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# Aging Mechanism and Material Ranking of PE Pipe Grades in Aqueous Chlorine Dioxide and Hypochlorite Solutions

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July 2020

# AFFIDAVIT

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# Aging Mechanism and Material Ranking of PE Pipe Grades in Aqueous Chlorine Dioxide and Hypochlorite Solutions

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# Abstract

With the ever-growing application of polyethylene (PE) as a piping material and the wide spread usage of secondary disinfection in the drinking water system, the effect of chlorine dioxide ($ClO_2$) and hypochlorite (HOCl) on the degradation of PE pipes has become a matter of interest. In spite of active research work, nowadays neither a commonly accepted aging mechanism nor alternative quick test methods are available. This dissertation aims to provide a thorough overview of the relevant scientific reports supporting the development and optimization of a new test method. Moreover, the major objectives are a deeper understanding of the PE aging mechanism in $ClO_2$ and HOCl, the mechanical and thermal performance screening of various PE grades in $ClO_2$ as well as a material ranking of PE pipe grades based on fast laboratory experiments.

The severe impact of these oxidizing agents on the performance of PE pipes is exemplified by many premature field failures. Relevant publications highlight the adverse effect of the two frequently applied oxidizing agents on the degradation of polyolefin pipes. Furthermore, the literature overview draws attention to the different physical and chemical properties of $ClO_2$ and HOCl, implying their distinct effect on the aging of PE pipe grades. Considering the fast concentration decline due to decomposition and the oxidation reaction of $ClO_2$ and HOCl, precisely controlled aging experiments were found to be essential when investigating the effect of disinfectants. In fact, a comparison of various PE formulations and aging studies is extremely difficult due to the lack of constant aging parameters and different experimental set-ups. Nonetheless, a strongly surface limited material embrittlement and rapid consumption of antioxidants (AO) up to a 1 mm thick material layer have been reported. Currently, standardized pipe pressure tests with disinfected aqueous solutions are used to assess the effect of disinfectants. Due to high costs and long testing times, there is a clear need for accelerated, well-controlled laboratory aging experiments, which support customized set-ups and provide reliable and reproducible data within a short amount of time. Such tests would contribute to the determination of the dominating aging mechanisms and improve the aging resistance of PE pipe grades.

Therefore, in this work, an exposure device was used which provides constant aging conditions and frequently records the aging parameters. When studying the consumption of AO, the Oxidation Induction Times (OIT) and Oxidation Onset Temperatures (OOT) of aged samples were compared. The latter was found to be significantly more sensitive and a faster measurement method than the OIT. Moreover, tensile tests and Scanning Electron Microscopy (SEM) analyses indicate that aging of 1 mm thick specimens in 1 ppm $ClO_2$ at 50°C or a less aggressive medium provides suitable results to interpret and evaluate the progress of PE degradation. Immersion in HOCl solution led to a highly surface-limited aging process; hence the application of thinner, 0.3 mm thick specimens was found to be advantageous.

SEM analyses indicate that $ClO_2$ generates surface cracks and a degraded material layer, while immersion in HOCl resulted in surface erosion without any sign of polymer oxidation in the bulk phase. The different aging mechanisms were further confirmed by comparing the elongation at

break, the OOT and the Carbonyl Index (CI) evaluated over the aging time in $ClO_2$ and HOCl. The $ClO_2$ aged samples suggest that polymer chains are attacked before the complete loss of active AO. In the case of HOCl immersion, an accelerated auto-oxidative aging mechanism was detected. Considering the distinct PE aging products identified in the FTIR-ATR spectrum for each medium and chain scission reactions shown by GPC analyses, polymer degradation was presumably dominated by the following reactions. The decomposition of α-keto hydroperoxides in $ClO_2$ and the decomposition of allylic-hydroperoxides in HOCl seem to govern the chain scission of PE in the affected surface layer. The evolution of molecular wieght over the aging time implies that reactive chlorine species of HOCl attack selectively oxidized tertiary carbon atoms. The presence of $ClO_2$ resulted in a quasi-competitive reaction between chain defects, oxidized chain parts and tertiary carbon atoms of PE molecules.

To screen the performance of various material formulations, OOT, degree of crystallinity and CI were determined at different distances from the contact surface. The changes in these property profiles recorded during the immersion test in $ClO_2$ of three PE grades suggest that the rate-determining step is the $ClO_2$ diffusion. This process is strongly influenced by density, and AO diffusion to the surface seems negligible. The increased crystallinity of a 200 µm surface layer points out the gradual decrease in the $ClO_2$ diffusion rate, so with advanced chemical degradation, AO consumption became slower. Consequently, the material property profiles represent a high potential to rank various material formulations regarding their relative $ClO_2$ resistance. The degree of crystallinity and CI profiles of HOCl-exposed samples remained almost unchanged affirming the highly surface limited polymer degradation. The results also indicate that carbonyl products observed by FTIR-ATR are predominately derived from polymer degradation. Nevertheless, considerable AO consumption was observed in the bulk zone. The diffusion of $Cl_2$ molecules and selective reactions with phenolic AO groups were concluded as the most plausible explanation.

Since a clear material ranking based on these property profiles is rather complicated, further experiments were conducted in $ClO_2$ to identify suitable testing method. Immersion tests were performed with six PE grades in 1 ppm and 0.5 ppm $ClO_2$ at 50°C and 60°C. Recording the decline of elongation at break and OOT in 1 ppm $ClO_2$ at 50°C or lower concentration and temperature was found to be an optimal method for performance screening of various PE pipe grades. Based on mechanical and thermal characterization, three distinct groups with different $ClO_2$ resistance were detected of the six PE grades. The results presented emphasize the reproducibility and applicability of this approach for fast material screening, which can enhance the development time of PE pipe grades and AO packages with optimized $ClO_2$ resistance significantly.

## List of Publications

I Bredács M, Redhead A, Frank A, Bastero A, Pinter G. Development and implementation of an accelerated method for chlorine dioxide exposure. In: Proceedings PPS. doi:10.1063/1.4965541; 2015.

II Bredács M, Redhead A, Frank A, Amaia B, Pinter G. Implementation of a new chlorine dioxide device for accelerated aging of polyolefin pipe materials. In: Proceedings PPXVIII. Berlin, DE. doi:10.13140/RG.2.2.24112.35846; 2016.

III Bredács M, Bastero A, Frank A, Pinter G. Accelerated Aging of Polyethylene Pipe Grades in Chlorine Dioxide and Hypochlorite Solution. In: ANTEC 2017. Anaheim, CA, USA: Society of Plastics Engineers.

IV Bredács M, Frank A, Bastero A, Stolarz A, Pinter G. Accelerated aging of polyethylene pipe grades in aqueous chlorine dioxide at constant concentration. Polymer Degradation and Stability 2018;157:80–9. doi:10.1016/j.polymdegradstab.2018.09.019.

V Bredács M, Bastero A, Frank A, Pinter G. Performance of PE Pipe Resins in Chlorine Dioxide Containing Aqueous Solution. In: ANTEC 2018. Orlando, FL., USA: Society of Plastics Engineers.

VI Bredács M, Frank A, Bastero A, Stolarz A, Pinter G. Aging Mechanism of Polyethylene Pipe Material in Chlorine Dioxide and Hypochlorite Solution. In: Proceedings PPXIX. Orlando, FL, USA; 2018.

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# 1 Introduction

In the past decades, due to their superior properties and price-performance ratio, polyethylene (PE) pipes have gradually replaced the traditional metallic pipes in many water distribution networks in the pressure range up to 16 bar. At the same time, the disinfection of drinking water with the dosage of chlorine-based oxidizing agents has become widely used. In spite of the strong oxidizing nature of the disinfectants, their effect on PE pipes has not been adequately determined yet. Still, recent scientific publications have intensively investigated this matter [1–5]; however neither a commonly accepted aging mechanism nor material ranking and testing methods have been reported. The main objective of this work is to identify and describe the influence of disinfectants on the long-term performance of PE pipe grades.

## 1.1 Background and motivation

**The main objectives of this dissertation are the understanding of the dominating aging mechanism of PE in contact with HOCl and with $ClO_2$, and to develop an accelerated material ranking procedure. Such knowledge would be highly advantageous for the development of PE pipe grades and AO packages with improved disinfectant resistance.**

In order to provide safe drinking water and eliminate pathogenic microorganisms, a large variety of disinfection techniques are used [6–8]. These are ozonation, ultraviolet (UV) radiation, chlorination (HOCl), and the addition of chloramines and chlorine dioxide ($ClO_2$). The water treatment process is usually divided into primary and secondary disinfection [6, 8–10]. The primary process occurs in the water plant, while the latter takes place in the distribution system. If secondary disinfection is used, then PE pipes will be in contact with HOCl and $ClO_2$, which are widely used disinfectants due to their high effectivity [11–14]. Considering the high reactivity of these chemicals, their adverse effect on PE is a matter of interest. Field case studies [15–21] of failed polyolefin pipes have shown that disinfectants lead to advanced material degradation and ultimately to premature pipe failure. Nowadays pipe pressure tests such as ASTM F2023 [22] and F2263 [23] are used to determine the performance and disinfectant resistance of PE pipe grades. Despite elevated testing temperatures, these tests could take longer than a year. Beside the long testing times, the high cost of such experiments represents well the need for faster and more cost-effective characterization methods. In order to develop new testing methods, investigate PE aging mechanism and eventually prevent premature pipe failures, numerous research studies have been conducted [1–4, 17, 24–29]. These publications point out accelerated antioxidant consumptions, increased amounts of degradation products, advanced material embrittlement in a thin surface layer and an overall shortened crack initiation time. However, the detrimental effect of disinfectants on crack propagation is generally assumed, decisive experimental data has not been published yet. It is important to note that in laboratory aging experiments, the precise control of HOCl and $ClO_2$ concentration are crucial for a reliable and reproducible aging dataset. Both disinfectants undergo fast oxidation reactions and thermal decomposition, which leads to rapid concentration decrease, especially at high testing temperatures. Therefore, accurately controlled and constant aging conditions are essential in investigating the effect of HOCl and $ClO_2$

on the degradation of PE pipes. The importance of stable exposure conditions has been discussed in previous studies [30, 31].

## 1.2 Objectives

Considering the increasing application of polyolefin pipes and chlorine based secondary disinfectants, the effect of $ClO_2$ and HOCl on the aging of PE pipes is a matter of interest. The main goals of this dissertation are the development and optimization of an accelerated aging method under laboratory conditions as well as a deeper understanding of the PE aging mechanism in contact with $ClO_2$ and HOCl. Based on this knowledge material screening methods have been developed, which allows the relative performance difference of PE materials in $ClO_2$ medium to be idnetified. The following objectives will be investigated:

**A: Method development and optimization of accelerated aging in $ClO_2$ and HOCl solutions for PE pipe grades under constant conditions.**

**B: Determination of the aging mechanisms of PE in $ClO_2$ and HOCl solutions applying immersion tests without mechanical loading.**

**C: Development and application of material screening methods in order to identify the relative $ClO_2$ resistance of different PE pipe grades.**

It is important to note that a comprehensive lifetime assessment method for PE pipes in contact with disinfected water is not an objective of the current work. However, based on the results of this work a theoretical model for lifetime prediction is proposed.

## 1.3 Structure of this dissertation

This dissertation is divided into three major parts which focus on the different aspects of PE aging in contact with disinfected aqueous solutions. The content of these three major parts is summarized as follows as:

**PART I:** **INTRODUCTION, LITERATURE OVERVIEW, EXPERIMENTAL**

**PART II:** **OPTIMIZATION AND ACCELERATION OF AGING AND DEGRADATION MECHANISMS**

**PART III:** **ACCELERTED MATERIAL RANKING METHODS OF PE PIPE GRADES IN CONTACT WITH DISINFECTANTS**

Without being exhaustive, **PART I** gives an elaborated overview of the relevant scientific publications and a comprehensive summary about the state of the art. This critical review of published research works focuses on identifying the most pressing issues in this field. Completed experiments, materials used and characterization methods are described in the experimental chapter. **PART II** is divided into the chapters concerning the optimization of the aging conditions and the PE degradation mechanism in $ClO_2$ and HOCl. The former chapter concludes with aging parameters which are the most suitable to observe the PE degradation in a reasonable time frame, while the latter provides fundamental conclusions about the aging process of PE in both media. With the practical usage of the previous results, **PART III** aims to rank different PE grades based on mechanical, thermal and surface embrittlement and the AO depletion rate in $ClO_2$.

Moreover, material characteristics such as degree of crystallinity, thermal stability and degradation products are examined at different distances from the immediate contact surface. However, these property profiles are evaluated in both media, material ranking in HOCl was not an objective of this dissertation. Before the summary, a theoretical lifetime prediction model is discussed, which includes the effect of disinfectants as well as the effect of mechanical loading. This model could produce failure curves which are comparable with standardized pipe pressure tests, based on significantly faster aging experiments.

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# PART I – LITERATURE OVERVIEW AND EXPERIMENTAL

# 2 Literature overview

It is important to review the available relevant literature in order to have a deeper understanding of the effect of the disinfectants on polymer materials in general and on polyethene pipe grades specifically. The current chapter firstly discusses the general background such as properties and reactions of disinfectants. Secondly, field case studies and standardized pipe pressure test results will be reviewed. Finally, published scientific work related to the aging of polymer materials in contact with aqueous solutions of chlorine dioxide and hypochlorite will be summarized.

Physical and chemical properties and some basic reactions of disinfectants are important to be reviewed in order to critically interpret the results of polymer aging in contact with chlorine-based oxidizing agents. This chapter is dedicated to discussing disinfection techniques, chlorine dioxide and hypochlorite as disinfectants and the stability of these oxidizing agents in water. The effect of disinfectants on the degradation of antioxidants (AO) and polymer materials will also be mentioned.

## 2.1 Disinfection methods for drinking water

The ground or source water treatment in a water plant usually follows as [1–3]:

- coagulation,
- sedimentation of coagulated particles,
- filtration
- and disinfection.

In order to eliminate pathogenic microorganisms and ensure the high quality of drinking water, primary disinfection techniques such as UV radiation, ozonation and the dosage of chlorine-based disinfectants are used in water plants [4, 5]. In some cases, secondary disinfection is necessary, which includes the dosage of chloramines, chlorine and $ClO_2$ into the distribution system. Chlorine dioxide has the highest reactivity and thus the strongest bacterial inactivation effectivity, while chloramines have the lowest reactivity [4, 6]. From a practical point of view, the reactivity of disinfectants determines their shelf-life, which can be considered as the effective disinfection time period. In other words, the lower the reactivity of an oxidizing agent the longer it is active in the drinking water distribution system. Chloramines are often used in combination with $ClO_2$, or chlorine, in order to provide an effective disinfection over a longer time period. Since $ClO_2$ and chlorine are the most widely used secondary disinfectants, it is imperative to understand the effect of these oxidizing agents on the degradation of polymer materials. Further aspects of drinking water disinfection such as primary disinfection techniques, generation techniques, dosing methods, controlling measurements, etc. are not discussed in this dissertation. However, these fields are well described and investigated in various manuals, regulations and technical guidelines [1–4, 7–10].

### 2.1.1 Chlorine dioxide as an oxidizing agent

Chlorine dioxide was discovered by Humphrey Davy in 1811 [11, 12] as the reaction product of concentrated hydrochloric acid and potassium chlorate (see Equation 1).

$$HCl + KClO_3 \rightarrow ClO_2 + KCl + H_2O \tag{1}$$

The greenish-yellow gas is unstable at room temperature and in its concentrated form it is explosive at temperatures above 45 °C [8, 13]. At increased pressure or when the volume concentration in the air is higher than 10 %, $ClO_2$ is explosive [14]. Therefore, it cannot be stored and transported; it must be produced on site. It has a solubility of 70 g/l in water at 20 °C, and when it enters water it stays as an undissociated dissolved gas [15]. In aqueous solution, $ClO_2$ forms thermodynamically unstable free radicals, although these molecules could persist for longer time periods due to its special electron structure [15].

Chlorine dioxide first does not hydrolyze [8, 11, 12, 15] when entering pure water, but remains as an undissociated dissolved gas with approximately the same reactivity between pH 2 and 10 [16]. After a while (days) it reacts to $HClO_2$ and $HClO_3$ and further to HCl and $HClO_3$, so the reaction can be summarized as shown in Equation 2.

$$6ClO_2 + 3H_2O \rightarrow HCl + 5HClO_3 \tag{2}$$

Depending on the pH level, reduction and disproportion reactions of chlorine dioxide could take place. The reduction of $ClO_2$ to chlorite ($ClO_2^-$) ion happens with one electron gain in neutral solution at around pH 7 [17], as shown in Equation 3. According to Equation 4, further reduction of chlorite ion in an acidic environment, when the pH is lower than 2, leads to chloride ion ($Cl^-$). In alkaline solution above pH 9 the disproportion of $ClO_2$ [15] to chlorite and chlorate ($ClO_3^-$) ion could form significant yields. This reaction can be described by Equation 6. Exposure of $ClO_2$ to UV light leads to photodecomposition, forming similar products [18], although the exact reaction mechanism in solution has not been fully understood yet [9]. Myhstrad et al. [19] suggested that the reduction of $ClO_2$ to $ClO_2^-$ follows the pathway illustrated by Equations 3, 5 and 7, when organic compounds are present in drinking water. The main reaction products are $ClO_2^-$ ions with a 50 to 70 % conversion rate. Chlorate and $Cl^-$ ions are also formed to a lower extent in less than 30 % of the reaction products. Depending on the organic and inorganic composition of the water, slightly different conversion rates to $ClO_2^-$, $ClO_3^-$ and $Cl^-$ ions can be also observed [20]. Chlorate and $ClO_2^-$ ions can also originate from stock solution, since most $ClO_2$ production techniques provide incomplete conversion [7]. Furthermore, the decomposition of $ClO_2$ during storage could be an additional source of these ions, especially when these processes are catalyzed by higher temperatures or exposure to sunlight [14].

$$ClO_2 + 1e^- \rightarrow ClO_2^- \tag{3}$$

$$ClO_2^- + 4H^+ + 4e^- \rightarrow Cl^- + 2H_2O \tag{4}$$

$$2ClO_2 + 2OH^- \rightarrow H_2O + ClO_2^- + ClO_3^- \tag{5}$$

$$ClO_2^- + H^+ \rightleftharpoons HClO_2 \tag{6}$$

$$4HClO_2 \rightarrow 2ClO_2 + HCl + HClO_3 + H_2O \tag{7}$$

In practical water treatment applications, the maximum allowed concentration of $ClO_2$ is mostly limited by state or country regulations. The amount of $ClO_2$ applied for drinking water disinfection is generally within the range of 1.0-1.4 mg/l in the United States [3] while in the European Union it is usually kept between 0.05-1.0 mg/l [8]. In Austria, 0.4 mg/l of $ClO_2$ in drinking water is the maximum allowed concentration [21]. High concentrations of $ClO_3^-$ and $ClO_2^-$ ions are suspected to have adverse health effects [22, 23]; hence, the maximum allowed amount of them is 0.8 mg/l in the United States [7]. However, sodium chlorite is not classified as a carcinogenic substance [24]. Despite the limitation in concentration, a major advantage of $ClO_2$ over chlorine is that it does not produce harmful chlorinated by-products such as carcinogenic trihalomethanes (THMs) [9, 25, 26].

In order to understand the degradation of polyolefin pipes caused by $ClO_2$, the reactions of this disinfectant and its by-products with aliphatic hydrocarbons and phenolic compounds should be considered. Already known reactions of $ClO_2$ in aqueous solution with organic materials might be used as an initial point to understand the relevant mechanisms. As $ClO_2$ possesses one unpaired electron, it is highly reactive to organic materials, although it has been shown that it is not reactive enough to extract hydrogen from aliphatic saturated hydrocarbons [16, 25, 27]. More likely, it reacts in a rather complex way with alkenes forming a broad range of non-chlorinated and chlorinated products. In contact with phenol, $ClO_2$ can generate oxidized and chlorinated products such as quinones and chloro-quinones [4, 15, 28–30]. An excess of $ClO_2$ can lead to the rupture of the parent ring forming mostly maleic and oxalic acids. Generally, chlorine dioxide favors oxidation over chlorination, although chlorinated by-products are not absolutely absent when phenolic materials or alkenes react with $ClO_2$.

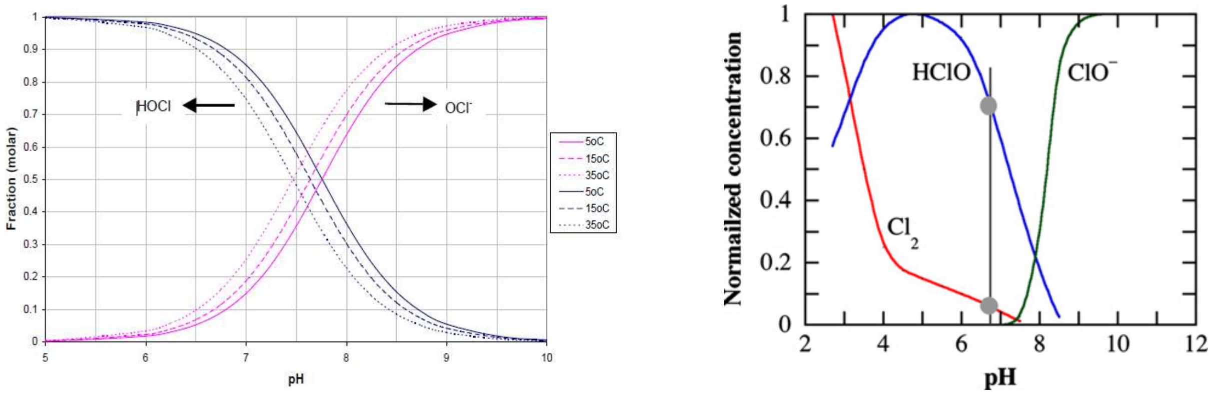
### 2.1.2 Hypochlorous acid as an oxidizing agent

The most widely used disinfection technique is the dosage of chlorine into drinking water, due to its advantages over $ClO_2$ such as its simple preparation, easy handling and lower safety risk. Applying chlorine as a disinfectant, the most frequently used techniques are the dosage of sodium hypochlorite (NaOCl) solution and chlorine gas into the water [3, 31, 32]. At pH 5 and above, the chlorine ($Cl_2$) gas in water will hydrolyze immediately and completely to hypochlorous acid (HOCl) and to hypochlorite ion ($OCl^-$), according to Equation 8 [26, 33]. Just a very low amount of hydrochloric acid of less than 0.01 % will be formed, which dissociates perfectly in water. Since HOCl is a weak acid, its partial dissociation can be expected as shown in Equation 9. Active species in water will eventually be HOCl molecules and $OCl^-$ ions, independently of the applied chlorination technique.

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl \tag{8}$$

$$HOCl \rightleftharpoons OCl^- + H^+ \tag{9}$$

Depending on the pH level, HOCl and $OCl^-$ ions are present in different ratios [2, 5, 34, 35]. The two chlorine derivatives are in equilibrium at a pH of approximately 7.5 at room temperature. At pH 5, mostly just HOCl molecules are present, while over pH 10, $OCl^-$ becomes the dominating molecule in the system, as it is illustrated in Fig. 2.1 (a) [1]. Previous studies [36–38] investigated active chlorine molecules in aqueous solution and the experimental data was summarized by Yu et al. [39]. In case of controlling the pH of the HOCl solution with hydrogen chloride (HCl), the equilibrium according to Equation 10 can be found. In case of acidification of the chlorine solution with HCl this equilibrium must be considered. In Fig. 2.1 (b), the experimental data of the chlorine species concentration depending on pH is illustrated. A maximum amount of HOCl is reached at around pH 5; at lower pH levels, dissolved $Cl_2$ concentration could become significant. At 15 °C and a pH level of 6, the $Cl_2$ fraction was found to be in the $10^{-5}$ magnitude [40]. The relative concentration of $Cl_2$ is about 5 % at room temperature, indicating a roughly three order of magnitude concentration increment with increasing the temperature by 10 °C [36–38]. This effect of temperature on the fraction of chlorine species in hypochlorite solutions should be considered, especially in the case of aging experiments and applications at elevated temperatures. Nevertheless, HOCl is a stronger oxidizing agent than $OCl^-$ ion, so it is beneficial to shift the pH to slightly lower levels in order to increase the efficiency of disinfection. As Fig. 2.1 (a) shows, beside the pH, the equilibrium between HOCl and $OCl^-$ ion is also influenced by the temperature applied.



(a) (b)

Fig. 2.1: Hypochlorous acid and hypochlorite ion ratio dependency of pH and temperature in water solution [1] (a), concentration of chlorine species in aqueous solution at different pH values in case of acidification with HCl [36–38] (b).

$$HOCl \; + \; HCl \; \rightleftharpoons \; Cl_2 + H_2O \tag{10}$$

Hypochlorite, $OCl^-$ and chlorine $Cl_2$ molecules are frequently referred to as free chlorine or free available chlorine (FAC). Chloramines are usually mentioned as combined chlorine, and the sum of free and combined chlorine is called the total chlorine. In this dissertation, HOCl and $OCl^-$ ion will be not distinguished, and will be referred to as hypochlorite, HOCl. The generation and addition of hypochlorite to potable water networks are well discussed in literature [1, 3, 34]. In diluted aqueous solutions of HOCl, HOCl decomposes slowly in the dark, but fast in sunlight according to Equation 11.

$$2HOCl \rightarrow 2HCl + O_2 \tag{11}$$

According to Equation 12, in higher concentrations the HOCl molecules decompose slowly to $ClO_3^-$ and $Cl^-$ ions. As intermediate products $ClO_2^-$ ions are also formed, although they react rapidly further forming $ClO_3^-$ and $Cl^-$ [10]. Even under ideal storage conditions – low temperature, no UV radiation, etc. – the decomposition reaction could lead to a significant NaOCl concentration decrease [14].

$$3OCl^- \rightarrow ClO_3^- + 2Cl^- \tag{12}$$

The decomposition rate depends strongly on the pH level, temperature and ionic strength. Moreover, the presence of metal ions could catalyze the decomposition process, just like exposure to direct sunlight [41, 42]. Similar to the $ClO_2$ solution, this process is probably a considerable source of chlorate ions in municipal water.

Chlorinated by-products, such as THMs and further chlorinated organic molecules which are proven to be carcinogenic [2, 25, 34] represent a significant drawback of this disinfection technique. Consequently, in the United States, the maximum residual disinfectant level is regulated to 4 mg/l, measured as FAC [7]. Currently, in the European Union, only the maximal allowed THM concentration in potable water is limited to 0.1 mg/l, as it is provided in the EU Regulation S.I. No. 278/2007 [43]. A recent regulation of the World Health Organization limits the maximal HOCl concentration to 5 ppm [44]. Austrian regulations set the upper HOCl concentration limit as 1.2 ppm, measured in FAC [21]. Hypochlorite molecules have a lower disinfection capability so they are frequently dosed into the drinking water network in higher concentrations than $ClO_2$. In case of pipe replacement in the distribution network, shock chlorination or so-called “superchlorination” up to 500 ppm of HOCl concentration is occasionally applied for a short time period [45].

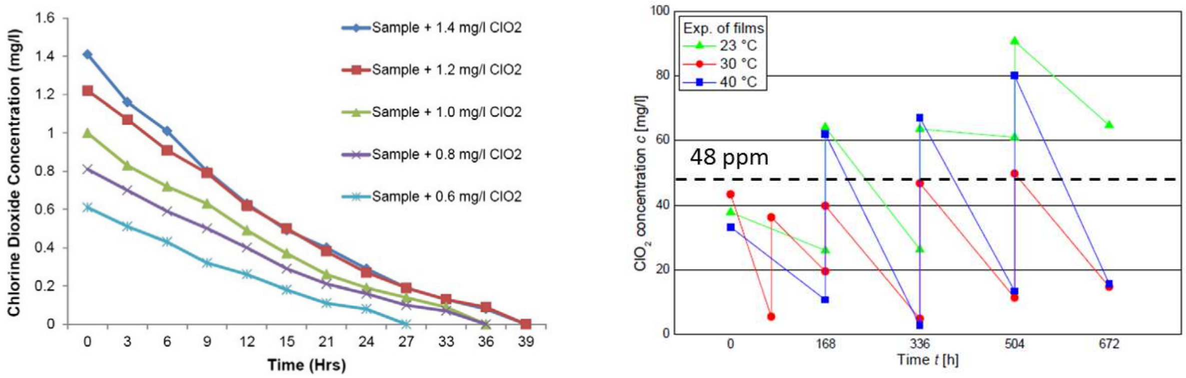
The most important reactions of HOCl with organic materials can be classified as addition, substitution and oxidation [26, 33]. The yield of the chlorinated products from these reactions strongly depends on the nature of the organic substance. As a strong oxidizing agent HOCl oxidizes various functional groups [46], reducing itself to chloride. The oxidation of aldehyde groups (RCHO) to carboxylic acid (RCOOH) groups illustrates this group of reactions well. It is well known that HOCl is highly reactive with carbon double bonds. Addition reaction of HOCl on alkenes results in chlorohydrin products [25]. It reacts rapidly with phenolic functional groups by replacing one hydrogen atom from the phenolic ring with a chlorine atom in a substitution reaction [14, 35]. In excess of HOCl further diverse chlorinated products can be expected [25, 26], and eventually it could lead to the rupture of the phenolic ring. Generally, these chlorophenol molecules are responsible for odor and taste issues in drinking water, which is one of the main reasons to apply $ClO_2$ and other alternative disinfectants. Considering the aforementioned reactions, chemical consumption of AO by oxidative reactions in contact with HOCl can be expected. The reaction of HOCl with aliphatic saturated hydrocarbons is only expected if radical chain reactions take place. The initiation of such a reaction requires light, thermal energy or initiator molecules. Therefore, in application direct attack of HOCl on polyolefin molecules is highly unlikely. It should be noted that the reaction of HOCl or its derivatives with chain defects – double bonds, functional groups from oxidation, catalyst residue – can be anticipated. Moreover, based on the work of Holst [47], a mechanism for hydroxyl radical ($OH^*$) formation from the reaction of HOCl and $OCl^-$ molecules was also introduced. The presence of such radicals will significantly accelerate the consumption of stabilizers and also the degradation of the polymer itself. Additionally, radical molecules could lead to an increased hydroperoxide amount, further accelerating the AO consumption and eventually the auto-oxidative PE degradation.

## 2.2 Stability of disinfectant in aqueous solution

To ensure stable conditions during laboratory aging experiments applying HOCl and $ClO_2$ solutions, their concentration should be frequently monitored and adjusted. Considering the reactive nature and fast decomposition reactions of both oxidizing agents, their concentration may decrease significantly in a matter of a few hours. Concentration decay of the two disinfectants can be classified into two main groups. Bulk decay leads to the loss of the oxidizing agent due to the reaction with organic and inorganic materials in the water. Reactions with the pipe wall, wall decay, can also result in a significant decrease of the disinfectant concentration [48]. Moreover, decomposition reactions at elevated temperatures could cause a considerable loss of the disinfectants. In this section, an investigation of the bulk decay due to different source water quality will be not included, as it is well studied in other research fields. The main focus is put on the reactions of the disinfectants with PE. Reproducibility and the evaluation of laboratory aging experiments could become highly difficult without proper monitoring and continuous controlling of exposure parameters like pH, oxidation reduction potential (ORP), temperature, and especially the concentration of disinfectants. In addition, the comparison of aging experiments is highly limited due to the different and sometimes unknown operation or laboratory aging conditions.

### 2.2.1 Chlorine dioxide decay in aqueous solutions

Considering the slow disproportion even at neutral pH and the fast oxidation of inorganic and organic substances of $ClO_2$, the disinfectant concentration could decline rapidly. Chlorine dioxide is considered to be stronger oxidizing agent than HOCl; hence a faster concentration decrease could be expected. In spite of that, the stability of this disinfectant is not well investigated in relevant literature, especially in the case of contact with polymer materials. Nevertheless, Ammar et al. [49] reported an approximately 50 % decrease in the $ClO_2$ concentration after about 10°h as shown in Fig. 2.2 (a), by monitoring five different $ClO_2$ solutions. The authors also proposed a decay model, which is in good agreement with the published experimental data. Li et al. [50] studied the self-decay of $ClO_2$ in pure water solutions, revealing a first order reaction kinetics. Furthermore, an increasing reaction rate with increasing temperature was reported, supporting previous findings discussed in 2.1.1. In the work of Redhead et al. [51] PE films were subjected to immersion in 48 ppm of $ClO_2$ and the concentration was monitored as it is illustrated in Fig. 2.2 (b). Aging media were replaced with the 48 ppm $ClO_2$ stock solution on a weekly basis applying 23, 30 and 40 °C temperatures. Fumier also reports that $ClO_2$ concentration decreases rapidly over time [52] during the immersion of polyvinylchloride (PVC) pipe samples in closed tanks as shown in Fig. 2.3.



(a) (b)

Fig. 2.2: Decrease in $ClO_2$ concentration at 20 °C [49] (a), monitoring the concentration of $ClO_2$ during a laboratory aging experiment at various temperatures [51] (b).

Similar to data presented by Redhead et al., high scattering was observed in the disinfectant concentration. Fast reduction and increased deviation of the $ClO_2$ concentration clearly points out the importance of stable aging conditions. Such results can hardly be used to compare different aging experiments of polymers, since the actual aging conditions are not known. Due to the rapid thermal decomposition and reactions of $ClO_2$ with organic or inorganic compounds, a continuous monitoring and adjustment of aging conditions is crucial to gain reliable information about the material performance.

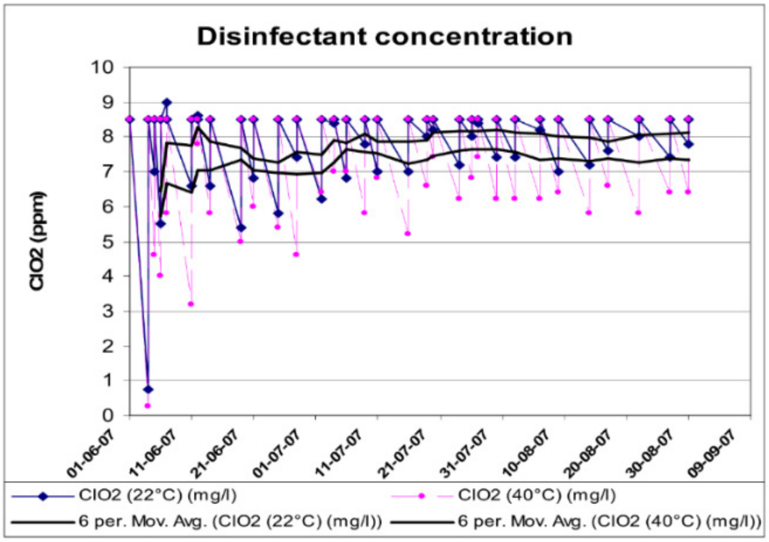
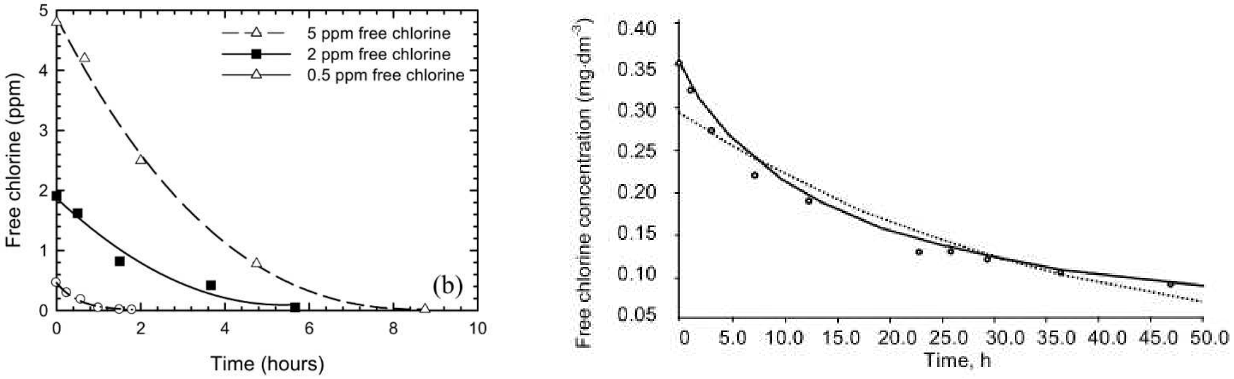


Fig. 2.3: Concentration of $ClO_2$ aging time recorded at 22 °C and at 40 °C, [52].

### 2.2.2 Hypochlorite decay in aqueous solutions

The stability of HOCl solution is frequently discussed, although only few research studies focus on the detailed analysis of concentration changes over exposure time. Abdelaal and Rowe [53] report rapid free chlorine decline, resulting in almost zero chlorine concentration from the initial 5 ppm in about eight hours at 85 °C, as it is shown in Fig. 2.4 (a).



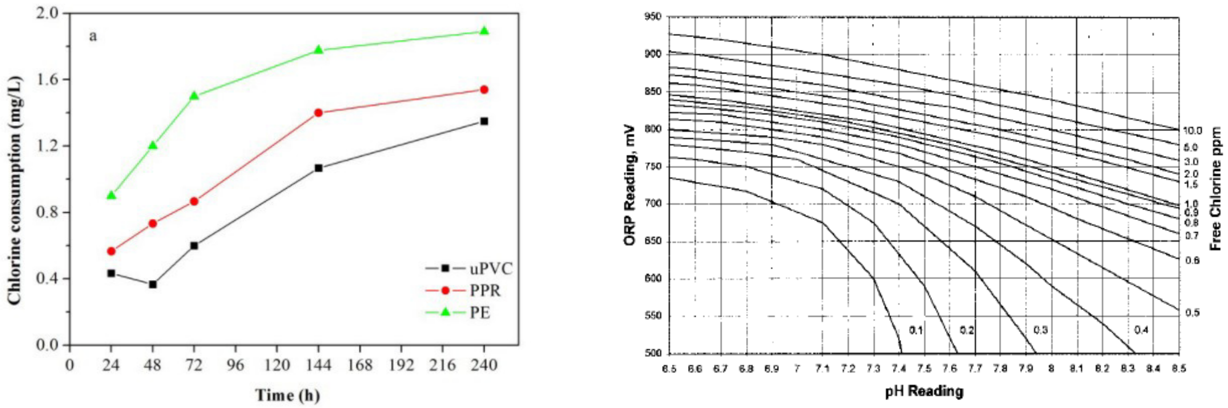
(a) (b)

Fig. 2.4: Decrease in the free chlorine concentration at 85 °C (a) applying three different initial dosages [53], and at 9 °C (b) modeling the decay with a first- (solid line) and second- (dashed line) order reaction [54].

Moreover, the influence of exposed material surface (S) to aging medium volume (V) ratio on the chlorine consumption rate has been reported. The surface to volume ratio was found to be directly proportional to the decrease in free chlorine. Similar findings were reported by Lu et al. [31], although in new polymer pipes, the decline of disinfectant concentration due to wall reactions was found to be negligible compared to the bulk reactions. Kowalska and his coworkers

[54] published chlorine decay models based on experimental data obtained from an operating pipe network at a water temperature around 9 °C, which is illustrated in Fig. 2.4 (b). The model presented describes chlorine decay in a water distribution system with the combination of a first and a second order kinetic model. Despite the slower decline at this temperature, a decrease in the free chlorine concentration should be considered as the most important parameter during laboratory aging experiments.

In the framework of a migration study, Zhang and Liu [55] reported that the initial 2 ppm of HOCl concentration decreased to less than 0.1 ppm during a ten-day-long internal exposure test of PE pipes. The chlorine consumption rate of PE, polypropylene random copolymer (PPR) and unplasticized PVC (uPVC) pipe segments was also studied at room temperature. As it is presented in Fig. 2.5 (a), the fastest chlorine consumption was reported for PE and the slowest for uPVC. Moreover, published data indicates that the test water did not consume free chlorine molecules, highlighting reactions between the polymer pipe materials and the disinfectant. Similar findings were presented by Al-Jasser [56], pointing out that chlorine consumption due to reactions with the internal pipe wall decreases with increasing service time for PE, PVC and uPVC pipes.



(a) (b)

Fig. 2.5: Chlorine consumption at room temperature of three polymer pipes [55] (a), the relationship between free chlorine concentration, ORP and pH level [57, 58] (b).

In the comprehensive work of Gill et al. [59], the concentration dependency of pH and ORP was investigated. This work clearly demonstrates a non-linear increase of ORP with increasing HOCl concentrations. At a given pH, increasing HOCl from 0.1 to 1 ppm results in a higher ORP increment than increasing HOCl concentration from 1 to 10 ppm, as it is presented in Fig. 2.5 (b). Moreover, the ORP of municipal water was found to be between 300 and 550mV. The “aggressivity” of a solution is frequently described by the ORP, which refers to the overall oxidative or reductive nature of a medium. Since this value represents the total electrode potential of all molecules and ions in the solution, characterizing a solution purely based on ORP can be misleading. In fact, applying different buffer solutions or a pH controlling method, it is possible to reach the same ORP value of two media with different HOCl concentrations. It is worth noting that this relationship between ORP, pH and free chlorine is used in current standardized pipe pressure tests in order to assess the performance of PE pipes in contact with disinfectants.

The literature overview presented above clearly draws attention to the complexity of chlorine chemistry and more importantly to the basic chemical reactions as well as to the stability of $ClO_2$ and HOCl solutions. Reactions of these oxidizing agents with phenolic molecules and hydrocarbons can be used as an initial theoretical approach to a deeper understanding about the effect of $ClO_2$ and HOCl on the degradation of AO and polymer materials. However, the decrease in disinfectant concentration over storage time presented must be considered and addressed in order to produce reliable and reproducible aging experiments. Without well-controlled aging experiments, the evaluation of long-term performance and different polymer pipe grades is very limited.

## 2.3 Failure mechanism and applied test methods

Unfortunately, most studies concerning the influence of disinfectants on polymer pipes do not provide detailed data about the aging medium concentration over laboratory exposure time. Nevertheless, the subsequent sections of this chapter will give an overview of recent findings in the field of polyethylene pipe aging in contact with disinfected water. In the following section, field case studies dealing with premature pipe failures in contact with chlorinated drinking water will be discussed. Moreover, studies investigating the failure mechanism based on standardized pipe pressure tests will be reviewed.

