Deterioration of Polyethylene Exposed to Chlorinated Species in Aqueous Phases:
Test Methods, Antioxidants Consumption and Polymer Degradation

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To my families
ABSTRACT

This thesis presents a study of antioxidant depletion in water containing chlorinated species (water containing 10 ppm either Cl₂ or ClO₂, buffered to pH = 6.8), the degradation products in the aqueous phase, and polyethylene pipe degradation scenarios. A low molecular weight hydrocarbon analogue (squalane) was used instead of solid polyethylene as the host material for the antioxidants, and the depletion of antioxidants has been studied. The phenolic antioxidant Irganox 1010 was consumed ca. 4 times faster in water containing 10 ppm ClO₂ than in water containing 10 ppm Cl₂. The different degradation products in extracts from the aqueous phase identified by infrared, liquid chromatography and mass spectrometry revealed the different degradation mechanisms between ClO₂ (β cleavage) and Cl₂ (hydrogen substitution). The squalane test shows no energy barrier between 30 and 70 °C, and the activation energy of the antioxidant in solid PE was found to be ca. 21 kJ mol⁻¹. A linear relationship has been established between the time to reach antioxidant depletion in the polyethylene tape samples and the time to reach depletion in samples based on squalane containing the same antioxidants. The surface oxidation and surface embrittlement of PE tape on long time exposure have been studied by IR and SEM. Pressure testing on medium density PE pipes with a controlled pH aqueous media (6.8 ± 0.2) containing 4 ppm either ClO₂ or at 90 °C showed that the stabilizers were rapidly consumed towards the inner pipe wall and the rate of consumption in ClO₂ was 4 times greater than in Cl₂ solution. The subsequent polymer degradation was an immediate surface reaction. It was confirmed by differential scanning calorimetry, infrared spectroscopy and size exclusion chromatography that, in the surface layer which came into contact with the oxidizing medium, the amorphous component of the polymer was heavily oxidized leaving a highly crystalline powder with many carboxylic acid chain ends in extended and once-folded chains.

Key words: Antioxidant; Polyethylene pipes; Chlorine dioxide; Degradation
LIST OF PUBLICATIONS

This thesis is a summary of the following publications:

I  “A new method for assessing the efficiency of stabilizers in polyolefins exposed to chlorinated water media”

II “Deterioration of polyethylene pipes exposed to water containing chlorine dioxide”

III “Antioxidant consumption in squalane and polyethylene exposed to chlorinated aqueous media”
   Polymer Degradation and Stability 2012; 97: 2370-2377.

IV  “Assessing the long-term performance of polyethylene stabilized with phenolic antioxidants exposed to water containing chlorine dioxide”
   Accepted in Polymer Testing.
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1. **PURPOSE OF THE STUDY**

The purpose of this study was to gain further knowledge about the deterioration of polyethylene pipes distributing water containing disinfectant (Cl₂ and ClO₂). The goals of the work were to elaborate and discuss:

1. **The development of efficient testing methods.**
   A new test method was developed to assess the capacity of the antioxidants using a liquid analogue, squalane, instead of solid polyethylene (referred to as the squalane test) to study the consumption of squalane containing antioxidants exposed to Cl₂ and ClO₂, to analyze degradation species by infrared, liquid chromatography and mass spectrometry, and to study the phenolic antioxidant degradation mechanism.
   The long-term performance of stabilized polyethylene tape samples after exposure to Cl₂ and ClO₂ in an aqueous phase using an over-flow system (referred to as the tape test) to assess the efficiency of the antioxidants as a function of exposure time, study the surface embrittlement and crack-growing study by infrared and SEM and to establish the relationship between the time to reach antioxidant depletion in the tape test and in the squalane test.

2. **To study the deterioration mechanism of PE pipes with inner pressurized water containing Cl₂ and ClO₂.**
   Attempts were made to evaluate the antioxidant concentration profiles from the contact inner surface into the pipe wall, and to analyze the degradation products in terms of crystallite, molar mass distribution and infrared spectrometry, and to study the degradation-assisted crack propagation mechanism.
2. INTRODUCTION

2.1. Background

Water-distributing pipes made of polyethylene undergo degradation due to disinfectant in the water. Chlorine (Cl₂) and chlorine dioxide (ClO₂) are the most common water treatments [1, 2] and they are strong oxidants even at a very low concentration. Polyethylene is chosen for piping materials due to its chemical stability and it performs equally well for buried, trenchless, floating and marine installations [3]. In spite of all the advantages, polyethylene pipe degradation is unavoidable and visible cracks can be observed on the inner wall of the pipe with time. The deterioration of polyethylene pipes with internal chlorinated media has been studied [4-10]. Due to the unstable nature of chlorine and chlorine dioxide, the strict definition of the pH and concentration of the chlorinated species in water is essential in any study of the degradation mechanism [11]. Usually the degradation of polyethylene needs a long period of time and earlier attempts have been made to accelerate aging using empirical methods (mechanical loading, hydrostatic pressure, UV exposure thermal degradation) [12-18]. A three-regime mechanism of pipe failure has been established [19-21] to describe the failure of pipe distributing water with an inner pressure: Regime I: the formation of micro-scale cracks (fractures are ductile and chemical effects in the polymer are insignificant); Regime II: the development of brittle fracture due to crack growth (physical brittleness regime) and Regime III: chemical degradation predominates and the failure is generally brittle at low stress levels (Fig 2-1). The distinct difference between regime II and regime III is the molar mass of the polymer. The molar mass distribution is not affected even with the presence of micro-cracks in regime II, whereas it is shifted to low values in regime III. The strong oxidizing disinfectant in water may accelerate the chemical degradation process and regime III can totally supplant regime II [21].
Fig. 2-1: Lifetime of pipe subjected to internal pressure (hoop stress) as a function of time at constant temperature. Schematic curve for illustration of regimes I, II, and III. Drawing after Viebke et. al.[20] original from [21].

Commercial polyethylene products are stabilized to reduce oxidation during processing. With added antioxidants, polyethylene pipes had a 12 % longer lifetime in regime III in the hot-water distribution systems [20]. Hassinen et. al. [22] have observed that antioxidant consumed rapidly even far into the pipe wall, which may be caused by the diffusion of chlorine species into the solid plastic material. Colin et al. [23] showed a rapid consumption of a phenolic antioxidant in a 1.2 mm thick layer near the inner pipe wall, after which essentially no propagation of the antioxidant-free layer occurred. These authors suggested that chlorine dioxide reacts not only with the antioxidant but also with polyethylene, but at a considerable lower rate. However, Stevens and Seeger [24] provided evidence that the reactivity of saturated hydrocarbons to chlorine dioxide is strictly zero. Dear and Mason [4] found that chlorine can penetrate polyethylene in amorphous regions without reacting with the polymer chains. Similar findings were obtained for aliphatic olefins [25]. In 1957, Russell [26] reported the autoxidation of aralkyl hydrocarbons and peroxy radicals was a cause of the failure of polymer materials. Hence, the deterioration of polyethylene may be due not to the disinfectant but to the by-products (radicals) of chlorine or chlorine dioxide dissolving in water.

Polyolefin pipes distributing tap water are usually placed underground, and it is important to replace the aged ones before the pipes reach the failure stage. Thus, the service time
prediction is practically and academically important. Usually the failure of a pipe material occurs in regime III. Hoàng et al. [14] claimed that the extrapolation method from the hydrostatic pressure test provides an unrealistic lifetime and it intended to assess the lifetime of the antioxidants in the water pipe to define service time of the water pipes. Antioxidants play an essential role in prolonging the service time of polymeric materials, and this thesis presents a study of the selective antioxidants consumption in polyethylene exposed to water containing 10 ppm Cl₂ or ClO₂ at pH = 6.8 with regard to test method development, degradation mechanism study and polyethylene pipe deterioration mechanism.

2.2. Oxidation mechanism

Oxidation is responsible for aging, rusting, cracking and the destructive failure of materials. Chemically, oxidation is due to the loss of electrons. Oxidizing species are those that tend to lose electrons during reaction, such as chlorine and chlorine dioxide. The oxidation of hydrocarbons and polymers has been investigated [27-32]. Bolland and Gee [33, 34] described the degradation in two steps: radical formation (1) and the addition of oxygen (2). In the presence of a free radical R•, the addition of oxygen leads to the fast generation of peroxyl radicals (RO₂•) with a speed of 10⁹ M⁻¹ s⁻¹ [28]. A further step of the hydrogen atom exchange process (3) leads to the formation of hydroperoxides (ROOH) and initiates autoxidation [26]. The hydrogen atom exchange is much slower than to oxygen addition, whose typical speed is of the order of 10 M⁻¹ s⁻¹ [28].

\[
\text{Initiation:} \quad \text{RH} \rightarrow \text{R•} \quad (1) \\
\text{Addition of O₂:} \quad \text{R•} + \text{O₂} \rightarrow \text{RO₂•} \quad (2) \\
\text{Hydrogen atom exchange:} \quad \text{RO₂•} + \text{RH} \rightarrow \text{ROOH} + \text{R•} \quad (3)
\]

The migration of low-molecular-weight compounds due to bond breakage has been investigated [5, 22, 32, 35-40]. The hydrogen atom exchange mechanism induces radicals in the system without any change in polymer molar mass. Bolland reported one-electron oxidation mechanism that leads to chain breakage [41]. The one-electron mechanism is
divided into three steps: the initiation of unpaired electrons (4, 5); the propagation stage through the absorbance of oxygen (6, 7); the termination step through the formation of stable oxidation products (8-10). The two oxidation mechanisms are not independent and they always appear in parallel in the polymer. The hydroperoxide group is the product from hydrogen atom exchange and exposure to UV radiation, or in the presence of metal deactivator, the hydroperoxide groups decompose and form carbonyl groups in the polyolefin chains and generate organic radicals and hydroxyl radicals. The additional oxygen in organic radicals promotes the breaking of chains with more unpaired electrons and turns the polymer chain into radicals and another source of hydroperoxide. Radicals are not stable, and all the organic radical and peroxides with unpaired electrons couple with each other, and stable products are generated by the termination reactions. The process of chain breakage is also described in Fig. 2-2.

