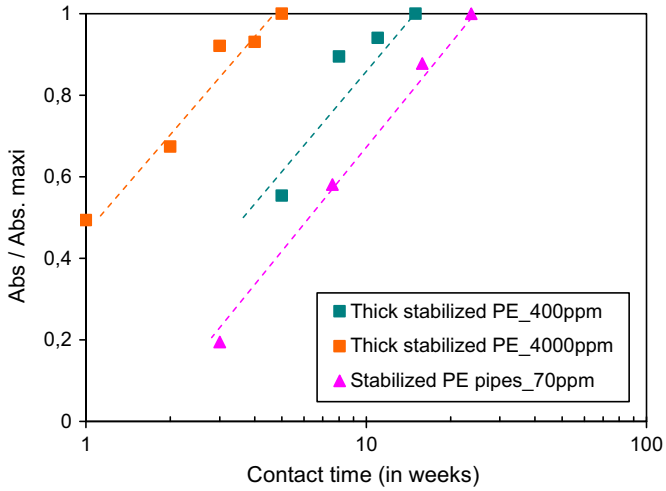

Fig. 4. Carbonyl absorbance for thick samples (70, 400 and 4000 mg/l using a log scale).

close to 40 kg mol^{-1} for the unstabilized polyethylene and 60 kg mol^{-1} for the stabilized polyethylene. With respect to the 400 mg/l experimental conditions, after 15 weeks of contact, the M_w values were found to be, about 40 kg mol^{-1} for the unstabilized polyethylene and 35 kg mol^{-1} for the stabilized polyethylene. On closer examination, one can notice a slight discrepancy between the results for both polyethylenes; the initial M_w decrease is little more pronounced in the case of the stabilized polyethylene. This slight discrepancy can be attributed to the macromolecular architecture of the virgin material since some branching is present in the case of the unstabilized polyethylene.

Using SEC measurements, the polydispersity index (PI) changes were followed during the immersion times. The PI values for the polyethylene films were plotted as a function of the contact times for the two concentrations under study (Fig. 5c, d). From an initial value of 20, the PI values dropped to a value close to 8 after 5 weeks for the 4000 mg/l experiment and to about 5 after 15 weeks for the 400 mg/l one. Moreover, the results shown in Fig. 5c, d clearly show that there is no difference in the PI decrease (as least none that can be observed) between the two polyethylenes. This confirms that there no detectable influence of the stabilizer on the chain scission kinetics under the chlorine concentrations studied.

From the observed drop in PI, values, it can be concluded that the chain scission process occurs homogeneously throughout the whole thickness of the film. In addition, it should be remembered that if the scission process exhibits a random change character, then this behaviour should theoretically lead to an asymptotic PI value of 2. This is in fact consistent with the experimental PI evolution observed. Indeed, if the polyethylene degradation was limited by diffusion processes (by oxygen, chlorine or stabilizer for instance), it would led to heterogeneous film degradation [11]. In that case, the existence of an oxidation front would induce an increase in the PI values. The studies published by Gedde et al. showed clearly that degradation can reach several hundred of μm into the depth [8], this is consistent with the fact that degradation is homogeneously distributed in our films showing a thickness of 100 μm. As a result, degradation rate is governed by temperature and/or chlorine concentration in our case.