### 2.3.1 Failure mechanism and field case studies

Characteristic failure behavior of PE pressurized pipes is discussed extensively in the relevant literature [60–63]. It can be divided into three different stages, as it is presented in Fig. 2.6 [64]. In stage I at high internal pressure, ductile failure is dominant with large plastic zones and with relatively short failure times. This stage is mostly controlled by the yield stress of the material. At lower loads, in stage II, the failure mode changes from ductile to quasi-brittle failure dominated by crack initiation and slow crack growth (SCG) with only small plastic deformation in the tip area of the crack [65]. The sum of the crack initiation and the SCG time is the total failure time. In the third stage, brittle failure dominates and the failure time is almost independent of the hoop stress. Stage III only became significant after long service times, when advanced thermo-oxidative aging and polymer degradation led to large-scale material embrittlement. Failure resistance is mostly controlled by stabilizer systems. However, the overall thermo-oxidative resistance of a polymer material is determined by the combination of the base polymer and stabilizer package. The use of disinfectant in the drinking water network has a significant effect on the failure mechanism of polymer pipes. Since the $ClO_2$ and HOCl are strong oxidizing agents, these molecules could accelerate the consumption of stabilizers and consequently the thermo-oxidative aging related to stage III.

Several scientific works and technical reports discuss premature pipe failure due to the presence of disinfectants, including numerous field case studies. Chung et al. [66, 67] examined polyolefin pipe samples after field failure. In Fig. 2.7, the two images of failed pipe samples display cracks on the fracture surface. However, exact operation conditions are not reported. The authors proposed that after an oxidative crack initiation, the crack growth is determined by mechanical propagation and in some cases oxidative propagation. Overall, the stage III failure mechanism in case of advanced oxidation was found to be a combination of Stages II and III. Moreover, findings of the field case study were consistent with results of laboratory aging experiments. Considering the high reactivity of HOCl and $ClO_2$ it is possible that their effect is limited to a certain surface layer resulting in the mixed failure mode observed, where only the crack initiation is accelerated by disinfectants. In agreement with this hypothesis, cracks, low antioxidant (AO) content and increased amount of carbonyl groups were detected in the degraded inner surface layer. In contrast with the results of Pinter et al. [68], the authors report that no increase in the carbonyl ratio was found in the crack front.

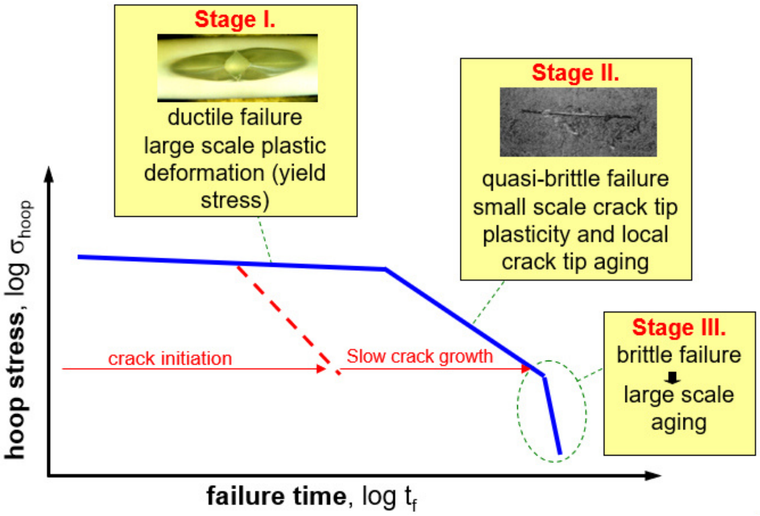


Fig. 2.6: Characteristic failure behavior of PE pressurized pipes [64].

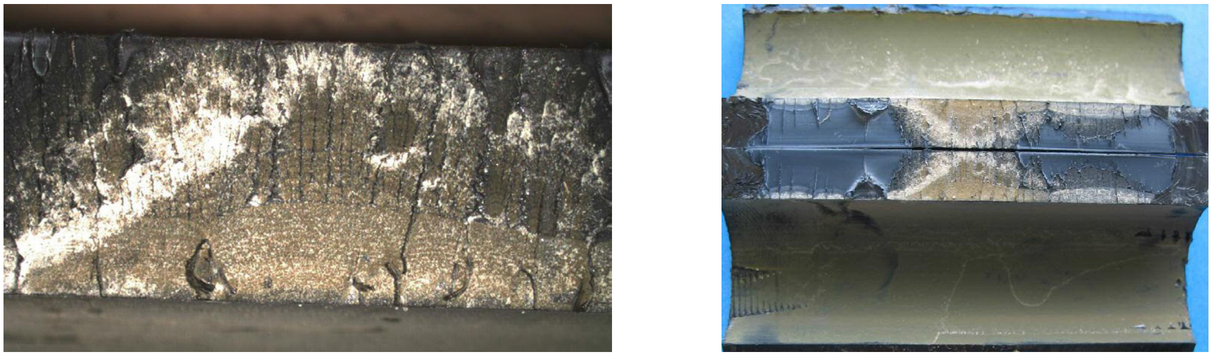

(a) (b)

Fig. 2.7: Images of two polyolefin field samples that failed during operation according to the findings of Oliphant et al. (a) [66] and Chung et al. (b) [66, 67].

As part of the research of Rozental-Evesque et al. [69, 70], more than 200 PE pipe samples from different countries were excavated and analyzed. The field samples were in contact with disinfectants and operated at a pressure range of 2-16 bar. The service temperature varied between 6 and 30 °C. Images of two selected field samples are presented in Fig. 2.8. Similar to the field samples (Fig. 2.7) highly advanced oxidation was observed leading to the appearance of cracks in the inner pipe surface (Fig. 2.8 (a)). The failure mechanism after a critical crack depth was found to be SCG (Fig. 2.8 (b)), confirming the previously assumed limited surface effect of disinfectants. Duvall [71] examined the effect of HOCl solution on polypropylene (PP) pipes by analyzing field samples after failure. Several leaks of a PP pipe network were reported during a few years of operation, transporting HOCl-disinfected water with a concentration range between 8 and 12 ppm. Although the applied PP materials contained no AO, it was concluded that most of the failures were attributed to poor material selection, processing and installation. In contrast with data published by Chung et al. [66, 67] and Rozental-Evesque et al. [69, 70], the impact of HOCl was not considered as the main reason for the observed leaks.

(a) (b)

Fig. 2.8: Inner surface cracks of the PE pipe field sample on the pipe surface (a), and fracture surface of another PE pipe field sample after failure [69, 70] (b).

In a later extensive work of Duvall [72], several PE pipes were investigated thoroughly after operation in disinfected water. A cross-section image of a failed water pipe is shown in Fig. 2.9 (a). A highly degraded inner surface layer was found with a thickness of about 0.5 mm. A high amount of degradation products and near to zero oxidation induction times (OIT) were reported, which highlight the advanced material degradation. Moreover, the AO level in the core of the pipe was also significantly reduced. The examination of 23 field samples, pointed out that disinfectants shortened the lifetime of PE pipes, especially the crack initiation time period. Hassinen and Jacobson [73] also reported a case study discussing premature pipe failure. In Fig. 2.9 (b), the cross-section of a PP field sample is shown. The sample was removed from service due to leakage after 8 years of service at 55 °C in contact with 0.5 ppm of $ClO_2$ solution. Cracks from the inner surface were observed with a depth of about 1.6 mm. As in previous case studies, the degraded layer showed an increased amount of degradation products and a reduced AO level. These changes were attributed to the effect of the $ClO_2$. Diffusion of $ClO_2$ into the bulk was found to be limited to a certain depth.

(a) (b)

Fig. 2.9: Cross section images of a failed PE pipe [72] (a) sample after 22,5 years of operation and one PP pipe [73] (b) field sample showing internal surface cracks.

As a conclusion of the field studies, the following general failure mechanism can be concluded:

- At first, stabilizers in the internal contact surface layer are consumed due to their reaction with disinfectants.
- After a rapid AO consumption period, oxidative aging of the polymer leads to the embrittlement of the inner surface.
- Advanced material aging and internal pressure eventually lead to the appearance of surface cracks.
- After reaching a critical crack depth, SCG becomes the dominating process, which finally results in pipe failure.

There are some discussions about the exact role of the oxidizing agents after the appearance of surface cracks. If $ClO_2$ and HOCl can diffuse into the crack tip, they may assist in crack propagation by continuously reacting with AO molecules and chain defects. This process would shorten the SCG time; however, the continuous contact of disinfected solutions with the crack tip has not been yet experimentally proven. Moreover, AO could also diffuse from the bulk material into the surface, slowing down the AO consumption. Diffusion of AO in the pipe material takes a rather long time period, so this process could be neglected in case of a short operation – less than a decade long – at low temperatures [74, 75]. The role of disinfectants in the polymer degradation, after the consumption of AO is still being debated.

Fischer et al. [76–78] reported fatigue tests executed in a media cell. Cyclic testing of crack round bar (CRB) specimens [79] made of PE, PP and glass fiber reinforced polyamide (PA) showed faster crack growth when increasing the testing temperature or HOCl concentration. The proposed explanation for this phenomenon was local crack tip aging and hence degradation of polymer molecules, especially tie molecules and entanglements, due to the presence of HOCl. However, local crack tip aging during the creep crack growth test determined with IR spectroscopy has been reported [68]; a direct chemical attack of HOCl on saturated hydrocarbon is not possible (see 2.1.2). Regarding the local crack tip aging, the following factors should be considered.

- First, the polar nature of aqueous solutions and the non-polar polymer matrix clearly hinders the diffusion of the medium into the matrix.
- Second, due to the small size of the crack (~micron region) and its size and shape changing over the propagation process, it makes capillary forces most likely a determining factor.
- Third, the dynamic nature of crack growth and material degradation gradually increases the polymer surface polarity gradually. This process could play an essential role in the actual aging process of polymer pipes in contact with disinfectants, especially in terms of local crack tip aging accelerated by disinfectants.

In fact, in terms of SCG resistance, no differences between the three PP grades – non-stabilized, hindered phenolic AO stabilized, hindered phenolic and amine stabilized specimens – have been reported [78] in case of testing in HOCl medium, further confirming the importance of the three aforementioned factors.

### 2.3.2 Standardized test methods to assess the performance of pipe grades in contact with disinfectants

To assess the effect of disinfectants on the lifetime of polyolefin pipes, two standardized test methods, ASTM F2023 [57] and ASTM F2263 [58], are currently available. Both tests are internal pipe pressure tests applying a continuously controlled disinfectant solution. The test measures the time to failure at given a concentration, temperature and hoop stress.

The ASTM F2023 describes the requirements to evaluate the oxidative resistance of cross-linked polyethylene (PEX) pipes in contact with chlorinated water. In this method, $ClO_2$ is not included as an oxidizing agent. Vibien et al. [80] published results of PEX pipe pressure tests performed in accordance with ASTM F2023, applying 4.3 ppm of HOCl solution with a pH level of 6.8 at 95, 105 and 115 °C. During exposure pipes were subjected to a hoop stress from 1 to 2.6 MPa, and except for two, all 16 samples failed within 5800 h of testing. Shortly after starting the exposure a fine degraded surface layer on the inside of the pipes was observed, which became thicker with aging time, presenting surface cracks. Advanced surface degradation led to crack growth and propagation and finally to pipe rupture. The failure time was found to be over 2 times shorter compared to the non-disinfected aging medium. The authors proposed that this difference in failure time is more significant at lower temperatures. Based on extrapolation of the results, a pipe lifetime around 93 years was reported at a service temperature of 60 °C. Even though chlorinated water seems to accelerate the oxidative aging of PEX pipes, an overall good resistance against HOCl was reported. Effects of different HOCl concentrations on PEX pipes were further investigated by Chung et al. [81]. Samples were exposed to HOCl media at 105 and 115 °C in a concentration range of 0 to 5 ppm. The pH level was set to 6.5 or 8.5. At both temperatures, exposure to 0.1 ppm HOCl shortened the time to failure significantly. The authors reported a strongly degraded internal surface layer with several cracks. Under this layer, cracks penetrated further into the bulk, presenting signs of further oxidation. Near the failure the cracks have coalesced and propagated through the pipe wall by SCG. In good agreement with the result of Gill et al. [59], the correlation between the ORP values of the aging medium and the time to failure was reported. Higher ORP levels resulted in shorter times to failure. As expected the pH level of 8.5 led to longer failure times, since less oxidative $OCl^-$ molecules are dominant in alkaline solution. Additional experiments based on ASTM F2023 were performed by Chung et al. [82] to investigate the effect of the $ClO_2$, HOCl and chloramines on PEX pipes with a disinfectant concentration of 4.3 ppm. All the pipes showed degraded surface after failure, including several cracks around the point of failure. After exposure to the three disinfectants, highly reduced OIT values were recorded across the pipe wall, indicating an almost complete AO depletion. The increased amount of carbonyl groups confirmed the advanced oxidation of the samples. Based on SEM-EDX analysis, increased oxygen content was reported in the cross-section of aged pipes. In agreement with the chemical reactions discussed in 2.1, pipes exposed to HOCl solution showed higher chlorine content on the inner surface and mid wall than samples aged in $ClO_2$. In a later study by Duvall [83], internal pressure tests were conducted with PP-R and glass fiber reinforced PP-R pipe samples according to ASTM F2023, applying 4.4 ppm of HOCl solution at an exposure temperature of 95, 105 and 115 °C. Lifetime prediction showed that this material would not reach the expected 50 years lifetime under 0.55 MPa internal pressure at 60 °C. The reduced lifetime was attributed to advance surface degradation caused by HOCl.

Laboratory tests based on ASTM F2263 are often used to examine the resistance of pipe materials against disinfected water. Chung et al. [84, 85] investigated the effect of $ClO_2$ on PE pipes in pressure testing applying 1 ppm concentration, in a temperature range of 60 to 90 °C, with a pH level of 6.8. After 350 h of testing at 80 °C, a highly degraded surface layer, increased CI and very low OIT values were detected. The authors report no AO consumption in the mid pipe wall, similar to the work of Conrad et al. [86]. At the beginning of the aging experiment, the aged samples showed sharp OIT reduction simultaneously with the increase in CI values. After a short induction time, surface embrittlement and surface cracks were observed, indicating advanced material degradation. A fine degraded surface layer with a thickness of about 0.1 mm was reported. Despite the strong effect of the disinfectant, over 100 years of lifetime was projected for the investigated pipes. A technical report by Oliphant et al. [87] focused on further internal pressure tests according to ASTM F2263. Tested PE pipe grades, similar to the results of Conrad et al. [86], showed a strong decrease in the OIT and an increase in the CI. Furthermore, a residual lifetime extrapolation of pipe grades after about five and eight years of service resulted in more than 200 years of lifetime expectancy.

Beside the contradicting results of standardized test methods, long testing times, high costs, and the applied high temperature demonstrate well the need for faster and more precise testing methods. This dissertation aims to offer complementary materials testing concepts in order to facilitate the improvement of pipe material screening in contact with disinfectants.

## 2.4 Effect of disinfectants on polyolefin degradation

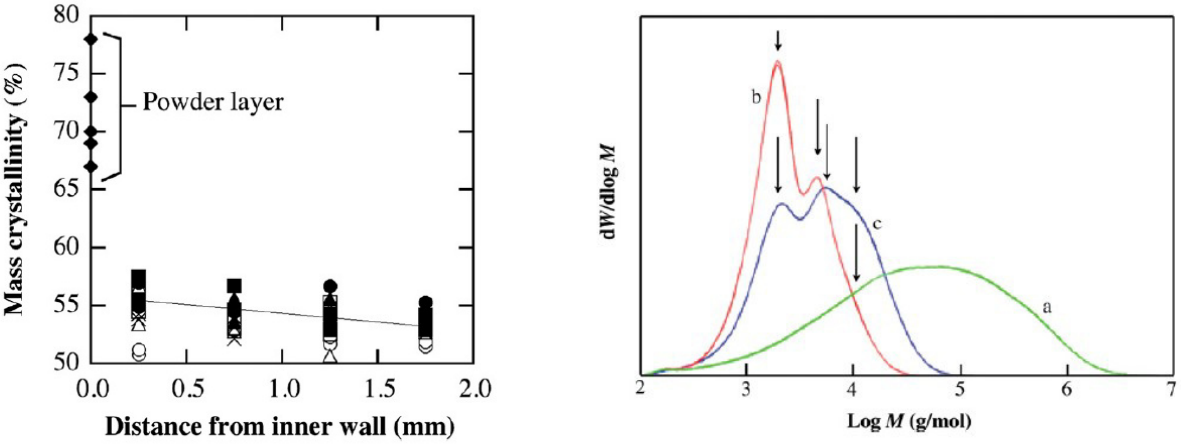
Beside standardized techniques for pipe aging setups, degradation of pipe material can be examined by various measurements such as electron microscopy (SEM), light microscopy, gel permeation chromatography (GPC) and Furier transform infrared spectroscopy (FTIR). The activity of the stabilizer system is usually characterized by dynamic, or in some cases, static oxidation measurements. It has been shown in polyolefins such as PP and PE that the oxidation induction time, OIT, can be correlated with the amount of active AO. Moreover, the oxidation onset temperature (OOT) is also used to assess the effectivity of stabilizers [88, 89]. For further analysis of the AO, high pressure liquid chromatography (HPLC) measurements are applied in some cases. These techniques have a high potential in providing deeper insight into the degradation process of laboratory and field-aged samples. In this section, relevant literature concerning polyolefin degradation in disinfected media will be reviewed. Furthermore, a comparison of field and laboratory-aged pipes will be also discussed. One should keep in mind that generally, HOCl solution favors chlorination over oxidation and regards $ClO_2$ mostly non-chlorinated products are expected. It should be mentioned that the direct reaction of a saturated hydrocarbon chain with HOCl or $ClO_2$ is only possible if effective catalyzators are present, as discussed in 2.1.

### 2.4.1 Chlorine dioxide

Since the reactivity of $ClO_2$ with saturated hydrocarbons should be close to zero, the reported alteration in the material properties and polymer structure is probably caused by intermediate reaction products and derivatives of chlorine dioxide. Several authors have published changes in mechanical properties, molecular weight distribution, chemical structure, as well as advanced material embrittlement and in case of application, even structural failures. These publications also indicate that thermo-oxidative degradation of polymer materials is considerably accelerated by the presence of $ClO_2$.

Colin et al. [90] investigated the impact of 80-90 ppm $ClO_2$ solution at 20 and 40 °C on compression molded PE samples at pH 2-3 and 6. Tensile tests showed approximately 20 % decrease in the strain at break after 2 weeks of exposure at 40 °C. Material embrittlement was detected around 500 h and 1200 h of aging at 40 °C and at 20 °C respectively. Tensile tests and overall aging mechanism indicate no pH dependency of the degradation in particular, which is in accordance with the approximately constant $ClO_2$ reactivity in a wide pH range (see 2.1.1). Applying a 500 h failure time as an end-life criterion, a critical molecular weight of 70 kg/mol was determined as an indication of material embrittlement and failure. An analysis of the chemical structure revealed a gradually increasing CI with increasing immersion time, highlighting the effect of $ClO_2$ on PE degradation. Moreover, 0.11 mol/l of grafted chlorine to the polymer was reported after 1200 h of immersion at 20 °C, similar to the findings of Chung et al. [82]. The amount of carbonyl groups was found to be about four times greater than the calculated number of chain scissions at 40 °C. No chain scission was reported after 1200 h of aging at 20 °C, although increasing carbonyl formation was observed. These results might be explained by the accumulation of hydroperoxides (ROOH). If the ROOH molecules reach a critical amount, then due to bimolecular decomposition, they could accelerate the oxidation rate significantly. Probably at 20 °C, this critical concentration of ROOH was not reached and consequently, no chain scission was detected. Furthermore, tensile results showed over 60 % decrease in the strain at break values, indicating material embrittlement. This effect could originate from highly increased crystallinity, which is unlikely at 20 °C, or from significant changes in the molecular structure.

Yu et al. [39] investigated the effect of $ClO_2$ and HOCl applying pipe pressure testing, performed at a pH of 6.8, a temperature of 90 °C and a hoop stress of 1.65 MPa in 4 ppm $ClO_2$. Fig. 2.10 (a) shows increased degree of crystallinity in the contact layer after specific aging periods, indicating polymer degradation. Digestion of the amorphous phase and the chemi-crystallization [91, 92] processes can serve as an explanation for the increased degree of crystallinity.



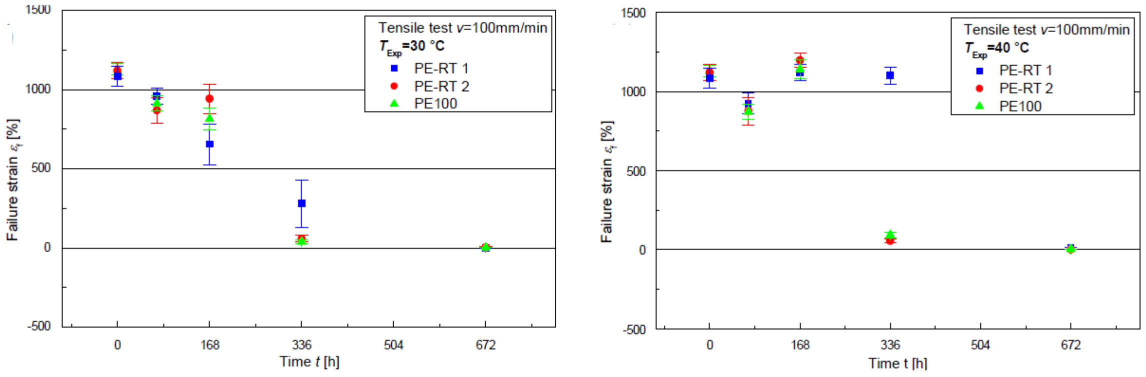
(a) (b)

Fig. 2.10: Crystallinity through the pipe wall, after different aging periods (a) and the molecular weight distribution of unaged (green), and degraded surface layers (blue and red) of PE pipes [39].

The relative carbonyl absorption was found to be lower after exposure to $ClO_2$ solution than aging in hot water, which could be caused by the wash-out of the highly degraded surface powder layer. The initial unimodal molecular weight ($M_w$) distribution shifted to lower molecular weights, and eventually displayed a multimodal distribution of the surface powder layer, as it is illustrated in Fig. 2.10 (b). The first peak at lower $M_w$ of the two samples appeared around 2500 g/mol, which probably corresponds with the extended chains between the crystallites. The appearance of the second peak was linked to once folded chains, and the weak shoulder around 14000 g/mol could indicate a less degraded polymer fraction.

Redhead et al. [51] also investigated the effect of $ClO_2$ on three PE pipe grades, applying 48 ppm of concentration at 23, 30 and 40 °C. After 3 weeks of conditioning tensile tests, it resulted in reduced mechanical properties, as it is presented in Fig. 2.11. Material degradation was also confirmed by FTIR measurements revealing continuously growing CI values. Deviations in material properties were attributed to poor control of aging parameters (see Fig. 2.2 (b)), further highlighting the importance of constant aging parameters.

In the work of Hassinen and Jacobson [73], the impact of $ClO_2$ on a new PPR pipe, a failed PPR pipe after 8 years of service at 55 °C in 0.5 ppm of $ClO_2$ and not stabilized ultra-high molecular weight polyethylene (UHMWPE) samples were investigated. Samples taken of UHMWPE exposed to 100 ppm of $ClO_2$ solution at 50 °C for one week and in air at 120 °C for 20 h showed very similar carbonyl and ROOH absorbance in IR spectrums. The authors point out that after initiation of the thermo-oxidative degradation, $ClO_2$ could catalyze the chain branching reaction at lower temperatures, similar to the effect of elevated temperatures. As $ClO_2$ reacts readily with ROOH groups forming ROO* radicals, bimolecular decomposition of hydroperoxides is most likely catalyzed by $ClO_2$. However, this process should lead to decreased activation energy ($E_A$), which was not confirmed by Vogt el al. [93, 94]. The strong surface degradative nature of $ClO_2$ could resolve this apparent contradiction.



(a) (b)

Fig. 2.11: Strain at break over exposure time at 30 °C (a), and at 40 °C (b) [51].

Carmier et al. [95] presented a new approach to protecting PE pipes against premature failure in disinfected water networks. During the processing of PE pipes, an additional inner polyvinylidene fluoride (PVDF) layer was extruded. Pipe samples with a PVDF inner layer were exposed to

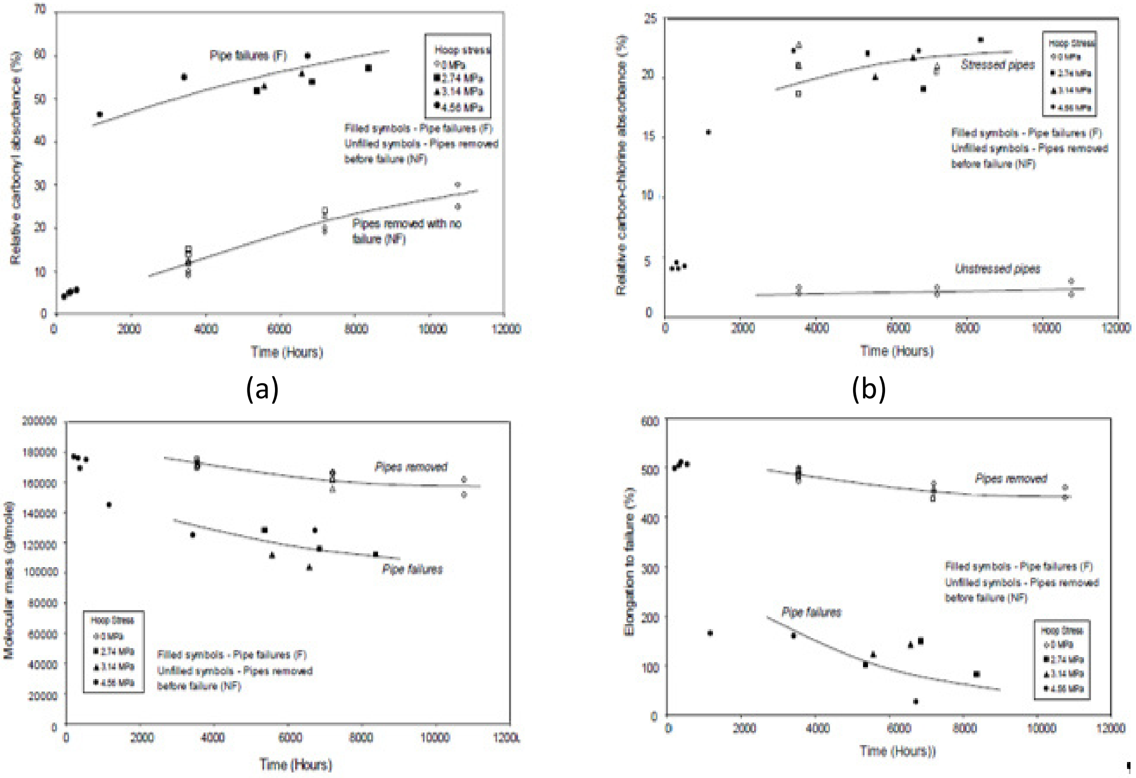
70 ppm of $ClO_2$ at 40 °C under 1 bar of pressure. In the adhesive PE layer, degradation products were identified by FTIR measurements, only after 1400 h of conditioning. At the immediate interface of the adhesive layer, the PE material did not show signs of oxidation in the terms of OIT and CI over the 4000 h-long aging. Furthermore, mechanical properties were intact after the aging experiment. In spite of the resistance of PVDF to $ClO_2$, in long-term applications, the diffusion of $ClO_2$ molecules through this protective layer could be considerable. This processing way ensures the expected pipe lifetimes, but increased costs must be considered.

### 2.4.2 Hypochlorite solution

Ifwarson and Aoyama studied [96] the effect of HOCl on three different polyolefin pipes applying internal pressure tests based on ISO 1167-19763 [97]. Pipe samples were exposed to 0, 0.5, 1 and 3 ppm of HOCl solutions at 95, 100 and 115 °C applying a hoop stress between 0.6 and 1.4 MPa. The presence of HOCl led to an advanced inner surface degradation and shorter failure times. Analysis with SEM-EDX showed no chlorine atoms in the bulk, but at the inner surface chlorine molecules were detected, in agreement with the results of Chung et al. [82], who reported increased chlorine amount on the contact surface and also a lower amount of chlorine in the mid wall layer after exposure to HOCl solution. Reported reduction in the pipe wall thickness points out the strong surface oxidative nature of HOCl solution. Furthermore, the authors have published that HOCl induces severe material degradation on the inner surface, resulting in cracks which can propagate through the pipe wall by SCG.

As previously discussed, the oxidizing potential of an HOCl solution can be related to its concentration; however, the ORP values should be handled with precautions. Gill et al. [59] reported that in the case of polybutylene-1 (PB) pipes failure times of pipe pressure testing are inversely proportional to the ORP. If the ORP value is used to determine the HOCl concentration then the nonlinear ORP increase in the 0.1 to 1 ppm concentration range (see Fig. 2.5 (b)) should be considered. Nonetheless, PEX pipes after hydrostatic testing with 3 and 5 ppm of HOCl at 105 and 115 °C showed several cracks on the internal surface and advanced AO consumption. Chemical degradation was only recorded after the total depletion of active AO.

In the comprehensive work of Dear et al. [98], MDPE pipes were pressure tested applying extremely high HOCl concentrations from 500 to 120000 ppm at 80 °C, with a hoop stress of 2.7, 3.1 and 4.6 MPa. Considering the fast HOCl concentration decline due to reactions and decomposition (see 2.2.2), the reported monthly medium replacement makes it difficult to evaluate the published data. Nevertheless, high HOCl concentration clearly resulted in faster brittle failure than pipes exposed to lower HOCl concentration. In Fig. 2.12, various material properties plotted against the aging time are displayed. As expected, increased hoop stresses shortened the failure time and amplified degradation. Infrared spectroscopic analysis of the inner pipe wall, in agreement with [82, 96], indicates the increment of carbonyl groups and carbon-chlorine (C-Cl) content. A maximum of CI was found for pipes removed after failure, while pipes removed before failure showed significantly lower CI values, indicating a plateau in CI after a certain aging period. The appearance of C-Cl bonds could be explained by the reaction of HOCl with AO and with the polymer, affirming the previously discussed chlorination potential of HOCl. The authors reported significantly reduced $M_w$ values for failed pipes, and less reduced $M_w$ for pipes removed before failure. Tensile specimens machined from the failed pipes showed reduced strain at break, pointing out advanced material embrittlement. Similar to the case study of Duvall [72], the presence of HOCl probably caused an accelerated crack initiation and an overall shorter failure time.

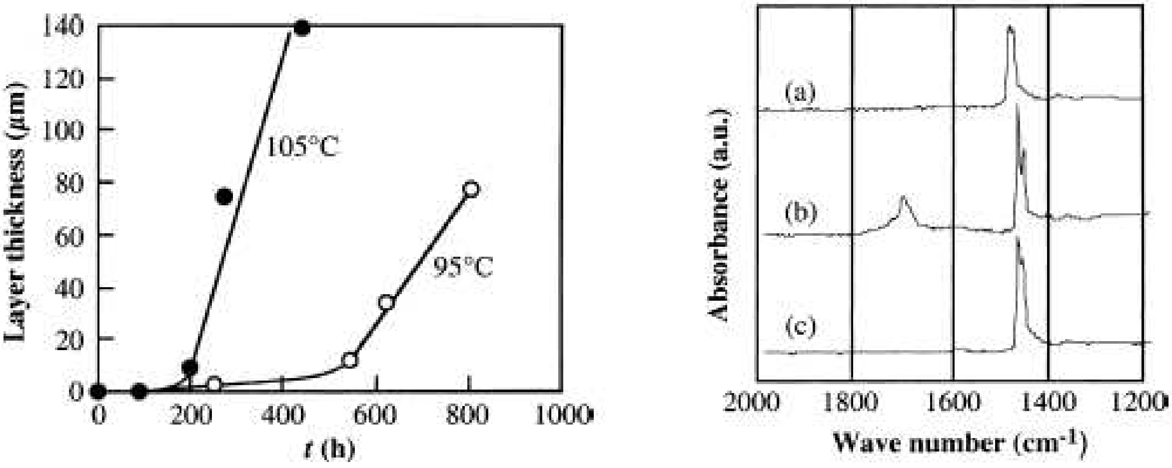


(a) (b)

(a) (b)

Fig. 2.12: Relative amount of carbonyl groups (a), relative carbon-chlorine content (b), molecular weight (c) and strain at break (d) over exposure time for failed and non-failed pipes after testing at different hoop stresses at 80 °C [98].

Hassinen et al. [99] published an extensive work investigating the effect of pressure testing at temperatures of 25, 95 and 105 °C applying 3 ppm of HOCl solution at 1 MPa hoop stress on HDPE pipes. The aging study was conducted in a circulation loop to ensure stable exposure conditions with a pH level of 6.45 ± 0.25. Advanced degradation of the internal surface layer was observed after 800 h of aging. In Fig. 2.13 (a), a constant increase in this degraded layer thickness can be seen after approx. 200 h of incubation time at 95 and 105 °C. Assuming applicability of the Arrhenius concept, 100 kJ/mol of $E_{akt}$ was calculated. Analogous to previously reviewed publications, increased carbonyl absorption was found in the porous surface layer, as shown in Fig. 2.13 (b). The surface powder layer showed a multimodal $M_w$ distribution.



(a) (b)

Fig. 2.13: Degraded layer thickness over exposure time (a) and the FTIR spectra (b) of unexposed sample (right a), degraded layer (right b) and the immediate layer under the porous layer (right c) [99].

Besides a slightly increased degree of crystallinity across the pipe wall, significantly higher crystallinity was detected in the surface powder layer. The loss of the amorphous polymer phase was estimated to be about 50 % on the internal surface. Similar results were published by Yu et al. [39] in the case of exposure to $ClO_2$, although a direct comparison of the findings is difficult due to different aging conditions.

The nonlinear correlation between the Arrhenius-based lifetime prediction and the HOCl concentration presented by Gill et al. [59] was also confirmed by Lundbäck et al. [100, 101]. Their study focused on PB pipe pressure testing applying 0.5, 1 and 3 ppm of HOCl solution at 95, 105 and 115 °C at a pH of 6.5. The predicted lifetime after increasing the HOCl solution concentration from 1 to 3 ppm resulted in lower lifetime shortening compared to the effect of raising HOCl concentration from 0.5 to 1 ppm. In fact, as it was shown previously (see Fig. 2.5 (b)), the ORP shows a higher increase by raising HOCl from 0.1 to 1 ppm than from 1 to 10 ppm. The pipe pressure test results are illustrated in Fig. 2.14. In agreement with previous findings [96, 102, 103] a highly degraded surface layer was detected. After a certain incubation time period, thickness of this porous internal surface layer increased constantly with the increasing exposure time. The presence of disinfectant caused nearly one order of magnitude decline in the lifetime. For the degradation process in 3 ppm HOCl, an $E_A$ of 140 kJ/mol was calculated, which is somewhat higher than the 108 kJ/mol value for non-disinfected water [104]. Despite the decrease in lifetime, which should lead to reduced activation energy, surprisingly a higher $E_A$ value was found for the HOCl solution, than for the non-disinfected water.

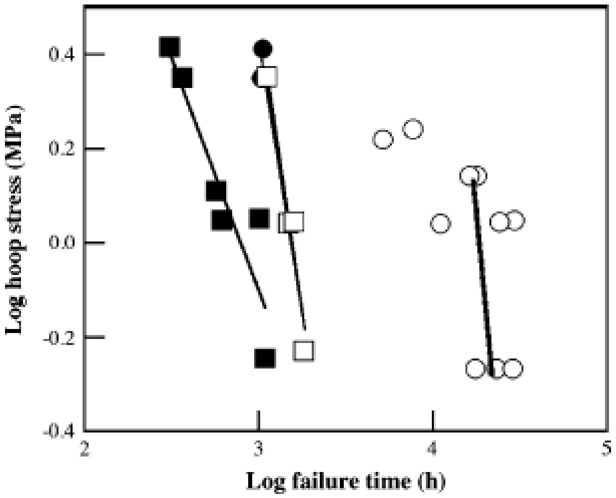
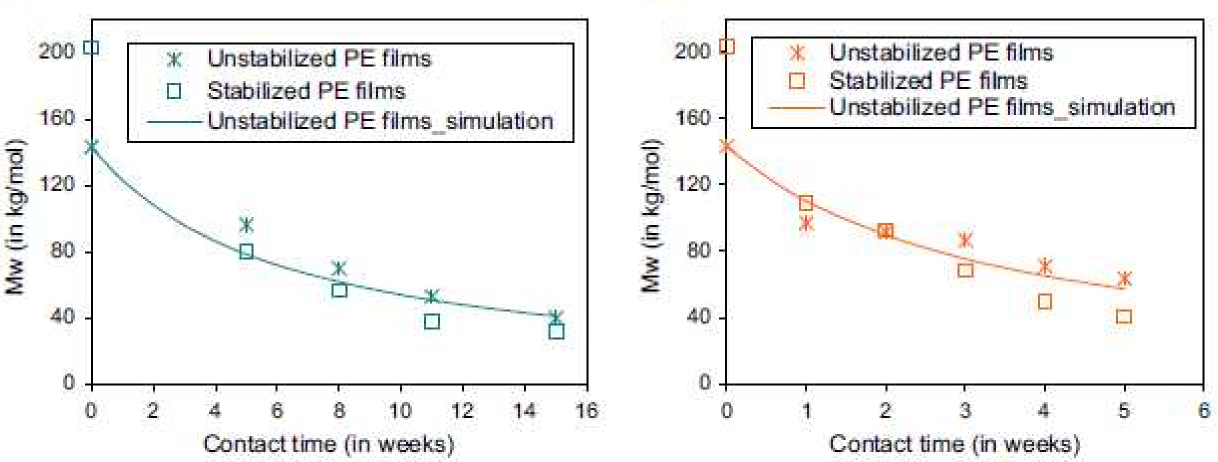


Fig. 2.14: PB pipe pressure test results, master curves for 115 °C after aging in 0 ppm (open circle), 0.5 ppm (filled circle), 1 ppm (open square) and with 3 ppm HOCl solution (filled square) [59].

A technical report published by the Plastic Pipes Institute [105] examined the effect of HOCl solution on newly installed PE pipes. The quick burst test according to ASTM D-1599 [106] showed no difference in the pipe failure times between pure water and water with 185 ppm of HOCl. Tests were performed for 3 days with a continuous rise in the internal pressure until failure. Despite the high concentration, the short test period could explain similar failure times in water and in HOCl solution. Tensile testing of compression molded samples after aging in water and in 200 ppm of HOCl again showed no influence on the elongation at the break and tensile strength. In contrast, previously reviewed studies clearly point out the adverse effect of disinfectant on the mechanical properties of pipe grades. In addition, Pennsylvania Edge-Notch Tensile tests (PENT) based on ASTM F1473 [107] further affirmed that HOCl has no effect on pipe performance. Generally, the adverse effect of HOCl on PE pipe grades was not confirmed.

Whelton et al. [108] summarized briefly the current literature concerning the aging of PE in contact with HOCl and also reported additional experimental data. Beside the fact that HOCl causes significant mechanical, morphological and surface changes, the importance of the stable exposure condition and the lack of detailed aging parameters in the relevant publications were highlighted. Especially the alkalinity of the aging medium was emphasized, since it could strongly affect the dominating chlorine species. This parameter further complicates the previous discussion regarding the temperature dependency of active chlorine species (see 2.1.2). Physical properties of active molecules in the aging solution are highly important for critical evaluation and for correct conclusions. Immersion tests of micro tensile specimens were performed in dark glass bottles. These were obtained from pipe segments and compression molded sheets, and immersed in a range of 23 to 70°C and 0 to 5000 ppm of HOCl solution. Both alkalinity and HOCl amount were measured by titration. In the 5000 ppm immersion test, the aging medium was renewed weekly and its concentration decreased to approximately 300 ± 100 ppm at 70°C after each week. Somewhat higher 680 ± 500 ppm HOCl concentration was reported after one week of conditioning in case of the reference bottles without PE samples, confirming the important effect of the S/V ratio pointed out by Abdelaal and Rowe [53]. As a consequence of HOCl decomposition, the pH gradually decreased from the initial 6.5 to 3 (see Equations 8 and 9). After a few days of aging, particles originated from the PE samples were observed at the bottom of bottles, indicating a highly advanced chemical aging leading to the digestion of the amorphous phase, similar to previous publications [39, 96, 99]. Tensile specimens were also immersed in 45 and 250 ppm of HOCl at 23, 37 and 70°C, at pH 6.5. Medium refreshment on a three-day basis led to significant HOCl concentration deviations, especially at higher temperatures. Initial alkalinity, 50 ppm of $CaCO_3$ and the pH level stayed basically constant after each three-day exposure period. In disagreement with previous PE aging studies [39, 59, 99] investigating the effect of $ClO_2$ and HOCl on polymer pipe grades, where raised CI was only observed after complete AO depletion, carbonyl groups were detected already after 40 % of AO consumption. Aside from high scattering in the mechanical values, significant changes were not reported after 2800 h and 3800 h at 37°C and 23°C, respectively, over the 250 ppm HOCl aging experiment. In agreement with Hassinen and Jacobson [73], reaction products of phenolic AO and $ClO_2$ molecules led to increased water absorption, which was determined by IR spectroscopy.