Initiation: \[ \text{ROOH} \rightarrow \text{R}^\bullet + \text{•OOH} \] \hspace{1cm} (4)
\[ \text{ROOH} \rightarrow \text{RO}_2^\bullet + \text{•H} \] \hspace{1cm} (5)

Propagation: \[ \text{R}^\bullet + \text{O}_2 \rightarrow \text{RO}_2^\bullet \] \hspace{1cm} (6)
\[ \text{RO}_2^\bullet + \text{RH} \rightarrow \text{RO}_2\text{H} + \text{R}^\bullet \] \hspace{1cm} (7)

Termination: \[ \text{R}^\bullet + \text{R}^\bullet \rightarrow \text{R} - \text{R} \] \hspace{1cm} (8)
\[ \text{R}^\bullet + \text{RO}_2^\bullet \rightarrow \text{ROOR} \] \hspace{1cm} (9)
\[ \text{RO}_2^\bullet + \text{RO}_2^\bullet \rightarrow \text{RO}_2 - \text{O}_2\text{R} \] \hspace{1cm} (10)

\[ \text{R} - \text{CH}_2^\bullet + \text{HCO} - \text{R}^\bullet \]

Fig. 2-2: Chain breaking mechanism (drawing after Scott [40] and originally from Bolland et al. [33, 34]).
The initiation of oxidation, hydrogen atom exchange and chain breakage reactions occurs continuously in the polyolefin materials and each reaction promotes the other reactions, for one product can be the reactant of another oxidation process (Fig. 2-3). The recycling reaction of the radicals and polymers can lead to extensive chain breakage, resulting in a mechanically weakened material. Nevertheless, Zebger et. al. [8] indicated that the amount of polyethylene degradation is pH-dependent, whereas the rate is stable in the pH range from 5 to 9 under the conditions of exposure to chlorinated water (NaOCl = 0.2 M for 3 h).

![Fig. 2-3: Scheme of autoxidation from Bolland-Gee [41]](image)

### 2.3. Antioxidants

Antioxidants are necessities in commercial polymers to counteract oxidative degradation. The oxidation mechanism in polyolefins has been simply illustrated in the previous chapter and the radicals are the key factor. In general, the function of the antioxidant is to eliminate radicals prior to the host materials. The antioxidant can be a hindered phenol, aromatic amine, phosphate or a natural antioxidants [42]. Based on their functionality, the antioxidants can be derived into two groups: primary antioxidants and secondary antioxidants. Primary antioxidants are capable of interrupting oxidation degradation by intercepting and reacting with free radicals faster than the substrate [28]. Secondary antioxidants, frequently referred to as ‘hydroperoxide decomposers’ [43, 44], decompose hydroperoxides (ROOH) that may...
generate free radicals during oxidation and yield non-radical, non-reactive and thermally stable products [45]. The solubility and the mobility need to be considered with respect to the efficiency of the antioxidants [37, 46-48]. It has been reported that the concentration of the antioxidant used can be up to 2 wt.% [49], but the commercial polyolefins preferably contain between 0.1 and 1 wt. %, due to the solubility of the antioxidant in the host material [50]. For a given polymer, the crystallinity and molecular weight distribution significantly influence the solubility of the antioxidant [51]. Antioxidants are typically mobile in host materials [52] and are able to diffuse to the radical region to dispose of the radicals. Nevertheless, the by-products of the antioxidants, such as chain sections and radicals may migrate from the host material to the aqueous phase, and a number of low molecular weight compounds have been documented in chlorinated tap water according to recent papers [36-38, 53, 54]. Thus, the selection of antioxidants depends not only on their ability to inhibit degradation but also on the possible toxicological effects of the sub-structures of the antioxidants [55].

2.3.1. Primary phenolic antioxidants

The phenolic compounds (ArOH) that protect host materials against oxidative degradation can prevent the peroxyl radicals (RO$_2^\cdot$) from reacting with the host materials because their hydroxylic hydrogens can form more stable hydroperoxides [56, 57]. The activity of phenolic antioxidants depends mainly on their ability to donate hydrogen atoms from the phenol groups to peroxyl radicals [49], i.e. the antioxidating capability increases with decreasing dissociation ability of the H-atom in the phenolic group [56]. The role of the phenolic antioxidant (ArOH) is to interrupt the chain reaction according to [58]:

$$\text{RO}_2^\cdot + \text{ArOH} \rightarrow \text{ROOH} + \text{ArO}^\cdot$$

Wright et. al. [28] have reported that the reaction rate of phenolic antioxidant with peroxyl radicals is about $10^6$ M$^{-1}$ s$^{-1}$ and this value is much higher than hydrogen atom exchange ratio ($10^6$ M$^{-1}$ s$^{-1}$), which is the reaction rate of peroxyl radical (RO$_2^\cdot$) with the substrate (RH).
In the presence of water, the peroxy l radicals can be deactivated by phenol through electron transfer. The deprotonation in solution is rapid and reversible. Water participates in the reactions but it is not consumed and the electron transfer is through protons (H⁺) that are hydrolyzed in water. The content of hydronium ions (H₃O⁺) that combine a proton with a water molecule (H₂O) is essential for the equilibrium reactions, i.e. the pH of the solution effects the direction of the equilibrium reactions. The role which the phenol antioxidant play in eliminating peroxy radicals in solutions is described in the following:

Electron transfer: \[ \text{RO}_2^* + \text{ArOH} \rightarrow \text{RO}_2^- + \text{ArOH}^+ \]  
(12)

Deprotonation equilibrium: \[ \text{ArOH}^+ + \text{H}_2\text{O} \rightleftharpoons \text{ArO}^* + \text{H}_3\text{O}^- \]  
(13)

Hydroperoxide formation: \[ \text{RO}_2^- + \text{H}_3\text{O}^+ \rightleftharpoons \text{ROOH} + \text{H}_2\text{O} \]  
(14)

The antioxidative activity is also influenced by polarity and steric effects [50, 59-62]. A less polar structure and ortho-substitution can efficiently increase the functionality of the phenolic antioxidants. Baum and Perun [58] suggested that alkyl substitution in the benzene ring of the phenol antioxidant can increase the efficiency. Their investigation showed that the induction time of tert-butyl phenol increased ca. 12 times with para-substitution of tertiary amyl. A recent study showed that fullerene substitution in a phenolic antioxidant increase the antioxidant capacity [63]. Irganox 1010 is one of the most commonly used primary antioxidants in polyolefins. Its typical four-arm structure (Fig. 2-4) with a phenolic group attached at the end of each arm and two tert-butyl ortho-substitutions on each side of the hydrogen substitution in the phenol. The highly symmetrical structure and the tert-butyl substitutions are capable of trapping radicals within the structure and this gives Irganox 1010 an efficient antioxidative activity [64].

Fig. 2-4: Chemical structure of Irganox 1010
2.3.2. Secondary antioxidant

Notwithstanding of the efficiency of the primary antioxidant, minimizing the overall loading of additives as well as retaining or increasing the stability in the products is the goal of the industry. The secondary antioxidants (typically phosphites, phosphonites, thio-co-stabilizers [65]) with the advantage of low molecule weight have been documented [50, 66]. Using a new highly efficient phosphine stabilizer, the concentration of secondary antioxidant can be reduced from the present typical levels of 0.07 – 0.15 wt.% of standard trivalent phosphorous based secondary antioxidants (phosphites, phosphonites) down to 0.01 - 0.02 wt.% of phosphine with the same antioxidative capacity in the host polyolefins [65]. Secondary (P(OR)_3) decomposes hydroperoxides (ROOH) to form stable alcohols (ROH) by the following mechanism:

$$\text{ROOH} + \text{P(OR)}_3 \rightarrow \text{ROH} + \text{O=P(OR)}_3$$  \hspace{1cm} (15)

The addition of secondary antioxidants to polymeric materials with the aim of preventing color changing and increase the thermal stability has been reported [67]. Phosphites provide color stability and the hydrolysis of phosphites can ultimately lead to the formation of phosphoric acid, which may corrode processing equipment [67]. Polymer products undergo pelletization and extrusion or other molding at high temperature, and thermal stability is essential. Thioesters have a high heat stability and they are used as secondary antioxidants to provide good heat stability of the host materials. Some thermal stabilizers, such as Sumilizer GM, contain phenolic groups but it preferably react with organic radicals (R•) instead of peroxyl radicals (ROO•) [68, 69] and they should not be mixed with primary antioxidants. Discoloration is attributed to the formation of quinone from a part of the primary antioxidant [70]. Although it is possible to improve the resistance to discoloration by modifying the primary antioxidant at the para-position with hydrogen substitution instead of a methyl group [68], its function as primary antioxidant to trap radicals in the structure is then greatly decreased.
In industry, a combination of two or more antioxidants is used, for each stabilizer has a specific temperature range for its optimum properties. More efficiently, a blend of a primary antioxidant (free radical inhibitor) and a secondary antioxidant (peroxide decomposer) is used to maximize the antioxidation properties.

2.4. Chlorine chemistry

When chlorine is dissolved in water, the following equilibrium reactions occur [8]:

\[
\begin{align*}
\text{Cl}_2 + \text{H}_2\text{O} & \rightleftharpoons \text{HOCl} + \text{H}^+ + \text{Cl}^- \quad (\text{pK}_a=3.4) \quad (16) \\
\text{HOCl} & \rightleftharpoons \text{H}^+ + \text{ClO}^- \quad (\text{pK}_a=7.4) \quad (17)
\end{align*}
\]

The relative amount of the three oxidizing chlorine species, \(\text{Cl}_2\), \(\text{HOCl}\) and \(\text{ClO}^-\), are determined by the pH of the aqueous environment. Fig. 2-5 shows the relative concentrations of these substances as a function of pH. At pH 6.8, \(\text{Cl}_2\) is a maximum of 5.5 % and the rest species are HOCl, which means that the concentration of the hypochlorous anion (\(\text{ClO}^-\)) is essentially zero (Fig. 2-5). In acidic solutions (pH < 7), singlet oxygen is also present. However, the comprehensive study by Zebger et al. [8] showed that neither singlet oxygen nor HOCl was responsible for the degradation of polystyrene and poly(styrene-co-butadiene).