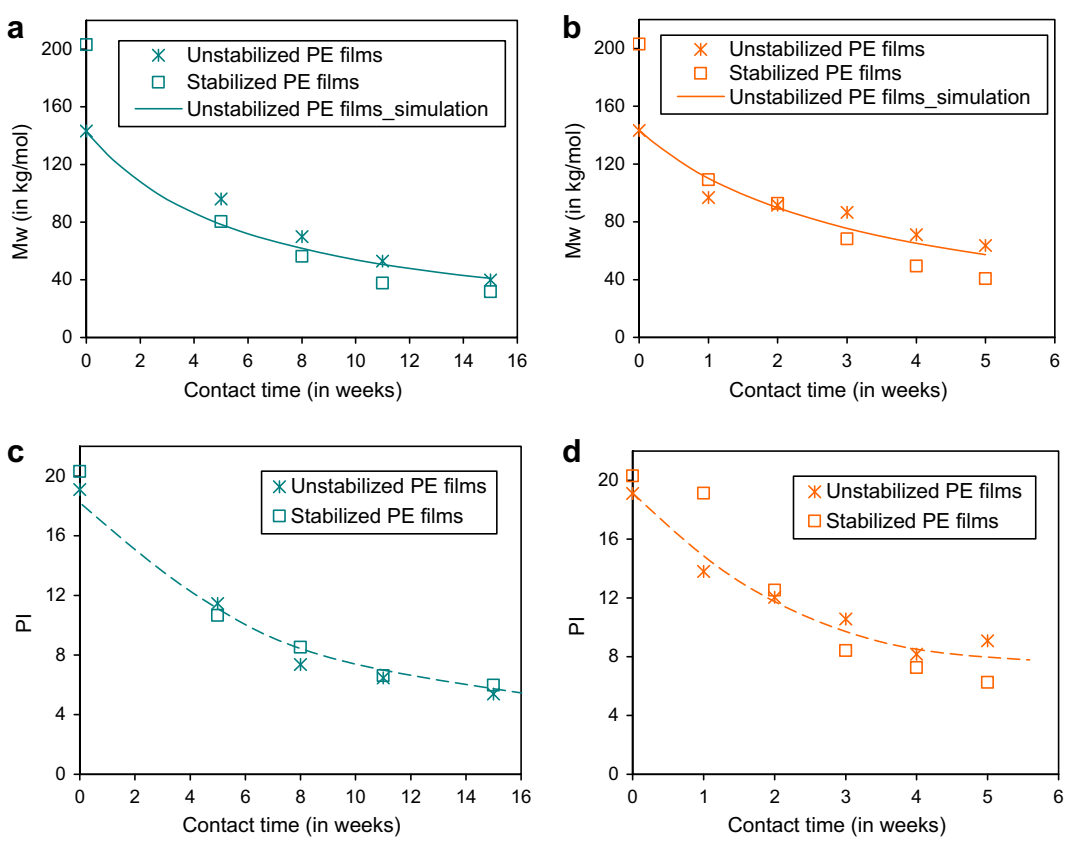

Fig. 5. Evolution of weight average molar mass (M_w) and polydispersity index (PI) as a function of contact time for stabilized and unstabilized polyethylene films at 400 mg/l (a) and (c) and 4000 mg/l (b) and (d), the full lines in (a) and(b) correspond to the simulations.

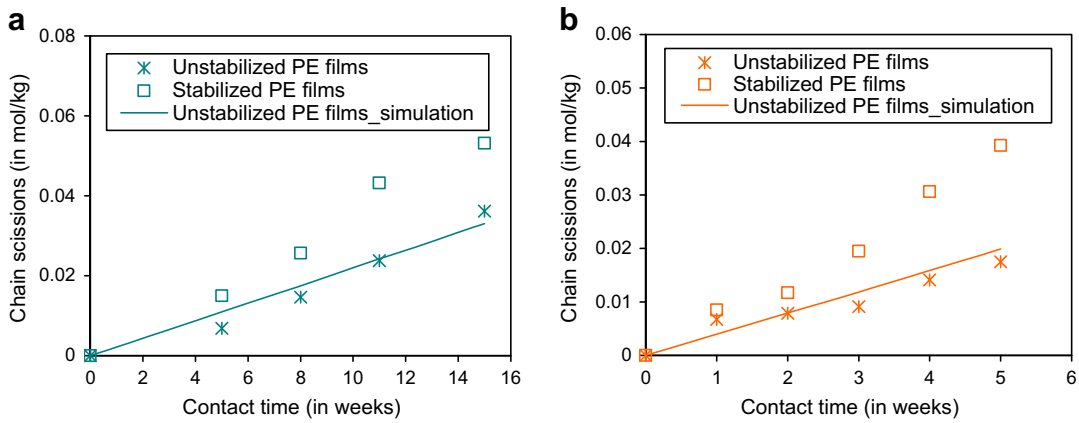

Fig. 6. Evolution of chain scission number as a function of contact time for stabilized and unstabilized polyethylene films at (a) 400 mg/l and (b) 4000 mg/l.