Devilliers et al. [109] performed immersion tests of 0.1 mm and 4 mm thick stabilized and unstabilized PE samples, including PE pipe segments, and injection molded specimens. The aging media contained 70, 400, and 4000 ppm HOCl and the experiments were conducted up to 40 weeks at room temperature. To ensure constant conditions, the aging solution was renewed three times a week. Samples immersed in 4000 ppm of HOCl showed a faster CI increase than those immersed in 400 or 70 ppm. Acceleration of the CI increase was found proportional to the HOCl concentration. The development of carbonyl groups indicates the hypochlorite induced oxidation. Under the applied aging conditions, the influence of stabilizers and sample thickness was found to be insignificant, implying that degradation in the surface layer is not determined by the AO diffusion. This conclusion is in accordance with the results of Colin et al. [90, 110], reporting that surface degradation is controlled by the disinfectant diffusion rate, in case of exposure to $ClO_2$. Gel permeation chromatography analyses a revealed strong $M_w$ decrease from the beginning of the aging test as it is illustrated in Fig. 2.15. A slightly stronger $M_w$ reduction of unstabilized samples was attributed to the different molecular structure. The amount of chain scissions showed an almost linear increase with increasing exposure time. The carbonyl index and chain scission number were found to be in the same range at any exposure time, indicating that most of the carbonyl groups are derived from chain scission reactions. The authors suggest that HOCl provides reactive radicals which can accelerate the initiation of the overall degradation process. Bradley et al. [111] suggested that OCl* radicals, originated from chlorite ions, can cause chain scission reactions. Furthermore, a kinetic model of the PE auto-oxidation process modified with an additional reaction between PE and HOCl was presented. In contrast with the findings of Colin et al. [90], a lower critical $M_w$ of 40 kg/mol was reported as an indication of material embrittlement. An explanation for this value was provided earlier by Fayolle et al. [112, 113]. Around this $M_w$ the chemi-crystallization process reduces the thickness of the amorphous layer, and under a critical thickness of 6 nm the material becomes brittle.



(a) (b)

Fig. 2.15: Molecular weight over the exposure time period after aging in 400 ppm (a) and in 4000 ppm (b) HOCl solution [109].

The effect of HOCl solution on the PE pipe grades was further studied by Montes et al. [114]. Multilayer PERT-Al-PERT semi-closed pipe segments were exposed internally to 1, 25 and 100 ppm of HOCl at 70°C for 270 days. The pH level was not controlled and it remained over 8 during the experiment. Control experiments in water and air were also performed. Even after one day of conditioning, the concentration dropped more than 50 %. In spite of this concentration drop, the aging medium was renewed daily. An increased degree of crystallinity, broadening of the melting peak and the lower melting peak temperature with increasing aging time were reported. In agreement with previous reports [108, 115], water uptake increased with longer aging periods, although the weight fraction increase stayed around 0.5 %. However, the formation of polar functional groups during advanced aging can lead to increased water uptake; no explanation was provided for the similar weight gain of HOCl and water-aged samples. Chemical structure analysis of the immediate surface layer was performed with FTIR-ATR, revealing an increased amount of hydroxyl, ether and vinyl groups with increasing exposure time. In disagreement with many other studies, no increment of the carbonyl region was reported with increasing exposure time.

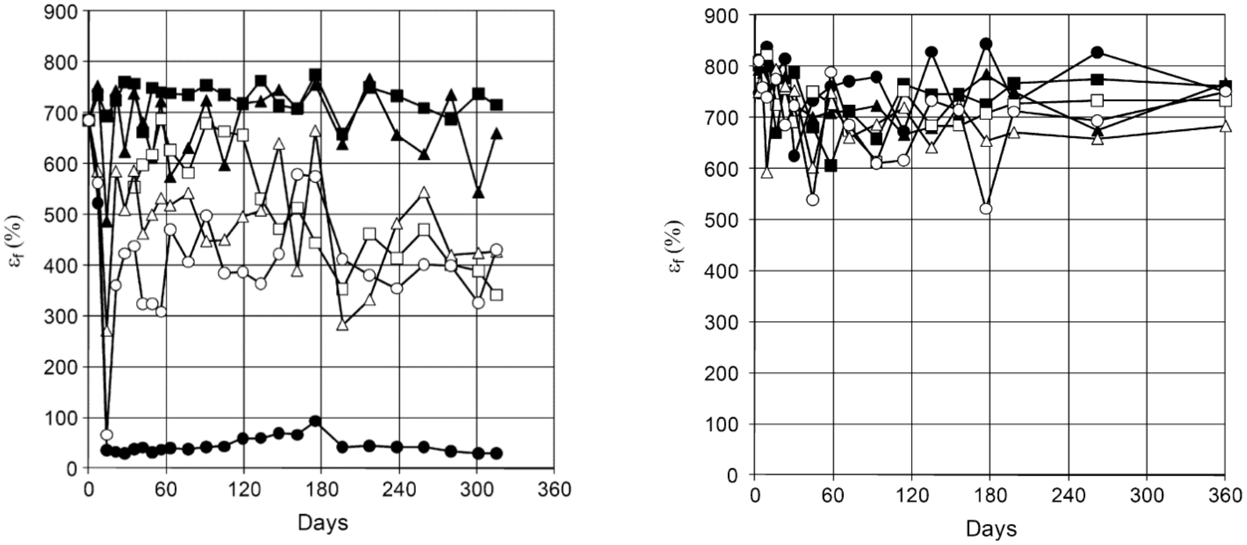
Mitroka et al. [45] investigated the effect of HOCl by immersing tensile specimens from HDPE pipes with AO, without AO, as well as samples after AO extraction, in 50, 250, and 500 ppm of HOCl at 37°C, with a pH of 6.5. The alkalinity of the aging solution was set with the addition of 50 and 100 ppm of $CaCO_3$. The aging media were replaced with new solution every three days during the 160-day experiment. Significant concentration and pH change during the three-day-long periods was only reported in the case of the 500 ppm of HOCl medium. Besides the increasing CI with increasing exposure time, chemical structural changes on the surface seemed to be independent of the HOCl concentration in case of the 50 and 500 ppm aging media. This is clearly in contrast with the findings of Devilliers et al. [109]. Nevertheless, ketone, aldehyde, hydroxyl and vinyl groups were also detected after 90 days of aging. Ketone and aldehyde groups are believed to be the reaction products of AO oxidation. Gas chromatography measurements showed two chlorinated hydrocarbon products, which were identified in case of non-stabilized samples as well. Thus, chlorinated degradation by-products can originate from the polymer, too, and not only from the AO. In fact, HOCl generally favors chlorination over oxidation (see 2.1.2). It should be note that silica-supported Ziegler-Natta polymerization catalyzers contain chlorine compounds, so chlorinated products could originate at least partially from polymerization. The Cl content of PE polymerized with such catalysts showed trace amounts of chlorine atoms [116]. Nevertheless, a direct proportional relation was reported between the chlorinated products in the water phase and the applied HOCl concentration, indicating that the effect of HOCl is strongly limited to the immediate contact surface.

Mikdam et al. [117] published extensive, thorough research about the kinetic modeling of non-stabilized PE aging in contact with HOCl. The published model simulates precisely the evolution of experimental CI and $M_w$ values over the exposure time. Samples were conditioned in 100 ppm of HOCl at 60 °C at a pH of 4, 5 and 7. The results suggest that $Cl_2$ and HOCl molecules can diffuse into the PE matrix and due to their low dissociation energy, form Cl* and OH* radicals. However, the thickness of the degraded surface layer showed no strong pH dependency and the highest oxidation rate was found at pH 5.

Recently published studies by Fischer et al. [78, 118, 119] examined the effect of HOCl on pipe grades with immersing PP micro-tensile specimens (0.1 mm sample thickness) in 5 ppm HOCl medium, at 60 °C maintaining a pH of 7. In agreement with previous publications, generally, the decrease of strain at break and molecular weight, as well as the increase of CI have been reported. Moreover, the essential work of fracture (EWF) concept has been used and compared to the results of the tensile test. The decrease in the specific total work of fracture over aging time showed very similar results to the strain at break values. The authors propose that due to easier specimen preparation and simpler testing procedures, tensile testing is more favorable than EWF. It should be mentioned that previous reports indicate the strong surface aging effect of HOCl, which could immensely impact the results of an aging experiment, especially in the case of 0.1 mm thick specimens.

### 2.4.3 Comparing the effect of disinfectants on PE pipes

In comparative studies conducted by Castagnetti et al. [120, 121], the effect of HOCl and $ClO_2$ on PE pipe grades was investigated. A new test plant was implemented with the capability to perform internal pipe pressure and immersion tests simultaneously. Disinfectant concentrations were measured and controlled based on the ORP values of the aging solution. It should be mentioned that disputes and issues of hypochlorite concentration control based on ORP are well discussed in Section 2.2.2. Considering the literature available, the relationship between ORP and $ClO_2$ concentration is not known. Even though the ORP and HOCl concentration function (see Fig. 2.5 (b)) is assumed to be applicable for $ClO_2$. Nonetheless, PE pipes were subjected to a 1.2 MPa of hoop stress at 40 °C. Tensile specimens were immersed in 2.5 ppm of $ClO_2$ and in a second experiment, the same HOCl concentration was applied at 40°C with a pH level of 7.1. As reference points, both the pipe samples and the tensile samples were aged in air and water. Changes in mechanical properties of the aged specimens are shown in Fig. 2.16. Tensile specimens exposed to $ClO_2$ showed about 90 % of reduction in the elongation at failure values after two weeks of aging. Samples taken from the pipe segment after exposure to air, water and $ClO_2$ solution also displayed an approximately 40 % decrease in the elongation at failure values after about one year of testing. The mechanical properties of HOCl-exposed specimens stayed more or less constant during the experiment.



(a) (b)

Fig. 2.16: Elongation at failure during an immersion test in 2.5 ppm of $ClO_2$ (a) and HOCl solution (b). Tensile specimens aged in air (filled squares), in water (filled triangles) and in disinfectant solution (filled circles); tensile specimens from pipes aged in air (open squares), in water (open triangles) and in disinfectant solution (open circles) [120].

Generally, the $ClO_2$ medium was found to be more aggressive than the HOCl solution, and the pipe samples showed better resistance than the immersed tensile specimens. Pipe pressure tests performed at 80°C, applying 5 MPa of hoop stress, up to 2000 h of testing time resulted in no premature failure. All the investigated pipes passed the test, indicating that mechanical properties were not negatively influenced by the disinfectants, similar to findings of the Plastic Pipe Institute [105].

Summarizing the above-discussed publications, it can be concluded that there are several contradictions in terms of how the HOCl and $ClO_2$ affect the polymer degradation. These conflicting results, aside from the very complex chemical and mechanical aspects, are probably caused by the exceptionally different and in some cases not-well-controlled aging conditions. Comparing data obtained after non-uniform aging conditions (e.g. concentration, pH, S/V ratio, circulation or stagnant medium, ORP, alkalinity, specimen geometry and fixture, temperature, various polymers and sample preparation) clearly leads to hardly explicable results and in some cases even to misleading conclusions. To resolve these issues, stable aging parameters and optimized conditions are obviously necessary.

## 2.5 Effect of disinfectants on stabilizers

In 2.1, general properties and the reactivity of $ClO_2$ and HOCl with phenolic compounds were discussed. As stabilization plays a key role to ensure a long lifetime of polymer pipes, numerous authors have investigated the effect of disinfectants on various hindered phenolic AO molecules. Disinfectants will react with antioxidant molecules, causing faster AO inactivation and shorter service time. In the course of recent years, the loss of stabilization in polymer pipes transporting disinfected drinking water has been intensively studied. Physical loss of AO refers to the leaching, diffusion and wash out of AO molecules from the matrix, while chemical consumption indicate reactions in which AO molecules becomes inactive and will not be able to neutralize radicals and or radical precursor compounds.

### 2.5.1 Antioxidant consumption by hypochlorite

Dear et al. [98] published AO profiles through the pipe wall expressed by the OIT, after PE pipe pressure tests applying extremely high HOCl concentrations, as it is illustrated in Fig. 2.17. Pipes exposed to higher concentrations (Fig. 2.17a, Fig. 2.17b) failed earlier and showed a homogenous AO profile with a slightly decreased amount of active AO in the bulk material. In the inner surface layer at approximately 1 mm depth, the AO was almost completely consumed. Physical loss of AO on the outer pipe surface (outer pipe samples are immersed in non-chlorinated water) was significantly lower than on the inner pipe surface due to chemical reactions with HOCl. Aging experiments with lower HOCl content (Fig. 2.17c, Fig. 2.17d) showed lower amounts of active AO through the pipe. Furthermore, the chlorine penetration depth detected by SEM-EDX moved gradually into the bulk with increasing exposure time reaching a maximum of 4 mm of distance from the surface. The 15 times higher HOCl concentration caused a different AO profile and longer failure times (see Fig. 2.17 (b) and Fig. 2.17 (d)). This contradicting finding can probably be traced back to the material conditioning. In fact, the experimental findings of Whelton et al. [108] suggest that the AO consumption rate increases with increasing temperatures and HOCl concentration.

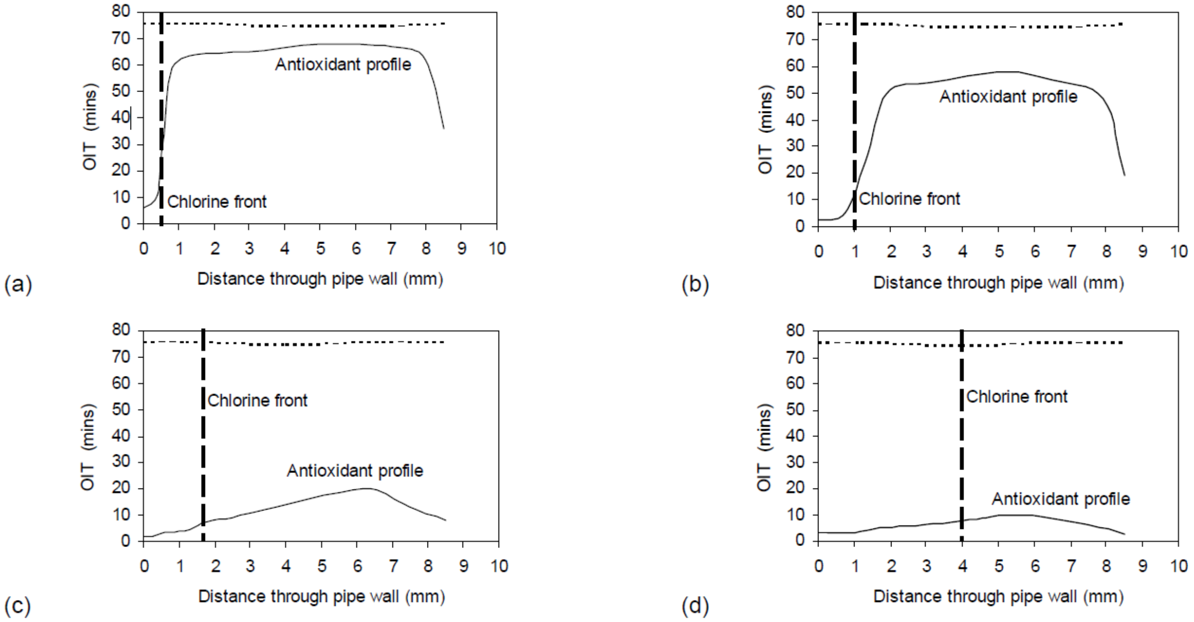
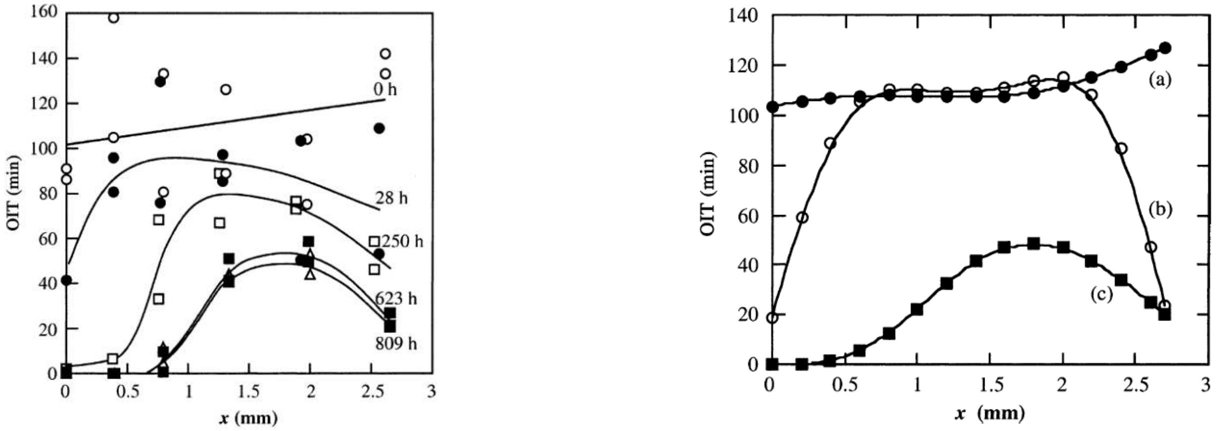


Fig. 2.17: Profiles of OIT of laboratory-aged pipe samples after pressure testing at 4.6 MPa hoop stress. Failures were recorded after 216 h in 120000 ppm (a), after 552 h in 15000 ppm (b), after 1176 h in 5000 ppm (c) and after 432 h in 1000 ppm (d) of HOCl solution [98].

Hassinen et al. [99] investigated the AO depletion and the internal surface degradation of PE pipe segments exposed to HOCl. The OIT profiles indicate significant AO loss on the inner surface even after 28 hours of exposure. Besides the gradually decreasing OIT values, the maximum of OIT shifted slightly to the outer surface, which is illustrated in Fig. 2.18 (a). Ifwarson and Aoyama [96] published almost identical OIT profiles after exposure to HOCl. This type of OIT profile was proposed to be an effect of increased AO diffusion on the inner side of the pipe segments compared to the outer side of the sample. Similar findings were reported for pipe aging studies, independently from the presence of disinfectants [74, 75]. Further analyses revealed that AO depletion on the internal surface occurred over 80 % due to chemical consumption. In case of internal water and outer air, reduced OIT was only expected only in the immediate inner and outer surface. Meanwhile, exposure to 3 ppm of HOCl at 95°C up to 810 h revealed significantly reduced OIT values through the pipe wall, with a maximum shifting to the outer surface. Experimental and predicted AO profiles shown in Fig. 2.18 (b) clearly display that in such aging experiments, AO diffusion is insignificant. The activation energy of AO depletion at a few hundred µm distance from the inner wall was assessed to be 80 kJ/mol.

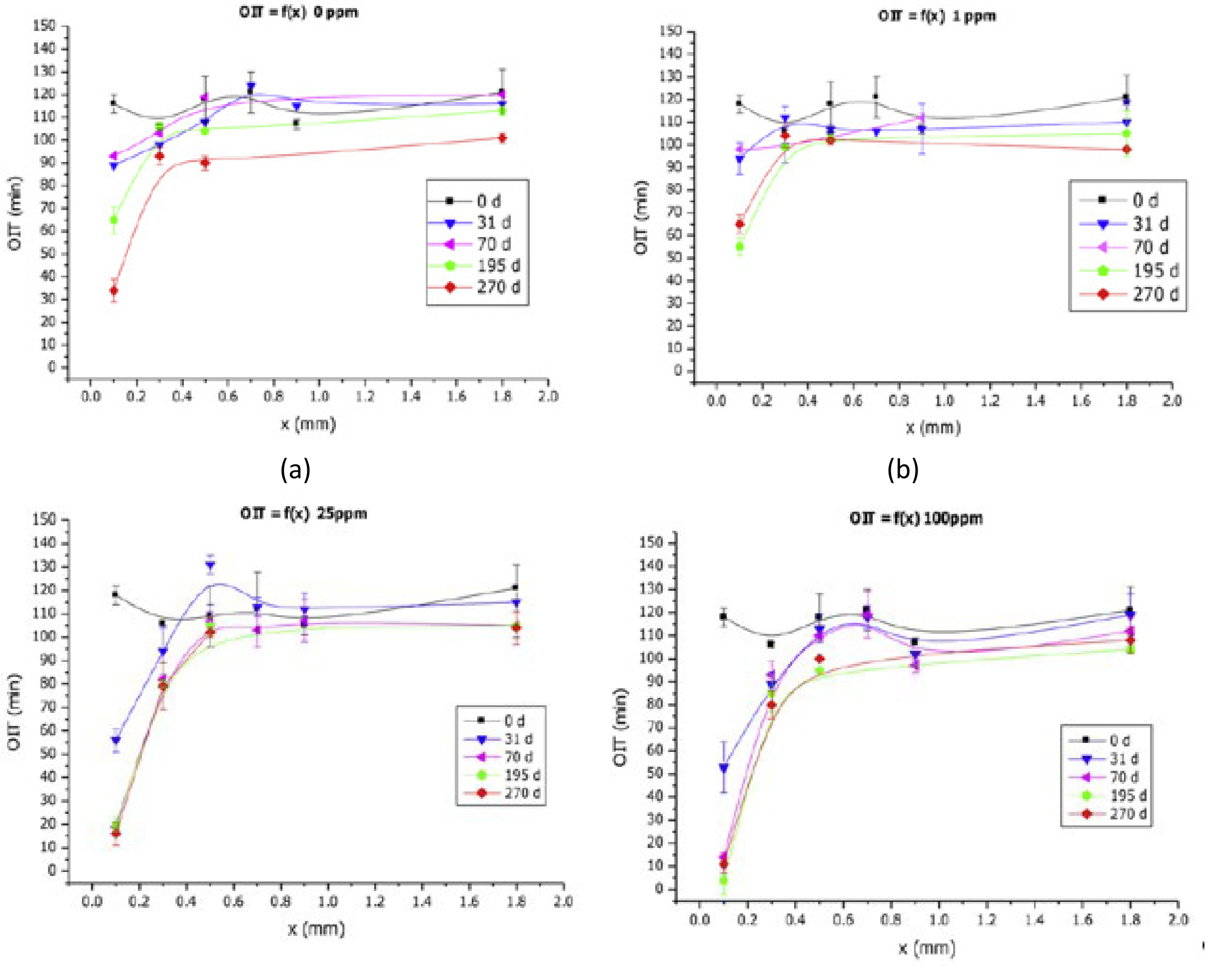


(a) (b)

Fig. 2.18: (a): Profiles of OIT of PE pipes aged at 95 °C with 3 ppm internal HOCl solution after various exposure times. (b): OIT profiles of unexposed (a), simulated OIT profile assuming only AO migration (b), and experimental of 3 ppm HOCl aging for 809 h at 95 °C [99].

Montes et al. [114] published OIT profiles of PE pipe grades indicating stronger AO consumption in the surface layer for 0 ppm than for 1 ppm HOCl-aged specimens (Fig. 2.19 (a) and(b)). As an explanation for this phenomenon, the formation of less reactive species than oxygen during the reaction of HOCl and oxygen was suggested. After conditioning in 25 and 100 ppm of HOCl media, OIT profiles for both conditions showed a 0.3 mm thick surface layer with reduced active AO content. Although the results imply that AO consumption is not influenced by 1 ppm HOCl, the 0.3 mm AO depletion front indicates that the diffusion of disinfectant or its derivatives plays an essential role in the overall degradation process. Previously presented studies [39, 99, 110] reported an approximately 1 mm thick surface layer with reduced AO concentration, which is significantly higher than the findings of Montes et al. [114]. Considering that over pH 8, mainly $OCl^-$ molecules are present and that pH was reported as being higher than 8, the lower diffusivity of polar $OCl^-$ molecules could clarify the thinner AO consumed layer observed.

Abdelaal and Kerry [53] also intensively investigated the effect of HOCl on AO consumption. The OIT analyses revealed that AO depletion is significantly faster at higher temperatures, in consisten with Whelton et al. [108]. Based on the Arrhenius concept for the AO consumption, 76 kJ/mol of activation energy in 1 ppm of HOCl was reported. The times to AO depletion at 20 and 60 °C were calculated to be 23 years and 0.5 years respectively. Fischer et al. [78, 118] investigated the effect of HOCl on PP samples focusing on the α and β polymorph crystalline phase, as well as on the effect of hindered phenolic and amine stabilizers. Micro-tensile samples were immersed in 5 ppm HOCl at 60 °C and a pH of 7. The slower AO consumption of β-nucleated PP was proposed to be the combined effect of higher AO content and the higher amount of tie and entangled molecules due to smaller spherulite sizes. Beside the better thermal stability of stabilized PP samples, a considerable antagonistic effect was reported between hindered phenolic and hindered amine stabilizer molecules. Since hindered amines are not active over 150°C, thus these molecules cannot be analyzed at elevated temperatures [122]. Conclusions about performance of hindered amine stabilizers based on OOT or OIT analysis are profoundly / scientifically unsound.



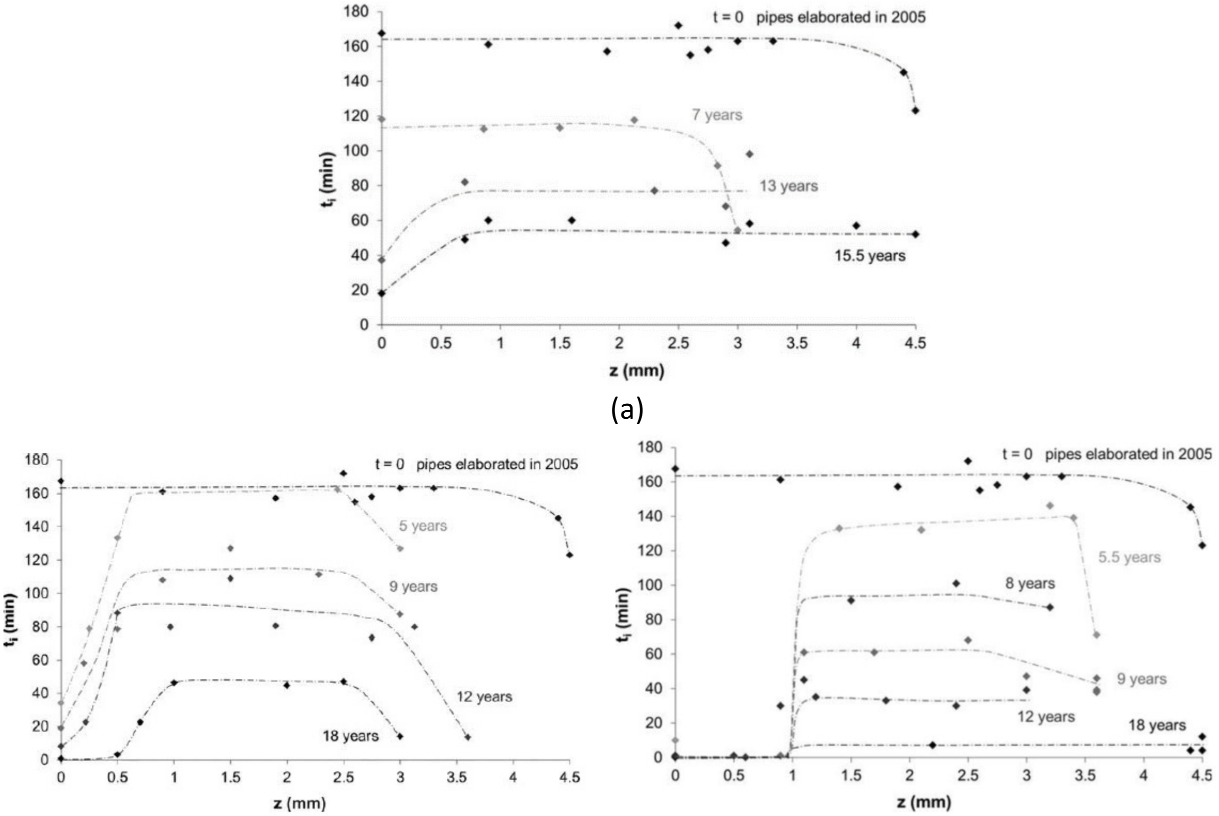
(a) (b)

(c) (d)

Fig. 2.19: Profiles of OIT after exposure to non-disinfected water (a), to 1 ppm (b), to 25 ppm (c) and to 100 ppm of FAC solution at 70 °C [114].

### 2.5.2 Comparing the effect of chlorine dioxide and hypochlorite on antioxidant consumption

In the extensive work of Colin et al. [110, 123, 124], the AO profiles of laboratory and field aged pipes were thoroughly examined. Published OIT profiles after various operation conditions represent well the detrimental impact of disinfectants on the AO consumption. In agreement with previous studies, only the physical loss of AO, as it is shown in Fig. 2.20 (a), plays a significant role in long-term applications [74, 75]. Homogenous AO distribution in the pipe core zone after several years of operation in HOCl (Fig. 2.20 (b)) and in $ClO_2$ (Fig. 2.20 (c)) demonstrates that the physical depletion of AO is more dominant than its chemical consumption in deeper material layers. The steep increase within the AO concentration between the chemically attacked layer, where AO was consumed by disinfectants, and the bulk, where AO depletion occurs by physical loss, might be a result of the decreasing diffusivity of disinfectants in the chemically attacked layer.



(a)

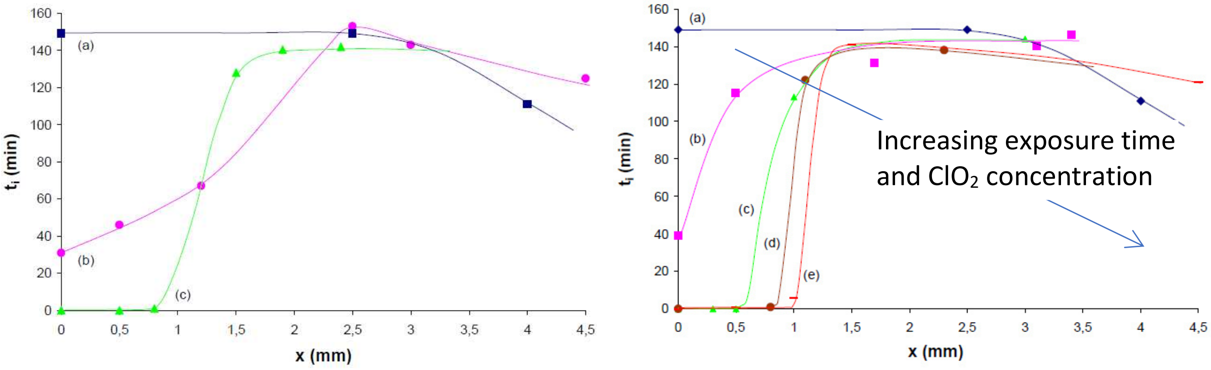
(b)

(c)

Fig. 2.20: Profiles of OIT of field-aged pipes after various service times without contact with disinfectants (a), in contact with HOCl (b) and in contact with ClO2 (c) [123].

This is probably caused by crosslinking [124] or an increased degree of crystallinity [39, 99]. Advanced digestion of the amorphous phase and chemi-crystallization can lead to a higher degree of crystallinity. The diffusion of disinfectants will be gradually suppressed by increasing degree of crystallinity of the chemically attacked surface layer, since the crystalline phase is believed to be impenetrable. Moreover, the quasi-asymptotic $ClO_2$ penetration depth (the chemical loss of AO limited to a 1 mm thick surface layer regardless of the service time) was proposed to indicate a diffusion-controlled aging, and the capability of $ClO_2$ to react with polymer chains. Although $ClO_2$ is not reactive enough to subtract hydrogen from saturated aliphatic hydrocarbons, chain defect points (e.g. double bonds) are likely to be attacked by $ClO_2$. The study reports an at least one order of magnitude shorter time to failure as an effect of disinfectants, predicted by regression analysis. The OIT profiles of laboratory-aged pipes (Fig. 2.21) in water,

$ClO_2$ and in HOCl samples display a good resemblance to field-aged samples (Fig. 2.20), confirming the reliability of laboratory experiments. Consumption of AO was found to be faster in case of exposure to disinfectants than to water, as it is illustrated in (Fig. 2.20 (a)). Chlorine dioxide consumed active AO in about a 1 mm thick surface layer, as long as in the bulk, only a slight decrease of AO was found. Between the internal surface layer and the bulk, a steep increase in the amount of active AO was detected, similar to the field-aged samples. Concenring HOCl exposure, on the internal surface, a less reduced stabilization was observed followed by a slowly increasing trend. In agreement with [53, 108], the AO concentration decreased faster with increasing $ClO_2$ concentration and with increasing aging time, as shown in Fig. 2.21 (b). In the bulk, no significant AO loss was detected.



(a) (b)

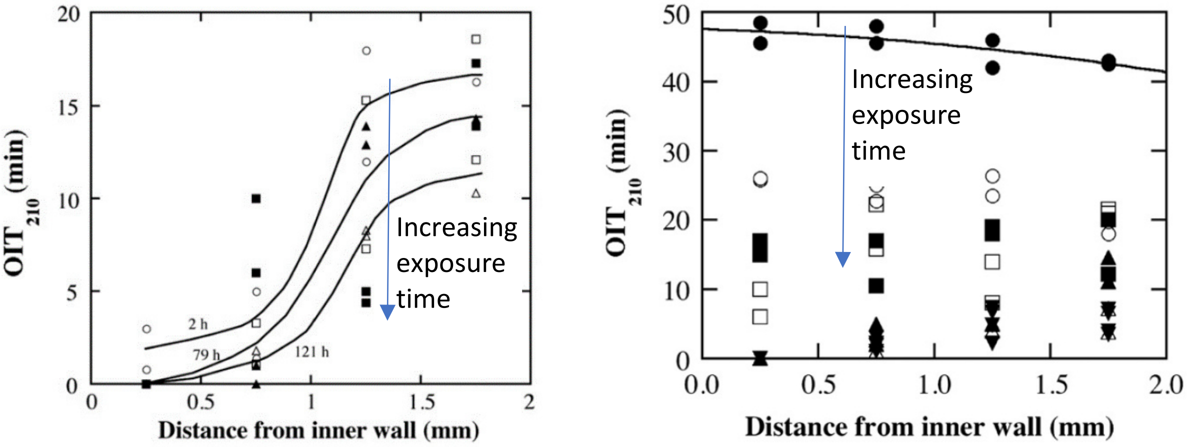
Fig. 2.21: (a): Profiles of OIT after aging at 90 °C for 19 weeks in deionized water (a), in 100 ppm HOCl (b) and in 100 ppm $ClO_2$ (c). (b): OIT profile of laboratory aged pipes where $ClO_2$ content was raised to 100 ppm and aging time to 99 days [124].

At a few hundred micrometers depth, a significant amount of carbonyl groups was observed, but only in the surface region containing almost no effective AO. The AO profiles of laboratory-aged samples revealed AO consumption in about a 1 mm thick surface layer in accordance with the field-aged samples. After a certain degradation level, the thickness of the chemically consumed AO layer appears to be independent from $ClO_2$ concentration and aging time. It should be noted that physical loss of AO in laboratory aging experiments due to higher temperatures might be significantly faster compared to field-aged samples. Elevated temperatures will increase the kinetic energy of molecules and the free volume of the polymer matrix, promoting a faster AO diffusion. Comparing AO loss in the bulk during laboratory (Fig. 2.21 (b)) and field (Fig. 2.20 (c)) aging, AO diffusion from the bulk seems to be negligible, in spite of the increased temperature.

Azhdar et al. [125] presented a new approach to investigate the effect of HOCl and $ClO_2$ on stabilizers used in polyolefin pipes. Instead of the polyolefin phase, a hydrocarbon analogue, squalane, was used. The liquid organic phase (squalane) containing an initial 0.2 wt.% of Irganox 1010 was exposed to 10 ppm of $ClO_2$ and HOCl at 70 °C. A continuous stirring was maintained, and the inorganic phase – the disinfected water – was replaced every 30 minutes to ensure stable exposure conditions. Comparing the effect of oxygen-free water and saturated water, only slightly faster AO depletion was detected, revealing a minor chemical consumption of AO in contact with water. Previous studies [74, 75] showed that AO loss in squalane was caused mostly by diffusion in non-disinfected water. In contact with HOCl and $ClO_2$, about 80 % of AO loss was assigned to chemical reactions between the disinfectant and the AO. A complete AO consumption was found, after 200 min of aging in $ClO_2$ solution, as long as non-disinfected water led to only 7 % active AO loss. Exposure to the two disinfectant solutions resulted in highly similar AO depletion times in squalane; however, $ClO_2$ is classified as a significantly stronger oxidizing agent, than HOCl. A linear decrease of OIT in squalane over exposure is reported for both disinfectants.

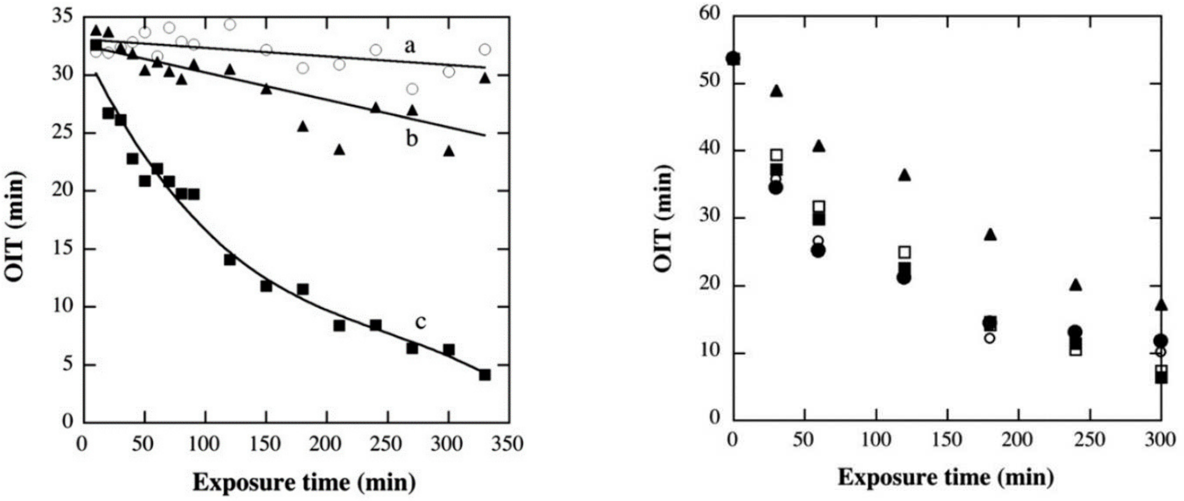
Yu et al. [39] investigated the effect of $ClO_2$ and HOCl solution on AO consumption in squalane and PE. The AO profile of MDPE pipes after exposure in a circulation loop at 90°C in 4 ppm of $ClO_2$ at a hoop stress of 1.6 MPa showed severe AO depletion through the cross section. After 2 h of testing on the inner surface an almost complete AO loss and at the outer surface, an over 50 % decline in the initial AO concentration was detected, as presented in Fig. 2.22 (a). Similar results were obtained in the case of aging in HOCl solution (Fig. 2.22 (b)). The effect of HOCl on AO consumption was not as drastic as it was for $ClO_2$. The appearance of a highly AO depleted surface layer was explained by the combined effect of the fast reaction between AO and $ClO_2$, and the diffusion of AO from the bulk to the surface. A comparison of OIT values at 0.75 mm distance from the contact surface showed an approximately four times faster AO depletion rate in $ClO_2$ than in HOCl. The AO consumption in squalane and in MDPE samples was further examined in 10 ppm HOCl and in 10 ppm $ClO_2$ solution in the temperature range of 30 to 70°C by Yu et al. [126]. For squalane samples, 10 % of AO loss was reported by diffusion into the water phase. The initial AO concentration decreased to about 75 % and 25 % in the presence of $ClO_2$ and HOCl, respectively. The OIT values in Fig. 2.23 (a) display the distinct effect of disinfectants. In contrast with the previous results [125], nonlinear OIT decrease was found regarding the $ClO_2$ aging.

Azhdar et al. [125] found a remarkably similar trend and time to AO depletion for both disinfectant solutions, opposing the data presented by Yu et al. Nevertheless, in the temperature range of 40 to 70 °C, AO concentration of PE and squalane samples showed a declining trend with increasing exposure time in $ClO_2$. At 30 °C, for PE samples, a somewhat slower OIT decrease was found, which is illustrated in Fig. 2.23 (b). The temperature dependency of AO consumption in squalane samples was found to be less pronounced. In agreement with the findings of Whelton et al. [108], overall AO consumption was reported to be moderately temperature-dependent. In accordance with the results of Colin et al. [110], a very low activation energy of $E_A$ <10 kJ/mol for the AO consumption in squalane was reported.



(a) (b)

Fig. 2.22: Profiles of OIT of PE pipes after exposure to 4 ppm $ClO_2$ solution at 90 °C (a), and after exposure to 4 ppm HOCl solution at 90 °C (b), applying different aging periods [39].



(a) (b)

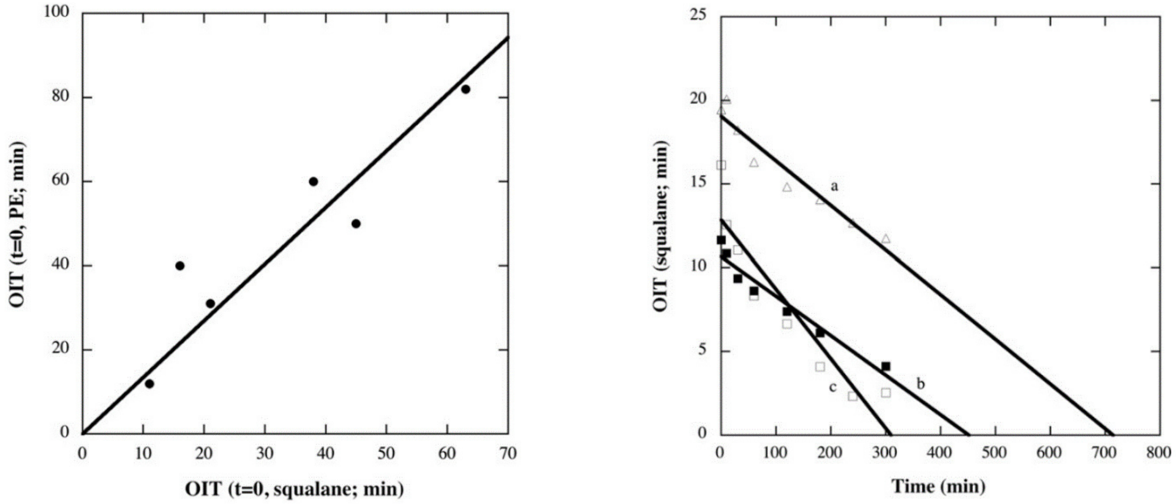
Fig. 2.23: (a): OIT of squalane samples containing Irganox 1010, after exposure to water (a), to 10 ppm HOCl solution (b) and to 10 ppm $ClO_2$ at 70 °C. (b): The effect of aging media temperature on AO consumption in PE samples caused by 10 ppm $ClO_2$, at temperatures of 30 °C (triangle), 40 °C (open square), 50 °C (filled square), 60 °C (open circle) and 70 °C (filled circle) [126].