It is suggested, based on these reports, that chemical consumption reaching far into the pipe wall is due to \(\text{Cl}_2\). The latter is soluble in the polymer, which is a necessary prerequisite for migration into the pipe wall. The polymer degradation, which is an immediate surface reaction, must be due to other species (‘superoxidants’) of ionic and/or radical character, e.g. the chloridyl radical \(\text{Cl}_2\bullet^-\). This water-bound radical is predominantly a strong one-electron oxidant \(e_{\text{red}} = 2.3 \text{ V vs. NHE}\) [71] and under the chosen reaction conditions it may even oxidize water and give rise to hydroxyl radical formation [72]:

\[
\text{Cl}_2\bullet^- + \text{H}_2\text{O} \rightleftharpoons \bullet \text{OH} + \text{H}^+ + 2\text{Cl}^- \quad (18)
\]

Hydroxyl radicals are strongly hydrogen abstracting and can thus attack the polymer and initiate auto-oxidative chain reactions in the presence of oxygen. In these chain reactions,
superoxide is formed, and this in turn is rapidly oxidized by chlorine to give another chloridyl radical [72]:

\[
\text{Cl}_2 + \text{O}_2^- \rightarrow \text{Cl}_2^- + \text{O}_2 \quad (19)
\]

Alternatively, hydroxyl radicals may also be created by a Haber-Weiss analogue reaction, i.e. by reductive cleavage of HOCl [72]:

\[
\text{HOCl} + \text{O}_2^- \rightarrow \cdot\text{OH} + \text{Cl}^- + \text{O}_2 \quad (20)
\]

Chlorine dioxide undergoes disproportionation reactions in water [72]:

\[
\begin{align*}
\text{ClO}_2 + \text{H}_2\text{O} & \rightleftharpoons \text{HOClO}_2^- + \text{H}^+ \quad (21) \\
\text{HOClO}_2^- + \text{ClO}_2 & \rightleftharpoons \text{HOClO}_2\text{ClO}_2^- \quad (22) \\
\text{HOClO}_2\text{ClO}_2^- & \rightleftharpoons \text{HOClO} + \text{ClO}_3^- \quad (23) \\
\text{HOClO} & \rightleftharpoons \text{H}^+ + \text{ClO}_2^- \quad (24)
\end{align*}
\]

The reaction scheme shows that the disproportionation can eliminate chlorine dioxide, and that the disproportionation is highly dependent on the pH in the water and on the concentration of chlorine dioxide. Under the reaction conditions used in this study, pH = 6.8 and a very low initial concentration of ClO₂ (ca. 10 ppm), the disproportionation should be very slow and the acting species in the reaction system is most probably ClO₂, which is a
moderately strong one-electron oxidant \( (E_{\text{red}} = 0.934 \text{ V vs. NHE}) \) [71]. Since chlorine dioxide shows practically no hydrogen abstraction reactivity, the attack on the polymer surface must proceed through species that arise when chlorine dioxide is reduced. This chemistry is difficult to outline in detail, but the initial reaction should lead to the formation of chlorite, \( \text{ClO}_2^- \), which by subsequent proton and electron transfer processes involving another phenolic antioxidant may generate strongly hydrogen-abstracting radical species such as chlorine monoxide, \( \text{ClO}^* \).

### 2.5. Squalane analogue

The pipe industry uses medium density polyethylene with a density between 920 - 940 kg m\(^{-3}\) [73]. The mixing of additives into polyethylene involves a masterbatch process, pelletization and an extruding process. During the processing, material is wasted in the pre-mixture and time is consumed during in heating and cooling. Squalane is a low molecular weight liquid hydrocarbon of a chemically inert nature (Fig. 2-6), which does not crystallize at room temperature. The squalane oil was selected as the analogue because it resembles and behaves in a manner very similar to that of the non-polar polymer chains in many engineering plastics (polyethylene). For the purpose of testing the efficiency of antioxidants, using squalane as a polyethylene analogue is beneficial because it is easier to test homogeneous antioxidant solutions in a liquid phase (squalane) than in a solid phase systems (polyethylene). This makes it possible to evaluate antioxidants on the basis of their intrinsic chemistry in an environment very similar to an optimal dispersion of the antioxidant in a polyethylene matrix.

![Fig. 2-6: Chemical structure of squalane.](image-url)
3. Experimental

3.1. Materials

Squalane (2,6,10,15,19,23-hexamethyldieicosane) with a purity higher than 95% was purchased from Sigma-Aldrich. The antioxidants used were supplied by Ciba Specialty Chemicals, Switzerland. Chemicals used for titration (sulphuric acid, potassium iodide, sodium thiosulfate and starch) were purchased from VWR international. Sodium chlorite, monopotassium phosphate and sodium hydroxide used for aqueous phase preparation were obtained from Sigma-Aldrich. Chlorine gas (containing less than 5 ppm water) was supplied by AGA Gas AB, Sweden.

3.2. Preparation of antioxidant-squalane solution and polyethylene containing antioxidant

A squalane solution with 0.2 wt.% of antioxidant was prepared by adding 40 mg antioxidant to 20 g squalane. The mixture was heated to 190 °C and stirred for 30 min under nitrogen flow. The resulting solution was clear, indicating that the antioxidant was properly dissolved in the squalane. The solution was then slowly cooled to 90 °C without any loss of clarity. The squalane solution was divided into 5 mL parts per test tube using a pipette with a heated tip.

The polyethylene strings containing 0.1 wt.% antioxidant were supplied by Borealis, and they were re-shaped according to the purpose of the experiment. The polyethylene plaques (4 mm thick, 10 mm wide and 100 mm long) and polyethylene tapes (0.5 mm thick, 15 mm wide and 200 mm long) were obtained by compression moulding using a Fontijne TP400 press (Fontijne, Netherlands) at 140 °C for 10 min followed by rapid cooling to room temperature.
3.3. Preparation of chlorinated aqueous media

A stock solution with 16000 ppm ClO₂ was prepared by a two-stage method. First, 210 g sodium chlorite was dissolved in 7 L water and chlorine gas was bubbled through the system for 4 h. Nitrogen gas was then gently bubbled through the solution for 8 h and the gas stream was led through a column with sodium chlorite to eliminate residual Cl₂, and the ClO₂ formed was transferred to an amber flask filled with pure water. A stock solution with ca. 10000 ppm Cl₂ was prepared by bubbling chlorine gas through deionized water for 40 min. Both the preparations were done at room temperature (ca. 22 °C) and the amber bottles containing the stock solutions were kept in refrigerator at a temperature at 5 °C.

The concentrations of ClO₂ and Cl₂ in the stock solutions were determined using the following procedure: 20 mL sulphuric acid (0.1 M) and 10 mL potassium iodide solution (80 g/L) were added to 3 mL of the stock solution and the solution turned yellow. The mixture was titrated with 0.1 M sodium thiosulfate (Na₂S₂O₃) drop by drop. When the yellow color of the mixture became very light, ca. 3 mL starch solution (0.2 wt. %) was added to the solution and which then turned almost black. The titration with sodium thiosulfate was then continued until the color completely disappeared. The concentration of ClO₂ was then calculated from the volume of sodium thiosulfate that was consumed, one mole of ClO₂ being equivalent to five moles of S₂O₃²⁻.

After titration, the stock solution was diluted with Milli-Q water to reach a concentration of 12.5 ppm ClO₂ or Cl₂ typically giving 500 mL of solution for a single exposure experiment. 125 mL of a buffer solution (67 vol.% 0.1 M KH₂PO₄ solution and 33 vol.% 0.1 M NaOH solution) of 125 mL was finally added to yield a 10 ± 1 ppm Cl₂ solution with pH = 6.8 ± 0.1. The pH was measured at room temperature using a WTW pH330i electrode.
3.4. The squalane testing method

Squalane samples exposed to water containing ClO₂ or Cl₂ was referred to as squalane test and the experiment setup is shown in Fig. 3-1. A test tube containing 5 mL squalane sample and 50 mL water containing 10 ppm ClO₂ or Cl₂ (pH = 6.8 ± 0.1) was heated on a hot plate and enclosing heater using the Eurotherm 914 PID control device, and the experimental temperature was varied between 30 °C to 70 °C. The duo-phase in the test tube was continuously stirred by a PTFE-coated magnetic stirrer bar with a rotation speed of 250 rpm. A condenser fed with cold water (ca. 10 °C) was placed on the top of the test tube to prevent volatiles from leaving the reaction phases. The squalane test setup was kept in a dark fume hood in order to avoid photolysis reactions. The aqueous phase was renewed with 25 mL every 30 min in order to ensure the stability of the pH and the concentration of the chlorine species.

![Fig. 3-1: Experiment setup of squalane test.](image)
3.5. The tape testing method

The exposure of polyethylene samples to water containing ClO₂ and Cl₂ was referred to as tape test using the same experiment setup as shown in Fig. 3-1. The polyethylene tape containing 0.1 wt.% antioxidants with the width of ca. 10 mm was placed in the test tube instead of the squalane solutions. There were two ways to refresh the aqueous phase in the test tube: (i) 25 mL of the aqueous phase was replaced manually every 30 min, as described in the squalane test. (ii) An overflow system was used and fresh 10 ppm chlorine dioxide solution at pH = 6.8 was added continuously to the test tube. The flow rate was 1 mL min⁻¹. L/S PTFE Tubing Pump was equipped with a variable speed drive model 7524-40, a pump head model 77800-60 and PTFE tubing (96412-13) supplied by Cole-Palmer, USA.