Finally, the experimental PI results clearly indicate that cross-linking can also safely be considered as negligible.

Knowing that the chain scission process can be considered as being homogeneously distributed, it is now possible to assess the chain scission number increase during immersion. Indeed, the chain scission number (s) can be calculated using the following relationship:

$$s = 2\left(\frac{1}{M_w} - \frac{1}{M_{w0}}\right) \quad (1)$$

where M_w is the measured molar mass during immersion and M_{w0} is the initial molar mass of unaged/virgin polyethylene.

The chain scission number was plotted as a function of the contact time and the results are seen in Fig. 6a, b. Already noticeable on the carbonyl curves in Fig. 2, here a linear increase in the chain scission is observed for samples immersed under the 4000 mg/l conditions. On the other hand, in the case of the 400 mg/l experiments, an induction period of 4 weeks is detected. A slight discrepancy is also obvious between the unstabilized and stabilized polyethylene under both chlorine contact conditions: the chain scission number is systematically lower in the case of the unstabilized polyethylene for any given contact time. As previously discussed, this can be attributed to a slight difference in the macromolecular architecture namely the branching. However, one can conclude that both polymers present roughly the same evolution when exposed to such chlorine concentrations. Comparing Figs. 2 and 6, another interesting feature is obvious: for the same given contact conditions, the carbonyl concentration is of the same order of magnitude as the chain scission number. This clearly indicates that chain the scission event is closely linked to carbonyl formation. Again this is characteristic of an oxidative process [12].

4. Discussion

4.1. Degradation mechanism

Although to date there have been several studies devoted to chlorine-induced degradation by in model chlorine solutions [3–6], the degradation mechanism involved is still unclear. The experimental results presented here confirm that the oxidation kinetics are closely associated with the chlorine concentration. This leads to the conclusion that the chlorine solution provides some species which are responsible for initiating the polyethylene oxidation process. These species are then capable of diffusing and reacting further with the polyethylene (PH) to give free radicals (P•). Let us recall some hypotheses proposed in the literature.

Historically, already in 1954 the first study that dealt with chlorine degradation proposed the following scheme as that occurring in the chlorine solution [13]:

$$HOCl + ClO^- \rightarrow ClO^\bullet + Cl^- + OH^\bullet$$

$$OH^\bullet + ClO^- \rightarrow ClO^\bullet + OH^-$$

$$ClO^\bullet + ClO^- + OH^- \rightarrow 2Cl^- + O_2 + OH^\bullet$$

Based on this scheme, it is proposed that the ClO• and OH• radicals are susceptible to attacking polyethylene to give P•. More recently, using Electron Spin Resonance Utsumi et al. showed that OH• radicals are present in chlorine solution [14]. However, due to their high reactivity, these radicals are unlikely to diffuse to any great extent deep into the polyethylene [8]. Indeed, the correlation length (l^*) of these species is determined by the scaling law $(D/k^*)^{1/2}$ where D is the diffusion coefficient for the radical and k^* their reactivity with PE. A rough assessment of l^* leads to the conclusion that ClO• and OH• can only diffuse into polyethylene over a short distance (smaller than 1 μm). Knowing that the degradation is homogeneous for the 100 μm films in this study (see §3.3), it is more than likely that another less reactive species exists that is responsible for homogeneous degradation observed. Following a similar argument, Khatua et al. proposed that the other reactive species could be a hydroperoxide such as Cl_2OOH which is formed according to the following scheme [15]:

$$HOCl + HOCl \rightarrow Cl_2O + H_2O$$

$$Cl_2O + OH^\bullet \rightarrow Cl_2OOH$$

The low reactivity of Cl_2OOH could explain the fact that the oxidation induced by chlorine is homogeneously distributed throughout the film thickness.

However, it must be acknowledged that the real mechanism responsible for oxidation initiation is still unclear. Hence, in the next section a kinetically equivalent scheme which takes into account all the experimental results reported here, especially influence of the chlorine concentration, will be proposed.