Furthermore, in PE samples, an increasing $E_A$ with increasing distance from the surface was detected. The activation energy of AO consumption reached a plateau at about 1 mm depth with a constant value of 21 kJ/mol. The AO consumption was suggested to be controlled by diffusion of $ClO_2$ molecules into the PE matrix. During the squalane experiment the organic phase displayed a discoloration in the case of $ClO_2$ exposure, revealing the presence of quinones, oxidized phenolic AO molecules. Due to its sterically hindered structure the phenolic ring rupture is unlikely, and some traces of chlorinated by-products were also found in IR spectrums.

Previously presented reactions (see 2.1.1) of phenolic compounds with $ClO_2$ are in good agreement with the aforementioned studies [39, 110, 123–126]. After HOCl and $ClO_2$ exposure, the degradation product analysis of the aqueous phase revealed ketone and ester groups, indicating oxidized reaction products of AO and squalane molecules. In the case of $ClO_2$ exposure, chlorine-carbon bonds were reported, implying $ClO_2$ reactions with AO. In fact, an excess of $ClO_2$ can lead to chlorinated by-products of phenolic molecules (see 2.1.1).

### 2.5.3 Antioxidants with increased disinfectant resistance

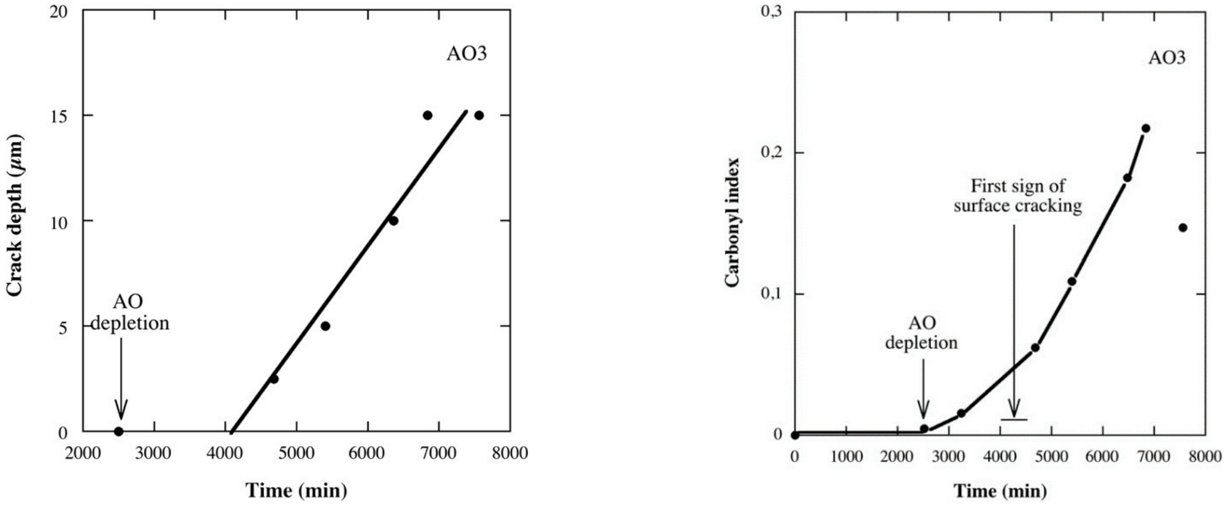
Yu et al. [103] studied the degradation of six different phenolic AO in squalane and in PE polymer matrices. After exposure to 10 ppm of $ClO_2$ solution at 70°C, a linear correlation was identified between the initial OIT values of PE and squalane samples for all six AO, which is shown in Fig. 2.24 (a). In squalane a linear AO depletion with increasing exposure time was found. However, PE samples only showed linear AO depletion in the first period of testing.



(a) (b)

Fig. 2.24: Linear correlation of OIT between PE and squalane samples (a), and OIT of three different AOs in squalane, after exposure to 10 ppm $ClO_2$ solution at 70 °C [103] (b).

With longer exposure times a nonlinear and slower AO loss was recognized for PE samples compared to the squalane experiment. In squalane a linear AO depletion with increasing exposure time was found (Fig. 2.24 (b)); however, PE samples only showed linear AO depletion in the first period of testing. With longer exposure times, a nonlinear and slower AO loss was recognized compared to the results of the squalane experiment. Longer AO depletion times were attributed to higher phenolic molar concentrations. In other words, the higher the phenol group amount / molecular weight of the AO molecule, the better the performance of the given AO in contact with $ClO_2$. The squalene-based methodology presented is potentially applicable to rank stabilizers based on their resistance against disinfectants within reasonable testing times. Cross-sections of tensile specimens after being drawn beyond necking were analyzed with scanning electron microscopy (SEM) at a 60° angel. Samples before complete AO depletion revealed a smooth texture, in contrast with longer exposed samples displaying a pattern of surface cracks. Surface cracks appeared after about 4000 h incubation time, well beyond the 2500 h of AO depletion time. After this incubation time period, the crack depth increased approximately linearly with increasing exposure time. For this sample an exponentially increasing CI was detected immediately after AO depletion as presneted in Fig. 2.25. This CI increment indicates that degradation products detected by FTIR are mostly formed by the polymer aging.



(a) (b)

Fig. 2.25: Growth of surface crack depth over exposure time (left), increasing carbonyl index with longer aging time (right) [103].

The resistance to 10 ppm of $ClO_2$ solution of eight phenolic AO added to thin MDPE films was further analyzed at 70 °C and at a pH level of 6.8 in a later study of Yu et al. [127]. Comparable with the previous work, a linear AO loss rate was reported in the first few hours of exposure, which was followed by a continuously reducing AO loss rate. Depletion times for each AO varied from a few hours up to 40 h. Yu et. al [127] proposed that AO with an aromatic core could possess higher resistance against $ClO_2$, since these molecules may be able to form clusters. Organochalcogen stabilizers were found to be outstandingly resistant against $ClO_2$ in squalane compared to conventional phenolic stabilizers [128]. The stabilizers studied showed constant OIT values after 91 h of exposure, but their toxicity and applicability in PE pipe grades were not tested.

## 2.6 Discussion

Beside the highly valuable experimental results, the publications discussed above also provide further insight into the relevant aging mechanisms of PE pipes in disinfected water. Based on the different physical and chemical properties of the two disinfectants and the experimental data, different aging mechanisms can be deduced for each disinfectant. In this chapter, these theoretical models will be reviewed and compared.

### 2.6.1 Proposed aging mechanism in chlorine dioxide

Colin et al. [90, 110, 123, 124] found that the aging process is controlled by the diffusion of $ClO_2$, and the disinfectant itself can react with the polymer chains as well. Considering that $ClO_2$ is a dissolved gas in water it is likely to diffuse fast into the polymer; thus, AO on the surface of polymer will be rapidly consumed. Diffusion of AO from the bulk takes longer and only becomes relevant after years of operation. Based on field samples and laboratory aging a 1 mm surface layer was found to be affected by $ClO_2$. The thickness of this layer seems to be constant, which can be attributed to the gradually decreasing diffusion rate of the $ClO_2$. The crystallinity ratio could be increased significantly by chemi-crystallization and by the loss of the amorphous phase. Both effects could lead to reduced $ClO_2$ diffusion.

The comprehensive work of Yu et al. [39, 103, 126, 127] suggests that rapid AO consumption is caused by $ClO_2$ in the surface layer. Polymer degradation in this layer is probably induced by ClO* radicals, formed by the AO and $ClO_2$ reactions. Chemical degradation assisted crack propagation was proposed as an explanation for premature pipe failures during operation and internal pressure tests. However, direct contact of the crack tip with the aging medium (e.g. local crack tip aging [68, 78]) was not proposed. In fact, for such effect polar and non-polar nature of the medium and the polymer, respectively, capillary forces and surface polarity change over the exposure time should be considered. Moreover, in the immediate superficial layer for AO consumption, 10 kJ/mol of $E_A$ and around 1 mm distance from the surface $E_A$=22 kJ/mol were reported. Fast AO depletion through the pipe wall is most likely caused by $ClO_2$, and in the degraded surface layer chlorine monoxide radical (ClO*) was suggested as the responsible species. Discoloration of the squalane solution was attributed to the presence of quinonoid compounds originated from the reactions of AO and $ClO_2$. Furthermore, an improved $ClO_2$ resistance of AO molecules with higher molar phenolic concentrations was reported. Costa et al. [129] confirmed the different behavior of some selected AO regarding contact with disinfectants, reporting synergetic and antagonistic effects between various AO packages exposed to $ClO_2$.

The experimental work of Vogt et al. [93, 94] confirmed the influence of oxidizing agents on the AO consumption, although thermo-oxidative polymer aging was found to be unaffected. An $E_A$ of 90 kJ/mol was reported for the polymer degradation based on pipe pressure testing up to 110 °C. Published data indicates that oxidizing agents like oxygen, HOCl, $ClO_2$ or nitric acid accelerate AO consumption, without influencing the polymer aging. Similar $E_A$ for unstabilized and stabilized samples exposed to different oxidizing agents suggests that the degradation process follows the thermo-oxidative aging mechanism.

Hassinen and Jacobson [73] suggested that the reaction of ROOH groups with $ClO_2$ produce peroxy radicals (ROO*) and catalyze the chain branching reaction. However, some authors have reported unchanged auto-oxidative material degradation in the presence of disinfectants. Nevertheless, as potential species, $Cl_2$, $Cl_2O$ and $ClO_2$ were suggested which are able to diffuse into the bulk and react with the AO. Radicals are probably too reactive to diffuse into deeper material layers.

### 2.6.2 Proposed aging mechanism in hypochlorite solution

Colin et al. [123] reported similar findings for HOCl solution compared to $ClO_2$, although for accelerated AO consumption and material degradation on the surface layer, the ClO* radical was suggested as the responsible molecule. Considering the lower oxidizing potential of HOCl, a significantly slower process was observed than in the case of $ClO_2$.

Yu et al. [126] put forward that OH* radicals are responsible for polymer degradation in HOCl. In accordance with literature, OH* are highly reactive and could abstract hydrogen from the polymer chain, initiating polymer auto-oxidation. As the responsible species for AO consumption in deeper material layers, $Cl_2$ molecules, which are soluble in PE, were proposed. Since $Cl_2$ should not be present (Fig. 2.1) or only in a very low amount around neutral pH levels, this conclusion might seem misleading. According to the Le Chatelier principle, variation in the temperature will shift the equilibrium between $Cl_2$, HOCl and $OCl^-$. Therefore, presence of a low amount of $Cl_2$, especially at elevated temperatures, can be assumed. Moreover, the authors propose the following aging mechanism for pressurized PE pipe failure in contact with disinfected water: After the consumption of active AO, presence of radicals (including OH*) initiate the chemical attack of polymer chains, which eventually leads to crack formation. At the crack tip, disinfectant could react with AO in a deeper material layer, leaving polymer chains unprotected against radical attacks. The AO consumption followed by material degradation and crack growth continues until a critical crack depth is reached, which leads to SCG and finally to rupture.

In contrast with the proposed radicals by Yu et al. [126] and Colin et al. [123] for polymer degradation, Devilliers et al. [109] suggested that these molecules are too reactive to diffuse into the bulk deeper than a few micrometers. Their study pointed out other more stable molecules (e.g. $Cl_2OOH$), which could cause accelerated material degradation. Based on the work of Holst [47] the ClO* and HO* radicals originated from HOCl can accelerate PE degradation, although the authors propose that these radicals are too reactive to diffuse in a sample more than 1 µm. The formation of a less reactive species was proposed by Khatua et al. [130] too, indicating that $Cl_2OOH$ as hydroperoxide could accelerate the degradation process significantly.

In the study of Hassinen et al. [99], $E_A$ of AO consumption at a few hundred micrometers distance from the surface was found to be 80 kJ/mol. A somewhat higher value was reported for the highly degraded immediate surface layer. In agreement with these findings, Abdelaal and Kerry reported 76 kJ/mol of $E_A$ for AO consumption in HOCl. As a potential reactive species responsible for reduced AO activity, $Cl_2$, $Cl_2O$ and $ClO_2$ molecules were suggested.

Montes et al. [114] and Mitroka et al. [45] reported that in case of higher disinfectant concentration, polymer degradation is independent of the HOCl amount applied. A new auto-oxidation mechanism was proposed by Mitroka et al [45]. Decomposition of HOCl could produce radicals and oxygen molecules. Non-selective and highly reactive radicals, such as HO* and Cl*, are able to abstract hydrogen from the polymer chain, producing carbon radicals in the carbon chain. As oxygen is also present, it could react with the carbon radical resulting in peroxyl or peroxide formation on the polymer chain. The decomposition of these molecules can follow several reaction pathways, but eventually lead to the formation of further radicals and carbonyl groups. The authors suggest that over time, HOCl concentration decreases mainly by decomposition and reacting with the polymer and not dominantly by reacting with AO. Moreover, decomposition of the hydroperoxide in chain scission reactions would be a logical explanation for the decreased molecular weight reported by several authors [73, 78, 90, 98, 99, 102, 109, 118].

Mikdam et al. [117] proposed that in HOCl exposure the $Cl_2$ and HOCl molecules could diffuse in the PE matrix and by dissociation to Cl* and HO* radicals and promote the degradation process. The reported kinetic model fits well to the experimental CI and $M_w$ change over exposure time; therefore the suggested mechanism seems highly plausible.

## 2.7 Summary and conclusion

Applying $ClO_2$ or HOCl as an oxidizing agent in drinking water is an obvious choice considering their excellent disinfection properties. Both disinfectants possess high reactivity, which is why their effect on polyolefin and especially PE pipes needs to be examined. In order to perform reliable and reproducible laboratory aging studies, exposure parameters should be well controlled and kept at a constant level. For such experiments, due to rapid thermal decomposition and oxidative reactions of disinfectants, continuous adjustment of the aging conditions is essential. Unfortunately, in the research studies available, exact exposure parameters over the aging period are not usually published; just average values of the conditioning are included. Furthermore, most currently used aging setups are either not well controlled (bottles), or feasible sample geometry is highly limited (pipe pressure tests). Nevertheless, an overview of the relevant literature draws attention to the adverse effect of disinfectants on AO consumption and polymer degradation. The two oxidizing agents are markedly different in many aspects. Without being exhaustive, these differences are summarized in Table 2.1. To understand the relevant aging mechanism, the different nature of oxidizing agents should be considered. Field studies have pointed out that the application of disinfectants in the drinking water network will lead to an advanced internal surface degradation and eventually to premature pipe failure. The case studies reviewed indicate that surface degradation leads to severe material embrittlement and surface cracks. After a certain crack depth – embrittlement depth –, SCG seems to dominate the crack propagation through the unaffected bulk material.

Table 2.1: Different properties of $ClO_2$ and HOCl media.

| | **$ClO_2$** | **HOCl** |
|---|---|---|
| Behavior in water | Dissolved gas | Temperature and pH dependent EQM:<br>$Cl_2+H_2O \leftrightarrow HOCl+Cl^-+H^+$<br>Solved ions / molecules |
| Influence of pH in water | Form 6 – 9 no reported influence on reactivity | pH ~7.5 equilibrium between HOCl, and $ClO^-$ molecules |
| Oxidation | 2.5 times stronger than HOCl (based on oxidation state difference) | pH<7.5 Increased amount of HOCl, which has higher disinfection capability |
| Disinfectant capability | High, effective against almost any microorganism | High, ineffective against some microorganisms |
| Dosage | Limited to 1 mg/L due to by-products | No limitation, well established technology |
| By-products due to oxidative reactions | Chlorite and chlorate ions, with adverse health effects | Carcinogen THMs, chlorinated phenolic molecules causing taste and odor issues |
| Diffusion into polymer matrix | Probably fast, since it is in gas phase | Probably slow, due to sterically hindered reactions |
| Behavior in polymer matrix | Polar molecules are insoluble, effect only in thin (0,1-1 mm) surface layer are expected due to limited diffusion, diffusion of radicals also limited by their high reactivity | |
| Reactions | Highly reactive, nonselective oxidation, no or low amount of chlorinated product | Highly reactive, selective oxidation and chlorination reactions |
| Reactions with phenolic compound | Oxidation to quinone, in excess ring rupture | Chlorination and oxidation, in excess ring rupture |

According to standardized methods, laboratory aging experiments generally showed a good agreement with field samples, although physical loss of AO in the pipe wall due to the short testing time was not reported. The results clearly display the effect of disinfectants on the inner pipe surface regarding the development of surface cracks, high amount of degradation products, reduced AO activity and decreased $M_w$. Despite the good agreement with field samples, testing based on these standards has some disadvantages. Internal pipe pressure experiments could require long testing times even at elevated temperatures. Beside considerably high testing costs, in some cases, the failure time exceeds one year of testing. Moreover, contradictions in the predicted pipe lifetimes also represent the need for another improved testing methodology. To overcome these challenges, several researchers have investigated the effect of disinfectants on pipe grades in laboratory-scale aging experiments.

The scientific papers reviewed point out that the presence of disinfectants will lead to accelerated material degradation and AO consumption in the superficial material layer. Overall material degradation leads to reduced mechanical properties, fast chemical consumption of AO, an increased amount of degradation products and reduced $M_w$. Nonetheless, some important aspects of the aging mechanism of PE in contact with disinfectants are still debated.

An increasing amount of polymer degradation products on the contact surface with increasing exposure time is has been recorded by numerous authors, although the appearance of carbonyl groups was detected before the complete loss of active AO in some cases. A possible explanation for this phenomenon would be that disinfectants or their reaction products react with the polymer molecules too, causing chain scission and various degradation products. To confirm this idea for both disinfectants, the origin of the carbonyl groups should be examined, including determination of the ratio between degradation products formed by polymer and by AO degradation. Considering that polymers always contain at least a low amount of processing stabilizera and that high $ClO_2$ or chlorine concentration could lead to the rupture of the phenolic ring, the observed chlorinated products could originate at least partially from AO.

Beside the demonstrated reduction in mechanical properties of PE samples exposed to disinfectants, a decreased $M_w$ in the powder surface layer was also observed. In spite of the fact that $ClO_2$ should not react with saturated hydrocarbons, significantly reduced $M_w$ was reported, including the appearance of new peaks at lower $M_w$ in the molecular weight distribution curves. Similar to the effect of $ClO_2$ on PE, exposure to HOCl also resulted in reduced $M_w$, although the decline was less conspicuous. The change in modality of the $M_w$ distribution curve after exposure to HOCl has also been reported. Both stabilized and unstabilized samples showed a similar decrease in $M_w$ values over exposure time implying that reactive chlorine species or radicals might react simultaneously with the AO and with the polymer. In case of exposure to $ClO_2$ the same hypothesis has already been proposed in literature.

As a result of advanced surface degradation, the authors highlight the digestion of amorphous phase in the immediate surface layer. The thickness of this degraded surface layer in the case of exposure to $ClO_2$ tends to increase up to about 1 mm. The existence of this limitation is probably linked to digestion of the amorphous phase, which eventually inhibits the diffusion of reactive chlorine molecules. Slower diffusion could be explained by the increased crystallinity ratio as well as with crosslinking, but only the increment of crystallinity has been experimentally confirmed. A similar thickness of the degraded surface layer has been published concerning aging in HOCl. At extreme high HOCl concentrations chlorine atoms were detected a few millimeters from the surface, indicating that material degradation caused by HOCl may not be limited to a 1 mm thick surface layer.

Loss of active AO of PE pipes exposed to disinfected water clearly indicates the different nature of the two oxidizing agents. Aging in $ClO_2$ led to a fast and almost complete AO consumption in a 1 mm thick surface layer, while exposure to HOCl solution caused only reduced AO activity in the same material layer. Even though the effect of $ClO_2$ on AO consumption in the bulk material seems almost negligible, exposure to HOCl solution caused decreased AO activity deeper than at a depth of 1 mm.

As the reviewed studies indicate, in order to fully understand the relevant aging mechanism of PE pipes in the case of contact with disinfectants several aspects yet to be understood. In the development of AO packages and PE pipe grades with improved disinfectant resistance, a well-known and predictable aging mechanism would be crucial.

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# 3 Experimental

This chapter provides an overview of the applied aging technique, exposure device, materials and characterization methods. In order to avoid unnecessary repetition, the following chapters will refer to this part. Since aging paramters plotted over immersion time are important for reproducible experiments the chapters include additional figures of immersion test values. In this chapter, certain paragraphs have been quoted verbatim from Bredács et al. [2].

## 3.1 Exposure device

While studying the aging mechanisms of PE under well-controlled aging conditions, a specialized exposure device was developed at PCCL in cooperation with Mechatronik Moharitsch GmbH (Austria) [1, 2]. The structure of the apparatus is schematically illustrated in Fig. 3.1. The instrument can be used for accelerated aging experiments in aqueous HOCl and $ClO_2$ solution with a maximum temperature of 60°C. The technical specifications of the device are shown in Table 3.1. Hypochlorite solution is prepared from sodium hypochlorite (NaOCl) stock solution.

(a) (b) (c)

Fig. 3.1: Schematic structure (a) of the exposure device, (1) stock solutions, (2) sample chamber, (3) metering station and control panel, (4) $ClO_2$ production and dosing unit. Picture of the metering and dosing unit (b), as well as (c) of the exposure device [2].

Table 3.1. Technical specifications of the applied exposure device adapted from [1, 3, 4].

| Test medium | chlorine dioxide ($ClO_2$) or<br>sodium hypochlorite (NaClO) |
|---|---|
| Temperature | max. 60 °C ± 1 °C |
| Vol. sample chamber | 50 l |
| Flow rate | max. 500 l/h |
| Concentration $ClO_2$ | max. 10 ppm ± 0.1 ppm |
| Concentration NaClO | max. 100 ppm ± 0.1 ppm |
| pH measurement | ± 0.1 |
| Free chlorine measurement | ± 0.1 ppm |
| ORP measurement | ± 10 mV |

To control the pH of the aging medium sodium hydroxide and sulfuric acid are applied. For the formulation of $ClO_2$, the hydrochloric acid-chlorite technique was used, which is shown in Equation 13 [5]. The $ClO_2$ stock solution was prepared by a device of the type Legio Zon® CDL (ProMinent Dosiertechnik GmbH, Austria) and injected into a closed-loop system including the sample chamber via an integrated dosage pump.

$$5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 5NaCl + 2H_2O \tag{13}$$

A flow rate of 500 l/h was applied in the closed-loop system. Continuous monitoring of the concentration of ClO2, pH, ORP and the temperature were verified by metering stations for acids/leaches and by a measurement and control plant of the type DULCOMARIN® II (ProMinent Dosiertechnik GmbH, Austria). All parts of the instrument were made of materials resistant to chemical, mechanical and thermal loadings and meet the demands of ÖNORM M 5879-3 [6]. As a water supply, deionized water was used, prepared by an ion exchange column of the type Thermo Scientific DI1500. During accelerated aging experiments, all parameters were recorded every five minutes and stored for further analysis. Moreover, to ensure constant aging conditions, pH and concentration values were measured and adjusted every five seconds. The device recorded all exposure parameters every five minutes, also including the dosage values. Although the ORP – HOCl relationship at various pH levels is well known (see Fig. 2.5 (b)), the correlation between ORP and $ClO_2$ concentration has not been published yet. In Fig. 3.2, the nonlinear saturation-like curve increase of the ORP with increasing $ClO_2$ concentration can be recognized.

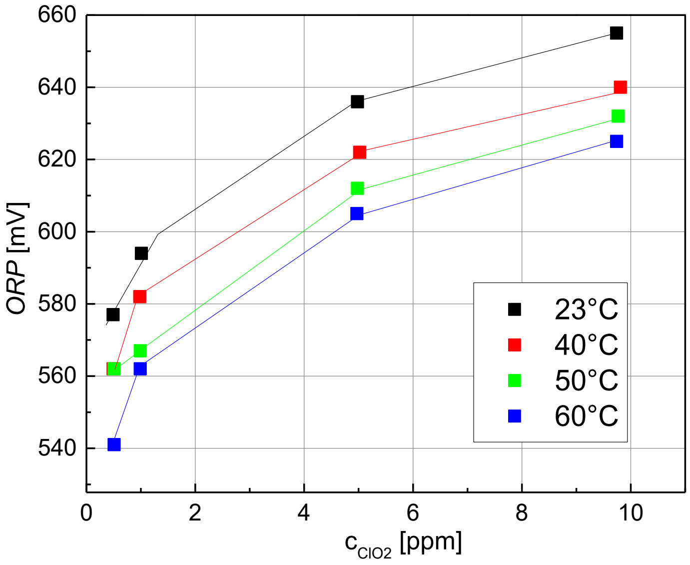


Fig. 3.2: Characteristic ORP-$ClO_2$ concentration curve at different temperatures.

This behavior is comparable to the relationship between ORP and HOCl; however, the actual values are likely to depend considerably on pH controlling solutions (see Section 2.2). In fact, the ORP at a given $ClO_2$ concentration is somewhat lower than values available in the relevant literature publications. The characteristic ORP-$ClO_2$ concentration curve draws attention to a faster ORP increase in between 0.1 and 1 ppm, compared to the concentration range of 1 to 10 ppm. This phenomenon is similar to the ORP-HOCl concentration relationship [7]. Moreover, a gradual decrease in the ORP with increasing temperature can be also recognized. The effect of temperature on the ORP seems to follow a linear relationship.

## 3.2 Selected materials

From compression molded sheets with a press of type COLLIN P 300E+ (Dr. COLLIN GmbH, Germany) dogbone-shaped specimens (SHT) with a thickness of 1±0.1 mm were prepared in accordance with ISO 18488 [8]. From 0.3 ±0.05 mm thin cast films tensile specimens were punched out based on the ASTM D1708 [9]. The applied specimens are illustrated in Fig. 3.3 (a). All tensile specimens were fixed in polytetrafluoroethylene sample holders in accordance with [6] to avoid floating and ensure the complete immersion of each specimen. The photos shown in Fig. 3.3 (b) represent the anchoring of tensile specimens. Preliminary experiments showed that continuous contact of aging media with the sample surface is crucial for reliable and reproducible test results.

(a) (b) (c)

Fig. 3.3: Applied tensile specimens with a thickness of 1 mm (1) and 0.3 mm (2) (a), and anchoring of the tensile bars with PTFE sample holders (b) and (c).

From 15 mm thick compression molded plates, 10 mm wide and 30 mm long block specimens (BCK) were prepared. To investigate the changes in material properties at various depths, thin film specimens were cut from the surface into the bulk before exposure and after each sample removal. The 50 µm thin films were prepared via sectioning using a rotary-microtome of the type RM 2255 (Leica Microsystems, Austria). In Fig. 3.4, the block samples and sectioning of thin films are illustrated schematically. Six PE resins were selected for accelerated aging in disinfected aqueous solutions. The basic material properties of the samples chosen are shown in Table 3.2. The stabilizer package labeled as 1* indicates a higher amount of AO from stabilizer package 1. Due to confidentiality, no further information about the AO used can be provided in this dissertation. The highly distinct molecular morphologies of the six PE grades are shown in Fig. 3.5. The selected PE grades were prepared with hexen comonomer with different polymerization techniques, which is why different side chain distributions are represented. Despite similar molecular weight distribution of PE2 and PE4, these materials were prepared by different polymerization processes.

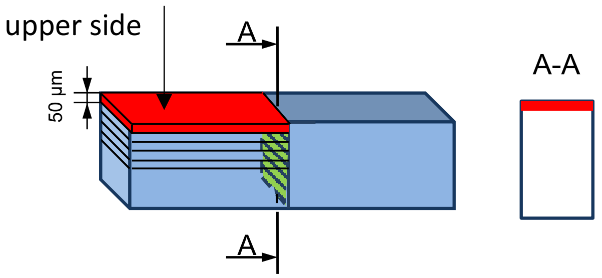


Fig. 3.4: Illustration of a block specimen, and the preparation of thin film specimens.

Table 3.2: Material properties of the six PE pipe grades selected ($M_w$: molecular weight, $\rho$: density, $\varepsilon_b$**:** elongation at break, *OOT*: oxidation onset temperature, *X:* crystallinity) [10].

| | **AO** | **$M_w$ [g/mol]** | **$\rho$ [g/cm$^3$]** | **$\varepsilon_b$ [%]** | ***OOT* [°C]** | ***X [%]*** |
|---|---|---|---|---|---|---|
| PE1 | 1 | 115660 | 0.941 | 509±63 | 276 | 52 |
| PE2 | 1 | 131340 | 0.933 | 577±24 | 274 | 45 |
| PE3 | 1*+2 | 256500 | 0.950 | 437±46 | 279 | 57 |
| PE4 | 1 | 112920 | 0.931 | 517±24 | 280 | 49 |
| PE5 | 3 | 102270 | 0.940 | 350±10 | 248 | 44 |
| PE6 | 4 | 261350 | 0.950 | 400±22 | 273 | 59 |

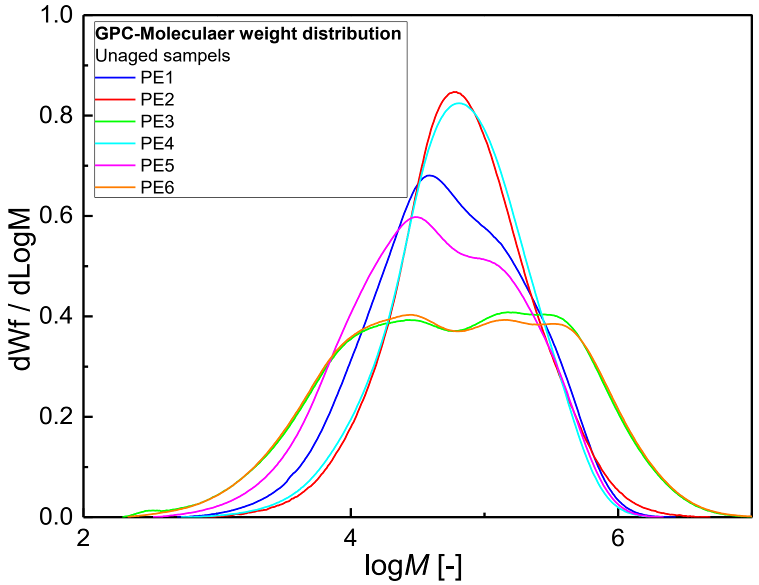


Fig. 3.5: Molecular weight distribution curves of the selected six PE pipe grades [10].

## 3.3 Applied aging and material characterization methods

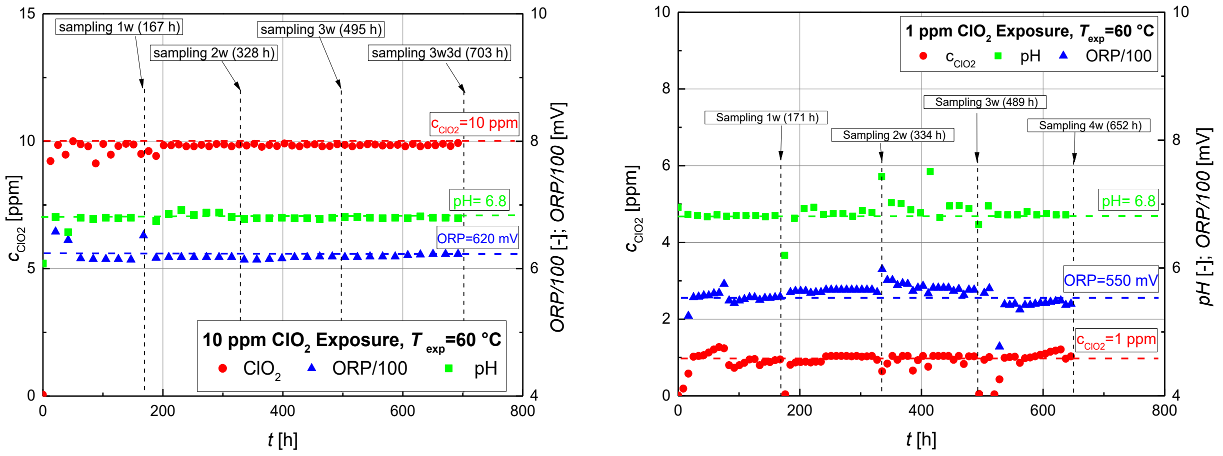
In Table 3.3 the aging experiments conducted are listed, including the exposure conditions, total immersion times and specimen geometries. Before each sample removal, the closed loop system, including the specimens, was flushed through several times with deionized water.

Table 3.3: Aging experiments and testing times ($c_{ClO2}$: controlled disinfectant concentration, $T$: controlled conditioning temperature, *ORP*: measured oxidation-reduction potential, $t$: maximum conditioning time, $d$: specimen thickness) adapted from [10].

| **Experiment** | $c_{ClO2}$ **[ppm]** | $c_{HOCl}$ **[ppm]** | $T$ **[°C]** | ***ORP*** **[mV]** | $t$ **[h]** | $d$ **[mm]** |
|---|---|---|---|---|---|---|
| **1.** | 10 | | 60 | 620-650 | 1038 | 0.3, 1, BCK |
| **2.** | 5 | | 60 | 610-630 | 165 | 0.3 |
| **3.** | 1 | | 60 | 540-590 | 652 | 0.3, 1 |
| **4.** | 1 | | 50 | 570-620 | 452 | 1 |
| **5.** | 1 | | 40 | 520-570 | 1909 | 1 |
| **6.** | 0.5 | | 60 | 560-610 | 514 | 1 |
| **7.** | 0.5 | | 50 | 530-600 | 597 | 1 |
| **8.** | | 100 | 60 | 900-950 | 3218 | 0.3, 1, BCK |
| **9.** | 0 | 0 | 60 | 150-300 | 1909 | 1 |

As control experiments, 1 mm tensile samples were immersed in distilled water without disinfectants, applying closed glass bottles at a temperature of 60 °C. In spite of the lower ORP value of the $ClO_2$ aging experiments compared to the immersion test in HOCl (Experiment 8), an overall faster material aging was observed in $ClO_2$. The significant ORP difference of the two disinfectants is probably related to the different chlorine chemistry of aqueous $ClO_2$ and HOCl solutions [5, 11–15]. In the case of $ClO_2$, several reaction products such as chlorite ($ClO_2^-$), chlorate ($ClO_3^-$), chloride ($Cl^-$) and further ionic products may be present, which could influence the ORP reading. Moreover, temperature, pH controlling solutions and ionic strength play an important role in the ORP readings, as it was previously discussed in 2.2.

In the literature overview chapter, the importance of controlled and constant aging parameters was discussed exhaustively. The evolution of the concentration, pH and ORP values over the aging time for two $ClO_2$ and one HOCl immersion tests are shown in Fig. 3.6 and Fig. 3.7. The concentration of $ClO_2$ was well-controlled and kept constant in case of high, 10 ppm and also at low, 1 ppm of $ClO_2$. The pH and ORP values were also stable over the aging time, displaying considerable deviations only by the restart of the exposure after sample removal. In Fig. 3.7, the aging parameters of the 100 ppm HOCl aging experiment are plotted over the immersion time. Similar to the $ClO_2$ immersion test, constant aging parameters with a very low deviation from the preset conditioning values were recorded, which represents well the potential of the device for stable conditioning experiments in disinfected water. The evolution of aging parameters of Experiments 2 and 5 are shown in Fig. 3.8. Concentrations over the immersion time of Experiments 4, 6 and 7 are discussed later.



(a) (b)

Fig. 3.6. Exposure parameters over the aging time with a concentration of (a), Experiment 1, 10 ppm [3] and (b), Experiment 3, 1 ppm $ClO_2$ at 60 °C, adapted from [1], [2].

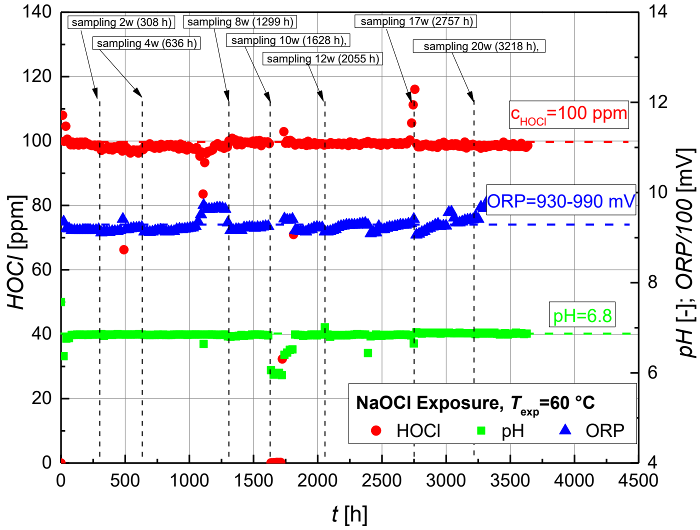
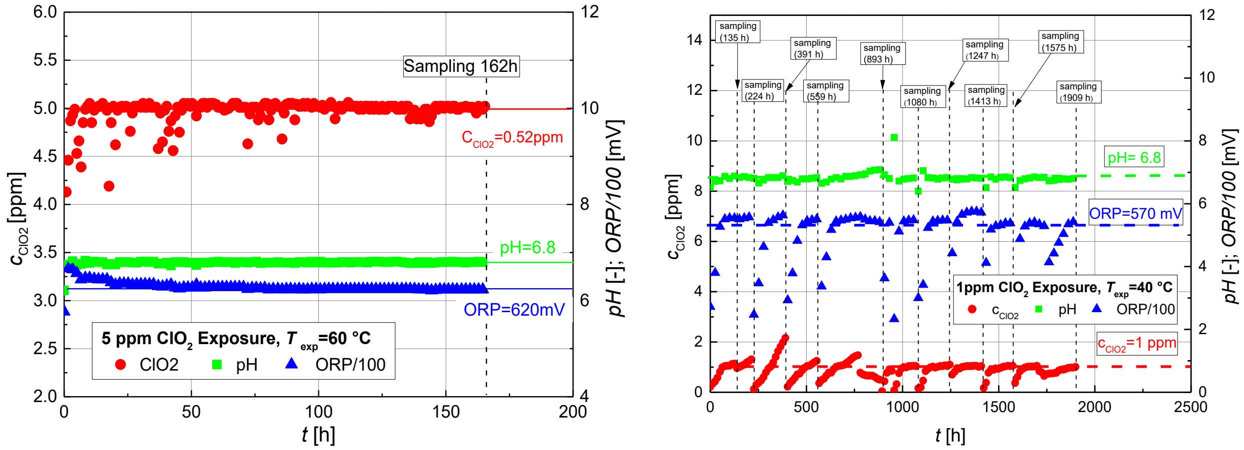


Fig. 3.7: Exposure parameters over the aging time of PE immersed in HOCl, Experiment 8.

Mechanical tests were carried out with a tensile test machine of the type Z001 (Zwick/Roell GmbH & Co. KG, Germany), equipped with a 1 kN load cell. The determination of stress-strain curves was conducted at ambient temperature with a speed of 50 mm/min, completing at least three tests for each material. Characterization of the surface morphology was carried out with scanning electron microscopy (SEM) of the type TESCAN VEGA II (Elektronen-Optik-Service GmbH, Germany). The device was equipped with Energy Dispersive X-ray detector (EDX), which allowed the analysis of elements and their distribution. The samples were subjected to oxidation tests with a differential scanning calorimeter (DSC) of the type DSC 4000 (Perkin Elmer GmbH, Germany). In order to measure their oxidation onset temperature (*OOT*), cross-sections of 1 mm thick samples and films cut from BCK specimens were continuously heated up from 25 °C to 300 °C with a heating rate of 20 K/min in synthetic air atmosphere until they reached the onset of the oxidation. The calculation of the *OOT* was carried out by the shifting the baseline by 0.2 mW [16]. The oxidation induction times (*OIT*) were also determined, to confirm the correlation between *OOT* and *OIT* [17, 18] in case of aging in $ClO_2$ solution. The measurements were carried out with a DSC 1 (Mettler Toledo GmbH, Germany) in accordance with ISO 11357-6:2008 [19] at 220 °C. With each sample, at least three oxidation measurements were performed. To characterize potential changes in the chemical structure during the exposure time FTIR spectroscopy measurements were completed with a device of the type Spektrum GX (Perkin Elmer, Germany). The spectrums were recorded in ATR mode with a resolution of 4 $cm^{-1}$. The 50 µm thin films were measured always on upper side (see Fig. 3.4). The carbonyl index (*CI*) was calculated based on the area ratio between wavenumbers of 1850-1650 and 1396-1330 $cm^{-1}$.



(a) (b)

Fig. 3.8: Aging parameters over the Experiment 2 (a) and Experiment 5 (b).

Mechanical tests were carried out with a tensile test machine of the type Z001 (Zwick/Roell GmbH & Co. KG, Germany), equipped with a 1 kN load cell. The determination of stress-strain curves was conducted at ambient temperature with a speed of 50 mm/min, completing at least three tests for each material. Characterization of the surface morphology was carried out with scanning electron microscopy (SEM) of the type TESCAN VEGA II (Elektronen-Optik-Service GmbH, Germany). The device was equipped with Energy Dispersive X-ray detector (EDX), which allowed the analysis of elements and their distribution. The samples were subjected to oxidation tests with a differential scanning calorimeter (DSC) of the type DSC 4000 (Perkin Elmer GmbH, Germany). In order to measure their oxidation onset temperature (*OOT*), cross-sections of 1 mm thick samples and films cut from BCK specimens were continuously heated up from 25 °C to 300 °C with a heating rate of 20 K/min in synthetic air atmosphere until they reached the onset of the oxidation. The calculation of the *OOT* was carried out by the shifting the baseline by 0.2 mW [16]. The oxidation induction times (*OIT*) were also determined, to confirm the correlation between *OOT* and *OIT* [17, 18] in case of aging in $ClO_2$ solution. The measurements were carried out with a DSC 1 (Mettler Toledo GmbH, Germany) in accordance with ISO 11357-6:2008 [19] at 220 °C. With each sample, at least three oxidation measurements were performed. To characterize potential changes in the chemical structure during the exposure time FTIR spectroscopy measurements were completed with a device of the type Spektrum GX (Perkin Elmer, Germany). The spectrums were recorded in ATR mode with a resolution of 4 $cm^{-1}$. The 50 µm thin films were measured always on upper side (see Fig. 3.4). The carbonyl index (*CI*) was calculated based on the area ratio between wavenumbers of 1850-1650 and 1396-1330 $cm^{-1}$.