3.6. The pressure testing method

The circulation loop at the Exova AB facility at Studsvik, Sweden, was used for the pressure tests. The water was taken from the dosage unit using sodium chlorite and hydrochloric acid with a well-defined concentration and was then heated to the testing temperature, pressurized and finally brought back to the dosage unit (Fig. 3-2). The concentration of ClO₂ was continuously measured before the water entered the dosage unit. All the components of the circulation loop were made of inert materials - titanium, poly(vinylidene difluoride) and polytetrafluoroethylene. The pressure testing was carried out on pipe specimens with a length of 250 mm at 90 ± 1 °C with internal water containing ClO₂ (4.0 ± 0.1 ppm) at a hoop stress of 1.65 ± 0.05 MPa and with external air. The pH of the internal medium was 6.8 ± 0.2. The flow rate of the internal medium was 32 L min⁻¹. A few pressure tests were performed using water containing 4.0 ± 0.1 ppm Cl₂ (pH = 6.8 ± 0.2) at 90 ± 1 °C with external air. The water was taken from the chlorine dosage unit (based on sodium hypochlorite) with a well-defined chlorine concentration and was then heated to the test temperature, pressurized and finally brought back to the dosage unit. The concentration of chlorine was continuously measured before the water entered the dosage unit. The flow rate in the circulation loop was 23 L min⁻¹.
3.7. Sampling from pressure – tested pipes

Cylindrical pieces with a diameter of 5 mm were punched through the pipe wall at two different positions. From each piece, four samples with an approximate thickness of 0.5 mm and a weight of 5 ± 1 mg were obtained by cutting with a scalpel. The samples were taken at the following distances (x) from the inner wall: 0 - 0.5 mm (average x = 0.25 mm), 0.5 - 1.0 mm (x = 0.75 mm), 1.0 - 1.5 mm (x = 1.25 mm) and 1.5 - 2.0 mm (x = 1.75 mm).

3.8. Liquid-liquid extraction of aqueous phase

The aqueous phase (25 mL) from the squalane test was collected after each 30 min period of exposure up to total exposure time of 300 min. The 250 mL aqueous phase collected was extracted five times using 5 mL dichloromethane each time. The dichloromethane phase containing the migration species was concentrated with regard to the analytes by evaporation of dichloromethane at 50 °C for 4 h in nitrogen flow. Only ca. 100 µL of liquid, referred to as the concentrated extracted solution, remained and it was diluted in 1 mL acetonitrile before being analyzed by high-performance liquid chromatography-electrospray ionization tandem mass spectrometry (HPLC-ESI MS).
3.9. Characterizing techniques

3.9.1. Size exclusion chromatography (SEC)

The molar mass distribution was obtained by size exclusion chromatography using a Polymer Laboratories GPC220 with 1,2,4-trichlorobenzene with antioxidant as solvent at 160 °C. Refractive index and differential pressure detectors were used. The elution volume (time) was converted to molar mass by calibration with polystyrene standards and the application of a mathematical correction using the universal calibration procedure. Smithers Rapra Technology Ltd., UK, carried out the size exclusion chromatography analyses.

3.9.2. Scanning electron microscopy (SEM)

A field emission scanning electron microscope (Hitachi S-4300) was used to study a few selected samples obtained from pipe samples after exposure to water containing chlorine dioxide. Samples were coated with a thin gold layer using an Agar High Resolution Sputter Coater (Model 208HR) before examination.

3.9.3. Differential scanning calorimetry (DSC)

A Mettler-Toledo differential scanning calorimeter (DSC) with Mettler Toledo STARe software V9.2 was used to assess the mass crystallinity, the melting peak temperature and the oxidation induction time (i.e. the concentration of the effective phenolic antioxidants). Polyethylene samples of ca. 5.0 ± 1.0 mg enclosed in 40 μL aluminium pans with covers. The heating rate was 10 °C min⁻¹ and the purge gas used was nitrogen. The mass crystallinity (w_c) was calculated from the area under the melting trace yielding the enthalpy of fusion (Δh) according to:

\[
w_c = \frac{\Delta h}{\Delta h^0}
\]

(25)

where \(\Delta h^0\) is the enthalpy of fusion of 100 % crystalline polyethylene, 293 J g⁻¹ [74].
The effective phenolic antioxidant concentration in the squalane or polyethylene tape samples was determined by assessing the oxidation induction time (OIT) by the DSC. A 100 µl aluminium pan was filled with either a 35 µL (ca. 25 ± 3 mg) squalane sample or a ca. 5 mg polyethylene tape sample. Three holes were punched in the lid to allow access of oxygen. Each sample was heated from 100 °C to 190°C at 10 °C/min in nitrogen at a flow rate of 50 mL/min. The sample was held at 190 °C for 5 min and then switch from nitrogen to oxygen gas keeping the same gas flow rate. The oxidation induction time was obtained as the time elapsing between the onset of the oxygen gas flow and the intersection of the isothermal base line and the tangent at 0.2 W g⁻¹ (squalane solutions) or 1.5 W g⁻¹ (polyethylene samples) deviation with the isothermal base line.

3.9.4. Infrared spectroscopy (IR)

The samples collected from the squalane test and the tape test were analyzed by attenuated total reflection fourier transform infrared spectroscopy (ATR-IR) using an Elmer Spectrum 2000 (Wellesley, MA, USA) equipped with a golden gate single-reflection accessory from Graseby Specac (Kent, United Kingdom). Each spectrum was based on eight scans between 500 and 4000 cm⁻¹. All absorbance spectra presented were normalized with respect to the 2950 cm⁻¹ band.

3.9.5. High performance liquid chromatography and mass spectrometry

The chromatograms of the extracted solution were recorded by a LCQ ion trap Surveyor Plus LC System equipped with a Surveyor PDA detector (UV detector recording analytes at 270 nm) provided by Thermo Finnigan Corporation, San Jose, USA. The mobile phase used in the high performance liquid Chromatography consisted of 98.5 wt.% acetonitrile (LC-MS grade, Fisher Scientific, USA) and 2.5 wt.% Milli-Q water, and the flow rate was 0.8 mL min⁻¹. A Discovery C18 HPLC column (reversed phase) with 5 µm particle size and 18 nm pore size was used. The thermostat of the column was set to room temperature at ca. 24 °C. The injection volume was 20 µL. The mass spectrometry used an electron spray ionization system.
The analyses were run with positive mode and the ion source from LC was operating at 5 kV. It was adjusted to reveal ions in the mass range from 600 to 1200 m/z.
4. RESULTS AND DISCUSSION

4.1. Methodology development

4.1.1. The squalane test method

In these studies, the degradation of polyolefins was due to exposure to aqueous media either containing either chlorine (Cl₂) or chlorine dioxide (ClO₂). The pressure test is the most adequate test to assess the efficiency of antioxidants in polyolefins. However, the aqueous medium containing chlorine or chlorine dioxide makes the pressure test complicated and expensive due to the unstable nature of the chlorine and chlorine dioxide. The squalane test was developed using a liquid hydrocarbon analogue, squalane, in which antioxidants were dissolved. A two-phase system was formed during the squalane test when the squalane-antioxidant solution was exposed to the aqueous phase containing Cl₂ or ClO₂ (Figs. 4-1a-b).

![Fig. 4-1: Water-squalane system during squalane test: (a) photograph and (b) scheme of the two-phase system.](image-url)
In the squalane test, the volume of the aqueous phase (50 mL) was 10 times greater than that of the squalane phase (5 mL), and the intensive stirring at the bottom of the test tube could not disintegrate the squalane solution, but made the squalane solution form a conical shape, which showed the effective increase in the contact area between the aqueous phase and squalane solution (Note: the description in the first paper concerning the phase scheme during stirring in the squalane test was incorrect). The aqueous phase containing 10 ppm of either ClO₂ or Cl₂ was replaced every 30 min of exposure to ensure invariant experimental conditions. Results obtained by monitoring the pH and the concentration of the chlorine species showed that the pH remained constant at 6.8 ± 0.1 and that the concentrations of Cl₂ or ClO₂ remained constant at 10 ± 1 ppm over a time period of 30 min.

Fig. 4-2: Thermograms obtained at 190 °C after switching to an oxygen atmosphere for: (a) pure squalane; (b) squalane containing 0.1 wt.% Irganox 1010; (c) squalane containing 0.2 wt.% Irganox 1010. From Azhdar et. al. with permission from Elsevier [75].
Typical thermograms showing the oxidation induction time (OIT) are displayed in Fig. 4-2. The OIT of squalane samples was defined as the time period between the onset of oxygen flow until the intersection between the isothermal baseline and the tangent at 0.2 W g⁻¹ exothermal deviation from the baseline (examples of OIT assessments are shown in Fig. 4-2, curve c). Pure squalane showed zero OIT (no stable time period of the isothermal baseline in the thermograms under oxygen flow), and the OIT of squalane solutions containing 0.1 wt.% and 0.2 wt.% Irganox 1010 were 13 min and 30 min respectively (Fig. 4-2). Fig 4-3 shows a linear relationship between the OIT and the concentration of antioxidant in the squalane solutions, which confirms that the indirect OIT measurement to assess the concentration of hindered phenolic antioxidants established for polyolefins also applies to the squalane containing phenolic antioxidants.

Fig. 4-3: OIT plotted as a function of the initial concentration of Irganox 1010 in squalane. The line is a linear fit to the experimental data. From Azhdar et. al. with permission from Elsevier [75].
The thermograms of the squalane solutions with 0.2 wt.% Irganox 1010 exposed to deionized water and water containing ClO₂ at 70 °C for different periods of time are displayed in Figs. 4-4 and 4-5. In both aqueous media, the OIT value decreased with increasing exposure time, and the decrease in OIT of the squalane solution exposed to the aqueous phase containing 10 ppm ClO₂ was faster than that of the solution exposed to pure water (Figs. 4-4 and 4-5). The thermal traces obtained from DSC showed a flat isothermal baseline followed by a steady exothermal signal in most cases. A bimodal exothermal drop with a plateau at the early stage of oxidation was observed in the squalane samples exposed to water containing ClO₂ as shown in Fig. 4-5. Though the reason for the bimodality is not clear, the first slight decrease tendency in exothermal reaction did not have an impact on the OIT data.
In the squalane test, air could access the test tube. **Fig. 4-6** displays the influence of oxygen on the OIT values obtained after exposure to 0.1 wt.% Irganox 1010 - squalane solutions. The solution containing 0.1 wt.% Irganox 1010 have exposed to two aqueous media: one saturated with air (the common squalane test case), and the other one saturated with nitrogen (oxygen-free water). Although the scatters were large, the consumption of Irganox 1010 followed a linear trend in both cases and the time to depletion was ca. 480 min for the oxygen-free squalane test and ca. 380 min for the test open to air. The difference of 20 % in the depletion time suggests the consumption of antioxidant by oxidation, and that the major loss in stability was due to migration to the aqueous phase. It needs to be noticed that the OIT of the 0.1 wt.% Irganox 1010 solutions are low and that the scatter in the data is significant. The data show that presence of oxygen in the squalane test system moderately decreases the loss rate.