4.2. Kinetic scheme

In order to model the degradation induced by chlorine, the homogeneous case involving the films, will be considered. The main hypothesis of our model consists in the postulation that

Table 2
Parameter values used in simulation.

	$k_{Cl}[Cl]$	γ_{1s}	$[POOH]_0$	M_{w0}
400 mg/l	7.5×10^{-10} s^{-1}	0.6	10^{-4} mol l^{-1}	143 kg/mol
4000 mg/l	7.5×10^{-9} s^{-1}	0.4	10^{-4} mol l^{-1}	143 kg/mol

the chlorine species are responsible for the formation of alkyl radicals (P•). All the other reactions arise from the closed loop mechanism already used to simulate polyethylene oxidation under oxygen excess [10]. The resulting scheme proposed for the polyethylene oxidation induced by chlorine is described below:

$$(1u)\quad POOH \rightarrow 2P^{\bullet} + \gamma_{1S}s + \gamma_{1CO}PO \quad k_{1u}$$

$$(1b)\quad 2POOH \rightarrow P^{\bullet} + PO_2^{\bullet} + \gamma_{1S}s + \gamma_{1CO}PO \quad k_{1b}$$

$$(2)\quad P^{\bullet} + O_2 \rightarrow PO_2^{\bullet} \quad k_2$$

$$(3)\quad PO_2^{\bullet} + PH \rightarrow POOH + P^{\bullet} \quad k_3$$

$$(3b)\quad Cl + PH \rightarrow P^{\bullet} \quad k_{cl}$$

$$(6a)\quad PO_2^{\bullet} + PO_2^{\bullet} \rightarrow [PO^{\bullet}\,{}^{\bullet}OP]_{cage} + O_2 \quad k_{6a}$$

$$(6b)\quad [PO^{\bullet}\,{}^{\bullet}OP]_{cage} \rightarrow POOP + ret \quad k_{6b}$$

$$(6c)\quad [PO^{\bullet}\,{}^{\bullet}OP]_{cage} \rightarrow P{=}O \quad k_{6c}$$

$$(6d)\quad [PO^{\bullet}\,{}^{\bullet}OP]_{cage} \rightarrow 2P^{\bullet} + 2\gamma_{1S}s \quad k_{6d}$$

Using this scheme, it is possible to write the necessary differential equation system (see Appendix 1). The differential equation system (DES) was solved numerically by using Matlab. The kinetic constant k_{1u}, k_{1b}, k_2, k_3, k_{6i} values at 20 °C and the initial hydroperoxide concentration $[POOH]_0$ have been already reported in [16]. The only unknown is the value of $k_{Cl}[Cl]$. Since the solubility of chlorine in polyethylene is unknown, considerate is assumed that $[Cl]_{4000\ mg/l}/[Cl]_{400\ mg/l} = 10$ to simulate the 400 and 4000 mg/l conditions. Here, the value of k_{Cl} is considered as being independent of the chlorine concentration.

In order to predict the molar mass change, the chain scission (s) rate was calculated from the POOH and $[PO^{\bullet}\,{}^{\bullet}OP]_{cage}$ values obtained using DES and the following equation:

$$\frac{ds}{dt} = \gamma_{1s}k_{1u}POOH + \gamma_{1s}k_{1b}POOH^2 + 2\gamma_{1s}k_{6d}[PO^{\bullet}\,{}^{\bullet}OP]_{cage} \quad (2)$$

After integration of s, the weight average molar mass (M_w) is given by:

$$M_w = \left(\frac{s}{2} + \frac{1}{M_{w0}}\right)^{-1} \quad (3)$$

where M_{w0} is the initial weight average molar mass of polyethylene.

Simulations are shown in Figs. 5a, b and 6a, b for the unstabilized polyethylene. A good agreement between simulations and experimental data for both ageing conditions with parameters values reported in Table 2 is observed.