The polymer molecular weight and distribution was characterized by high temperature triple detector gel permeation chromatography (3D-HTGPC). The chromatographic system consisted of a 'PolymerChar HT-GPC-IR' high temperature chromatograph, equipped with a 'Precision Detectors' (Amherst, MA) 2-angle laser light scattering detector, Model 2040, and a 4-capillary differential viscometer detector, from PolymerChar. The 15° angle of the light scattering detector was used for the experiments. Concentration was measured by using the PolymerChar IR4 InfraRed detector in the PolymerChar HT-GPC-IR. The system was equipped with a (HPLC-) pump and on-line solvent degassing device from PolymerChar/Agilent. The solvent used was 1,2,4 TriChloroBenzene. The samples were prepared at a concentration of 1.5 g/L of polymer in approx. 8 milliliters of solvent. The solvent used to prepare the samples contained 200 ppm of butylated hydroxytoluene (BHT). The samples were dissolved for 60 min. in a carousel compartment operated at 160 °C, and then 200 microliters were injected on to the columns. The flow rate was 1.0 milliliter/minute. The column set consisted of four Agilent PLgel Mixed-A, 20 µm particle columns: Length/I.D.: 300 x 7.5 mm. The columns were operated at 145 °C. Calibration of the GPC column set was performed with narrow molecular weight distribution polystyrene standards (Easical GPC/SEC Calibration Standards) purchased from Agilent. The calibration of the detectors was performed in a manner traceable to NBS 1475 using an in-house linear polyethylene homopolymer with databook number 53494-38-4. The viscometer detector was calibrated based on an intrinsic viscosity value of 1.01 deciliters/gram, and the light scattering detector was calibrated based on a molecular weight of 96,000 Daltons. Data reduction and sample calculations were done with GPC-One software, obtained from PolymerChar and integrated macros made by Dow.

## 3.4 References

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# PART II – OPTIMIZATION OF AGING CONDITIONS AND DEGRADATION MECHANISMS IN CLO$_2$ AND HOCL SOLUTIONS

# 4 Optimization of exposure conditions in $ClO_2$ and HOCl solution

In this chapter, the optimization of immersion conditions and specimen geometry for $ClO_2$ and HOCl media exposure will be discussed. It is necessary to identify aging parameters which provide sufficient data to observe the aging process and the changes in various material properties over the exposure time. Moreover, the changes in various properties over exposure time support a deeper understanding of the relevant aging mechanism and consequently the screening of various PE pipe grades´ performance in disinfected solutions.

Due to numerous advantages, polymer pipes have become an obvious choice for the transportation of potable water [1, 2]. To ensure high quality of drinking water and inactivate all pathogenic microorganisms, $ClO_2$ and HOCl as secondary disinfectants [3–6] are applied more and more frequently. With the widespread application of PE pipes and chlorine based oxidizing agents, the effect of $ClO_2$ and HOCl on the aging mechanism and long-term performance arise as essential questions. However, before examining these questions optimization of exposure conditions and sample geometry were performed in order to gain reliable data. The importance of the stable aging conditions was thoroughly discussed in Chapter 2. Considering the published results, the reason for contradicting findings is not only the various aging parameters, but also different sample preparations. In fact, the effect of different morphologies and material properties cannot be ignored especially in the case of strong surface oxidative aging. For example, injection and compression molded specimens will have a different overall resistance to the surface oxidative disinfectants. Several field case [7–10] and laboratory aging [11–15] studies have concluded that the effect of disinfectants is limited to a thin surface layer.

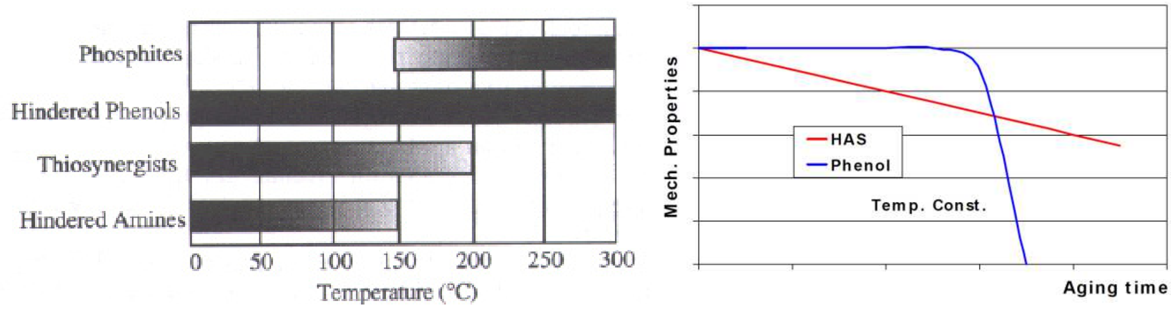
In relevant publications, the effect of various aging conditions on the aging characteristic of polymer pipe grades has not been thoroughly and systematically investigated. Nonetheless, several authors point out that increased disinfectant concentration leads to faster material degradation. An increased HOCl content [13, 14, 16–18] resulted in an overall faster surface embrittlement and AO loss as well as earlier appearance of degradation products. Lundbäck et al. [19] pointed out that increasing HOCl concentration from 0.1 to 1 ppm has a higher effect on the material degradation rate than raising the HOCl content from 1 to 10 ppm (Section 2.2.2). Moreover, the importance of surface to volume ratio [20], alkalinity [21], and pH [22] have been studied extensively. As it is discussed above, $ClO_2$ is less sensitive to pH changes in the range of 2-10 pH [23] than HOCl. Most scientific reports addressing the effect of $ClO_2$ use only one concentration, without examining the impact of different $ClO_2$ content on the polymer degradation process. Nevertheless, increased $ClO_2$ concentration up to 100 ppm [15] resulted in a faster and more pronounced AO consumption in the superficial surface layer. Since only limited information is available in literature about aging conditions in $ClO_2$, this chapter focuses mostly on the optimization of aging conditions in $ClO_2$. Considerable variation in the applied exposure parameters, such as temperature, concentration, pH etc., highly limits the comparability of published studies. Thus, this chapter aims to provide comparable material properties over various aging times and conditions. Certain paragraphs have been quoted verbatim from Bredács et al. [49], and results described in Section 4.3 have been published in Bredács et al. [49].

## 4.1 Background: Thermal analysis of antioxidants

In order to protect the PE materials from undesired oxidative degradation primary and secondary AO molecules are added to these products [24]. While primary AO are radical scavengers used for preventing the polymer chain oxidation during the processing, secondary AO molecules are responsible for the long-term material performance during the service time of a certain product. However, several studies have been dedicated to this matter, so this section provides a short overview of the thermal stability characterization of PE.

To assess the thermal stability of PE, most widely *OIT* analysis are used, which is described thoroughly in ASTM D3895 [25]. The early work of Gugugumus [26] implies that the concentration of phenolic AO can be measured by *OIT*, which was confirmed by the findings of Epacher et al. [27]. Similar results were published by Hsuan and Koerner [28], demonstrating a proportional relationship between AO concentration and *OIT* in the same PE formulation. Furthermore, it is essential to consider that PE resins have an intrinsic oxidation stability even without phenolic AO molecules [28, 29]. It is worth noting that Dobkowski [30] suggested that the scattering of repeated *OIT* measurements is caused by an inhomogeneous side chain distribution in linear low density PE. This further affirms the importance of the intrinsic oxidation stability of PE grades. Hence, comparing absolute *OIT* values of different non-aged PE materials can be misleading, even though the time to exothermic oxidation is measured at the same temperature. In fact, AO molecules depending on their chemical structure have a wide effective temperature range [31, 32]. As shown in Fig. 4.1 (a), phosphite-based primary AO molecules only react with radicals above 150 °C, while phenolic AO are able to react with hydroperoxides in a much wider temperature range. The comprehensive study of Földes et al. [33–35] draws attention to the possible interaction of different AO molecules in a stabilization system, which can lead to synergetic and antagonistic effects, depending on the temperature. Moreover, partially hindered phenolic AO molecules can associate via hydrogen bonds above 240 °C, resulting in a two-sided effectivity [36]. First, the hydroxyl groups become more available sterically, increasing the effectivity of phenolic AO in the case of lower concentration. Secondly, in higher AO concentration due to less available hydroxyl groups, the effectivity decreases. Additionally, this specific binding energy within molecular associations decreases with decreasing temperatures. This also means that the extrapolation of AO effectivity measured at higher temperatures cannot be extrapolated to lower application relevant temperatures. A comparison of primary and secondary AO mixtures indicates that a synergetic effect, higher effectivity than the sum of two AO, is only possible when specific interaction between the two AO molecules is absent.

Hindered amine light stabilizers (HALS) cannot be measured by means of the *OIT* technique, since at lower temperatures, oxidation can take too long. As shown in Fig. 4.1 (a) HALS molecules are not active at higher temperatures. In certain applications, such as geomembranes, the performance of HALS has to be monitored. To resolve this issue, the high pressure *OIT* (*HP-OIT*) test [37, 38] was developed. Increased oxygen pressure during the *OIT* measurement leads to faster oxidation; thus, this test allows the determination of the AO depletion rate in HALS-containing stabilization packages [39]. The fundamental effect of a stabilization package on the long-term material performance is well represented in Fig. 4.1 (b). In principle, phenolic AO stabilization leads to an abrupt decrease in mechanical properties after a given induction period, as long as HALS antioxidants contribute to a slow gradual decrease [31].



(a) (b)

Fig. 4.1: Effective temperature range of various AO molecules (a) and evolution of mechanical properties over the aging time for HALS and phenolic AO (b) [31, 32].

Nonetheless, monitoring *OIT* during an accelerated aging experiment provides valuable information to assess the thermal and long-term performance of a certain PE and AO stabilization package. Wang et al. [40] in accordance with Epacher at el [27] found that first order reaction kinetics is applicable to describe and calculate *OIT* during PE aging experiments. The hydrogen atom transfer [41] mechanism dominates the oxidation of hindered phenolic AO molecules to quinonidal structures. In other words, these molecules compete with the PE chains for hydroperoxides. In the course of an aging process, AO loss can be caused by several processes, such as evaporation, diffusion, leaching and chemical consumption. Kinetics of this rather complex AO depletion was well described in the work of Richaud [42].

Considering the limitations of the *OIT* test, several publications address and discuss alternative measurements to assess the thermal performance of stabilization packages. Beside thermal gravimetric analysis and chemiluminescence [43], oxidation onset temperature (*OOT*) measurement is a frequently used technique. This test measures the time to oxidation, applying a dynamic and continuous temperature increase in oxygen rich atmosphere. Dörner et al. [44] reported a correlation between the *OIT* and *OOT* values of PE samples aged in air and water. However, *OIT* was found to be more sensitive for residual AO assessment and quality assurance purposes, presenting better differentiation between the depletion rate of various AO packages [45]. Subsequent publications [43, 46, 47] showed that the *OIT* and *OOT* relationship can be described with second degree polynomial regression. Moreover, a high uncertainty of low *OIT* values was reported in an interlaboratory Round Robin test [46], indicating that *OOT* can be advantageous for monitoring fast PE oxidation and AO depletion processes. Applying *OOT* to characterize the AO loss rate, the temperature of complete active AO depletion is a matter of interest, especially considering the intrinsic oxidation stability of PE grades. Dörner et al. [44, 48] reported that PE without phenolic AO shows an *OOT* value in the range of 190 °C and 220 °C, depending on the exact PE molecular structure. This temperature range is most likely determined by the distribution and homogeneity of side chains, as it was discussed earlier. Considering the relevant literature and the experimental data obtained in this work the *OOT* of 210 °C and below will be used as an indication of complete active AO loss in the following part of this dissertation.

## 4.2 Experimental

The PE1 and PE2 pipe grades were selected for accelerated aging in $ClO_2$ and HOCl solution. The properties of the unaged materials are summarized in Table 3.2. The PE2 has a unimodal molecular weight distribution, while the weak shoulder of PE1 at higher molecular weights represents a bimodal distribution (see Fig. 3.5). These two selected PE pipe grades represent well the most commonly used PE materials in piping applications. Tensile specimens with a thickness of 0.3 mm and 1 mm were prepared from compression molded sheets (see Fig. 3.3). According to Experiments 1-5, 8 and 9 (Table 3.3), samples were immersed in $ClO_2$ and HOCl solution. Conditioning parameters over the aging Experiment 4 are shown in Fig. 4.2. The aging parameters of the other experiments are illustrated in Section 3.3. and in Fig. 4.3.

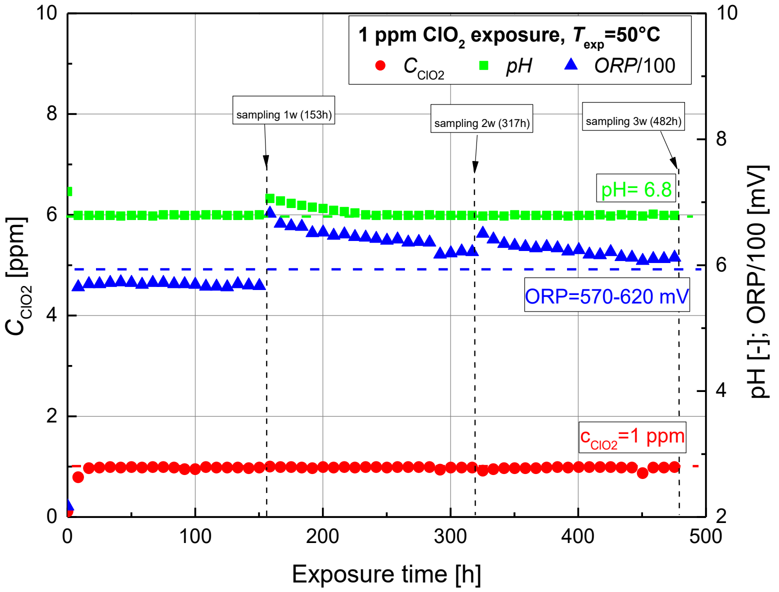
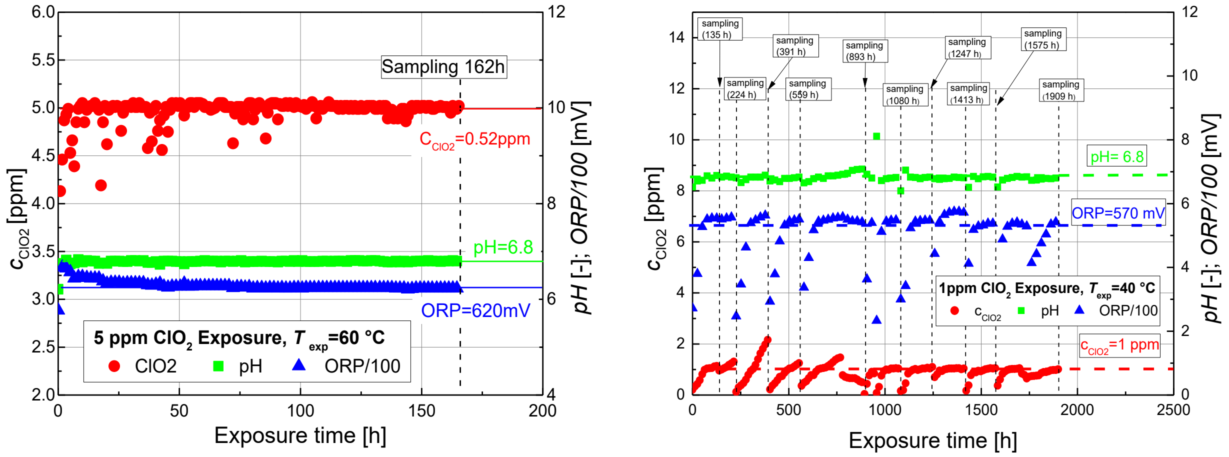


Fig. 4.2: Exposure parameters of aging Experiment 4.



(a) (b)

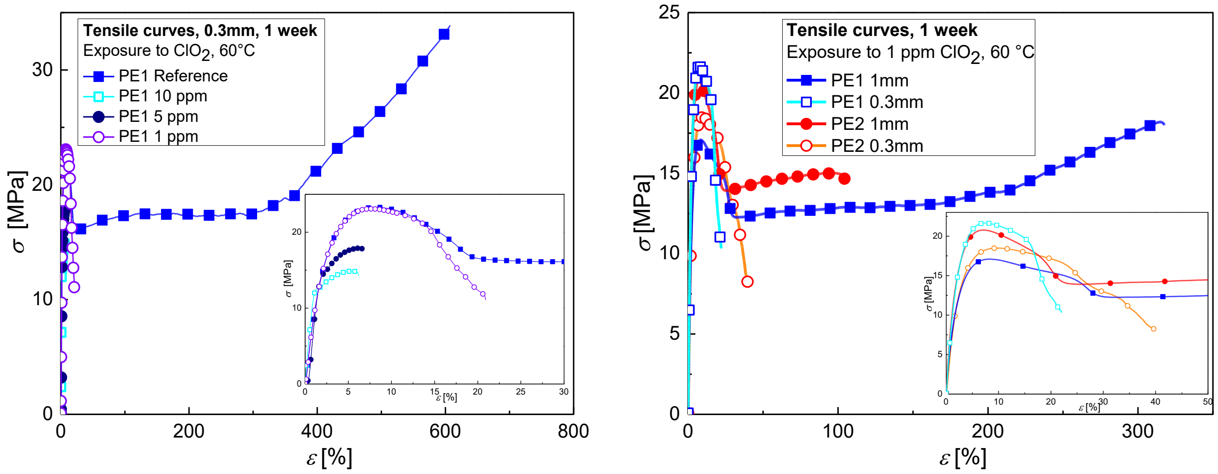
Fig. 4.3: Aging parameters over the Experiment 2 (a) and Experiment 5 (b).

## 4.3 Optimization of exposure conditions and specimen geometry in $ClO_2$

In this part, the effect of temperature, concentration and specimen thickness on the degradation rate of two selected PE grades will be examined. As it is described in Section 1.21.2, objective A will be discussed. Moreover, for the assessment of active AO loss during the aging period, the applicability of *OIT* and *OOT* will be compared. For this purpose, the *OIT* is usually used, but the determination of *OOT* was found to be more advantageous. The benefits of *OOT* will be discussed later. Additionally, the results will be evaluated in terms of aging mechanism and material screening according to objectives B and C.

### 4.3.1 Effect of concentration, temperature and sample thickness

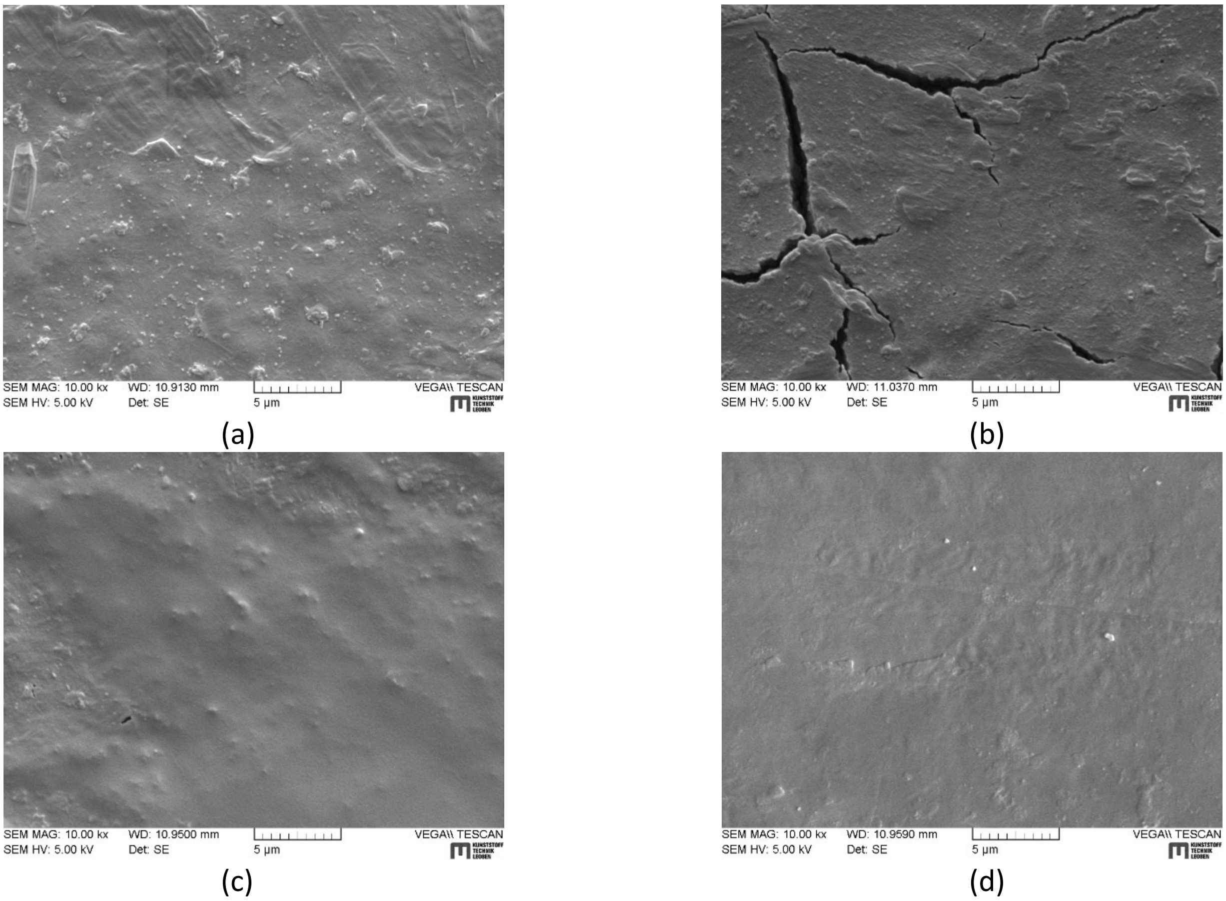
The first aging experiment was conducted with 10 ppm $ClO_2$ containing aqueous medium at 60 °C applying 0.3 mm thin film samples, in order to reach material degradation as fast as possible. Since the elongation at break ($\varepsilon_b$) value of a tensile test is the most sensitive parameter for chemical degradation, this mechanical value is considered as one of the main indicators of material aging and embrittlement. Compared to the unaged sample (reference), strongly decreased elongation at break ($\varepsilon_b$) was already observed after a week of immersion. Hence, for the following experiments, the $ClO_2$ concentration was reduced to 5 and to 1 ppm, sequentially. In Fig. 4.4 (a), the tensile curves of PE1 after aging at 60 °C show a significant reduction of $\varepsilon_b$, confirming an extremely high chemical degradation of the polymer. While the tensile samples after exposure to 10 and 5 ppm broke before the yield point of the reference, the specimens conditioned in 1 ppm of $ClO_2$ solution show some remaining ductility as it passes strain at yield stress until an elongation of about 20 %. The 1 mm tensile specimens show less reduction of $\varepsilon_b$ after immersion in 1 ppm $ClO_2$ for one week than the thinner 0.3 mm samples, as it is illustrated in Fig. 4.4 (b).



(a) (b)

Fig. 4.4: Effect of $ClO_2$ concentration (a) and sample thickness (b) on stress-strain curve after one week of aging at 60 °C adapted from [49].

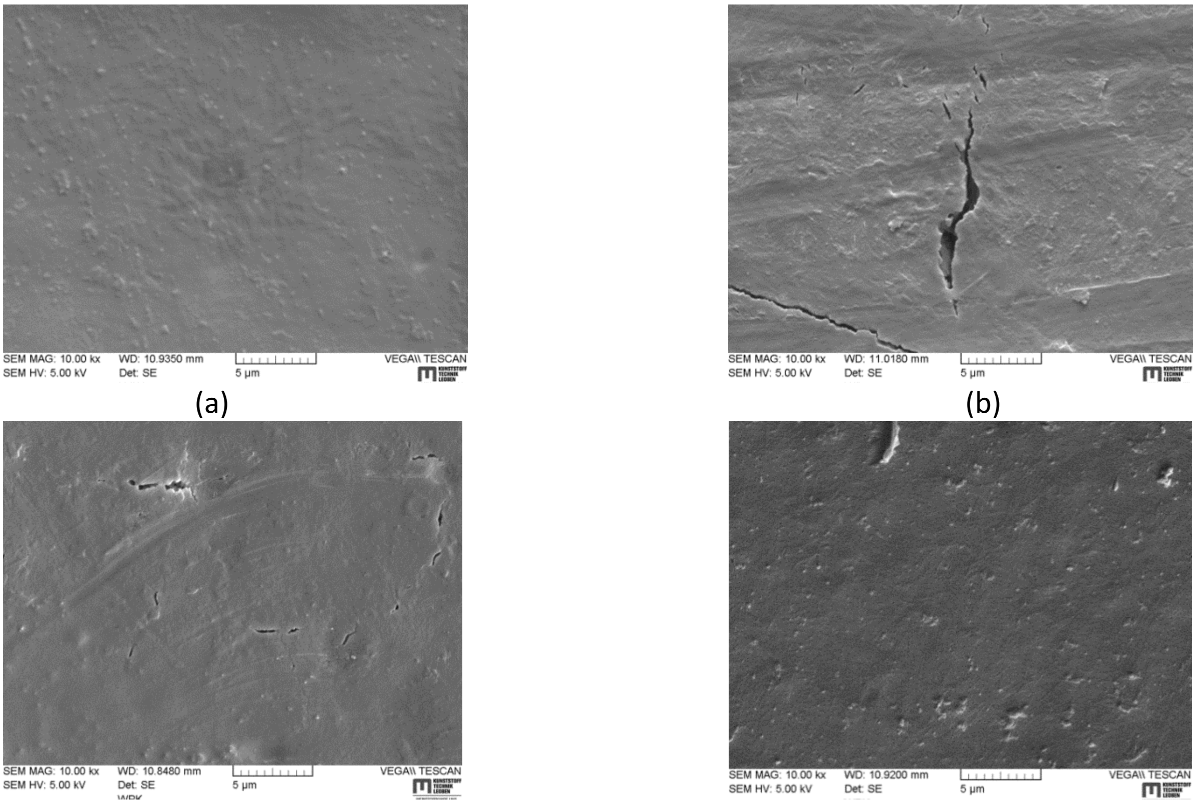
In agreement with the experimental findings [20], samples with lower surface to volume ratio (1 mm thick) should be less affected by aqueous oxidizing agent, since $ClO_2$ only causes an accelerated degradation in a thin surface layer. The SEM surface images of the 0.3 mm thick PE1 tensile test specimens after conditioning for 1 week in 10, 5 and 1 ppm $ClO_2$ at 60 °C are shown in Fig. 4.6. Surface cracks are clearly visible after exposure to 10 and 5 ppm $ClO_2$, highlighting advanced material embrittlement. However, surface cracks were not detected after one week of conditioning in 1 ppm $ClO_2$; strong decline in $\varepsilon_b$ (Fig. 4.4) indicates advanced material embrittlement. Considering that the overall material degradation was found to be too fast for a detailed examination of the aging processes in the 0.3 mm samples, in subsequent experiments only 1 mm thick samples were used. The SEM images of PE2 showed highly similar surface characteristics (see Fig. 4.5).



(a) (b) (c) (d)

Fig. 4.5: SEM surface images of 0.3 mm thin PE2 tensile test specimens unaged (a) and after one week of aging in 10 ppm (b), 5 ppm (c) and 1 ppm (d) $ClO_2$ solution at $T$=60 °C.

To evaluate the effect of different aging temperatures on the material degradation, normalized strain at break values of PE1 and PE2 were plotted against the logarithmic exposure time, as it is illustrated in Fig. 4.7. In the following figures, except in Fig. 4.10, linear lines represent only a visual guide for the eye. The accelerating effect of $ClO_2$ on the PE degradation is quite striking. Specimens immersed in distilled water showed constant $\varepsilon_b$, while the presence of $ClO_2$ resulted in a fast reduction of $\varepsilon_b$. Applying $T$=50 and 60 °C, significantly reduced strain at break values were detected already after the first sample removal from one week of aging. With longer aging times, highly scattered data was observed. Reducing the exposure temperature to $T$=40 °C, a constant $\varepsilon_b$ was found for both materials during the first 400 h of aging. Subsequently, a continuous decrease in $\varepsilon_b$ was recorded with increasing exposure time. Although the reduction of this mechanical property can be well monitored applying 1 ppm of $ClO_2$ at $T$=40 °C, a qualitative material differentiation is uncertain.



(a) (b)

(c) (d)

Fig. 4.6: SEM surface images of 0.3 mm thin PE1 tensile test specimens unaged (a) and after one week of aging in 10 ppm (b), 5 ppm (c) and 1 ppm (d) $ClO_2$ solution at T=60 °C, [49].

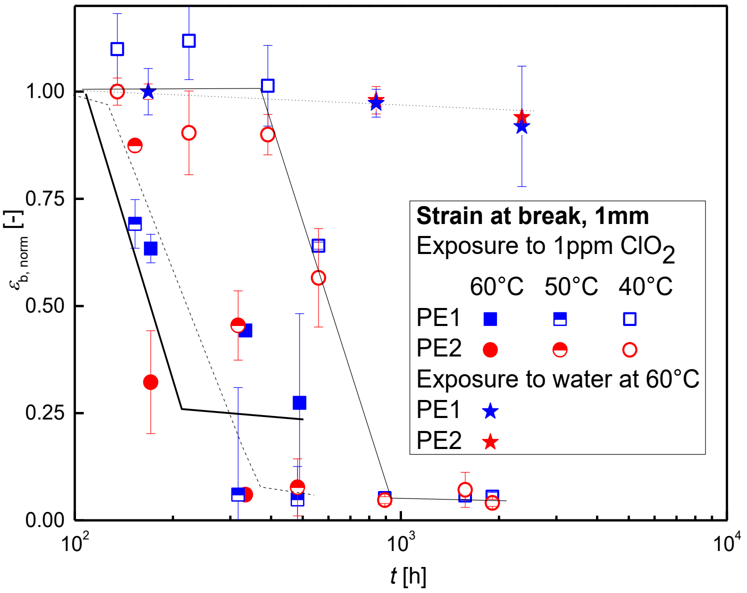
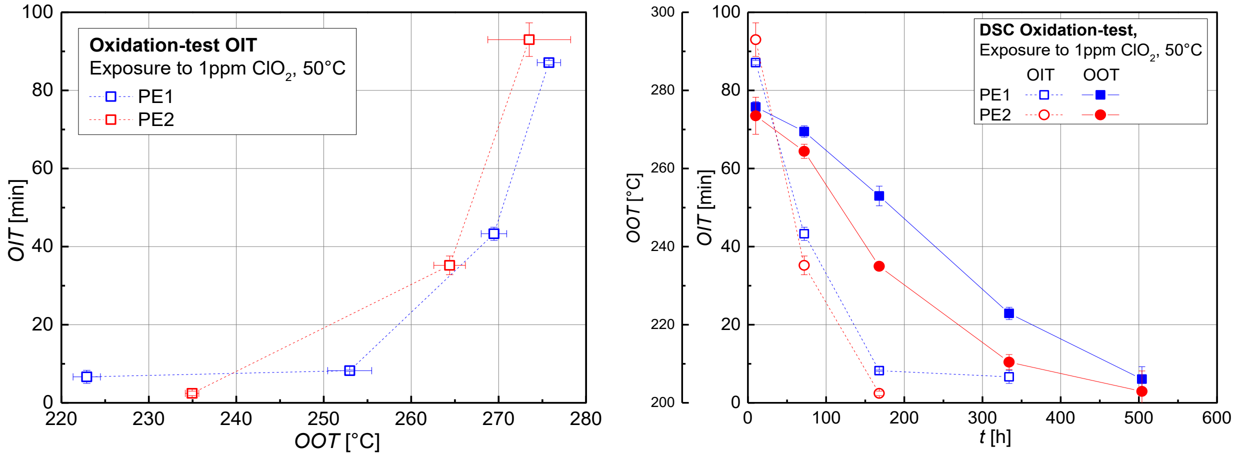


Fig. 4.7: Effect of testing temperature on the normalized strain at break as a function of aging time, adapted from [50–52].

Furthermore, lower exposure temperatures or concentrations could be advantageous in order to study the aging process of PE materials in $ClO_2$ and to differentiate between the performances of various material formulations.

### 4.3.2 Antioxidant consumption and material aging

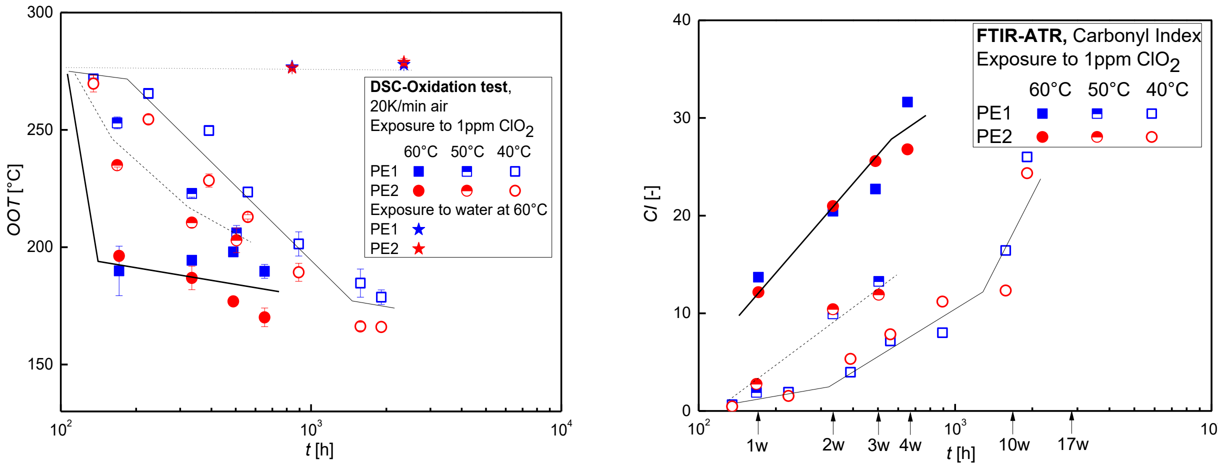
In case of highly accelerated aging experiments, the measurement of *OIT* monitoring the loss of active AO has some disadvantages. On the one hand, choosing a constant testing temperature which delivers *OIT* times between 100 min and 60 min for unaged reference samples can be too high for aged samples. On the other hand, a much lower temperature for *OIT* tests could result in huge differences between the unaged and aged samples. Moreover, the differentiation between very short *OIT* values of aged samples can be difficult. Thus, oxidation onset temperature (*OOT*) tests were carried out, which resulted in a better resolution of the oxidative resistance of aged samples over exposure time. Nevertheless, ensuring the relationship between *OIT* and *OOT* and confirming the advantages of *OOT* over *OIT* for aging experiments in strongly oxidative media, both measurements were performed in case of 1 ppm $ClO_2$ conditioning at 50 °C. In Fig. 4.8 (a), an exponential relationship between *OOT* and *OIT* can be seen, which is in accordance with findings of other studies [46, 47]. Monitoring *OOT* during immersion tests in disinfected solutions seems to be more sensitive to AO depletion than *OIT* as it is displayed in Fig. 4.8 (b). A further advantage of applying *OOT* instead of *OIT* is the significantly shorter testing time.



(a) (b)

Fig. 4.8: Correlation between *OOT* and OIT (a), and a comparison of the *OOT* and OIT evolution over exposure time (b) [49].

Values of *OOT*<210 °C are assumed to demonstrate the complete inactivation of stabilizer molecules (Fig. 4.9 (a)). Similar to the tensile test results, oxidation tests showed no change for samples immersed in distilled water, so the effect of $ClO_2$ can be easily recognized. At an aging temperature of *T*=60 °C, both samples already showed very low *OOT* after the first sampling, indicating advanced active AO depletion. At lower aging temperatures (*T*=50, 40 °C), the chemical consumption of AO increased continuously with longer sampling intervals. Although higher aging temperatures resulted in faster AO loss, a significant difference between the thermal stability of the two PE grades cannot be identified. A parallel loss of active AO and the reduction of normalized strain at break (Fig. 4.7) indicate that $ClO_2$ or its derivatives are able to attack the AO and the polymer molecules simultaneously too, similar to the conclusion drawn by Colin et al. [53]. However, $ClO_2$ is not reactive enough to subtract hydrogen atoms from the polymer backbone [23, 54]. Based on the physical and chemical properties of $ClO_2$, a theoretical explanation can be formed to overcome this apparent contradiction. When $ClO_2$ enters water, it stays as an undissociated dissolved gas [23, 55, 56]. Moreover, it is a thermodynamically unstable radical [56] in aqueous solutions, but $ClO_2$ could persist for longer time periods due to a special electron structure. Reactions of $ClO_2$ in water with other molecules will result in mostly ionic products (see 2.1.1). These ions are unlikely to diffuse into the bulk since their hydrate shell can hinder this process sterically. In fact, diffusion and reaction with chain defects of $ClO_2$ molecules in deeper material seems to be probable. To explain the material degradation in deeper layers, Yu et al. [57, 58] suggested chlorine monoxide (ClO*) radicals as the reactive species towards the polymer formed by the reaction of AO and $ClO_2$. Hassinen and Jacobson [59] proposed that $ClO_2$ could form peroxy radicals (ROO*) from hydroperoxides, consequently reducing the initiation time of radical chain scission. Both hypotheses assume diffusion of $ClO_2$ into the polymer matrix in accordance with above assumption. The seemingly random appearance of surface cracks (see Fig. 4.6) might be the result of a locally suppressed $ClO_2$ diffusion. The crystalline phase is impermeable, hence higher crystallinity ratio could be advantageous to decrease the effect of $ClO_2$ on the aging process. A higher degree of crystallinity of PE1 could be the reason for the slightly slower loss of active AO compared to PE2 (see Fig. 4.9). However, several other properties such as the change in crystallinity ratio, density, molecular weight and its distribution may also play a significant role in the overall resistance of PE against $ClO_2$. These properties will be discussed later. As an indication of the amount of thermo-oxidative degradation products, *CI* was determined and plotted against the aging time for each exposure program. In Fig. 4.9 (b), the effect of aging temperature on the development of *CI* is shown for both materials. At *T*=60°C, the increment of *CI* was found to be faster than at 50 and 40 °C.

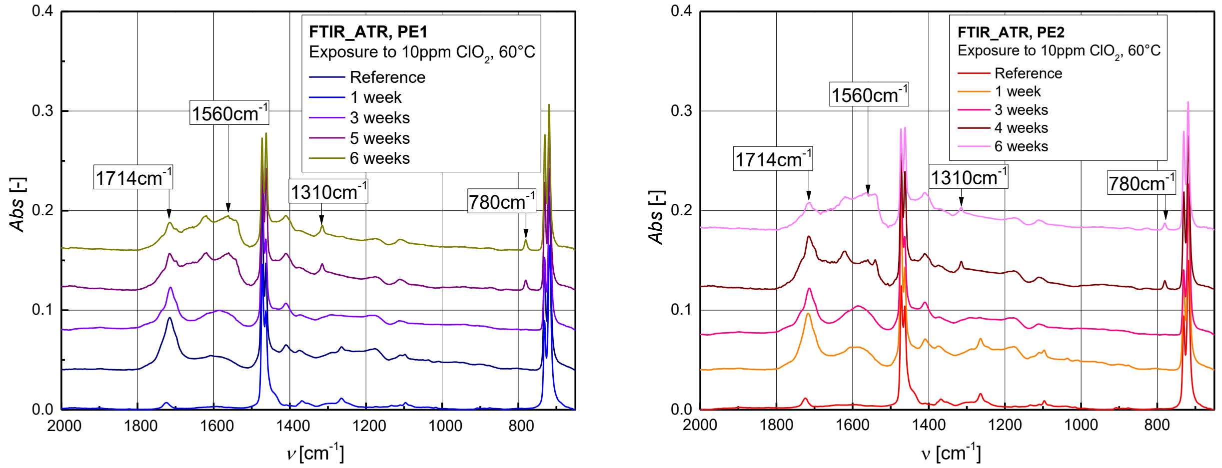


(a) (b)

Fig. 4.9: Effect of aging temperature on the evolution of *OOT* (a) and CI (b) of PE samples exposed to 1 ppm $ClO_2$ solution, adapted from [50–52].

In fact, at the lowest temperature, increased *CI* were detected after only 3 weeks of exposure, whereas aging at 60 °C resulted in strongly raised *CI* values already after one week of aging. Comparing PE1 and PE2, both materials show similar characteristics in the development of *CI* throughout all 1 ppm $ClO_2$ immersion tests, presenting an identical change in chemical structure caused by $ClO_2$.

Exposure of 1 mm thick samples to 10 ppm $ClO_2$ was further continued up to 6 weeks to monitor the changes in the chemical structure. Besides a gradual increase in the carbonyl peak (Fig. 4.10) at 1714 $cm^{-1}$, both materials showed new peaks around 1600 $cm^{-1}$. Signals of 1560, 1540, 1400 and 1310 $cm^{-1}$ are attributed to carboxyl functional groups derived from the degradation products of phenolic AO. After 5 weeks of aging, a new peak appeared at 780 $cm^{-1}$, indicating carbon-chlorine bonds. The appearance of this signal presumably demonstrates the degradation products of phenolic AO, since the reaction of $ClO_2$ and phenol could yield chlorinated products [56, 60–62]. Yu et al. [11] reported similar FTIR results after reacting $ClO_2$ with various AO types, concluding that chlorinated AO degradation products are formed.