The squalane test as a new method to assess the protective efficiency of phenolic antioxidants in polyolefins exposed to water containing ClO₂ or Cl₂ has significant advantages: (a) the usage of a low molar mass liquid analogue, squalane, instead of polyolefins, efficiently simplifies and shortens the time for samples containing antioxidants; (b) the phenolic
Results and discussion

Antioxidants can be easily and homogeneously dispersed in squalane; (c) the squalane containing antioxidants is readily exposed to chlorinated aqueous media by intensive stirring; (d) easy sampling of the squalane solutions by pipette when the stirring is stopped because the squalane phase and aqueous phase can automatically separated; (e) exposure for 300 min is capable of providing valuable data demonstrating the consumption of phenolic antioxidants determined by DSC (OIT). The squalane test method shows advantages when screening a large number of phenolic antioxidants.

4.1.2. The tape test method

With the same experimental setup, instead of squalane solution, a piece of polyethylene tape containing antioxidant was exposed to ClO₂ or Cl₂ aqueous media, referred to as the tape test. Besides the study of antioxidant consumption, the samples obtained from the tape test could be used to study the morphology by scanning the surface of the tape after exposure. The stability of the polyethylene-antioxidant system is greater than that of the squalane solution, and longer exposure times were required. A modification of the experimental setup was used by introducing an over-flow device (Fig. 4-7). A pump continuously pumping in fresh water containing 10 ppm ClO₂ or Cl₂ realizes automated refreshing of the aqueous phase.

Fig. 4-7: Sketch of the experiment setup using an over-flow system.
Results and discussion

The activation energy was calculated at different depths in a 4 mm thick polyethylene specimen initially containing 0.1 wt% Irganox 1010 exposed to ClO$_2$ aqueous medium at 30 °C and 70 °C, and Fig. 4-8 displays the activation energy plot according to the depth of the specimen. The activation energy increased with increasing distance from the specimen surface and reached an almost constant value of $21 \pm 2$ kJ mol$^{-1}$ in the specimen center, which is in agreement with data obtained by Colin et al. [39] who reported an activation energy of 26 kJ mol$^{-1}$ from data for polyethylene stabilized with Irganox 1010. The activation energy for the diffusion of small molecules (carbon dioxide) in polyethylene is, according to Flacconièche et al. [76], ca. 30 kJ mol$^{-1}$. Hence, the results obtained suggest that the antioxidant consumption rate was mainly controlled by the diffusion of chlorine dioxide.

Fig. 4-8: Activation energy of the antioxidant consumption rate (30 – 70 °C in water with 10 ppm ClO$_2$) plotted as a function of the depth (i.e. distance from the sample surface). From Yu et. al. with permission from Elsevier [77].

Fig. 4-9 presents the dependence of the oxidation induction time (OIT) of polyethylene tape (initial containing 0.1 wt.% Irganox 1010) on the time of exposure to water containing 10 ppm chlorine dioxide at the temperatures between 30 and 70 °C, and the rate of antioxidant consumption is higher at the higher exposure temperature. The moderate temperature dependence of the consumption rate corresponds to an activation energy of the order of 10 kJ mol$^{-1}$. Fig. 4-10 shows that the rate of consumption of the antioxidant in squalane solution is independent of the experimental temperatures (the initial concentration of Irganox
The oxidation induction time is proportional to the concentration of phenolic antioxidants in both polyethylene matrix and squalane solution. Fig. 4-11 shows the OIT data for the stabilized squalane and polyethylene samples containing different phenolic antioxidants. The
OIT of the polyethylene samples showed a linear relationship with the OIT of the corresponding squalane samples. The average deviation along the y-axis from the straight line was 15 % of the absolute oxidation induction time values of the polyethylene samples. It can be noted that the antioxidant concentrations in the different samples showed individual variations within 10 % of the absolute values (0.1 wt.%). The difference in oxidation induction times between the different samples was partly due to differences in the molar concentration of the phenolic groups per gram sample ($C_{\text{OH}}$); the samples with low $C_{\text{OH}}$ generally showed short oxidation induction times.

![Graph showing linear relationship between OIT of PE tape samples and squalane samples](image)

*Fig. 4-11*: Initial oxidation induction time of PE tape samples plotted as a function of initial oxidation induction time of squalane for the six different antioxidants. The line is a linear fit to the experimental data with the constraint that the line shall pass through the origin. From Yu et. al. [78] with permission.

The data of oxidation induction time of the stabilized polyethylene tapes exposed to ClO$_2$ aqueous medium showed an initial linear decrease, consuming 60 to 75 % of the initial antioxidant content. A significantly slower and non-linear decrease in the oxidation induction time was observed until antioxidant depletion was finally reached. The OIT data for the squalane solutions displayed a linear consumption rate during 300 min exposure period to water containing 10 ppm ClO$_2$ and the depletion time of the antioxidants was obtained by extrapolating the trend line to zero. *Fig. 4-12* shows a linear relationship between the time to reach antioxidant depletion in the polyethylene samples and the time obtained by
extrapolating the OIT data for the squalane samples. The slope of the trend line is 6.6, which indicates that the depletion time data showed a better ‘resolution’ in the polyethylene samples than in the squalane samples. The rates of antioxidant consumption are converted according to the initial OIT plots versus exposure time (linear decreasing OIT plots for polyethylene tape samples). Fig. 4-13 displays a linear relationship between the antioxidant consumption rates in the two media (squalane and polyethylene). Hence, it is possible to rank different antioxidant systems with regard to their efficiency in these chlorinated aqueous media on the basis of the short-term data (<300 min) obtained by both the squalane test and the tape test.

The scanning electron micrographs of the unexposed samples and of the samples exposed for short periods of time (less than the time to reach antioxidant depletion) and drawn beyond necking showed a smooth and fibrous surface texture. The samples exposed for longer periods of time, i.e. significantly longer than the time to reach antioxidant depletion, displayed a characteristic surface crack pattern (Figs. 4-14a,b). Between the cracked ‘islands’, the surface texture resembled that of the fresh samples (Fig. 4-14b). This indicates that the surface cracks
stopped beneath the border between highly degraded and fresh polymer. The samples examined in the scanning electron microscope were tilted by an angle of 60° with respect to the electron beam, making it possible to measure the crack depth in the electron micrographs.

The crack depth was determined by SEM (samples were tilted at an angle of 60° with respect to the electron beam) and the crack depth of the polyethylene tape stabilized with a phenolic antioxidant is plotted versus exposure in Fig. 4-15. The phenolic antioxidant was depleted at ca. 2500 min when exposed to ClO₂ aqueous medium and the onset of surface embrittlement occurred after 4000 to 4500 min. For this polyethylene tape samples, the growth of the crack depth was of the order of 5 \( \mu \text{m} \) per 1000 min exposure time (Fig. 4-15). A similar behavior was observed in PE tapes stabilized by other phenolic antioxidants: the surfaces after stretching showed smooth fibrous surface textures immediately after the depletion of the stabilizers and the initiation of embrittlement required a longer exposure time in the oxidizing aqueous medium. Although this sampling method was adequate to find the crack depth, the determination of the precise time for the onset of surface embrittlement was insufficient.

The carbonyl index (the ratio of carbonyl absorbance at 1710 cm\(^{-1}\) and methylene band at 1465 cm\(^{-1}\)) of the polyethylene tape samples plotted as a function of exposure time in water
containing ClO$_2$ is shown in Fig. 4-16. These measurements relate to the structure of the surface layer with a penetration depth of a few micrometers using the ATR technique. No carbonyl absorbance signals were observed on the polyethylene tape sample before it had reached the state of antioxidant depletion based on the DSC-OIT measurement (OIT = 0). However, a gradual increase in the intensity of the carbonyl absorption peak was observed immediately after depletion of the antioxidant for a marginally longer exposure time (Fig. 4-16). The rapid upturn in the curve of carbonyl index versus exposure time occurred after the onset of marked surface embrittlement. In fact, all the tape samples reaching the state of antioxidant depletion (oxidation induction time = 0) were analyzed by infrared spectroscopy and none of them displayed surface oxidation.

The advantages of the tape test for assessing the efficiency of antioxidants in polyethylene on exposure to water containing ClO$_2$ or Cl$_2$ are: (a) the use of thin polyethylene tape and the consumption of phenolic antioxidants is readily assessed by the DSC-OIT method; (b) the over-flow system makes possible the assessment of the long-term performance with a constant aqueous volume and a reliable concentration of chlorinated species in the aqueous...
phase; (c) the solid polyethylene samples can be characterized by IR and SEM, and this facilitates the study of surface embrittlement and crack-growth; (d) there is a linear relationship between the time to reach antioxidant depletion in the polyethylene tape and the time to reach depletion in samples based on squalane containing the corresponding antioxidants, and it is possible to estimate the long-term antioxidant depletion in polyethylene by assessing the short-term exposure (typically 300 min) using squalane solutions.

4.2. Degradation of Irganox 1010 in water containing ClO$_2$ or Cl$_2$

The OIT of squalane solutions containing 0.1, 0.2 and 0.3 wt.% Irganox 1010 versus exposure time in 10 ppm ClO$_2$ aqueous phase is displayed in Fig. 4-17. The data obtained followed a linear tendency, and the OIT data were extrapolated to zero to obtain the depletion of the antioxidant. Fig. 4-18 shows the depletion time as a function of the concentration of the antioxidant and it suggests that the time to depletion of the antioxidant increases in a non-linear fashion (positive curvature) with increasing initial antioxidant concentration. The OIT data for the 0.2 wt.% Irganox 1010 solution was collected within 120 min and the linear extrapolation may result in an incorrect depletion time.