4.3. Time to embrittlement prediction

According to this model, it is now possible to simulate the molar mass drop as a function of the chlorine concentration at 20 °C. In order to predict mechanical behaviour changes during long-term ageing, the coupling between the chemical degradation and the mechanical properties is needed. For this purpose, it has been proposed that the chemical degradation induced by chlorine is responsible for the embrittlement mechanisms occurring at the inner surface [17]. In the case of polyethylene films, it is well known that polyethylene is brittle since M_w is below the critical molar mass (M'_C) value; close to 40 kg mol^{-1} [12]. More precisely, it has been shown that this critical molar mass value is intimately linked with the chemi-crystallization process leading to reduce amorphous layer thickness. Once the amorphous layer thickness is below a specific critical value (~6 nm for polyethylene), the mechanical behaviour starts to exhibit a brittle behaviour [7]. In a preliminary approach,

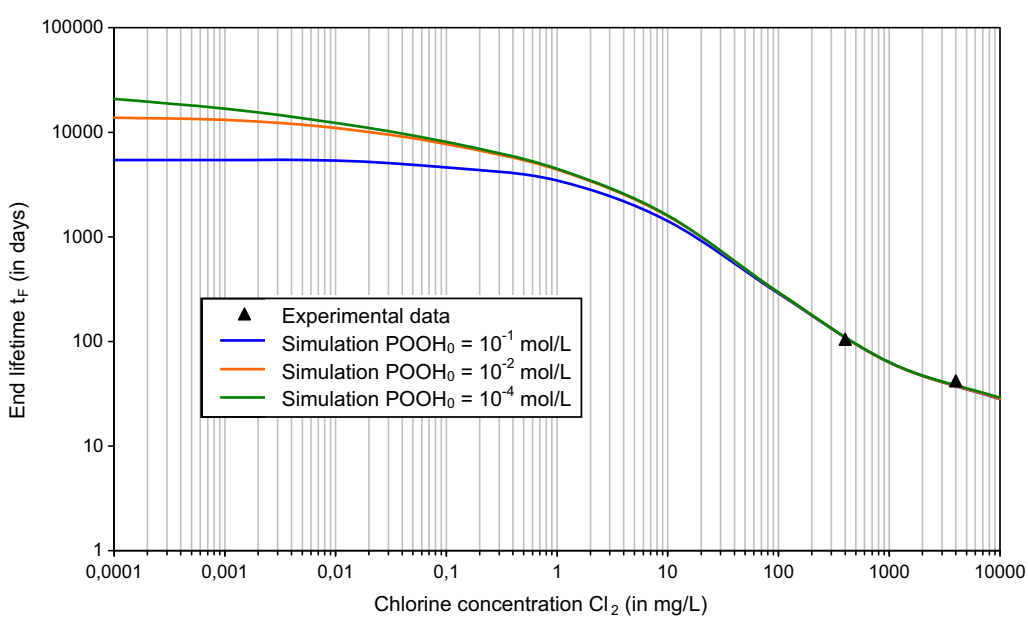

Fig. 7. Evolution of time to embrittlement of polyethylene surface in contact with water as a function of chlorine concentration—the curve corresponds to simulation by kinetic modelling for unstabilized polyethylene.

considerate can be assumed that the time to embrittlement (for films or oxidized layers) is closely associated with any M_w decrease lower than 40 kg mol^{-1}. According to Fig. 5a, b, the time to embrittlement for both stabilized and unstabilized polyethylene is roughly 5 days and 15 weeks for 4000 and 400 mg/l ageing conditions, respectively. These data are plotted in Fig. 7 where the *x*-axis is the chlorine concentration using a log scale. In this Figure, the curve corresponds to the simulation resulting from a combination of the kinetic model and the selected embrittlement criterion M'_C, for a chlorine concentration range from 0.01 to 10 000 mg/l as applied to an unstabilized polyethylene. Thanks to this curve, one can observe two domains: the first domains is where the chlorine concentration is below 0.01 mg/l and corresponds to the situation in which oxidation is mainly controlled by intrinsic polyethylene thermal oxidation, i.e hydroperoxide decomposition (no chlorine effect). The second domain corresponds to the 10–1000 mg/l range where the oxidation kinetics are governed by the chlorine concentration. This is most probably why no stabilizer impact has been observed in the latter case. In other words, the oxidative species generated by the chlorine concentration is higher than any generated by the stabilizers. Experimental results at 70 mg/l confirm this trend (see Figs. 4 and 7). For both situations (0.01–10 mg/l), the oxidation kinetics are controlled by the initiation processes: hydroperoxide decomposition and chlorine initiation. As a result, it is to be expected that the stabilizer efficiency in this 0.01–10 mg/range, which is the usual range observed in drinking water supply, is in operation.