(a) (b)

Fig. 4.10: FTIR spectrums of 1 mm thick PE1 (a), and PE2 (b) exposed to 10 ppm $ClO_2$ at 60 °C up to 6 weeks [49].

## 4.4 Optimization of specimen geometry for aging in HOCl solution

The SEM surface images taken after different aging times in 100 ppm HOCl of 0.3 mm thick PE1 samples are shown in Fig. 4.11. In contrast with $ClO_2$-caused surface cracks (see Fig. 4.6), the presence of HOCl led to voids, cavities and an overall porous-like surface. In other words, the HOCl solution caused etched-like, rough surface characteristics. This surface transformation became more obvious with increasing exposure time in HOCl solution. Similar surface characteristics were observed for PE2 and also for 1 mm thick specimens (see Fig. 4.12). In some cases, small surface cracks were also found after advance deterioration of the material. With longer aging times, these cracks and voids most likely support the formation of macro-cracks under mechanical loading of pipe samples, as it is reported in field case [9, 63] and laboratory studies [64, 65]. Nevertheless, the SEM images in Fig. 4.6 and in Fig. 4.11 point out both the different aging mechanism caused by HOCl and $ClO_2$ and the strong surface oxidative nature of disinfectants.

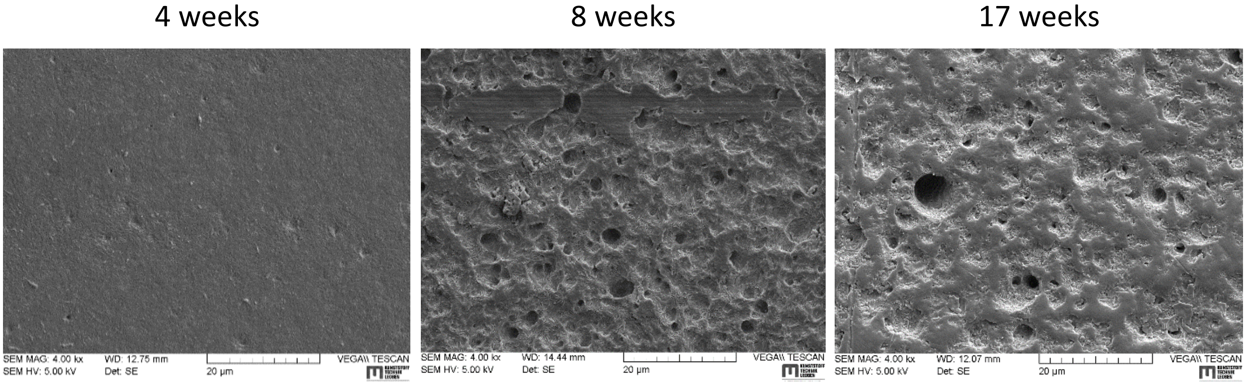


Fig. 4.11: SEM surface images 0.3 mm thick PE1 specimens after different aging times in 100 ppm HOCl at 60 °C, adapted from [66].

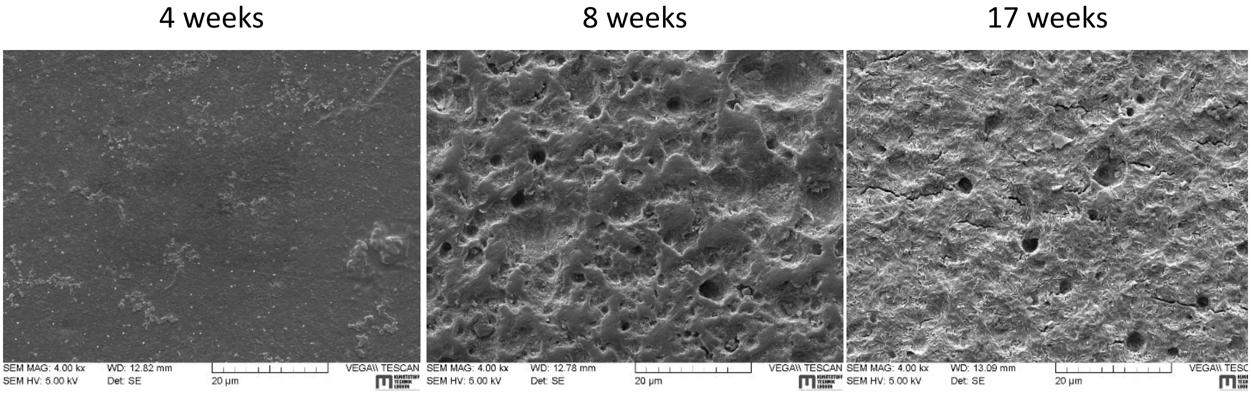
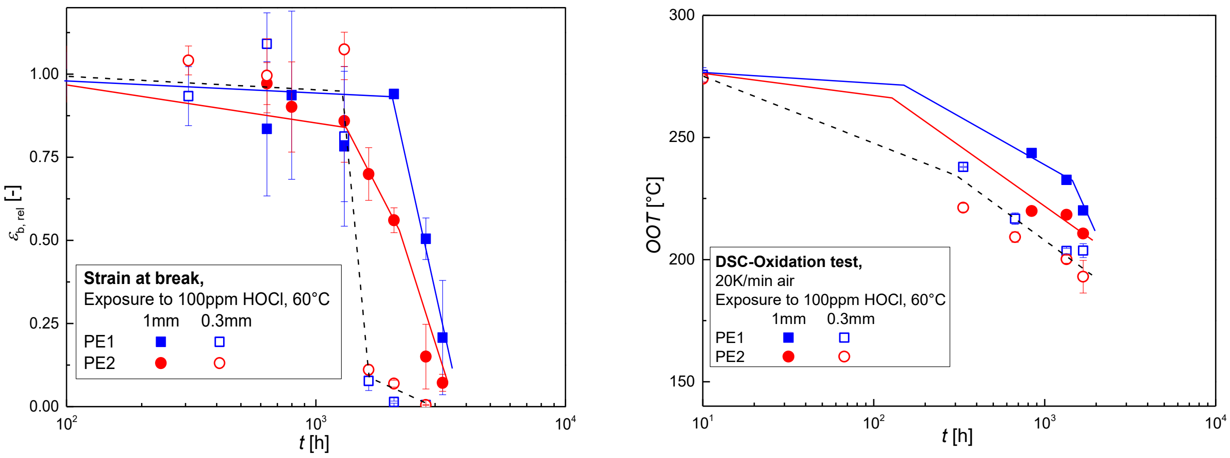


Fig. 4.12: SEM surface images 0.3 mm thick PE2 specimens after different aging times in 100 ppm HOCl at 60 °C.

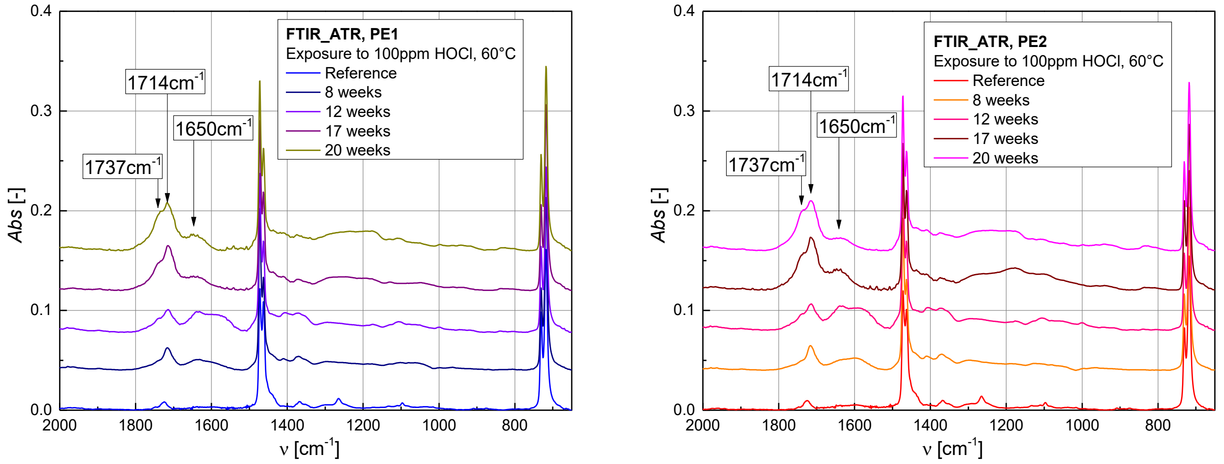
The $\varepsilon_b$ values showed a strong reduction for 0.3 mm thick specimens after a shorter aging time than the thicker samples, as it is illustrated in Fig. 4.13 (a). The longer aging time to embrittlement of 1 mm samples can be explained by a lower S/V ratio, confirming the assumed predominant surface aging characteristics. A further noteworthy difference is that while the 0.3 mm samples of PE1 and PE2 showed the same performance, the $\varepsilon_b$ decrease of the 1 mm thick PE1 samples took place after a longer aging time than PE2. This slight difference in the performance of the two materials can also be seen in Fig. 4.13 (b). In accordance with the tensile test results, thinner samples of both materials displays faster consumption of active AO than the 1 mm thick specimens. In spite of the longer aging time, a slightly slower *OOT* decrease was detected for PE1. In order to differentiate between various PE grades based on their mechanical and thermal stability by immersion tests, 1 mm thick specimens seem to be superior over thinner 0.3 mm specimens regardless of the longer aging time. Generally, the slower the degradation process the higher the chance to record different performances of various materials, which will be elaborately discussed later in Chapter 7 for the $ClO_2$ immersion tests.



(a) (b)

Fig. 4.13: Normalized strain at break values (a) and *OOT* (b) plotted over the aging time of PE1 and PE2 after exposure to 100 ppm HOCl at 60 °C.

The FTIR spectra of PE1 and PE2, shown in Fig. 4.14, display well a gradual evolution of degradation products caused by accelerated aging. In agreement with the recent work of Abdelaal and Rowe [67] new peaks at 1737, 1714 and 1650 $cm^{-1}$ can be related to the presence of ester, ketone and aldehyde functional groups, respectively. In spite of the increasing intensity of the degradation peaks with increasing aging time, a clear difference between the aging behaviors of the two materials has not been found. Since the ATR measurement technique is limited to approximately 10 µm thick surface layer, a comparison of 0.3 mm and 1 mm thick samples is unnecessary.



(a) (b)

Fig. 4.14: FTIR spectrum of 1 mm thick PE1 (a), and PE2 (b) exposed to 100 ppm HOCl at 60 °C up to 20 weeks of aging time.

## 4.5 Summary and conclusion

The effects of various $ClO_2$ concentrations and conditioning temperatures on the degradation behavior of two PE materials have been investigated. In order to optimize the conditioning and specimen configuration comprehensive systematical studies with two PE materials were performed. Specimens with a thickness of 0.3 mm showed advanced aging and material embrittlement by surface cracks and reduced strain at break, even after 1 week of exposure to 10 ppm $ClO_2$ at $T$=60 °C. In spite of the significant reduction of strain at break, the SEM images of 0.3 mm specimens aged in 1 ppm $ClO_2$ displayed no signs of surface degradation after one week of exposure. This finding points out that material degradation is initiated prior to microscopically detectable surface degradation. Applying *OOT* values for the analysis of AO consumption was found to be more efficient and less time consuming than *OIT* measurements.

Since $ClO_2$ mainly accelerates the surface degradation, samples with a lower surface to volume ratio revealed slower aging. The use of 1 mm thick specimens resulted in slower aging than the 0.3 mm specimens. Exposure to 1 ppm of $ClO_2$ solution at 50 °C or in less aggressive medium provides reasonable results for the interpretation of the aging characteristics of PE pipe grades.

The simultaneous reduction of $\varepsilon_b$ and *OOT* indicates that $ClO_2$ or its derivatives can react at the same time with the AO and the polymer. Most likely, $ClO_2$ gas can diffuse into the polymer, causing enhanced AO consumption. The reaction of $ClO_2$ with AO molecules probably generates radicals which are able to react with the polymer and consequently accelerate the radical chain scission. Additionally, chain defects, e.g. double bonds, could further facilitate the attack of $ClO_2$ on the polymer molecules. The FTIR signals of carbon-chlorine bonds are assumed to correspond to the AO degradation products formed by the reaction with $ClO_2$.

The results presented in this dissertation show that providing constant $ClO_2$ concentrations, a relatively high acceleration of PE degradation can be achieved within a few days of immersion. On the other hand, it was demonstrated that thin film specimens are not fully suitable for the characterization of potentially different aging resistance, as effects created on the specimen surfaces are too similar under the given, aggressive media conditions. It can be concluded that thicker specimens may be more suitable in order to investigate not only surface degradation, but also diffusion effects from the surface into the bulk material.

Immersion in HOCl solution showed that when applying 1 mm thick specimens, different mechanical and thermal performances of the two PE grades can be recognized more easily. Beside the obviously longer aging times to reach material embrittlement in HOCl than in $ClO_2$, the SEM and FTIR results indicate a different aging mechanism caused by the two disinfectants. The following part of this dissertation will focus on these differences and attempts to provide the aging mechanism of PE pipe grades in both media.

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# 5 Aging mechanism of PE pipe grades in chlorine dioxide and hypochlorite

In heterogeneous systems, where the reaction partners are in two physical states, such as solid (PE resin), and liquid (disinfectant solution), the reaction is usually controlled by mass transport. The governing reaction will be either the diffusion of the reactive molecules (AO) from the PE matrix to the surface or the diffusion of the reactive species (disinfectants) from the liquid phase to the contact surface and into the solid phase. The experimental findings of Gedde et al. and Smith et al. [1, 2] showed that at ambient temperature, the physical loss of AO molecules by diffusion is negligible in short-term laboratory exposure. Therefore, the diffusion speed of the disinfectant molecules to the contact surface and into the PE matrix can be safely defined as the rate-determining step. Several researchers have claimed that disinfectants cause an accelerated degradation up to 1 mm of distance from the surface, based on laboratory exposure and field case studies of premature pipe failures [3–8]. In accordance with these studies, previous work has revealed that only a few hundred microns thick surface layer is degraded by accelerated aging experiments [9, 10]. These results further verify the diffusion controlled aging process of PE. However, the different physical and chemical properties of HOCl and $ClO_2$ in aqueous solutions could lead to two distinct aging mechanisms of PE. In fact, in HOCl, mostly molecules and ions in a hydrate shell are present, while in the case of $ClO_2$ dissolved $ClO_2$ gas molecules can be expected as a reactive species. Considering the different reactive molecules of the two disinfectants, different PE degradation mechanisms for each oxidizing agent can be assumed.

This chapter aims to identify and describe the characteristics of PE degradation caused by $ClO_2$ and HOCl disinfectants. The overall objective is to fulfill objective B, as it is defined in Section 1.2. Knowledge and understanding of different aging mechanisms in $ClO_2$ and HOCl would be highly beneficial to further develop PE pipe grades and AO packages. Although the results of HOCl and $ClO_2$ concerning the aging experiments are discussed separately, the main differences are summarized.

## 5.1 Experimental

The PE1, PE2 and PE3 materials were selected to investigate the degradation process of pipe grades in contact with $ClO_2$ and HOCl solutions. Grade PE2 has the lowest density of $\rho=0.932$ g/cm$^3$, while the density of PE1 and PE3 were measured at $\rho=0.938$ and $\rho=0.945$ g/cm$^3$, respectively. The different properties of PE grades are shown in Table 3.2. Furthermore, diverse modalities, presented in Fig. 3.5, may promote the observation of different aging mechanisms in HOCl and $ClO_2$ as well as the determination of various PE performances. Tensile specimen with a thickness of 0.3 and 1 mm, as well as BCK specimens, were subjected to immersion tests according to Experiments 1, 5 and 8 (see Table 3.3). Since the usage of 0.3 mm thick specimens was found to be disadvantageous (see 4.3.1) with regard to $ClO_2$ aging, only micro-tensile samples were immersed in HOCl. Both the BCK and the 1 mm thick specimens were exposed to $ClO_2$ and HOCl solutions. To reach severe material degradation in the immediate surface layer, which is assumed to represent the superficial inner pipe layer during long-term operation, Experiments 1 and 8 were performed. Since fast material embrittlement prevents detailed observation of the degradation process, the results of Experiment 5 are also included. In order to precisely detect material aging over the exposure time, various material characterization techniques, including SEM, SEM-EDX, tensile test, *OOT* and FTIR-ATR measurements and GPC analyses were applied. These methods are described in 3.3. From the SHT samples 1 mm thick small disks were punched out and sections of the 50 µm thick films were prepared for the *OOT* analysis.

## 5.2 Aging mechanism of PE in contact with chlorine dioxide

Since $ClO_2$ does not dissociate in dilute aqueous solution but remains a dissolved gas, diffusion of these molecules into the PE resin can be expected. Previous reports, as it is summarized in 2.6.1, point out that radicals formed in the aqueous phase are way too reactive to reach deeper layers, so their effect is strongly limited to the immediate contact surface. However, radicals which are formed by reactions between $ClO_2$ and polymer, as well as $ClO_2$ and AO, could lead to reactions with the bulk material. Furthermore, consumption of active AO molecules up to 1.2 mm thick surface layer has been reported. In spite of various theoretical and experimental approaches and different aging mechanism, the published results indicate that PE degradation is enhanced in the surface layer about 1 mm thick. To gain more profound knowledge about the effect of $ClO_2$, local properties such as SEM and FTIR-ATR, as well as global measurement methods such as GPC, *OOT* and tensile tests were used. The latter techniques focus on the overall aging of the specimens, applying either the whole or the cross-section of the given specimen.

### 5.2.1 Surface and superficial layer analysis

In Fig. 5.1, the SEM images of PE1 display the appearance and gradual progress of the surface cracks with increasing exposure time during Experiment 1. This surface characteristic highlights an advanced surface embrittlement. Generally, surface cracks indicate that the internal stresses in the superficial layer exceeded locally the polymer tensile strength. The relative increment of internal stresses and decline in tensile strength may be explained by the combined effects of chain scission and chemi-crystallization [11]. Nonetheless, for PE2 and PE3, highly similar surface degradation was detected (see Fig. 5.2 and Fig. 5.3) without any significant difference between the PE grades. Additional sample removals beside 168, 328, and 703 hours confirmed that surface aging is dominated by the development of micro-cracks. In fact, several authors have reported this process, caused by disinfectants during laboratory and field aging [5, 6, 12–18].

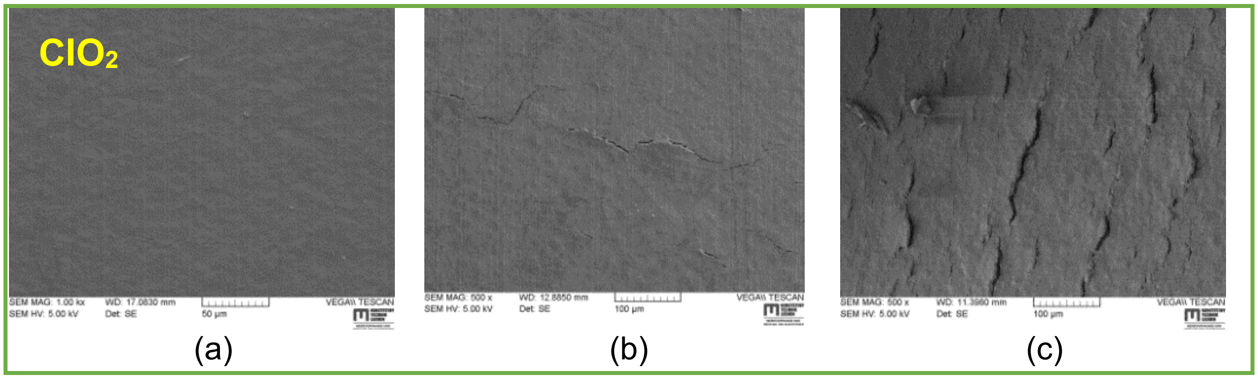


Fig. 5.1: Surface SEM images of PE1 samples after exposure to 10 ppm $ClO_2$ for (a) 168 h, (b) 328 h and (c) 703 h media at 60 °C [19].

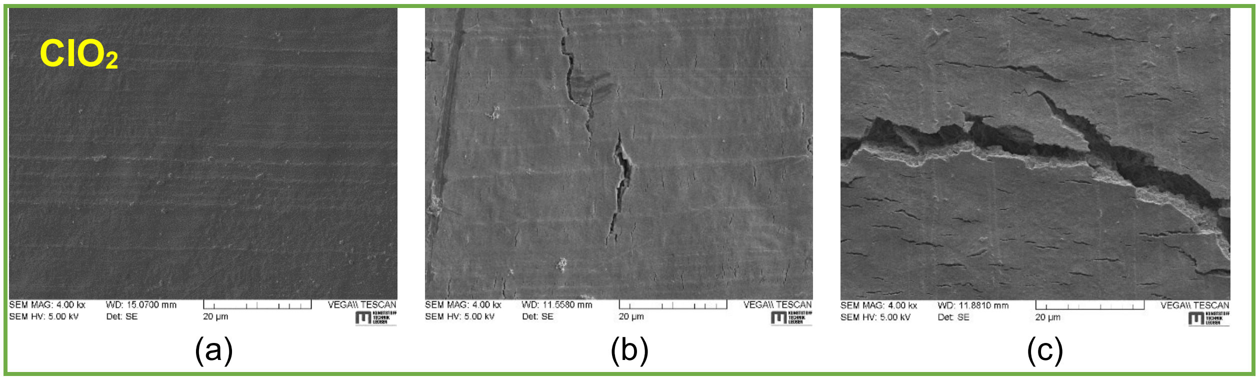


Fig. 5.2: Surface SEM images of PE2 samples after exposure to 10 ppm $ClO_2$ for (a) 168 h, ():328 h and (c) 703 h media at 60 °C [19].

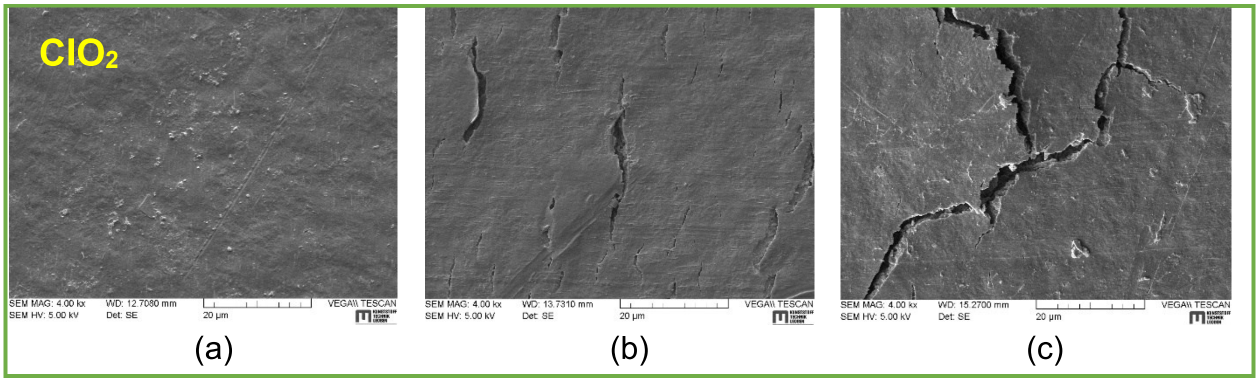
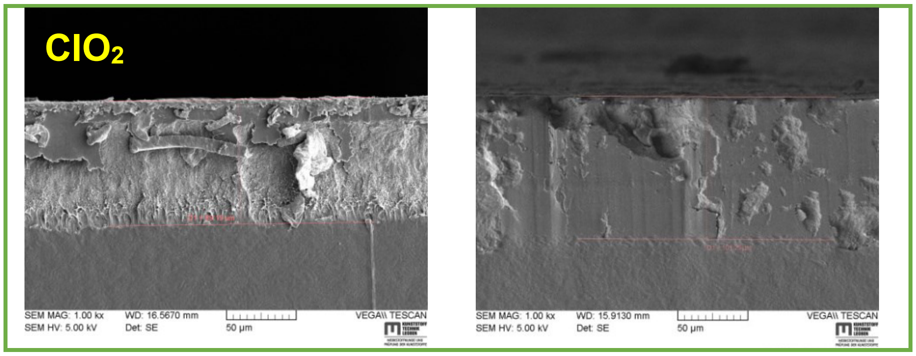


Fig. 5.3: Surface SEM images of PE3 samples after exposure to 10 ppm $ClO_2$ for (a) 168 h, (b):328 h and for (c) 703 h media at 60 °C.

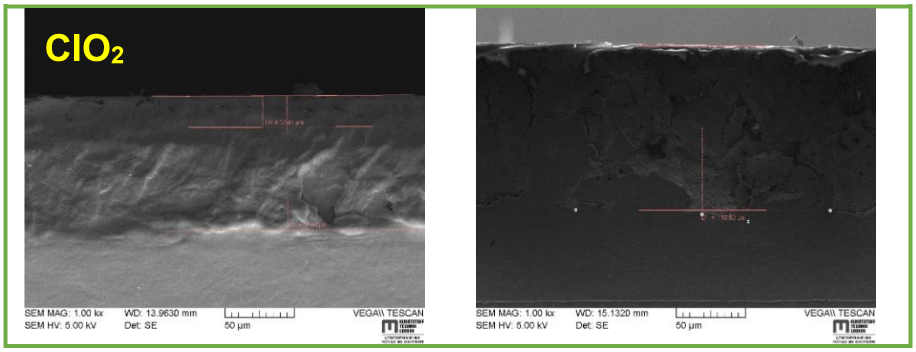
An overall conclusion of these studies is the surface degradation assisted crack initiation and growth; however, the different effect of HOCl and $ClO_2$ have not been considered, nor the effects of various application conditions been thoroughly analyzed. Cross-section of the BCK specimens were also analyzed with SEM to gain additional information about the embrittled surface layer. As Fig. 5.4 illustrates, after 168 h and 703 h of immersion times during Experiment 1, an approximately 100 µm thick highly degraded layer developed on the contact surface. For PE2 and

PE3 as well as for other sampling times, the thickness of the embrittled layer was between 100 and 250 µm (see Fig. 5.5 and Fig. 5.6). Indeed, field case studies of failed pipes (see 2.3.1) indicate that the crack growth process was initiated after reaching a certain constant thickness of the degraded layer. The smooth surface characteristics and embrittled surface layer of the 168 h aged samples on the one hand confirms the strongly local aging nature. On the other hand, implies the diffusion (and other $ClO_2$ derivatives) and reactions of $ClO_2$ in the bulk material.



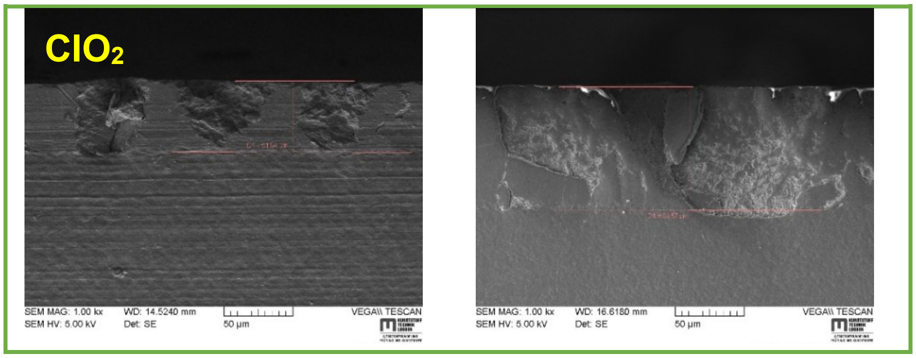
(a) (b)

Fig. 5.4: Cross-section SEM images of aged PE1 samples after exposure to 10 ppm $ClO_2$ for (a) 168 h and (b) 703 h media at 60 °C [19].



(a) (b)

Fig. 5.5: Cross-section SEM images of aged PE2 samples after exposure to 10 ppm $ClO_2$ for (a) 168 h and (b) 703 h media at 60 °C[19].



(a) (b)

Fig. 5.6: Cross-section SEM images of aged PE3 samples after exposure to 10 ppm $ClO_2$ for (a) 168 h and (b) 703 h media at 60 °C.

However, a direct reaction of $ClO_2$ with saturated hydrocarbons is not possible [20, 21]. Chain defects could serve as active reaction centers to induce the PE oxidation by $ClO_2$. Since ClO* radicals could be present in diluted solution of $ClO_2$ and also can be formed in bulk material, the appearance of the degraded layer is expected to be accompanied by advanced surface aging. The absence of surface cracks on the 168 h aged sample indicates that reactive radicals are more likely formed in the bulk zone. Intermediate and side products of AO and chain defects reactions with $ClO_2$ are a highly probable source of such radicals.

Considering possible reactions of $ClO_2$ with chain defects – e.g. double bonds, oxidized backbone atoms and catalyst residues – as well as with phenolic AO [22] in the bulk, the surfaces of cross-section samples were analyzed with SEM-EDX. In Fig. 5.7 (a) oxygen and chlorine can be seen, representing the accumulation of oxidative degradation products in the embrittled surface layer. In the bulk zone, only gold (Au) atoms were detected indicating the conductive coating from the specimen preparation.

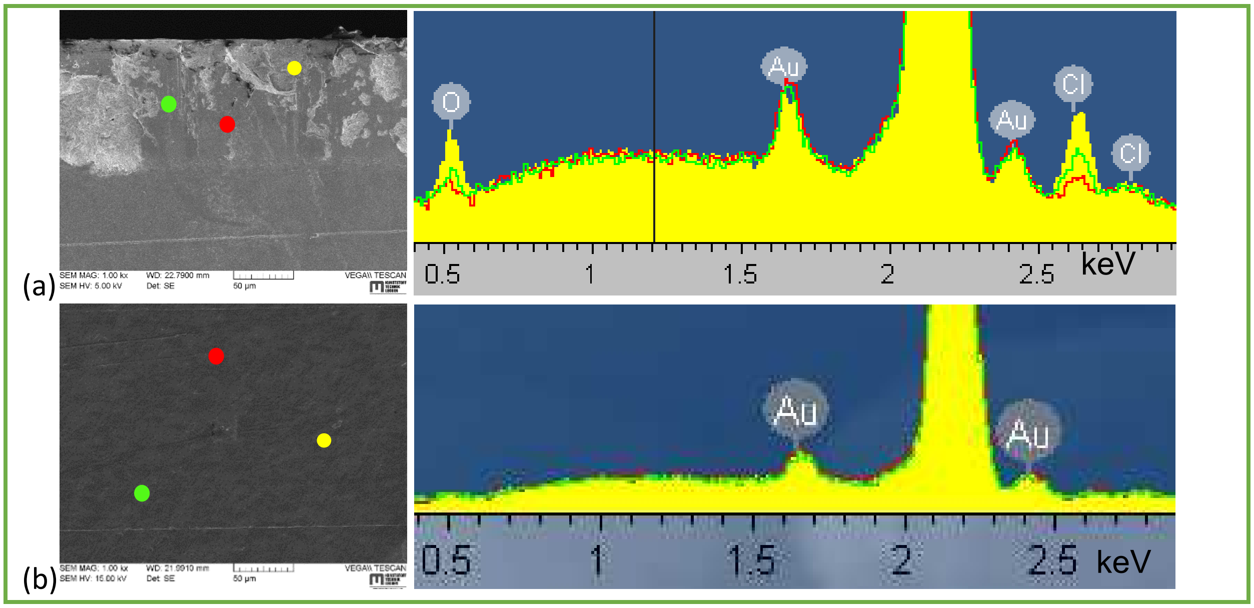


Fig. 5.7: SEM-EDX results of 703 h aged PE1 samples in $ClO_2$, (a) degraded surface layer and (b) analyses at about 1 mm distance from the contact surface.

The EDX method is not applicable for the quantitative evaluation of light chemical elements, although peak intensities imply that the closer the measurement spot to the immediate contact surface, the higher the amount of both elements can be detected. Firstly, this finding is in good agreement with the previously published study of Colin et al. [23]; however, this technique does not provide information about whether chlorine is grafted to the polymer or not. Secondly, the presence of chlorine atoms is clear evidence for the diffusion of $ClO_2$ molecules or its derivatives into the polymer matrix. As discussed above, $ClO_2$ molecules are the most likely candidates to diffuse into the bulk material. Interestingly, a sharp and distinct interface between the intact bulk and the degraded surface layer can be recognized. This distinct border suggests that the diffusion of reactive $ClO_2$ molecules becomes limited with increasing exposure time. Previous publications have pointed out that due to the increase of crystallite phase [24–27] in the degraded surface layer, which is impermeable, the diffusion process might be gradually suppressed. Further material properties at various distances from the contact surface are discussed in detail in the next chapter. In accordance with the limited diffusion of $ClO_2$, bulk material in about 1 mm distance from the surface showed no sign of degradation, e.g. the presence of chlorine or oxygen atoms.

To gain more information about degradation products and chemical structural changes over the aging time, aged and unaged samples were analyzed with FTIR in ATR mode. In Fig. 5.8, spectra of three PE grades after 972 h of exposure in 10 ppm $ClO_2$ are shown. Due to advanced oxidation, molecular vibrations of four important functional groups can be recognized, which are related to ketone at 1714 $cm^{-1}$, carboxyl at 1650-1550, 1410 and 1314 $cm^{-1}$, aryl conjugated vinyl in the range of 1590-1530 $cm^{-1}$ and alkyl carbon-chlorine (C-Cl) at 780 $cm^{-1}$ functional groups [28]. Alkyl C-Cl peaks probably indicate the presence of chlorine atoms grafted to the polymer chain or to the degradation products of AO molecules.

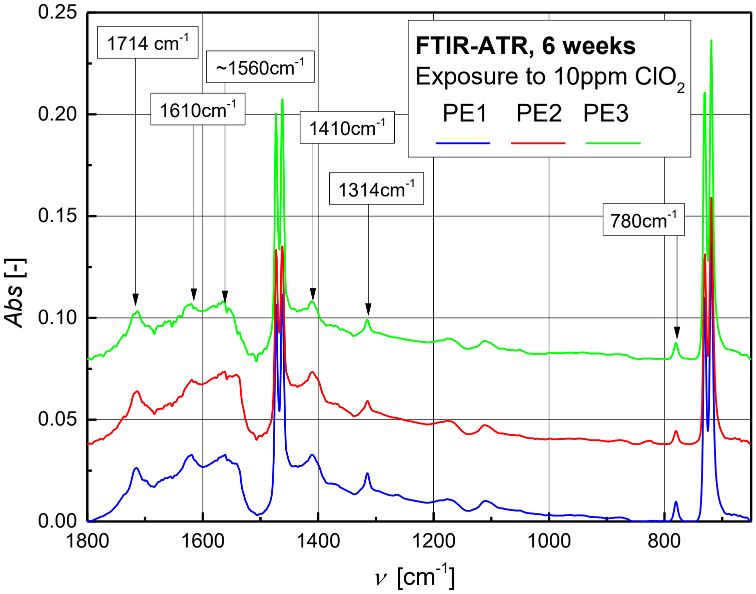


Fig. 5.8: Degradation products observed on FTIR spectra after exposure to 10 ppm $ClO_2$ at 60°C after 972 h of immersion test.

In accordance with the SEM-EDX data and with [22, 29, 30], in excess $ClO_2$ could form chlorinated products with phenolic AO. Based on experimental data, Colin et al. [23] anticipated that $ClO_2$ can react with PE chains; on the contrary, Yu et al. [31] suggested that chlorine atoms grafted to carbon atoms are derived exclusively from oxidized AO molecules. Considering chain defects and oxidized polymer molecules, both assumptions seem to be plausible. Nonetheless, these results only support the presence of alkyl C-Cl groups. Such groups could be derived from both the chlorinated polymer chain and the chlorinated products of AO after the ring rupture [22, 30]. Aryl conjugated vinyl groups can be safely assigned to the oxidation of phenolic AO products. Assuming that ketone and carboxyl groups are mostly, but not exclusively, formed by the degradation of polymer molecules the exact chain scission reaction based on the degradation products has been indirectly identified.

The exceptionally comprehensive work of F. Gugumus [32–34] investigating the oxidative chain scission mechanism of polyolefins, pointed out that the α-keto-hydroperoxide decomposition (see Fig. 5.9) should result in one ketone and one carboxylic acid group besides during one chain scission reaction. The FTIR-ATR data of $ClO_2$ aged samples showed good agreement with this reaction, at least in the case of advanced aging. The α-keto-hydroperoxide decomposition might be the dominating chain scission reaction during the degradation of PE in contact with $ClO_2$.

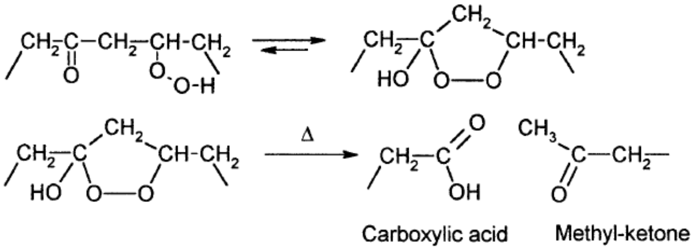


Fig. 5.9: Hypothetic reaction path for chain scission of PE caused by $ClO_2$; heat-catalyzed α-keto-hydroperoxide decomposition [34].

However, degradation products were only measured in the immediate surface layer after exposure to high $ClO_2$ concentration; similar products can be assumed in long-term applications with lower $ClO_2$ concentrations. Future experimental work could validate this theory by the inhibition of the α-keto-hydroperoxide formation and decomposition. Such results would have a tremendous effect on the development of PE grades with improved $ClO_2$ resistance.

### 5.2.2 Global material properties of PE in chlorine dioxide

To further understand the degradation mechanisms induced by $ClO_2$, tensile tests and *OOT* measurements were performed on the aged samples along with FTIR analyses. Since the elongation at break ($\varepsilon_b$) is the most sensitive value for chemical aging, $\varepsilon_b$ values normalized with the unaged values were used. The decline in $\varepsilon_b$ indicates advanced material embrittlement at least in the immediate surface layer. The *OOT* values can be related to Oxidation Induction Time (*OIT*) [35–37], and therefore can be used to describe the loss of active AO during aging. The *OOT* value of 210 °C is assigned to the complete consumption of active AO molecules. The development of degradation products can be assessed by the analysis of *CI*. By plotting these three properties against the aging time, as it is shown in Fig. 5.10, important conclusions can be drawn.

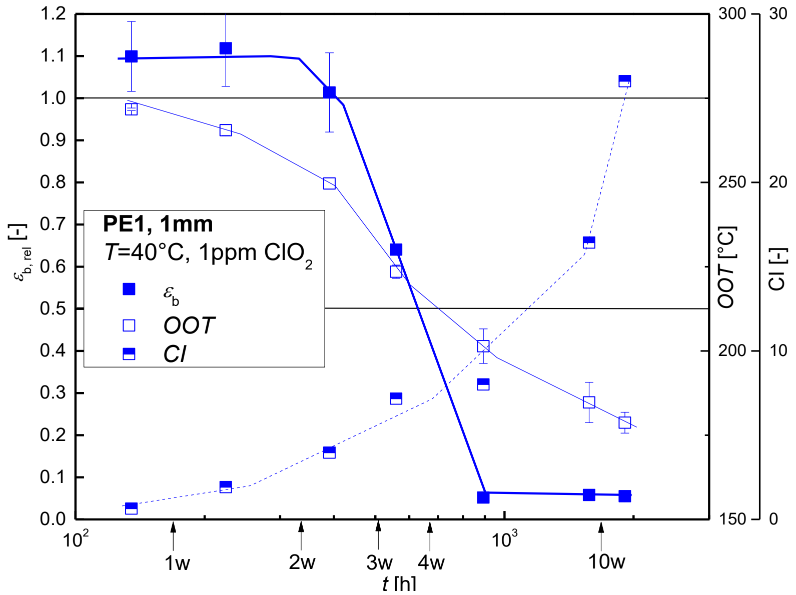


Fig. 5.10: Comparison of $\varepsilon_b$, *OOT* and *CI* over logarithmic aging time during immersion in 1 ppm $ClO_2$ at 40 °C.

Generally, auto-oxidative aging can be separated into three main steps.

- At the beginning, the material is overall well protected until active AO molecules are available.
- After complete AO depletion, the accumulation of radical precursors starts. This second step is frequently referred to as the induction period of the radical chain scission.
- Reaching a critical concentration of radical precursors, decomposition of peroxides results in radicals and eventually in the initiation of the auto-oxidative degradation process. With the appearance of radicals, the chain scission process gradually leads to material embrittlement during this third step.

In case of exposure to 1 ppm $ClO_2$ at 40 °C these three steps cannot be clearly recognized. Parallel reduction of $\varepsilon_b$ and *OOT* indicates the simultaneous reaction of $ClO_2$ with the polymer and AO molecules. In fact, more than 30 % loss of the original $\varepsilon_b$ was recorded before a complete AO consumption. An exponential-like increase of *CI* further confirms the parallel oxidation of the AO and polymer molecules [19]. Since $ClO_2$ should not react with saturated hydrocarbons [21], the assumption of radical by-products formed by the reaction of AO and $ClO_2$ gains more credibility. In case of PE2 and PE3, a very similar evolution of $\varepsilon_b$, *OOT* and *CI* over the aging time has been detected (see Fig. 5.11), affirming the conclusions mentioned above. The lines in Fig. 5.10 and Fig. 5.11 only represents a visual guide for the eye. The evolution of the molecular weight distribution (MWD) curve of the three PE grades with increasing exposure time during Experiment 1 are shown in Fig. 5.12. For the measurements, aged SHT specimens were used. Considering the observed surface limited effect of $ClO_2$ (Fig. 5.4), these samples probably contain some intact, non-degraded bulk material. An overall shift to lower molecular weights and a slight broadening of MWD of the aged samples were detected.