![Figure 4-17](image_url)

*Figure 4-17: OIT of squalane phase containing Irganox 1010 exposure to ClO$_2$ with concentration of (a) 0.1 wt.% (filled circles), (b) 0.2 wt.% (filled squares) and (c) 0.3 wt.% (filled triangles). From Yu et. al. with permission from Elsevier [77].*
The OIT data of 0.2 wt.% Irganox 1010 exposed to pure water, to water containing 10 ppm ClO₂ and to water containing 10 ppm Cl₂ for 300 min at 70 °C are displayed in Fig. 4-19. Ca. 10 % of the antioxidant exposed to pure water for 300 min was lost mainly due to migration to aqueous phase (Fig. 4-19, curve a). The faster loss of antioxidant in the squalane phase on exposure to the chlorinated aqueous media (Fig. 4-19, curves b and c) was due to chemical reactions [79]. As mentioned before, the OIT is proportional to the concentration of the active phenolic antioxidant. The concentrations of Irganox 1010 remaining after 300 min of exposure was ca. 10 % of the initial concentration when exposed to ClO₂ aqueous media and ca. 75% when exposed to Cl₂ aqueous media. The difference in the concentration of remaining active Irganox 1010 in the two chlorinated water media indicated that the reactions between the phenol and Cl₂ and ClO₂ are fundamentally different.
Fig. 4-19: The dependence of OIT of squalane initially containing 0.2 wt.% Irganox 1010 on the exposure time to water (●; line a), to water containing 10 ppm Cl₂ (▲; line b) and to water containing 10 ppm ClO₂ (■; line c). From Yu et al. with permission from Elsevier [77].

Fig. 4-20: Time at depletion of the antioxidant in squalane exposed to water containing 10 ppm ClO₂ at 70 °C as a function of the initial concentration of Irganox 1010. The data were obtained from the data presented in Fig. 4-8 and Fig. 4-18.

Fig. 4-20 shows the data of Fig. 4-18 re-plotted using the data from Fig 4-19. The depletion time of 0.2 wt.% Irganox 1010 obtained by linear extrapolation of OIT data within 120 min exposure time was 180 min. After 330 min exposed to water containing ClO₂, ca. 10 % active antioxidant remained and the depletion time was expected to be ca. 350 min. A clear curvature can be observed in the OIT data of Irganox 1010 exposed to water containing ClO₂ indicating that the rate of consumption of Irganox 1010 decreased with increasing exposure period. A linear proportionality between the depletion time and the initial antioxidant concentration can be observed. However, it is difficult to apply this linear plot to the solid polyethylene because of the solubility of the antioxidant. Billingham has showed the solubility of Irganox 1010 in LDPE under 60 °C was less than 0.2 wt.% [80] and Irganox 1010 was supersaturated at the service temperature. A large physical loss of the antioxidant is expected due to the surface evaporation [81].

4.2.1. Analyses of the degradation products

The infrared absorbance (ATR) spectra of three condensed aqueous phase extracts are shown in Fig. 4-21. The presence of carbonyl absorption peaks which centering at 1745 cm⁻¹ can be
observed in the extracts samples from the ClO₂ and Cl₂ aqueous phases (Fig. 4-21a). Karlsson et. al. [82] and Viebke et. al. [20] have reported that a carbonyl absorption at 1715 cm⁻¹ can be observed in the oxidized medium density polyethylene, precisely matching the absorption peak of ketonic carbonyls [83, 84]. The absorbance peak at 1745 cm⁻¹ indicated that ester groups were presented in the aqueous phase [83, 84]. Both the intact form and a substantial fraction of the degradation products of the antioxidant contain ester groups. Hence, the observed carbonyl absorption in Fig. 4-21a should originate from the antioxidant species. Fig. 4-21b shows a small peak associated with a stretching vibration of the chlorine-carbon bond at ca. 760 cm⁻¹ which was only observed in the extract solution exposed to the ClO₂ aqueous medium. This indicates that chlorine was to some extent covalently bonded to the degraded antioxidant species.

![Infrared absorbance (ATR) spectra of extracts of the aqueous phase collected during 300 min of exposure of squalane containing 0.2 wt.% Irganox 1010 to the following aqueous phases: (i) water containing 10 ppm ClO₂; (ii) water containing 10 ppm Cl₂ and (iii) Milli-Q water. From Yu et. al. with permission from Elsevier [77].](image)

The fact that infrared spectroscopy revealed no difference between the squalane solutions before and after exposure, although changes in color were visible, was due to low concentrations of the antioxidant and its degradation species. The absence of the carbonyl absorption peak indicated the effective protection by the antioxidant and no oxidation in the squalane structure within 300 min exposed to either ClO₂ or Cl₂ aqueous medium.
Figs. 4-22 and 4-23 show the chromatograms of extracts collected during exposure to water containing 10 ppm Cl₂ and ClO₂ respectively. Pure Irganox 1010 displayed a single peak at a retention time of 15.3 min in the liquid chromatogram. Intact Irganox 1010 can be observed in both chromatograms, showing the presence of intact Irganox 1010 in both Cl₂⁻ and ClO₂⁻ aqueous phases (marked with a in the Figs. 4-22 and 4-23), which indicates that a fraction of the antioxidant had migrated from the squalane phase to the aqueous phase without undergoing any degradation. The peaks that appeared at other retention times are marked b to i in Fig. 4-22 and with b to h in Fig. 4-23 and the mass spectra associated with each peak are shown in Figs. 4-24 and 4-25. The chromatography of the condensed extract obtained from the aqueous medium during 330 min exposure to Cl₂ aqueous medium containing migration products from the squalane solution displayed peaks which were small and well resolved at the following retention times (Fig. 4-22): 5.1 min, 6.8 min, 7.3 min, 7.7 min, 8.3 min, 9.5 min, 16.4 min and 18.3 min. Fig. 4-23 shows the chromatography of the extract obtained from the ClO₂ aqueous phase: an intact Irganox 1010 peak, stronger peaks associated with the degradation products of the antioxidant at the following retention times: 5.0, 6.1, 6.6 and 7.3 min and a broad shoulder between 7.5 and 11 min. The extracts of the squalane solution showed no remaining antioxidant or fragments and all the species were supposed to have migrated to the aqueous phase.

In chromatography, the area of the peak corresponds to the concentration of the species; thus the relative concentration of intact Irganox 1010 is higher in the Cl₂ aqueous phase than in the ClO₂ aqueous phase, compared with the overall area of the degraded species in each chromatography. This argument is consistent with the significantly higher OIT of the squalane phase after 300 min of exposure to water containing Cl₂ (ca. 25 min) than that after similar exposure to water containing ClO₂ (ca. 5 min). The fact that retention times reveals the polarity of the compounds suggests that the degradation species extracted from Cl₂ aqueous phase were more polar than those extracted from ClO₂ aqueous phase. Figs 4-24a and 4-25a both display a mass of 1200 m/z which is intact Irganox 1010 with sodium adducts. The difference in the mass spectra (Figs. 4-24b-i and 4-25b-h) suggests that the degradation products are unique in the Cl₂ and ClO₂ aqueous phases, which also reveals the difference in
the phenolic antioxidant degradation mechanism in Cl₂ and ClO₂ water medium. In water containing Cl₂, most of the degraded products were in the mass range between 930 and 1020 m/z. The most prominent peaks, as judged from the UV-absorbance and the intensity of the peaks in the mass spectra, were peaks d-g (Fig. 4-22) and their mass spectra showed the mass values in Fig. 4-24: 955 (d), 955 and 1020 (e), 940 and 956 (f), and 931 and 953 (g) m/z. Two peaks had 1-2 min longer retention times than the peak of pristine Irganox 1010 and they revealed essentially the same with pristine Irganox 1010. The ester bond is the weakest bond in the Irganox 1010 structure, and it is probable that of Irganox 1010 loses one arm by scission of an ester bond, resulting in a three-arm structure with a mass of 887 m/z. The dominating species had masses between these limiting values.

![Liquid chromatogram of extracted solution obtained from the aqueous phase sampled during 330 min of exposure to water containing 10 ppm Cl₂ at 70 °C. From Yu et al. with permission from Elsevier [77].](image)

Two mass ranges can be found in Figs. 4-23 and 4-25 of the degraded species present in the extract after exposure to the ClO₂ aqueous medium: 700-800 m/z (prominent peaks were b/c and d with masses 743 and 777 m/z) and 970-1050 m/z (prominent peaks were e (1051 m/z), f (1035 m/z), g (1004 m/z) and h (972 m/z)). The presence of lighter molecules suggests that
two chain scissions occurred in some antioxidant molecules. A two-arm moiety without aliphatic cilia would have a mass of 596 m/z and with full-length aliphatic cilia, 768 m/z. The high polarity of this extract suggests that these species were more oxidized than the molecules exposed to water containing Cl₂. It should be noted that the mass spectrometry scans were adjusted between 600 to 1200 m/z, and single phenolic units with short aliphatic groups must have been present in the water phase but not shown in the spectra or evaporated during the sampling process.

![Liquid chromatogram of extracted solution obtained from the aqueous phase sampled during 330 min of exposure to water containing 10 ppm ClO₂ at 70 °C. From Yu et. al. with permission from Elsevier [77].](image)

**Fig. 4-23:** Liquid chromatogram of extracted solution obtained from the aqueous phase sampled during 330 min of exposure to water containing 10 ppm ClO₂ at 70 °C. From Yu et. al. with permission from Elsevier [77].
Fig. 4-24: Mass spectra of the peaks marked a to h in Fig. 4-13. From Yu et. al. with permission from Elsevier [77].