5. Conclusions

The impact of chlorine on the oxidation of PE has been investigated. Both unstabilized and stabilized polyethylene samples were exposed to chlorine solutions at different concentrations (70, 400 and 4000 mg/l). Care was taken with the experimental variables such as contact temperature, pH of solution and solution renewal to reduce the risk of unstable species. A suite of analytical techniques was used to analyze the experimental results. These included FTIR spectrophotometry and SEC measurements. This data coupled with kinetic modelling makes it possible to reach the following conclusions:

- An increase in chlorine concentration leads to a strongly increased level of oxidation under accelerated ageing conditions (70, 400 and 4000 mg/l). The oxidation/chain scission rate is strongly correlated with the chlorine concentration. Moreover, no evidence of the influence of the stabilizers on the oxidation rates was found under the ageing conditions studied.
- After ageing, thin samples (100 μm thick) were found to exhibit a homogeneous degradation throughout their thickness. This result confirms that the oxidative species produced by the chlorine solutions can penetrate into a depth greater than 50 μm. This can be explained by the diffusion of low reactive species such as Cl_2OOH.
- By introducing a new reaction between species arising from the chlorine solution and the polyethylene, the known closed loop scheme was modified to take into account the chlorine impact on oxidation. Good agreement was obtained between this kinetic model and the experimental data only by adjusting the kinetic constant associated with the new reaction proposed. By coupling the kinetic model and the molar mass criterion for embrittlement (M'_C), time to embrittlement simulations as a function of chlorine concentration were able to be estimated.

Finally, this work constitutes the first step in building a kinetic model with a view to predicting the lifetime of polyethylene pipes under operational conditions.

Appendix 1

A set of ordinary differential equations is derived from this scheme; it expresses the concentration changes of the reactive species involved. Equations (1) and (2) correspond to the alkyl radical (P•), peroxy radical ($PO_2^{\bullet}$), and hydroperoxide (POOH) concentrations respectively, and k_{1u}, k_{1b}, k_2, k_3, k_4, k_5, and $k_{6a,b,c,d}$ are rate constants for reactions I to VId.

$$\frac{d[P\bullet]}{dt} = 2k_{1u}[POOH] + k_{1b}[POOH]^2 - k_2[O_2][P\bullet] + k_3[PH][PO_2^{\bullet}] + k_{6d}[PO_2]^2 + k_{cl}[Cl][PH] \quad (1)$$

$$\frac{d[PO_2^{\bullet}]}{dt} = k_{1b}[POOH]^2 + k_2[O_2][P\bullet] - k_3[PH][PO_2^{\bullet}] - 2k_{6a}[PO_2^{\bullet}]^2 \quad (2)$$

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

$$\frac{d[PO\bullet\bullet PO]_{cage}}{dt} = k_{6a}[PO_2^{\bullet}]^2 - (k_{6b} + k_{6c} + k_{6d})[PO\bullet\bullet PO]_{cage} \quad (4)$$

$$\frac{d[PH]}{dt} = -2k_{1u}[POOH] - k_{1b}[POOH]^2 - k_3[PH][PO_2^{\bullet}] - k_{cl}[Cl][PH] \quad (5)$$

The initial and boundary conditions input to solve the system of differential equation were $[PO_2^{\bullet}] = 0$, $[P\bullet] = 0$, $[POOH] = [POOH]_0$, $[PO\bullet\bullet PO]_{cage} = 0$, $[PH] = [PH]_0$, $[O_2] = [O_2]_s$, where $[PH]_0$ and $[O_2]_s$ are the initial concentrations of the [PH] and $[O_2]$ species respectively.

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