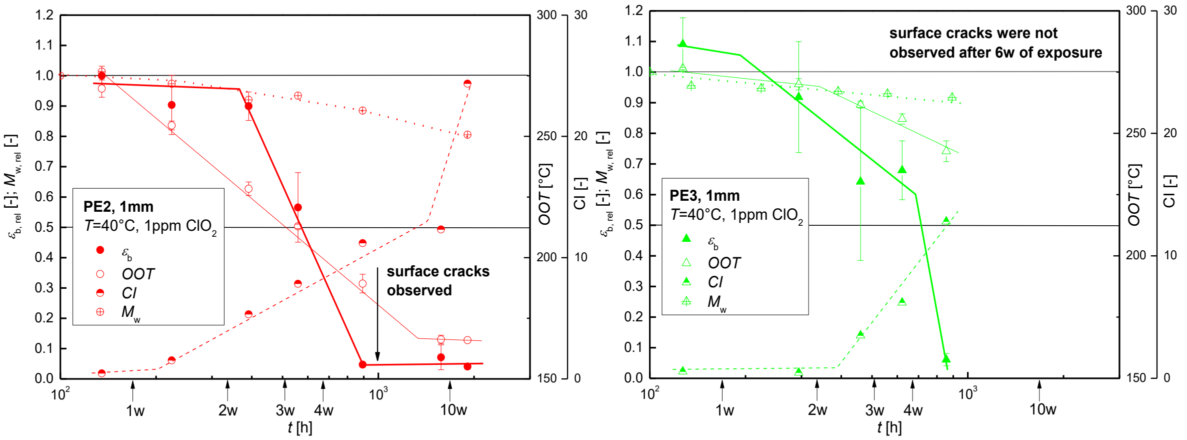
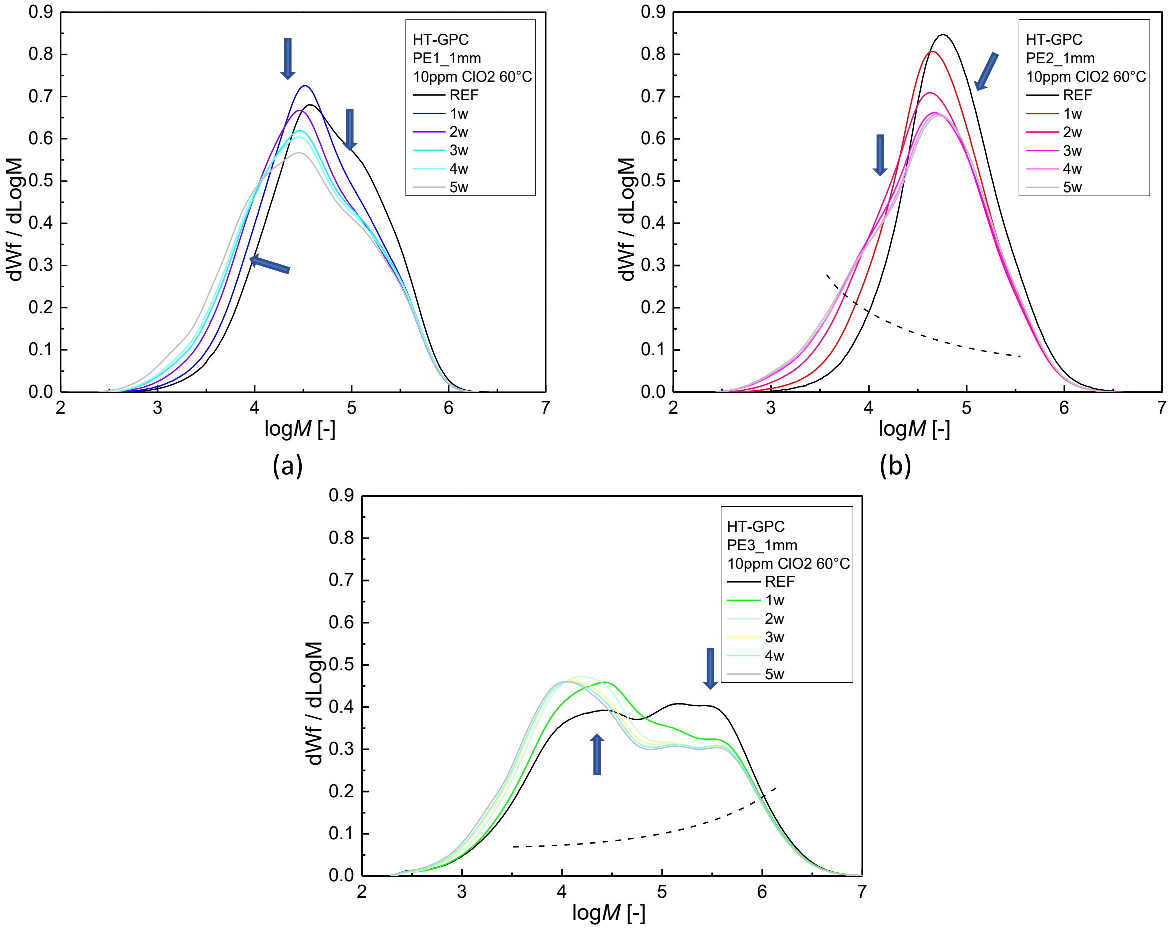


Fig. 5.11: Comparison of $\varepsilon_b$, *OOT* and *CI* over the logarithmic aging time during immersion in 1 ppm $ClO_2$ at 40 °C for (a) PE2 and for (b) PE3.

This change in the MWD curve becomes more pronounced with increased aging time. The GPC data clearly indicates advanced degradation and chain scission of the three PE grades, confirming the previously observed material embrittlement. Comonomers for short chain branches were added during the polymerization of the three PE grades; however, the MWD of PE1 and PE3 are bimodal, while PE2 displays a unimodal MWD. Compared to PE2, PE1 and PE3 MWD curves display somewhat stronger degradation of higher molecular weight fractions. The appearance of a weak shoulder in the lower molecular weight fraction of PE2 can be seen in Fig. 5.12 (b). As an effect of advanced aging in $ClO_2$, Yu et al. [27] suggested that peaks and shoulders in the low molecular weight range are probably linked to chain scission of once folded and to extended chains through single lamellae. To better interpret the change in MWD molecular weight moments, the first being the number average molecular weight ($M_n$), the second the weight average molecular weight ($M_w$), and the third moment, the Z average molecular weight ($M_z$) were calculated based on Equation 14 [38]. In the following sections, absolute moments determined with GPC measurements will be discussed.

$$\overline{M_x} = \frac{\sum N_i * M_i^x}{\sum N_i * M_i^{x-1}} \tag{14}$$

Typically, $M_n$, $M_w$ and $M_z$ values are used to observe changes in low, mostly middle and high molecular weight fractions, respectively. In Fig. 5.13 these three moments are plotted over the exposure time of the three PE grades.

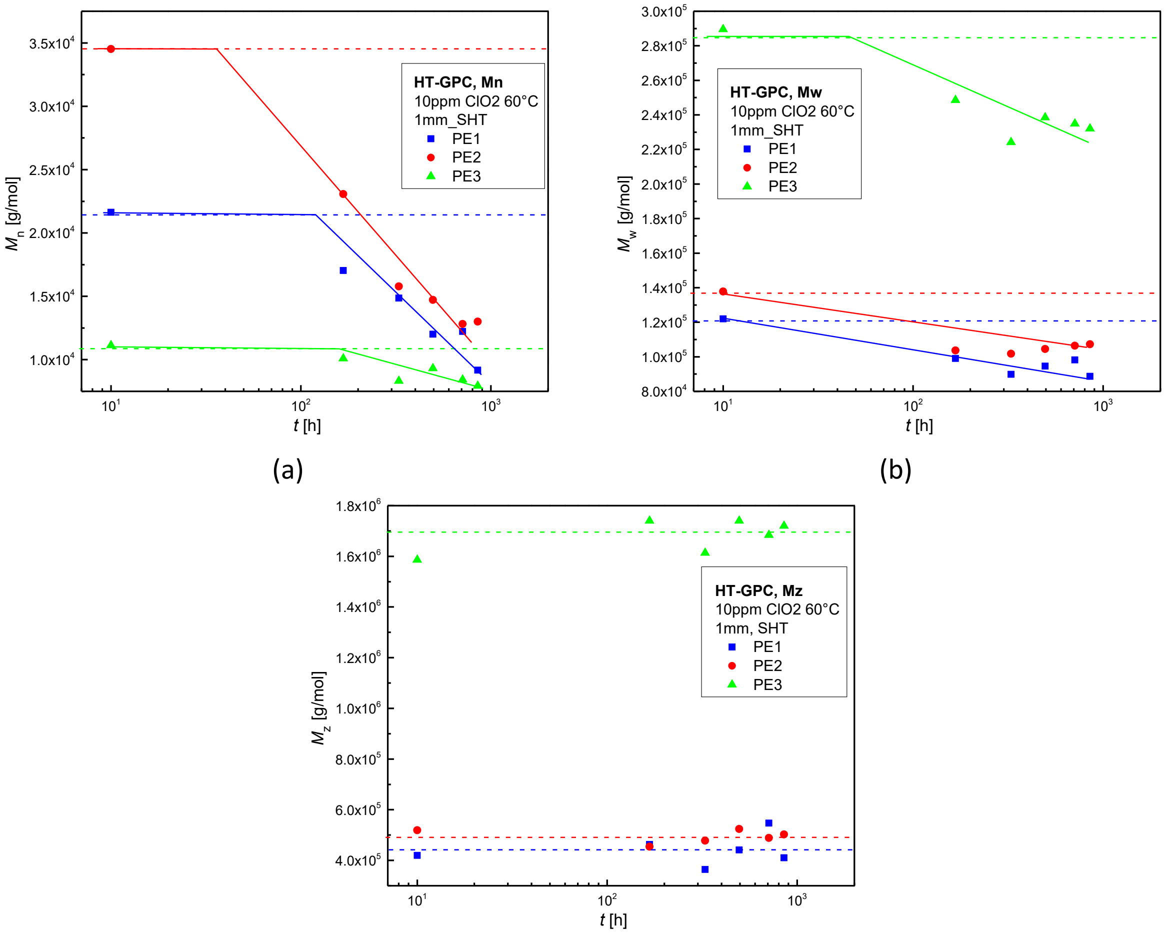


(a) (b)

(c)

Fig. 5.12: Molecular weight distribution of (a) PE1, (b) PE2 and (c) PE3 of SHT specimens after various aging times in 10 ppm $ClO_2$ at 60°C, up to 872 h of aging.

Considering that comonomer concentration for unimodal resins is greater on shorter polymer chains, and for bimodal resins is higher on longer polymer chains, a detailed observation of $M_n$, $M_w$ and $M_z$ values could result in important conclusions. The observed changes and assumed chain scission processes are summarized in Table 5.1, where chain scission refers to the most affected molecules. In case of PE3, a strong decrease in $M_w$, and a slight decline in $M_n$ can be recognized, indicating chain scission of longer molecules with higher side chain concentration. Similarly, for PE1 both $M_w$ and $M_n$ show reduced values, but the decrease in $M_n$ is greater than for PE3. Stronger decrease in $M_n$ of PE1, where the bimodality is less pronounced, indicate that $ClO_2$ caused chain scission does not occur exclusively on tertiary carbon atoms. The PE2 displays the highest decrease of $M_n$ and similar reduction of $M_w$ to PE1. Comonomer concentration and consequently the side chain as well as tertiary carbon atom concentration is the highest for PE3 on the longer and for PE2 on the shorter polymer chains, which is schematically illustrated by dashed lines in Fig. 5.12 (b) and (c). Thus, an attack of tertiary carbon atoms by $ClO_2$ can been assumed.



(a) (b)

(c)

Fig. 5.13: Molecular weight momentums plotted against the exposure time of $M_n$ (a), $M_w$ (b), and $M_z$ (c) plotted over the exposure time in 10 ppm $ClO_2$ at 60 °C.

Table 5.1: Molecular weight moment changes of PE due to $ClO_2$ immersion.

| **Material** | **Modality** | **Comonomer accumulation** | **Relative change: decrease** | | | **Chain scission** |
|---|---|---|---|---|---|---|
| | | | $M_n$ | $M_w$ | $M_z$ | |
| PE1 | light bimodal | longer chains | + | + | – | short and long chains |
| PE2 | unimodal | shorter chains | ++ | + | – | short chains |
| PE3 | bimodal | longer chains | - | ++ | – | long chains |

*Weak: -; Strong: +; Very strong: ++*

However, the chain scission of molecules with lower comonomer concentration cannot be ignored. Moreover, SEM results and the high reactivity of $ClO_2$ also suggest an unselective chain scission process. The MWD changes observed can be explained by the competitive reaction of $ClO_2$ with a tertiary carbon atom of polymer molecules and with chain defects as well as with oxidized backbone carbon atoms. In spite of the fact of $ClO_2$ cannot subtract hydrogen from saturated hydrocarbons, degradation and chain scission of polymer molecules were detected in accordance with literature. The above explanation enables to be described the polymer degradation in agreement with the experimental data and relevant literature.

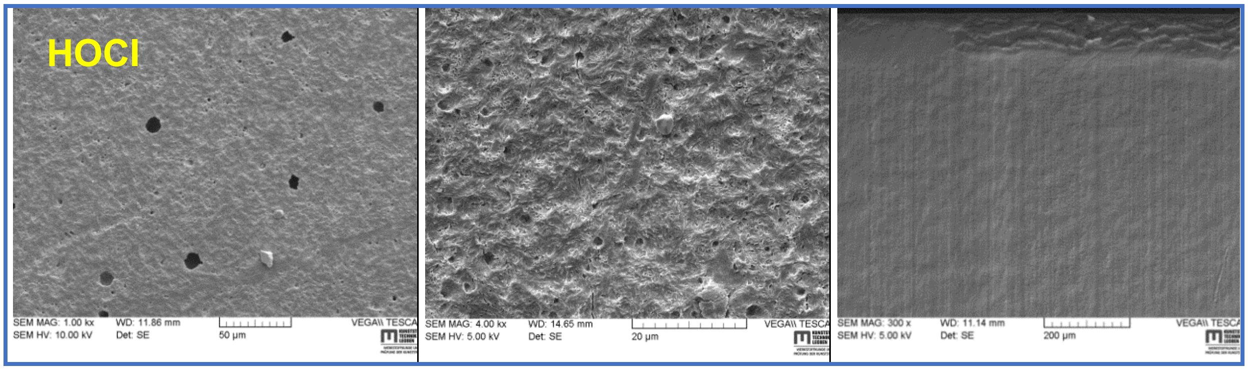
## 5.3 Aging mechanism of PE in contact with hypochlorite

Hypochlorite is one of the most used secondary disinfectants in drinking water treatment, with a strongly oxidative nature. Therefore the effect of HOCl on the degradation of PE pipes has been a matter of interest of several researchers [24, 26, 39–44]. Generally, material embrittlement has been reported as the effect of chain scission caused by hydroxyl (OH*) and ClO* radicals. In fact, the early work of Holst et al. [45] already pointed out the formation of these two radicals. However, due to the high reactivity of these molecules, they should only penetrate into a few microns of depth, in agreement with the proposal of Devillers et al. [24] and Khatua et al. [46]. Furthermore, $Cl_2OOH$ molecules were suggested as the species able to diffuse into deeper material layers. These molecules will shorten the time to critical hydroperoxide accumulation and the overall initiation of the radical chain scission process. Abdelaal and Kerry [47] proposed further molecules such as $Cl_2$, $Cl_2O$ and $ClO_2$ to explain the fast consumption of active AO molecules up to 1 mm distance from the contact surface. Montes et al. [25] and Mitroka et al. [48] reported that the polymer degradation is independent of the applied HOCl amount in the case of higher concentration, which is in good agreement with the diffusion-controlled aging mechanism. A recent study of Mikdam et al. [43] indicates that chloride (Cl*), hydroxide (OH*) and ClO* radicals are formed in HOCl solution. These species are reactive enough to cause accelerated degradation of the immediate contact surface. More stable species such as $Cl_2$ and HOCl can diffuse into deeper layers and dissociate to radicals, initiating an accelerated radical degradation process. Despite numerous scientific publications, aging mechanisms of PE in contact with HOCl have not been identified yet. This section aims to conclude further information about the dominating aging mechanism.

### 5.3.1 Surface and superficial layer analysis

The presence of HOCl caused voids, cavities and a porous-like surface with increased surface roughness, as displayed in Fig. 5.14. These etched-like surface characteristics became more pronounced in HOCl solution with increasing exposure time. In accordance with previous research works [5, 31, 49], on a macroscopic level, the surface cracks were found which were visible with the naked eye. Indeed, some minor, small micro-cracks can be seen in the SEM images as well. However, on a microscopic level, surface aging is dominated by voids and cavities, which is also confirmed by the data published in literature [50]. Loss of highly degraded powder-like surface material that likely originates from the oxidation of the amorphous layer could explain this kind of surface aging. Scanning electron microscopy images of the cross section (Fig.

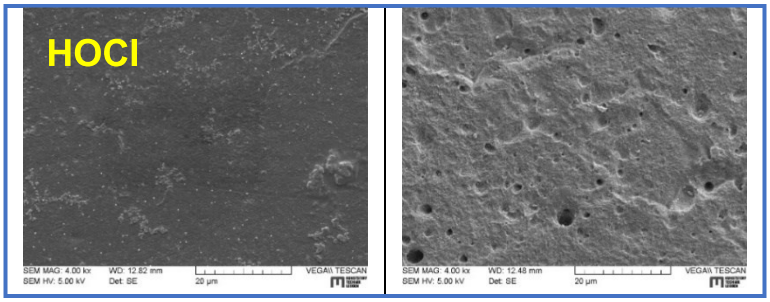
5.14 c) represent only a minor melting effect at the edge, likely initiated by the cutting process, without signs of an embrittled surface. Samples of PE2 and PE3 showed identical surface changes, without any significant differences between the three PE grades (see Fig. 5.15 and Fig. 5.16).



(a) (b) (c)

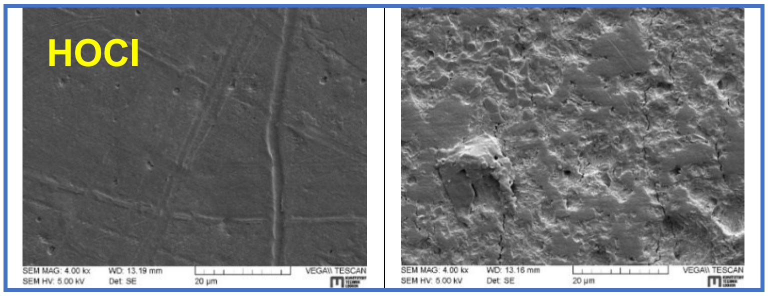
Fig. 5.14: Surface SEM images of aged PE1 samples after exposure to 100 ppm HOCl for (a) 799 h, (b) 2756 h and (c) cross section image after 2055 h of aging.

As previously discussed, in HOCl solution the presence of radicals such as HO*, ClO* and some other stable molecules (HOCl, OCl-, Cl-, $Cl_2$, $Cl_2OOH$) can be anticipated. High reactivity and very short shelf life of these radicals will restrain their diffusion into deeper material layers. Furthermore, diffusion into the bulk of ions and solved chlorine-based molecules is probably strongly limited due to their hydrate shell.



(a) (b)

Fig. 5.15: Surface SEM images of aged PE2 samples after exposure to 100 ppm HOCl for (a) 799 h, (b) 2756 h.



(a) (b)

Fig. 5.16: Surface SEM images of aged PE3 samples after exposure to 100 ppm HOCl for (a) 799 h, (b) 2756 h.

On the immediate contact surface, radicals will react unselectively with the AO and the polymer chains, resulting in a porous surface layer. For the reported AO consumption in the bulk [25, 26, 40, 51] by HOCl, the most probable candidate is the $Cl_2$ molecule. At 15 °C and a pH level of 6, the molar fraction of $Cl_2$ is in a negligible $10^{-5}$ magnitude [52], however at higher temperatures, this fraction can be increased significantly. At room temperature, the relative concentration of $Cl_2$ was found to be about 5 % [53–55] in HOCl solution. Considering the elevated exposure temperature, in a significant amount $Cl_2$ might be present. Increased concentration of $Cl_2$ gas can serve as an explanation for AO consumption in a few hundred microns of depth without significant embrittlement of this layer. In fact, Mikdam et al [43] concluded that $Cl_2$ and HOCl molecules are most likely to migrate into the bulk material. To investigate chemical composition, HOCl-aged samples were subjected to SEM-EDX analysis, as it is shown in Fig. 5.17. On the surface of the 1299 h-long immersed sample, oxygen and chlorine atoms were detected, indicating the oxidative degradation of the material. Bulk analysis at about 1 mm distance from the contact surface showed only a very low amount of oxygen and chlorine, which is around the limit of determination.

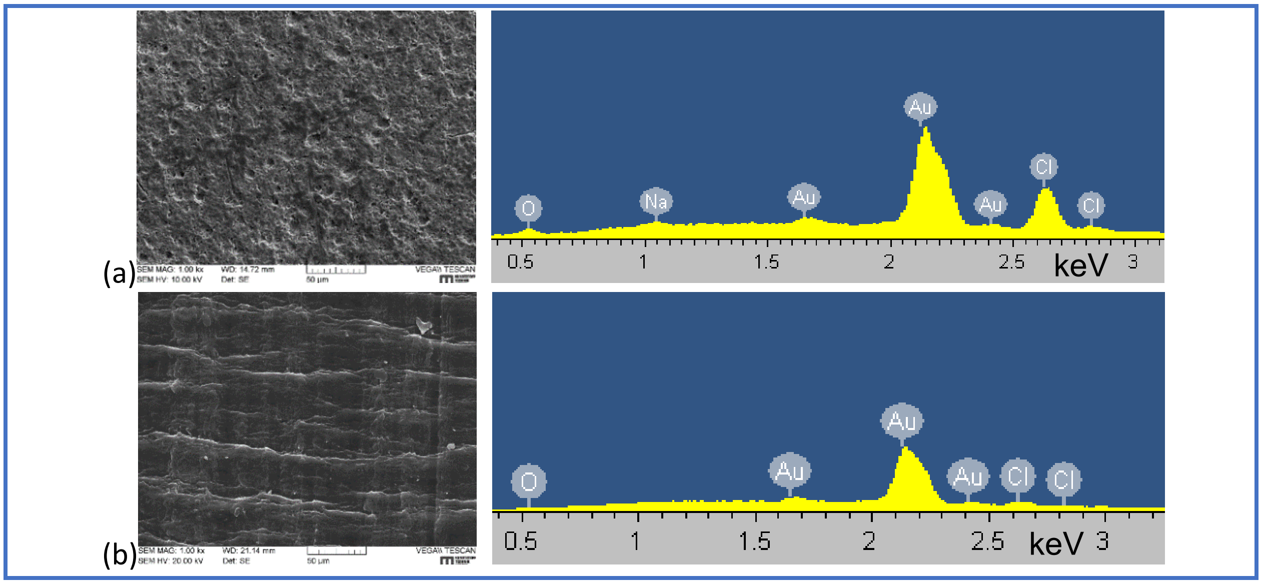


Fig. 5.17: SEM-EDX results of PE1 after 1299 h of immersion in 100 ppm HOCl solution at 60 °C (a) surface and (b) cross section analysis.

The chemical structure was further analyzed with FTIR-ATR, as it is illustrated in Fig. 5.18. After 3218 h of aging, peaks appeared at 1740-1720, 1714 and 1620 $cm^{-1}$ and correspond to various aldehyde, ketones, and ketoaldehyde functional groups [28]. Considering that chain scission reactions probably caused the loss of amorphous surface phase and the etched-like surface, these functional groups are at least partially the products of the chain scission. According to F. Gugumus [32–34], the reaction illustrated in Fig. 5.19 could result in aldehyde groups during one chain scission reaction. The highly surface limited reaction of HOCl is further confirmed by the absence of peaks in the 1600-1500 $cm^{-1}$ spectral region, where cyclic and aromatic AO degradation products usually appear [14]. Since an excess of HOCl can lead to ring rupture of phenolic compounds, the absence of AO oxidation products seems consistent with literature. Moreover, these oxidation products could be easily washed away during the aging experiment or lost with the surface powder layer during the handling of samples. It is essential to note that allylic hydroperoxide decomposition probably dominates the chain scission process, which is why prevention of such a reaction could lead to improved HOCl resistance of PE materials. Such a modification of the polymer would significantly increase the long-term performance of PE pipes.

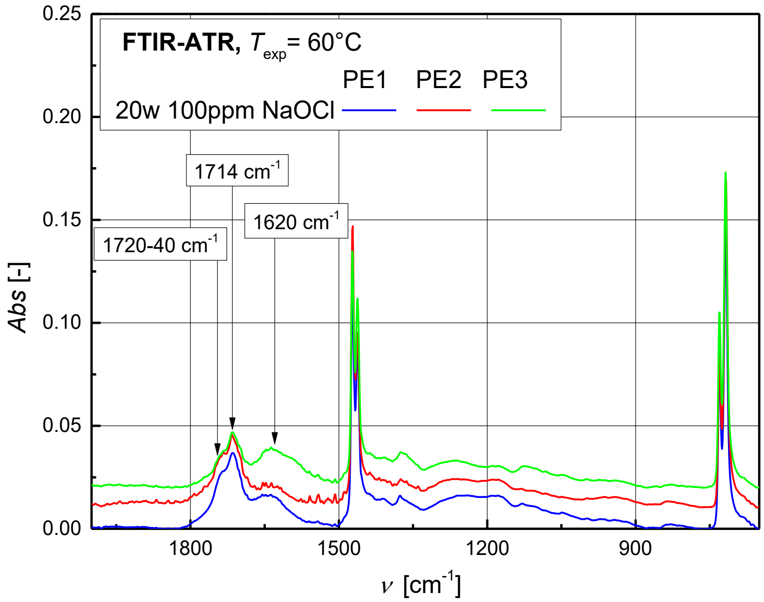


Fig. 5.18: Degradation products observed on FTIR spectra after 3218 h exposure to 100 ppm HOCl solution at 60°C.

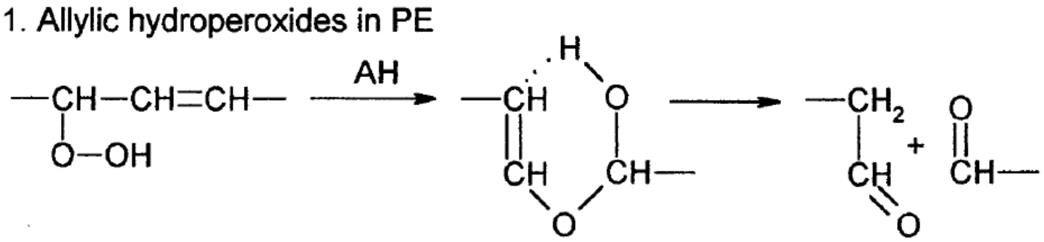


Fig. 5.19: Hypothetic reaction path for chain scission of PE caused by HOCl; heat-catalyzed allylic hydroperoxide decomposition [34].

### 5.3.2 Global material properties of PE in hypochlorite

Similar to Fig. 5.10, *OOT* and $\varepsilon_b$ values normalized with the unaged value and *CI* of 1 mm thick specimens were plotted over the exposure time. The three previously discussed main steps of autoxidative aging can be easily recognized in Fig. 5.20. After *OOT* values became lower than 210°C, a short induction period followed by the decline of $\varepsilon_b$ can be seen. This reduction of $\varepsilon_b$ is assigned to chain scission reactions and an overall advanced material embrittlement. A sharp increase in *CI* after the decline of $\varepsilon_b$ implies that degradation products on the surface became significant after material embrittlement. In other words, oxidation products recorded with FTIR-ATR measurements mostly originate from oxidation of the polymer and not from the AO degradation products. Furthermore, this observation confirms the above-assumed loss of oxidized AO products and represents a good agreement with the relevant literature (see discussion of Fig. 2.25). For PE2 and PE3, similar changes in the three material properties were recorded over the exposure time (see Fig. 5.21). An overall accelerated radical induced auto-oxidative PE degradation process can be observed due to the presence of HOCl. The MWD curves obtained from GPC analyses of 0.3 mm thick specimens are shown in Fig. 5.22.

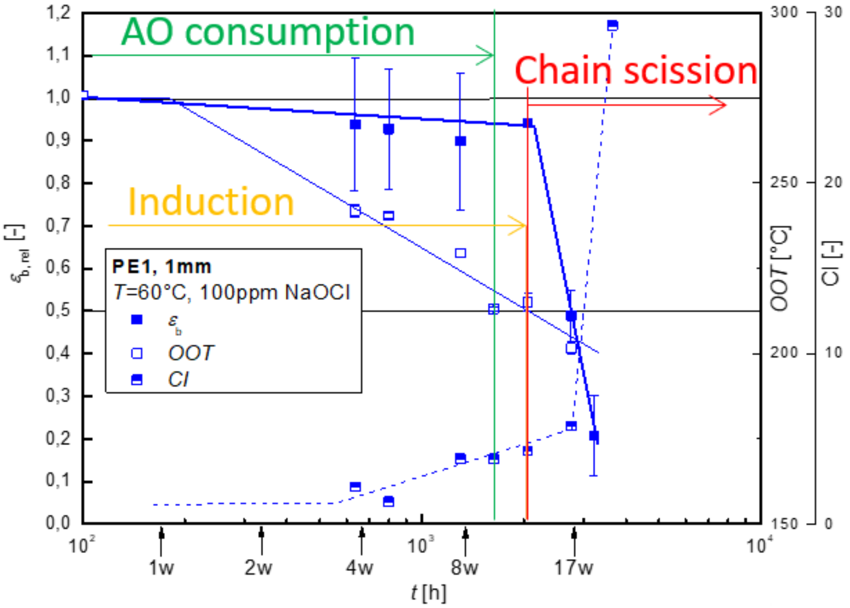
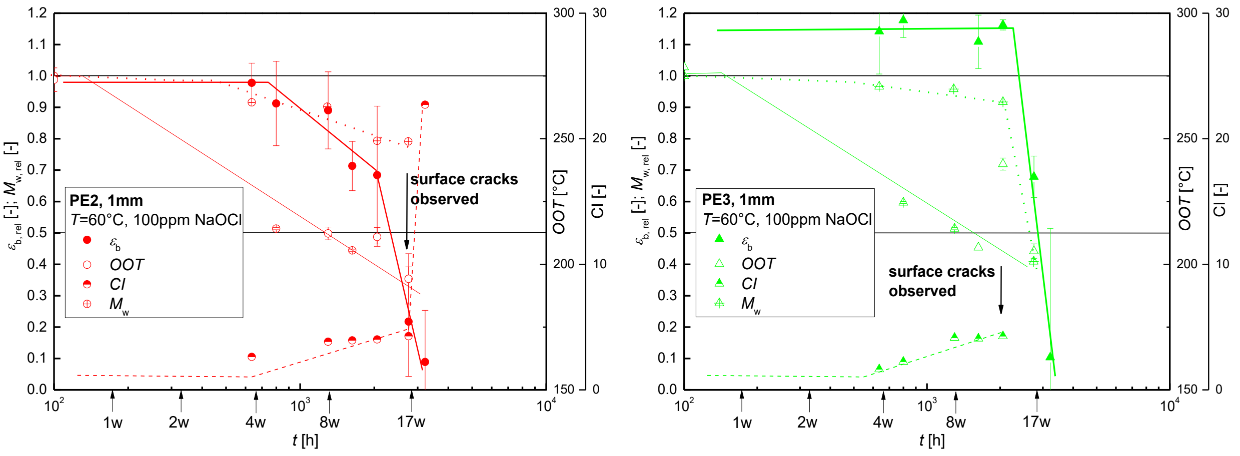
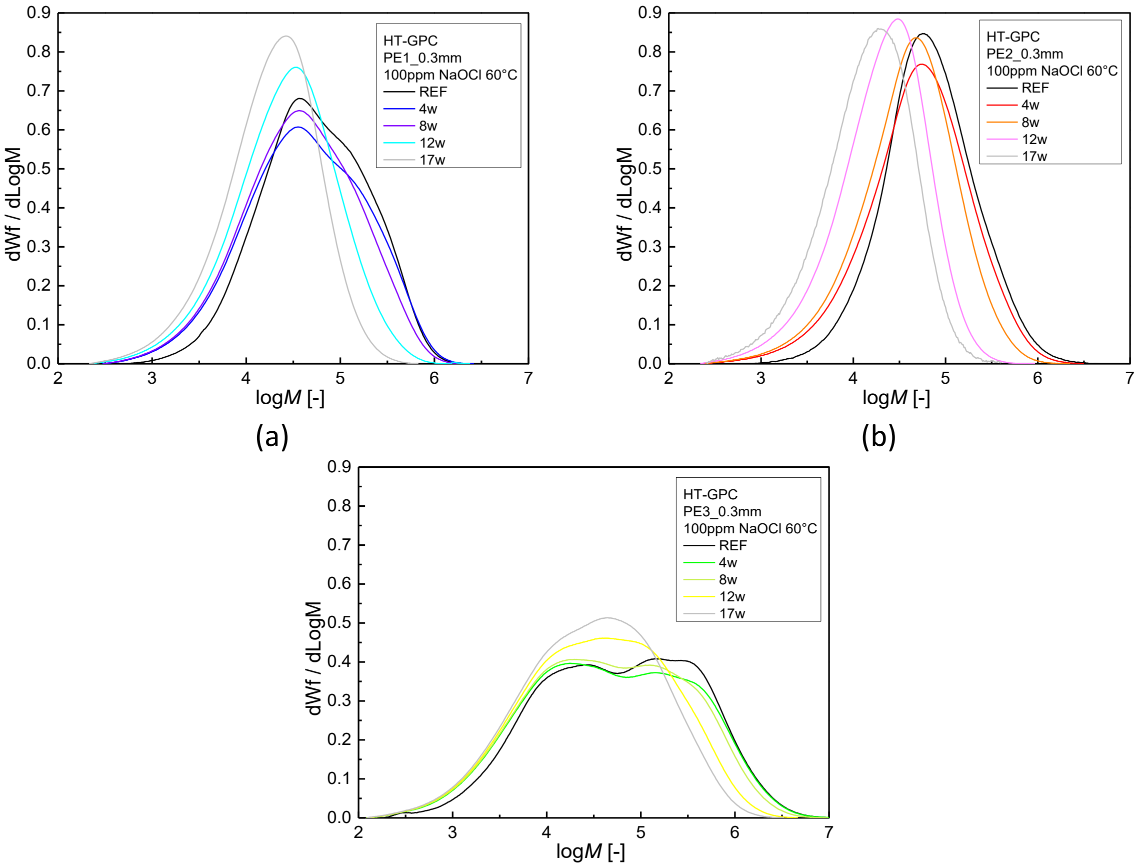


Fig. 5.20: Comparison of $\varepsilon_b$, *OOT* and *CI* after aging in 100 ppm HOCl at 60 °C [19].



(a) (b)

Fig. 5.21: Comparison of $\varepsilon_b$, *OOT* and *CI* after aging in 100 ppm HOCl at 60 °C for PE2 (a) and for PE3 (b).

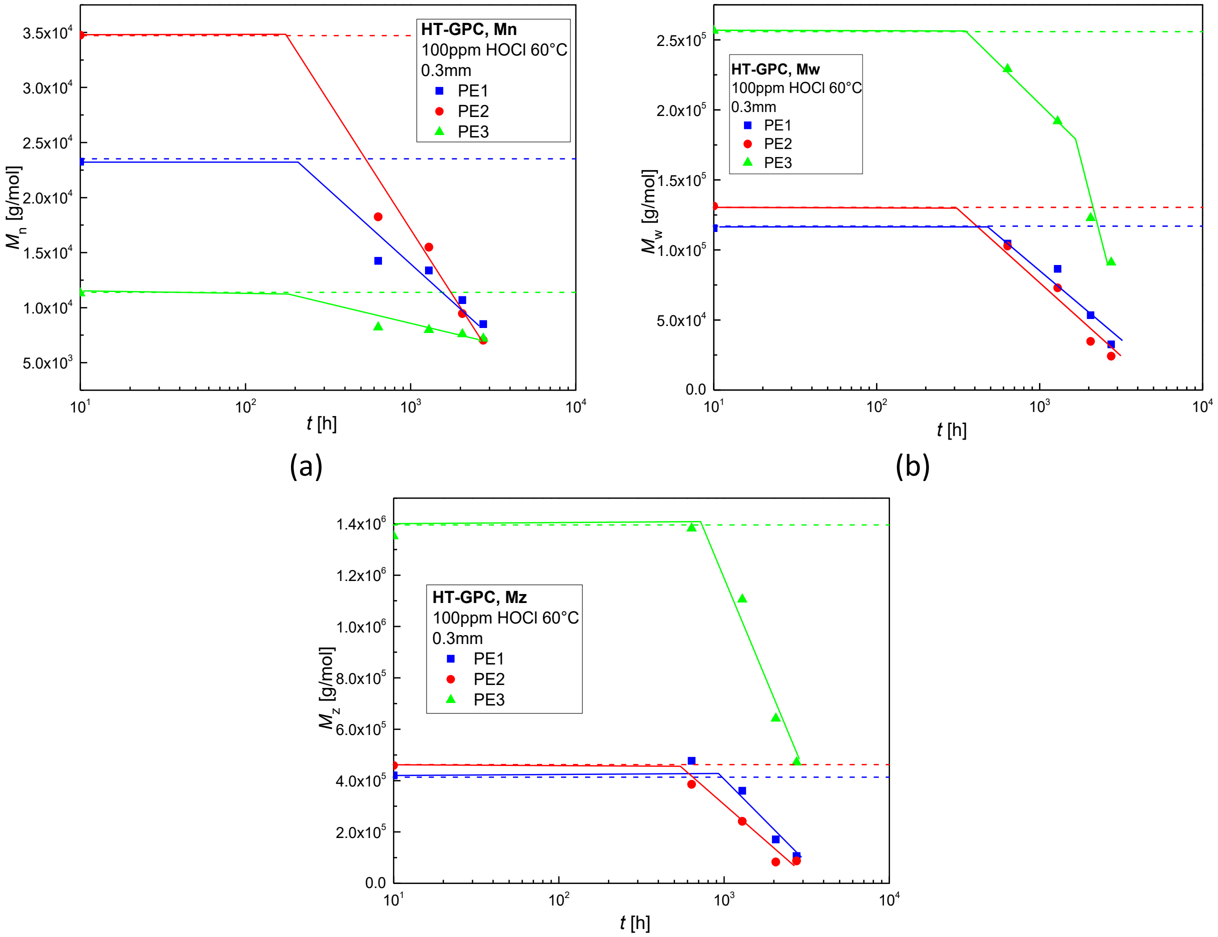


(a) (b)

(c)

Fig. 5.22: Molecular weight distribution of (a) PE1, (b) PE2 and (c) PE3 of 0.3 mm thick specimens after various aging times in 100 ppm HOCl at 60°C, up to 2757 h of aging.

Considering the strongly surface limited influence of HOCl, the 1 mm thick specimens showed only a minor change in MWD, due to their high amount of intact bulk material. Generally, a strong shift of MWD to lower molecular weight values can be seen for all three PE grades. Comparing the three PE grades, a shift of PE2 is the most, while for PE3 it is the least conspicuous. A decrease in the higher molecular weight fraction for all three PE grades is quite obvious. To gain a more detailed view of molecular weight changes over the aging experiment, moments of MWD, $M_n$, $M_w$ and $M_z$ were plotted over the immersion time, as shown in Fig. 5.23. With an evaluation analogous to Section 5.2.2, the following conclusions can be drawn from the GPC data presented: In case of PE3, where the side chain concentration is the highest in longer chains, the $M_z$ and $M_w$ decline is the most and the $M_n$ decrease is the least significant. This could indicate that longer chains with tertiary carbon atoms up to a certain extent were selectively attacked by HOCl. For PE1 and PE2, the decrease in $M_z$ and $M_w$ are inferior to the decline in $M_n$. The decline in $M_n$ of the PE2 sample is the greatest from the three PE grades. The observations are summarized in Table 5.2, where chain scission refers to the most affected molecules.



(a) (b)

(c)

Fig. 5.23: Molecular weight momentums plotted against the exposure time of $M_n$ (a), $M_w$ (b), and $M_z$ (c) after exposure of 0.3 mm thick specimens in 100 ppm HOCl at 60 °C.

Table 5.2: Molecular weight moment changes of PE due to HOCl immersion.

| **Material** | **Modality** | **Comonomer accumulation** | **Relative change: decrease** | | | **Chain scission** |
|---|---|---|---|---|---|---|
| | | | $M_n$ | $M_w$ | $M_z$ | |
| PE1 | light bimodal | longer chains | + | - | - | short and long chains |
| PE2 | unimodal | shorter chains | ++ | + | - | short chains |
| PE3 | bimodal | longer chains | - | ++ | ++ | long chains |

*Weak: -; Strong: +; Very strong: ++*

In fact, PE2 has the highest comonomer concentration on shorter chains; hence, the selective attack of HOCl on tertiary carbon atoms can be assumed. Reactive molecules derived from the HOCl solution quasi-selectively attack the tertiary carbon atoms independently from their position. It should be noted that the presence of radicals (Cl*, OH* and ClO*) may significantly influence chain scission reactions on the immediate contact surface. Since the effect of HOCl is extremely surface-limited, the abovementioned conclusion might not be true in deeper material layers. Nevertheless, with a special PE resin formulation and AO package selection, PE pipe materials with improved HOCl resistance can be prepared, without the loss of advantageous material properties of the bimodal MWD on the SCG resistance.

## 5.4 Summary: Differences in PE degradation caused by ClO2 and HOCl

The experimental data clearly highlights the different aging mechanisms caused by $ClO_2$ and HOCl. The following differences in the degradation of PE should be considered in case of applying secondary disinfection in drinking water networks:

The presence of $ClO_2$ led to surface cracks and a highly degraded surface layer with a thickness of about 150 µm, while HOCl predominantly caused surface abrasion with significant loss of degraded amorphous surface layer. Beside the absent degraded surface layer, surface cracks on the HOCl-aged specimens were detected by visual inspection. The surface aging characteristics observed are schematically illustrated in Fig. 5.24.

Fig. 5.24: Schematic illustration of the PE surface aging in contact with $ClO_2$ and HOCl disinfected aqueous solutions.