Fig. 4-25: Mass spectra of the peaks marked a to h in Fig. 4-14. From Yu et. al. with permission from Elsevier [77].
4.2.2. Hindered phenolic antioxidant degradation mechanism

The principal chemical difference between ClO₂ and Cl₂ is that ClO₂ is a one-electron oxidant \( E^0 = 934 \text{ mV} \) [85]) whereas Cl₂ preferentially reacts by hydrogen substitution [86]. The first reduction step of Cl₂ is \( \text{Cl}_2 + e^- \rightarrow \text{Cl}_2^- \), associated with a reduction potential of ca. 0.4 V [85]. Accordingly, Cl₂ is generally recognized as a very strong oxidant. Direct electron transfer from substrate to Cl₂ is much less efficient than for ClO₂, and electrophilic hydrogen atom substitution predominates in most cases. The water phase containing ClO₂ used in this study was buffered to pH = 6.8, and the major chlorinated component dissolved is hypochlorous acid (HClO) [8], but HClO does not efficiently oxidize phenolic antioxidant [87]. The chlorine that attacks the phenolic antioxidant is present at a low concentration (5.5 % of the maximum value). In water containing Cl₂, the initial reaction between the phenolic antioxidant and chlorine is substitution of hydrogen atoms, both in the aromatic ring and in the side chains by chlorine atoms. The reason that no carbon-chlorine absorption peak observed in the infrared spectra is that the chlorine substitutions may in turn be replaced by hydrolysis into hydroxy groups.

One-electron oxidation of a phenol, in this case by ClO₂, leads to radical cation formation, and to the formation of a phenoxy radical by prompt proton elimination. The addition of another ClO₂ molecule to a resonant radical site in the aromatic ring leads to the formation of chlorite ester, and the chlorite ester may undergo hydrolysis and ring opening, resulting in the formation of muonic acid derivatives [88]. However, due to the ‘hindered’ structure associated with the tert-butyl groups in Irganox 1010, it is probable that a β-cleavage in the side chain is induced resulting in the formation of yellow-colored quinoid structures. It has been observed that the squalane phase containing 0.2 wt.% Irganox 1010 turned dark yellow and hazy after exposure to water containing ClO₂ for 300 min, and the squalane solution remained transparent and colorless after exposed to water containing Cl₂ for the same exposure period. The remaining side chain radicals of Irganox 1010 tend to be further
oxidized by oxygen or ClO$_2$ to carbonyl sites or chlorine-containing products and the traces have been found by infrared spectroscopy.

Accordingly, chlorine mostly modifies the original structure leaving the functional phenolic group intact and, after modifications, the products act as efficient antioxidants. On the other hand, ClO$_2$ oxidizes the original structure into colored products with less value as antioxidants, so that the consumption of Irganox 1010 in water containing ClO$_2$ was faster than in water containing Cl$_2$.

### 4.3. DETERIORATION OF POLYETHYLENE PIPES

#### 4.3.1. Antioxidant concentration profiles

In this particular case, the assessment of antioxidant efficiency by the oxidation induction time (OIT) at 210 °C was used to optimize the evaluation of the stabilized piping materials [89]. **Fig. 4-26a** displays OIT data of pipe samples at different depth before and after exposure to water containing ClO$_2$ and **Fig. 4-26b** magnifies the OIT data obtained from samples after exposure on a layer scale. A rapid loss of stability, particularly near the inner wall exposed to water containing chlorine dioxide can be observed. The antioxidant was consumed ca. 90 % within 2 h close to the inner wall, while ca. 50 % loss of stability at the outer wall was observed in the same short exposure time (2 h). With a longer exposure period (21 h and longer), the antioxidant close to the inner wall reached depletion, and the antioxidant was consumed within the pipe wall due to the migration of the chlorine species. It may well be that Regime A loss, i.e., precipitation of a supersaturated solution of antioxidant [90] occurred during the initial period. The asymmetric component of the antioxidant loss, i.e., that part which was concentrated towards the inner wall, was significant far into the pipe wall.
Results and discussion

Fig 4-26: Oxidation induction time profiles for pipes exposed to internal water containing 4 ppm chlorine dioxide at 90 °C for the following times: • 0 h, ◇ 2 h, ■ 21 h, □ 79 h, ▲ 118 h and △ 121 h. (a) shows an overview and (b) shows a magnification of the low OIT-data region. From Yu et. al. with permission from Elsevier [87].

The corresponding data for the same piping material exposed to water containing chlorine is displayed in Fig. 4-27. A significant loss of stability (ca. 50 %) occurred in this case during the initial time period. The magnitude of the change was essentially the same as in the case of the pipes exposed to water containing chlorine dioxide, i.e., a 50 % loss of the initial concentration of effective antioxidant during the first 2 h, and the consumption of the antioxidant was of approximately the same order of magnitude through the depth of the pipe wall during each exposure time. Fig. 4-28 showed the OIT data for the samples taken from the pipe at a depth of 0.75 mm exposed to water containing ClO₂ and Cl₂ at different exposure times and the factorial difference in antioxidant depletion between the two cases was approximately four. The study of squalane test that squalane stabilized by 0.2 wt.% Irganox 1010 exposed to ClO₂ and Cl₂ aqueous phase were in accordance with the OIT plotting in Fig. 4-28 and also showed the factorial difference was four. Both former research [24, 25] and previous study of the squalane tests showed ClO₂ did not attack hydrocarbon chains. In the aqueous phase containing ClO₂, the phenol groups in the antioxidant molecules located in the inner wall are first degraded by ClO₂ by single electron transfer. With longer exposure time, the aggressive ClO₂ and chlorinated species diffuse further into the pipe wall, and thus consume the antioxidant deeper into the pipe. In the case of water containing Cl₂, the reaction
between the antioxidants and Cl₂ is mainly hydrogen substitution and results in chain scission. The phenol groups in the broken chains from the original antioxidant are still functional as stabilizers.

![Graph](Image)

**Figure 4-27**: Oxidation induction time profiles from pipes exposed to 4 ppm of chlorinated water at 90 °C for the following times: 0 h, ◊ 2 h, ■ 28 h, □ 140 h, ▲ 500 h and △ 1433 h and ▼ 1594 h. From Yu et al. with permission from Elsevier [87].

**Figure 4-28**: Oxidation induction time for samples at a depth of x = 0.75 mm as a function of exposure time at 90 °C after exposure in the following media: (a) internal ClO₂ - aqueous phase - filled symbols; (b) internal Cl₂ - aqueous phase - open symbols. From Yu et al. with permission from Elsevier [87].

### 4.3.2. Crystallinity profiles through the pipe wall

The crystallinity profile (Fig. 4-29) through the pipe wall of the unexposed pipe shows only a moderate radial dependence and the variations are within 2 wt.%. Exposure for 130 h at 90 °C had only a minor influence on the crystallinity profile. The variations at the same depth among the samples aged for different periods of time were small. The melting peak temperature was also essentially constant through the pipe wall and it remained constant even after ageing. The major alteration in crystallinity was in the powder samples. These samples were obtained by scraping off the white powdery material sitting on the inner pipe walls of the pipes aged for 79 h or longer. The powder samples showed significantly higher degrees of crystallinity than the bulk polymer samples, 67 - 78 wt.% compared with 55 ± 2 wt.%. These
results show that the increase in crystallinity was not accompanied by crystal thickening facilitated by oxidation-induced chain scission. The crystals thus remained intact and the increase in crystallinity can be attributed to oxidative digestion of the amorphous component. A calculation based on the crystallinity values suggests that 50 to 60% of the amorphous material had been removed from the powder samples.

**Fig. 4-29:** Mass crystallinity profiles through the pipe walls after exposure to 4 ppm chlorine dioxide in water at 90°C for the following times: ● 0 h, ○ 2 h, ■ 21 h, □ 79 h, ▲ 118 h, ▼ 121 h and ×130 h. Crystallinity data for the highly degraded powder layers are denoted with the symbol ◆. From Yu et al. with permission from Elsevier [87].

### 4.3.3. Oxidation products in degradation layer

The bulk of piping materials exposed to chlorinated water (including the material in the immediate proximity of the inner pipe wall) showed no difference from that before aging according to infrared spectra, and no carbonyl or hydroxyl absorption signals were observed. On the other hand, the powder samples collected from the highly degraded layers of the inner wall surface exhibits a carbonyl absorbance band which indicated the presence of characteristic oxidation products (Fig. 4-30). It has been reported that the ketonic carbonyl compounds exhibit an absorption band at 1715 cm⁻¹ and that carboxylic acid carbonyl compounds show a peak at 1705 cm⁻¹ [91, 92]. The main peak at 1709 cm⁻¹ is displayed in Fig. 4-30 and the variation in the peak wave number between different powder samples is
within ± 2 cm⁻¹. The location of the main peak between 1705 and 1715 cm⁻¹ suggests that both carboxylic and carbonyl compounds are present in the highly oxidized sample. Iring et al. [83] showed that the dominant oxidation product located at the chain scission sites are carboxylic acids. This is consistent with the carbonyl absorption spectra obtained and also with the data obtained by size exclusion chromatography. The high crystallinity powder consists mainly of extended chains and once-folded chains with a large number of chain ends and thus carboxylic acid groups. Furthermore, a shoulder at ca.1740 cm⁻¹ can be observed in Fig. 4-30 which is in the same spectral range as the absorption bands for ester carbonyls (1740 cm⁻¹) [91, 92]. The relative carbonyl absorption in the highly degraded powder samples is 0.4–0.5 (A₁₇₀⁹/A₁₄₆₅), which after exposure to Cl₂ aqueous phase is similar to that after exposure to ClO₂ aqueous phase. It may be surprising that the maximum value of the relative carbonyl absorption for unstabilized medium-density polyethylene was at least twice as high after exposure to hot water without disinfectants such as chlorine [20]. It should be remembered that the oxidation of the polymer in the chlorinated media is very rapid but that the majority of the oxidation products are washed out from the powder layer and are thus not accounted for in the infrared analysis.

![Image](image_url)

**Fig 4-30:** Infrared absorbance spectrum showing the carbonyl absorption bands of a powder (highly degraded) sample obtained from the inner wall of a pipe exposed internally to water containing 4 ppm chlorine dioxide at 90 °C for 120 h. The two main peaks appearing at 1709 and 1740 cm⁻¹ are marked with arrows. The ordinate shows the absorbance (A) divided by the absorbance of the methylene 1465 cm⁻¹ band (A₁₄₆₅). From Yu et. al. with permission from Elsevier [87].
4.3.4. Polyethylene degradation – molar mass

Fig. 4-31 shows the molar mass distributions of the virgin polymer and of two different samples obtained from powder layers showed large differences. The unexposed polymer had a wide molar mass distribution (curve a in Fig. 4-31), the average molar masses being: $\bar{M_n} = 5700 \text{ g mol}^{-1}$ and $\bar{M_w} = 155000 \text{ g mol}^{-1}$. The powder material showed extensive degradation $\bar{M_n} = 1800 \text{ g mol}^{-1}$, $\bar{M_w} = 3600 \text{ g mol}^{-1}$ (curve b in Fig. 4-31) and $\bar{M_n} = 2500 \text{ g mol}^{-1}$, $\bar{M_w} = 7600 \text{ g mol}^{-1}$ (curve c in Fig. 4-31). The polydispersity index (PDI), defined as the ratio of the weight average molecular mass to the number average molecular mass indicates the homogeneity of a polymer. The PDI of the unexposed polymer and the degraded powder samples marked b and c were 26, 2 and 3 respectively. The much lower values of both the molar masses and polydispersity indices (PDI) of the powder samples imply extensive degradation. Multimodal molar mass distributions are observed in the powder samples marked b and c. The presence of a weak shoulder in curve b locates the same molar mass as the high molar mass peak in curve c, which implies the difference in mass distribution between the two powder samples due to the difference in sampling, and the less degraded polymer may pollute the powder during recovery. The lowest molar mass peak that appears at practically the same molar mass for the two powder samples originated from chains that were extended through a single crystal. Most of the amorphous continuum was damaged by degradation surrounding this portion of the chain. It is suggested that the second low molar mass peak is suggested to be due to once-folded chains, which means that the length (molar mass) should be twice as high as the molar mass of the extended chains. Two distinct peaks at 2500 g mol$^{-1}$ and 5600 g mol$^{-1}$ can be observed in curve b, and the ratio between these two is 2.2. Curve c displays peaks at 2600 g mol$^{-1}$ and 6800 g mol$^{-1}$, and the ratio is 2.6. It is believed that the latter ratio value shows that the proximity of the third peak interfered and shifted the second peak to a higher molar mass value. A third peak (ca. 14000 g mol$^{-1}$) in the molar mass distribution marked c in Fig. 4-31 showed no reasonable integral relationship with the first peak, and the ratio between the third and the first molar mass is 5.6. Thus the third peak can be assigned to a fraction of less degraded material. Hassinen et. al. [22] also reported
the presence of extended chains and once-folded chains in the degraded powder oxidized in a chlorinated aqueous medium.

![Figure 4-31: Size exclusion chromatograms for virgin polymer (a; in green), and two degraded (powder) layer samples (b and c; in red and blue). Note the tri-modality of the molar mass distributions of the powder layer samples marked with arrows. From Yu et. al. with permission from Elsevier [87].](image)

4.3.5. Crack growth in pipe wall

**Fig. 4-32** shows a microtome section through a region with a crack formed during the hydrostatic pressure testing. On both sides of the major crack, there are zones of brittle material indicating the presence of small cracks due to the highly degraded polymers. The major crack presumably had at some stage grown into a zone of fresh material and stopped. Aggressive oxidizing species then attacked the material adjacent to the crack. In the case of pressure testing, the hydrostatic helps the growth of the crack. This crack growth mechanism as degradation assisted the crack propagation and different stages of degradation-assisted crack propagation are illustrated in **Fig. 4-33**. This crack growth mechanism is a probable cause of early fracture through a thick-walled pipe, despite the fact that the polymer degradation is strictly confined to the surface.
**Fig. 4-32:** Scanning electron micrograph of a specimen obtained by sectioning through a region with a crack in a pipe exposed to water containing 4 ppm chlorine dioxide for 121 h. From Yu et. al. with permission from Elsevier [87].

**Fig. 4-33:** Schematic representation of degradation-assisted crack propagation. Arrows with adjacent s indicate the first principal stress direction. From Yu et. al. with permission from Elsevier [87].

### 4.3.6. Degradation scenario of PE pipe exposed to water containing chlorinated species

**Fig. 4-34** illustrates the mechanisms involved in the deterioration of polyethylene pipes exposed to pressurized water containing chlorine dioxide. The initial stage (phase 1) is the loss of stabilizer protection which, in the case of a hindered phenolic antioxidant, is by a one-electron transfer from the phenol to ClO₂ followed by other reactions yielding inactive products. When the antioxidant system reaches depletion (phase 2, a significant part of the pipe towards the inner wall has no antioxidant protection), highly reactive radicals present in the aqueous phase (e.g. hydroxyl radicals) react in the immediate surface of the polymer by hydrogen abstraction. Hence, a large number of radicals (R*) are formed which react with
oxygen to form peroxyl radicals which react further according to the Bolland-Gee oxidation scheme [34, 41]. The degradation of the unprotected polymer starts at the inner wall. This immediate surface reaction yields a layer of degraded and porous material. The thickness of the layer increases with time (phase 3). The indication that phase 4 starts is the crack initiation in the porous layer, and the blunt in the fresh, undegraded material beneath the cracks. The cracks formed in phase 4 are on a micro-scale and can hardly be observed by the naked eye. Degradation occurs at the crack walls and the crack tip assisting further crack propagation in phase 5. When the size of the crack reaches a critical value, pipe failure occurs (phase 6).

Fig. 4-34: Sketch of mechanisms underlying failure of a pressurized polyethylene pipe exposed to water containing ppm levels of chlorine. From Yu et. al. with permission from Elsevier [77].
5. CONCLUSIONS

A new method has been developed for assessing the protective efficiency of phenolic antioxidants in polyolefins on exposure to chlorinated aqueous media (water containing Cl:\ or ClO₂, each at a concentration of 10 ppm, buffered to pH=6.8, at temperature 70 °C). The method is based on the use of squalane, which is a low molar mass liquid analogue of polyolefins. The concentration of effective antioxidant in the organic phase is readily determined by standard differential scanning calorimetry (oxidation induction time). The rate at which phenolic antioxidants are consumed by highly oxidizing chlorinated species is assessed within 300 min. The long-term performance of the stabilized polyethylene was evaluated by a modified experimental setup with an over-flow system keeping the concentration of chlorine species and the volume of the aqueous phase constant. A linear relationship was established between the time to reach antioxidant depletion in the polyethylene tape samples and the time to reach depletion in samples based on squalane containing the same antioxidants. Surface oxidation and surface embrittlement were detected by infrared spectroscopy and scanning electron microscopy of the polyethylene tape samples after they had been stretched beyond necking. Hence, the proposed methodology is capable of efficiently assessing different aspects of the long-term performance of polyethylene materials and their stability towards water containing chlorine dioxide.

The squalane samples stabilized with 0.2 wt. % Irganox 1010 exposed to water containing ClO₂ (buffered to pH = 6.8) at temperatures between 30 – 70°C suggested a surprisingly low activation energy which indicated no diffusion barrier in the squalane systems. Similar experiments conducted on polyethylene tape sample revealed an activation energy of 21 kJ mol\(^{-1}\). This value is of the same order of magnitude as the activation energy for diffusion of a similar sized penetrant molecule in polyethylene. The squalane solution
stabilized by the phenolic antioxidant, Irganox 1010, showed distinct differences in behavior exposed to water containing ClO₂ and Cl₂ at 70 °C. The reason is that chlorine dioxide degrades phenolic antioxidants by a β-cleavage in the side chain resulting in highly polar lower molar mass products containing yellow-colored quinoid structures, whereas the reactions between chlorine and phenol groups are usually hydrogen substitutions in the side chains and the functional phenolic groups are preserved. Under the prevailing experimental conditions, hydrolysis has probably replaced most of the chlorine substitution by hydroxyl groups. These modifications are fairly ‘innocent’; they lead to no color change and the loss of antioxidant activity is probably less pronounced.

Pressure tests on polyethylene pipes subjected to internal water containing ClO₂ and Cl₂, and the depletion of the antioxidant system occurred 4 times faster with internal water containing ClO₂ than with water containing Cl₂ and the ratio of the two cases was consistence with the results of the squalane test. Several direct indications of a digestive degradation of the amorphous component occurring at the aqueous and polymer interface leading to a significant increase in the degree of crystallinity of the degraded surface layer were obtained. Size exclusion chromatography indicated degradation near the crystal amorphous interface, leaving extended and once-folded crystal chains intact. Although polyethylene degradation is an immediate surface reaction, the chemical degradation propagates through a pipe wall with the aid of the cracks.
6. **FUTURE WORK**

The foregoing studies have shown the resistance of polyethylene piping materials against chlorine dioxide and chlorine by adding a combination of antioxidants. The multi-stabilizer system in polyethylene is usually a mixture of the primary and secondary antioxidants and the mixture is capable of eliminating both radicals generated in the first step of oxidation and hydroperoxides that are usually the product of the first step oxidation and trigger further oxidation. The stabilities of alternative antioxidants and their reaction products can be evaluated by the squalane test and tape test. Triple combinations can be attempted to improve the stability of polyethylene pipe materials against the degradation from chlorinated species.

Further efforts will be devoted to crack studies of PE piping material exposed to water containing \( \text{ClO}_2 \) or \( \text{Cl}_2 \) at elevated temperatures. A thin stream of aqueous solution can be induced to the narrow location of a bulk PE piping material under tension. The crack-growth ratio can be obtained and the service time of the piping material can be extrapolated. Different stabilizer systems can be attempted and the resistance towards the high oxidizing aqueous media containing chlorine dioxide or chlorine can possibly be improved.
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8. REFERENCES


A new method for assessing the efficiency of stabilizers in polyolefins exposed to chlorinated water media

Paper II

Deterioration of polyethylene pipes exposed to water containing chlorine dioxide

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*Polymer Degradation and Stability* 2011; **96**: 790-797
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*Polymer Degradation and Stability* 2012; **97**: 2370-2377.
Paper IV

Assessing the long-term performance of polyethylene stabilized with phenolic antioxidants exposed to water containing chlorine dioxide

Accepted in Polymer Testing