The SEM-EDX analyses showed oxygen and chlorine atoms on the surface and in the degraded layer of HOCl and $ClO_2$-aged specimens, respectively. Cross-section measurements indicated that no significant amount of oxygen and chlorine are present at about 1 mm distance from the contact surface.

In terms of reactive species, the diffusion of $ClO_2$ molecules and the generation of radical molecules in the affected surface layer is the most probable explanation. Radicals such as ClO* and OH* most likely play an important role in surface aging. As far as HOCl goes, for surface abrasion and degradation various radicals and more stable molecules are assumed to be responsible. Consumption of active AO in deeper material can be explained by the diffusion of $Cl_2$ molecules, which are most likely present in increased concentration at elevated exposure temperatures.

The inverse approach to identify chain scission reactions based on the oxidation products detected by FTIR-ATR measurements resulted in the following conclusions, which are:

- In case of $ClO_2$ the chain scission mechanism is probably dominated by the α-keto-hydroperoxide.

- For HOCl allylic hydroperoxide decomposition reactions presumably govern the chain scission process.

These findings are highly valuable for the further development of current PE grades with improved resistance to disinfectants.

The evaluation of the GPC results allowed conclusions to be drawn between the molecular structure and the disinfectant initiated chain scission reactions. In contact with PE, $ClO_2$ (and / or its derivatives) probably reacts competitively with tertiary carbon atoms, with chain defects and with oxidized parts of the polymer chains. The HOCl-aged samples showed a quasi-selective chain scission reaction to the tertiary carbon atoms. These reaction paths are probably predominant during the aging of PE in HOCl and $ClO_2$, but other chain scission processes cannot be fully excluded. Further research, additional model experiments with special material, AO packages and filler formulation are recommended, in order to prove the deduced conclusions and develop PE grades with improved $ClO_2$ and HOCl resistance.

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# PART III – ACCELERTED MATERIAL RANKING METHODS OF PE PIPE GRADES IN CONTACT WITH DISINFECTANTS

# 6 Material properties at various distances from the contact surface

Over the past decades, researchers [1–6] have actively studied the changes in PE pipe materials at various distances from the contact surface caused by disinfectants. It is crucial to understand and describe the diffusion of AO and the reactive disinfectant molecules. Such knowledge would be highly beneficial for the further development of AO packages and PE resins. The diffusion of active AO molecules to the inner pipe surface was only found to be significant in long-term operation in non-disinfected water at ambient temperatures [7, 8]. If oxidizing agents such as HOCl and $ClO_2$ are added to the drinking water system, the AO depletion process might be strongly influenced. Disinfectants cause a fast and complete AO consumption on the immediate contact surface [1, 2, 6, 9, 10]. The increased AO concentration difference between the bulk and the surface can result in a greater diffusion coefficient [11] than for non-disinfected water. Therefore, an overall faster diffusion of the bulk AO to the inner surface can be expected even at lower temperatures. As discussed in Section 5.4, $ClO_2$ and $Cl_2$ molecules have the highest potential to diffuse deeper into the PE matrix. The diffusion rate of these molecules is essentially determined by the PE matrix, assuming a more or less constant operation or laboratory aging conditions. Polyethylene with a higher crystallinity ratio is probably less influenced by disinfectants in the bulk, since the crystallite phase is impermeable. Moreover, the dynamic change of crystallinity ratio and morphology can play an in important role in the diffusion of disinfectant derivatives (e.g. the initial and the change in crystallinity ratio and morphology over the aging period). Naturally, the composition, amount and distribution of the AO package will fundamentally determine the diffusion and hence the AO depletion rate, including chemical and physical loss.

In accordance with Objectives B and C, this chapter has the following two major goals:

- First, to determine material properties at various distances from the contact surface for PE pipe grades immersed in $ClO_2$ and HOCl.
- Secondly, to identify possible differences in these property profiles for various PE pipe grades.

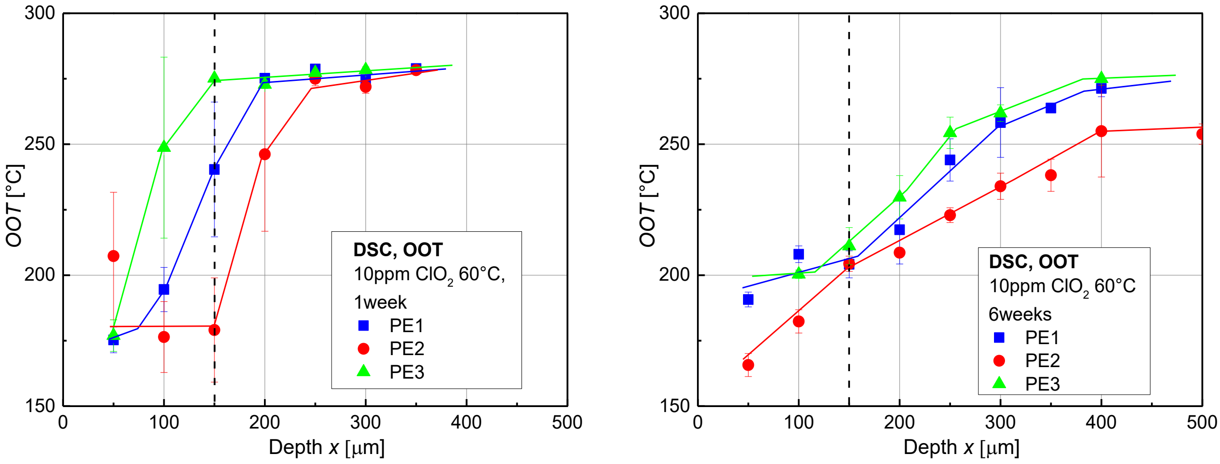
Such data would allow comparison of the performance of different PE resins and AO packages in disinfected solutions. Generally, the expected results would contribute to further understanding the relevant processes and ultimately support the further development of PE grades.

## 6.1 Experimental

This chapter focuses on the interpretation and discussion of the results from aging Experiments 1 and 8 (see Table 3.3). The former was performed in 10 ppm $ClO_2$ at 60°C, while the latter corresponds to the immersion test in 100 ppm HOCl at 60°C. For the aging experiment the BCK specimens of PE1, PE2 and PE3 grades were used. A detailed description of the selected materials is given in Section 3.2. Samples of PE1 and PE2 have the same type and amount of AO package (S1), while PE3 has an increased amount of S1 and an additional AO package (S1*S2), as it is presented in Table 3.2. These AO packages contain hindered phenolic antioxidants and probably processing stabilizers. That said, the exact composition is subjected to a confidentiality agreement with the project partner. Film specimens with a thickness of 50 µm were prepared from unaged and conditioned specimens using a rotary-microtome (see Fig. 3.4). Thin films were subjected to DSC-OOT to study the thermal stability evolution over the aging time. Furthermore, the crystallinity ratios were also measured and evaluated via DSC [12]. To investigate changes of the chemical structure, FTIR-ATR measurements were performed and the results were plotted against the distance from the immediate contact surface.

## 6.2 Thermal analysis of AO profile and crystallinity after exposure to $ClO_2$

Active AO molecules in the polymer sample can be estimated well with oxidation tests. It is known that oxidation induction time (*OIT*) values measured are in a linear relationship with the amount of AO available. To examine the AO depletion process, the oxidation onset temperatures (*OOT*) were measured, which can be well correlated to the *OIT* test [13–15]. The average *OOT* values plotted against the distance from the surface of the block specimens are illustrated in Fig. 6.1. The lines represent only a visual guide. The *OOT* values below 210°C are considered as an indication of complete active AO loss, while values above 270 °C correspond to unaged material conditions, representing the initial AO amount.



(a) (b)

Fig. 6.1: *OOT* profile of three PE grades after (a) 168 h and (b) 1038 h of immersion in 10 ppm $ClO_2$ at 60 °C, adapted from [16].

Generally, the three PE samples show a strongly reduced *OOT* on the surface and approximately the reference values in the bulk. In the case of PE2, low *OOT* values indicate a complete AO consumption in a 150 µm thick surface layer, while for PE3, this layer is around 50 µm thick after 168 h of aging in 10 ppm $ClO_2$. Since PE3 has the highest and PE2 has the lowest density and crystallinity (see Table 3.2), the *OOT* profiles observed might be dominated by this material property. It is somewhat difficult to draw clear conclusions about the overall thermal stability of the three PE materials, due to different resins and AO packages. Nonetheless, different AO loss rates of the three PE indicate that the *OOT* profiles are applicable to assess the thermal performance of different PE grades in $ClO_2$. The *OOT* profiles are shifted to deeper layers and the gradient of *OOT* reduction seems to decrease with increasing exposure time. Moreover, the decreased slope after 1038 h of immersion time and lower *OOT* values in the bulk indicate that the diffusion of active AO from the bulk took place up to a certain extent. Due to fast chemical consumption, an increased AO concentration gradient can be assumed between the surface and the bulk zone. Thus, diffusion of AO to the contact surface is likely. The differences between the AO consumption rates can be easily recognized. It should be noted that the sampling interval between 168 h and 1038 h of aging times showed similar trends and the same performance difference between the three PE grades (see Fig. 6.2). The previously observed ~150 µm thick degraded surface layer (Fig. 5.4) is in accordance with the complete consumption of active AO in this layer, as it is displayed in Fig. 6.1.

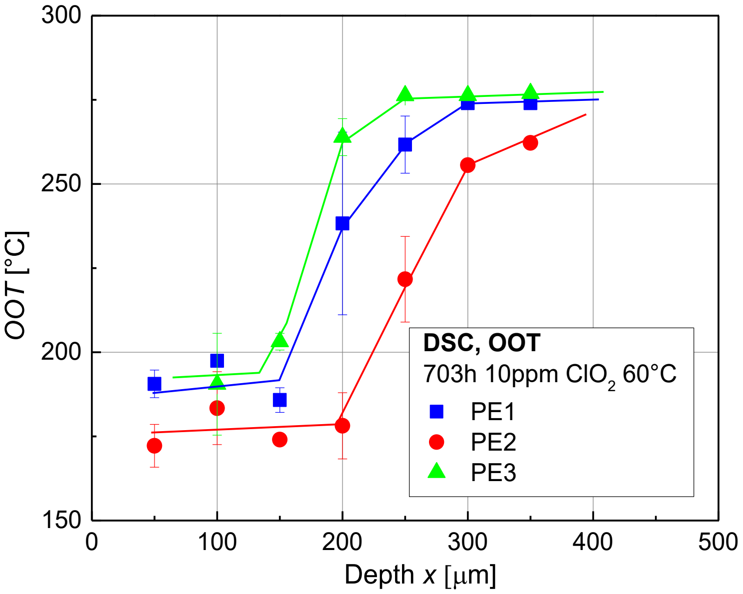
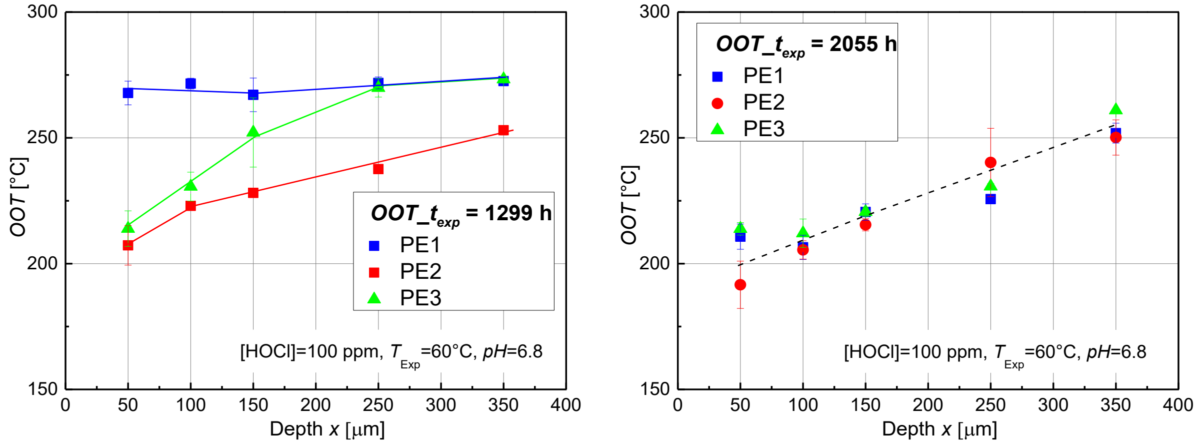


Fig. 6.2: *OOT* profile of three PE grades after 703 h of immersion in 10 ppm $ClO_2$ at 60 °C [16].

A similar approach was applied to the HOCl-aged specimens. The *OOT* profiles of the three PE materials, shown in Fig. 6.3, indicate a significantly different AO consumption process compared to $ClO_2$. After 1299 h of aging, the *OOT* values of PE1 remained unchanged. Considerably decreased OOT values were found for PE2 and PE3 in the analyzed surface layer. In spite of this difference, the 2055 h-aged specimens represent almost identical *OOT* profiles. In contrast with the $ClO_2$ results, the relationship between different densities and *OOT* profiles was not observed. This points out that in case of HOCl AO consumption is determined by other material properties. Comparing $ClO_2$ and HOCl *OOT* profiles, the different effects of disinfectants on the AO consumption are clear. The reduction of *OOT* profiles seems more linear in HOCl solution than in $ClO_2$, representing a very good agreement with the field aged pipe samples [5, 17]. Furthermore, significantly longer aging times until considerable AO consumption in HOCl solution clearly indicate the higher oxidative potential of $ClO_2$, in accordance with previous publications [4–6, 17–19]. Different *OOT* profiles may also be attributed to the different nature of disinfectants.

- In case of HOCl, both chlorination and oxidation reactions could take place,
- while $ClO_2$ prefers oxidation over chlorination.

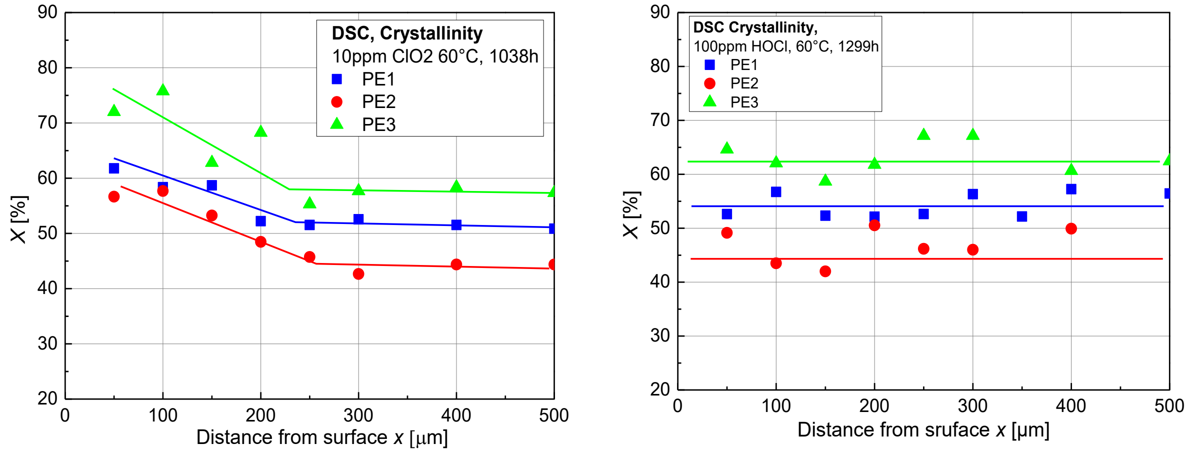
As discussed above, AO-reactive molecules in deeper material layers are most likely the $ClO_2$ and the $Cl_2$ molecules for $ClO_2$ and HOCl solutions, respectively.



(a) (b)

Fig. 6.3: *OOT* profile of three PE grades after (a) 1299 h and (b) 2055 h aging in 100 ppm HOCl at 60 °C, adapted from [16].

The crystallinity ratios of the film specimens were also analyzed and plotted against the distance from the surface, as it is displayed in Fig. 6.4. Despite considerable scattering of the data, an increased degree of crystallinity of $ClO_2$ aged specimens can be seen. The ratio of the crystalline phase increased by approximately 15 % and 10 % for PE3 and for PE1 and PE2, respectively. This phenomenon can be explained by the loss of highly degraded amorphous phase and by the chemi-crystallization [20, 21] processes. Comparing $ClO_2$ *OOT* profiles to HOCl *OOT* profiles, higher crystallinity on the surface corresponds to a slower disinfectant diffusion and a slower AO consumption in the affected surface layer.



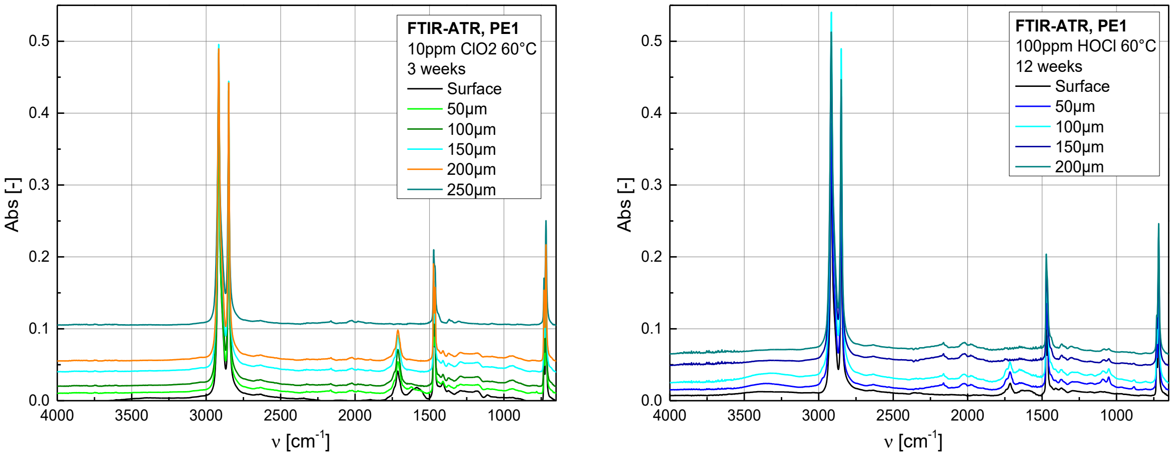
(a) (b)

Fig. 6.4: Crystallinity profile of (a) 1038h (6weeks) long 10 ppm ClO2-aged and (b) 1299 h long 100 ppm HOCl aged PE grades.

In fact, the crystallite phase is impermeable; hence, the diffusion of $ClO_2$ becomes progressively limited with the increase in crystallinity ratio. This also means that beside density, other material properties may also play an important role in the AO consumption, especially in deeper material layers. In contrast to the $ClO_2$-aged samples, exposure to HOCl resulted in a constant crystallinity ratio in a 400 µm thick surface layer. Considering strong abrasion like surface aging (see Fig. 5.14) caused by HOCl, this finding is not surprising at all. It should be noted that during the cutting and handling of the first film specimens, most of the surface powder layer was lost and not included in the DSC samples. In fact, a loss of degraded surface material (see Fig. 5.24) can lead to the measurement of quasi-intact bulk material. This assumption would explain the mostly constant crystallinity ratios shown in Fig. 6.4 (b). Identical sample aging and handling during the aging experiments ensures that the material properties obtained are comparable and applicable to identify different trends in the aging behavior of various PE grades.

## 6.3 Analysis of the chemical structure profile

Thin films were subjected to FTIR-ATR measurements to analyze the evolution of degradation products at various distances from the contact surface. In Fig. 6.5, the spectra of the $ClO_2$ and HOCl-aged samples up to 250 µm distance from the surface are shown. Carbonyl peaks around 1740 $cm^{-1}$ up to 200 µm clearly illustrate that $ClO_2$ caused a significant amount of oxidation in the affected surface layer. In case of HOCl exposure, significantly smaller carbonyl peaks were recorded up to 100 µm distance from the surface. This difference further emphasizes the distinct aging characteristics of PE caused by the two disinfectants.

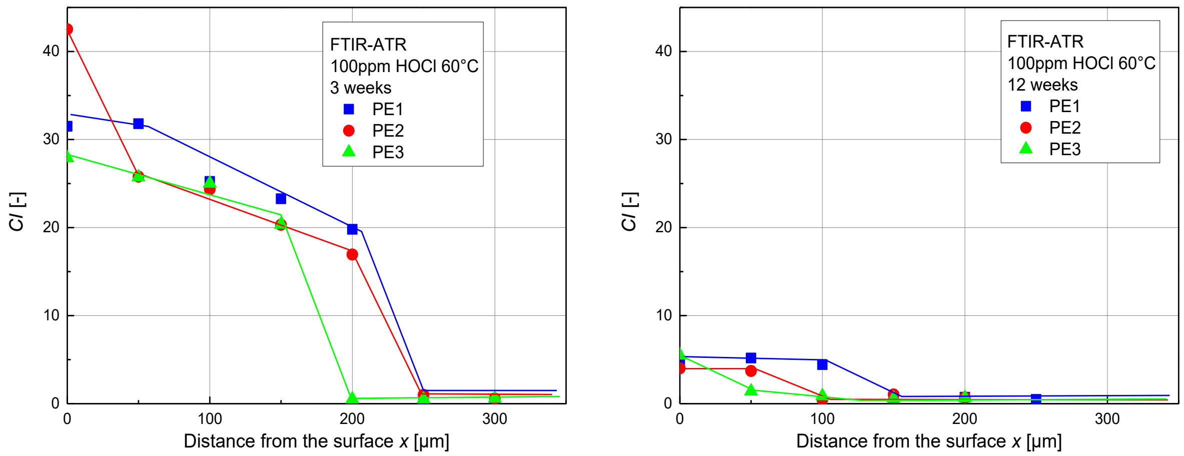


(a) (b)

Fig. 6.5: FTIR spectrum of PE1 at various distances from the surface after exposure (a) to 10 ppm $ClO_2$ for 703 h and (b) to 100 ppm HOCl for 1299 h at 60 °C.

For a more accurate interpretation, the evolution of degradation products and carbonyl index (*CI*) were calculated, as it is illustrated in Fig. 6.6. Samples immersed in $ClO_2$ show high *CI* values at 200 µm depth, while HOCl resulted in only slightly increased *CI* of an approximately 100 µm thick material layer. However, the different performances of the three PE grades are not as striking as in the *OOT* profiles. Slightly lower *CI* values of PE3 indicate moderately better resistance compared to PE2 and PE1.

Previous findings (see Section 5.3.1) demonstrated that polymer oxidation predominantly contributes to the *CI* increase. These results further affirm surface-limited HOCl aging and the oxidative effect of $ClO_2$ in deeper material layers. In other words, $ClO_2$ can diffuse into the bulk and cause chain scission reactions and chemically consume active AO.



(a) (b)

Fig. 6.6: Carbonyl Index depth profile of (a) 703 h long 10 ppm $ClO_2$ and (b) 1299 h long 100 ppm HOCl aged samples at 60 °C.

In contrast, immersion in HOCl leads to a highly surface-limited polymer degradation and AO consumption in the bulk. The latter process is most likely governed by the availability and diffusion of $Cl_2$ molecules. It should be noted that these findings also imply that $Cl_2$ reacts more or less selectively with AO molecules, without considerably inducing the polymer degradation in short-term aging experiments.

## 6.4 Summary and conclusion

The *OOT* and crystallinity profiles of the $ClO_2$-aged samples indicate that active AO molecules are rapidly consumed in a few hundred µm thick surface layer. In the course of this process, the diffusion of AO molecules to the surface may be initiated due to the high concentration gradient. On the one hand, the increased crystallinity ratio corresponds to chemi-crystallization and to the loss of the degraded amorphous phase. On the other hand, an increasing crystallinity ratio gradually limits the diffusion of $ClO_2$ molecules into the bulk. Therefore, beside density other material properties may play an important role in AO consumption as well. In agreement with the aforementioned assumption and literature, high *CI* values are originated mainly from the polymer oxidation, while AO oxidation products were found to be less significant. Despite the almost complete AO loss in the HOCl-aged samples, only low *CI* values were recorded at the same distance from the surface. In the surface layer analyzed, constant crystallinity ratios indicate that the polymer molecules stayed mostly intact in the HOCl solution. This finding is in accordance with the unaffected surface layer shown in Fig. 5.14.

The different *OOT*, crystallinity and *CI* profiles presented further confirm the significantly different aging characteristics of PE in $ClO_2$ and HOCl solution. Furthermore, the reported findings highlight the potential of this characterization method for material screening and a for better understanding of the AO and disinfectant diffusion relationship.

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# 7 Material ranking based on $ClO_2$ resistance

To assess the effect of disinfectants on the degradation of PE pipe grades ATSM 2023 [1] and ASTM 2263 [2], standardized methods are available. Since these tests are only specified for HOCl containing aqueous solution, their applicability is not clear regarding the $ClO_2$ test results. In these pipe pressure tests, the HOCl concentration is calculated from the ORP readings, which is also the controlled parameter. The relationship of pH, ORP and HOCl concentration is well established, but it is unknown for $ClO_2$. Nonetheless, several publications attempt to describe material aging in $ClO_2$ [3–8] and evaluate the performance of AO packages [9–13] in contact with $ClO_2$. Moreover, the effects of $ClO_2$ have also been actively investigated in various field case studies as well as with pipe pressure tests according to ASTM standards [5, 14, 15]. Since these studies used different aging temperatures and disinfectant concentrations as well as different PE grades and AO packages, the reported results are hardly comparable. Aging parameters are frequently not reported over the exposure time, which makes it more difficult to relate published data of different research papers to each other. Consequently, there is no publicly available data about the relative ranking of different PE grades based on their $ClO_2$ resistance.

This chapter aims to provide accelerated aging data on different PE pipe grades in $ClO_2$ containing solution in order to complete Objective C (see Section 1.2) of this dissertation. A major focus was put on the development of a fast ranking tool, in order to analyze the $ClO_2$ resistance of different PE formulations based on their mechanical and thermal performance. Moreover, a comparison of various material morphologies and stabilizer packages could provide further insight into the relevant degradation processes. The determination of the relative performance of different PE formulations, in a reasonable time frame, is imperative to support material and AO development.

## 7.1 Experimental

In Chapter 4, the immersion test of PE samples in 1 ppm $ClO_2$ at 50°C or lower concentration and temperature was found optimal to observe the decline in material properties over the aging time. Therefore, tensile tests and DSC-OOT measurements were performed on six PE grades after various aging times during Experiments 4, 6 and 7 (see Table 3.3). To identify and confirm the effect of $ClO_2$, a control immersion test was performed in distilled water according to Experiment 9. The $ClO_2$ concentration was kept at a constant level, as it is presented in Fig. 7.1. Considerable deviations from the set values were only recorded in a short time period during the restart of the exposure device after the sample removals. Across all three $ClO_2$ experiments, a pH level of 6.8 was applied and the ORP values were recorded between 520 and 610 mV. Although the selected materials are sufficiently described in 3.2, for easier interpretation, the PE resins and AO packages are classified and shown in Table 7.1. Considering the similar molecular weight distribution, the two unimodal, PE3 and PE6, and the two monomodal, PE2 and PE4, materials were categorized as C and B, respectively. Since PE1 and PE5 show a weak shoulder in the MWD curves (see Fig. 3.5), these materials are labelled as A. To evaluate the material embrittlement rate of the six PE materials, the elongation at break values from the tensile tests were normalized with the unaged material property. The *OOT* values under 210 °C are assumed to represent a complete loss of active AO. Furthermore, the GPC results of aging Experiment 4 are also included to better interpret the relationship of chain scission and material embrittlement detected with the tensile tests.

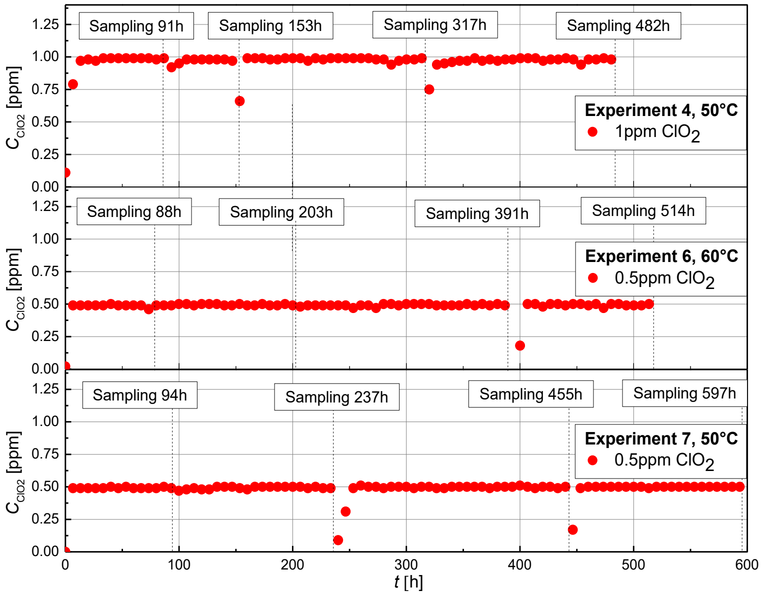


Fig. 7.1: $ClO_2$ concentration over the exposure time for the three aging experiments [16].

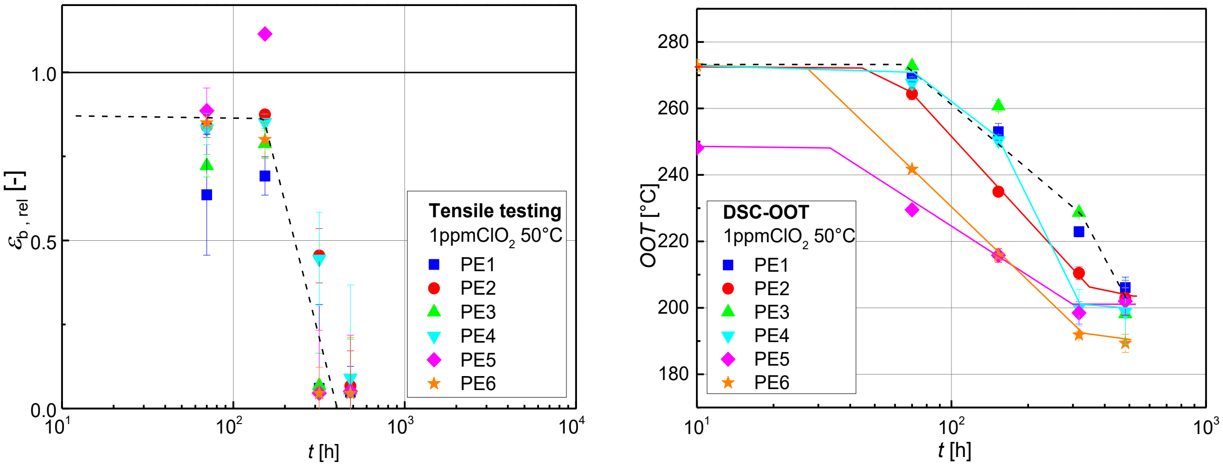
Table 7.1: Classification of the PE resins and AO packages selected.

| | PE1 | PE2 | PE3 | PE4 | PE5 | PE6 |
|---|---|---|---|---|---|---|
| Polymer | A | B | C | B | A | C |
| AO | S1 | S1 | S1*+S2 | S1 | S3 | S4 |

## 7.2 Material ranking of PE grades aged in $ClO_2$

As a critical mechanical value, elongation at break ($\varepsilon_b$) was chosen, since it is the most sensitive tensile parameter to material aging. After an arbitrarily selected 50 % reduction of $\varepsilon_b$, advanced material embrittlement and loss of functionality were assumed. In the following figures, the colored and dashed lines only serve as a visual guide.

In Fig. 7.2 (a), the change in $\varepsilon_b$ values over the aging time in 1 ppm $ClO_2$ at 50 °C indicate a similar behavior of the six materials; however, a slightly slower $\varepsilon_b$ decline for PE2 and PE4 can be recognized after 317 h immersion. The consumption of active AO was investigated with *OOT* measurements, presented in Fig. 7.2 (b). Concerning PE1 and PE3 higher *OOT* values, compared to other materials, they correspond to increased thermo-oxidative resistance. Considering the higher AO amount of PE3, this behavior is not surprising at all. Even though PE1 and PE2 have the same AO package, a faster AO consumption was recorded for PE2. The *OOT* values represent the combined performance of PE resin and AO. The fastest decline in *OOT* was found for PE5 and PE6, which is probably the consequence of a less $ClO_2$-resistant AO package.

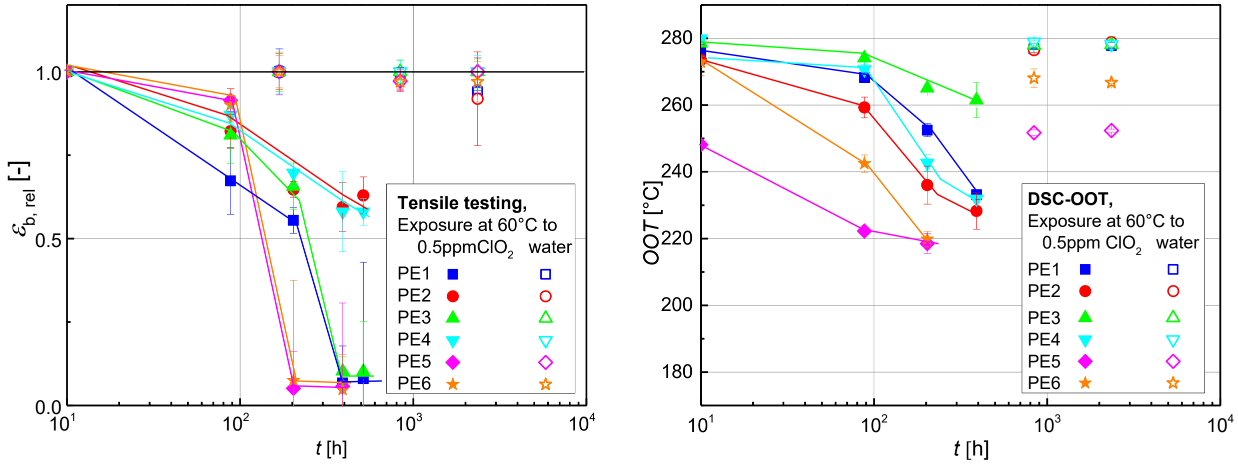


(a) (b)

Fig. 7.2: Elongation at break (a) and *OOT* values (b) plotted over the exposure time and after aging in 1 ppm $ClO_2$ solution at 50 °C [16].

Concentration of the aging media was lowered to 0.5 ppm in order to identify the different mechanical performances of the selected PE grades. The aging temperature was increased to 60 °C to avoid long testing times. The tensile test results and *OOT* analyses are shown in Fig. 7.3. The slower aging process allowed a more accurate observation of different material degradation rates, resulting in three distinct groups based on normalized $\varepsilon_b$. Samples PE2 and PE4 show the slowest, while PE5 and PE6 display the fastest material embrittlement rate. The samples aged in non-chlorinated water showed constant $\varepsilon_b$ values over the 1909 h long immersion test, highlighting the detrimental effect of $ClO_2$ on the degradation of PE grades. Beside the unaffected mechanical properties of the six materials over the control experiment, the *OOT* values stayed constant as well, as it is illustrated in Fig. 7.3 (b). The presence of $ClO_2$ leads to considerable AO consumption, which is well illustrated by the decreased *OOT* values. As expected, PE3 showed the slowest AO consumption rate due to the increased AO amount. Similar *OOT* evolutions of PE1, PE2 and PE4 correspond well to the effect of the same AO package. In accordance with Experiment 4, the effect of different PE grades can be recognized by slightly higher values of PE1 than PE2. Analogous to the previous immersion test, the fastest AO consumption was found for PE5 and PE6. These results undoubtedly affirm the substantial acceleration of polymer and AO degradation caused by $ClO_2$. It is important to note that both Experiments 4 and 6 led to very similar material classification, which draws attention to the applicability of the material characterization approach used.

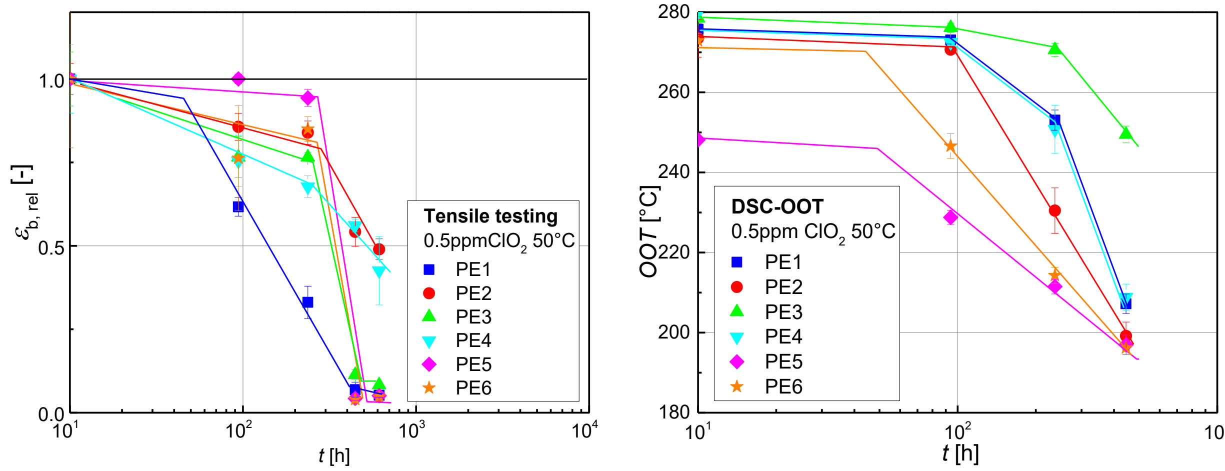
Normalized $\varepsilon_b$ data (Fig. 7.4) of the third aging experiment performed in 0.5 ppm of $ClO_2$ at 50 °C showed particularly different trends than the previous conditioning. However, for PE2 and PE4, the similar behavior during the three different immersion tests confirms that they belong to one material group as identified in previous experiments.



(a)

(b)

Fig. 7.3: Elongation at break (a) and *OOT* values (b) plotted over the exposure time and after aging in 0.5 ppm $ClO_2$ solution at 60 °C [16].

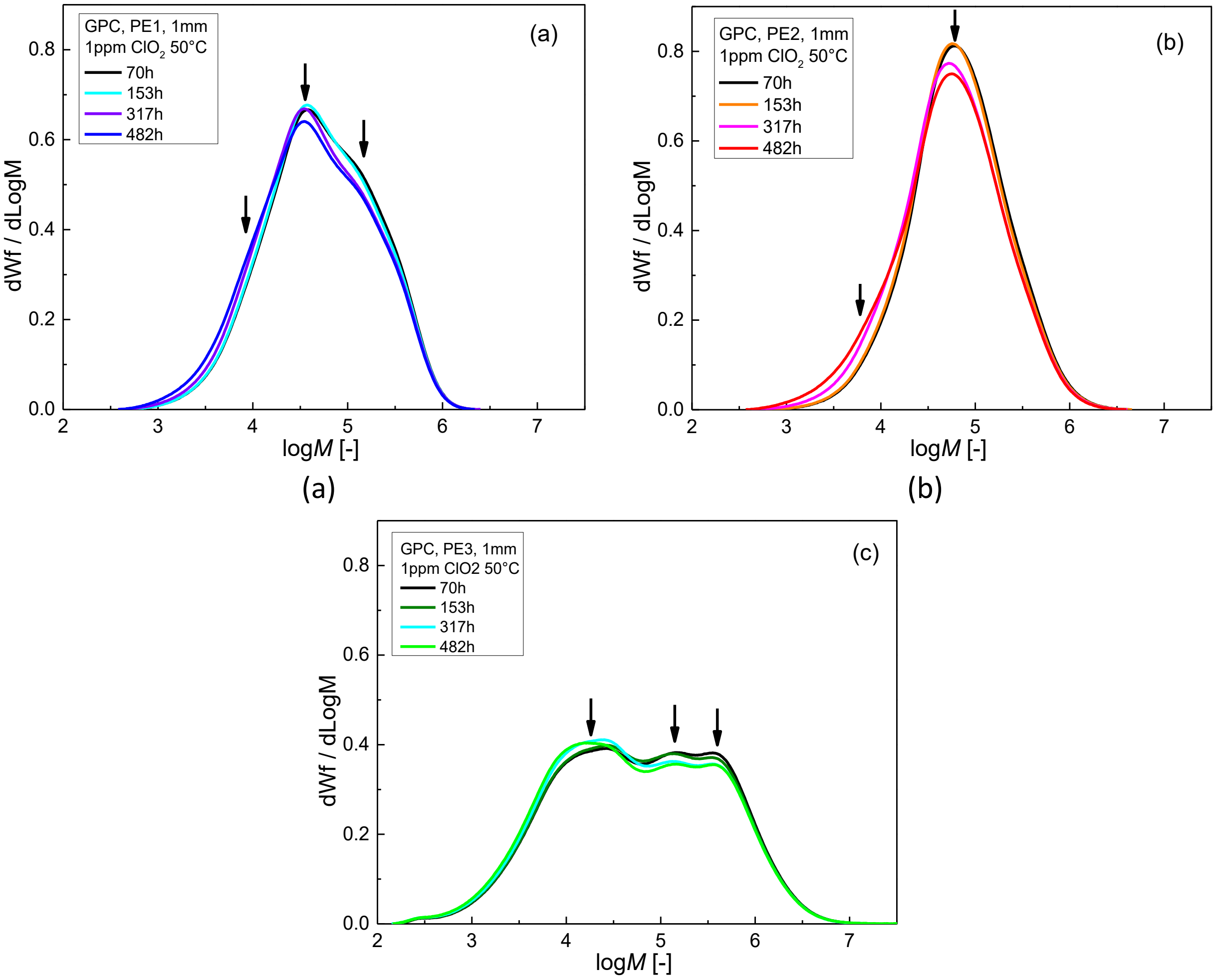


(a)

(b)

Fig. 7.4: Elongation at break (a) and OOT values (b) plotted over the exposure time and after aging in 0.5 ppm $ClO_2$ solution at 50 °C [16].

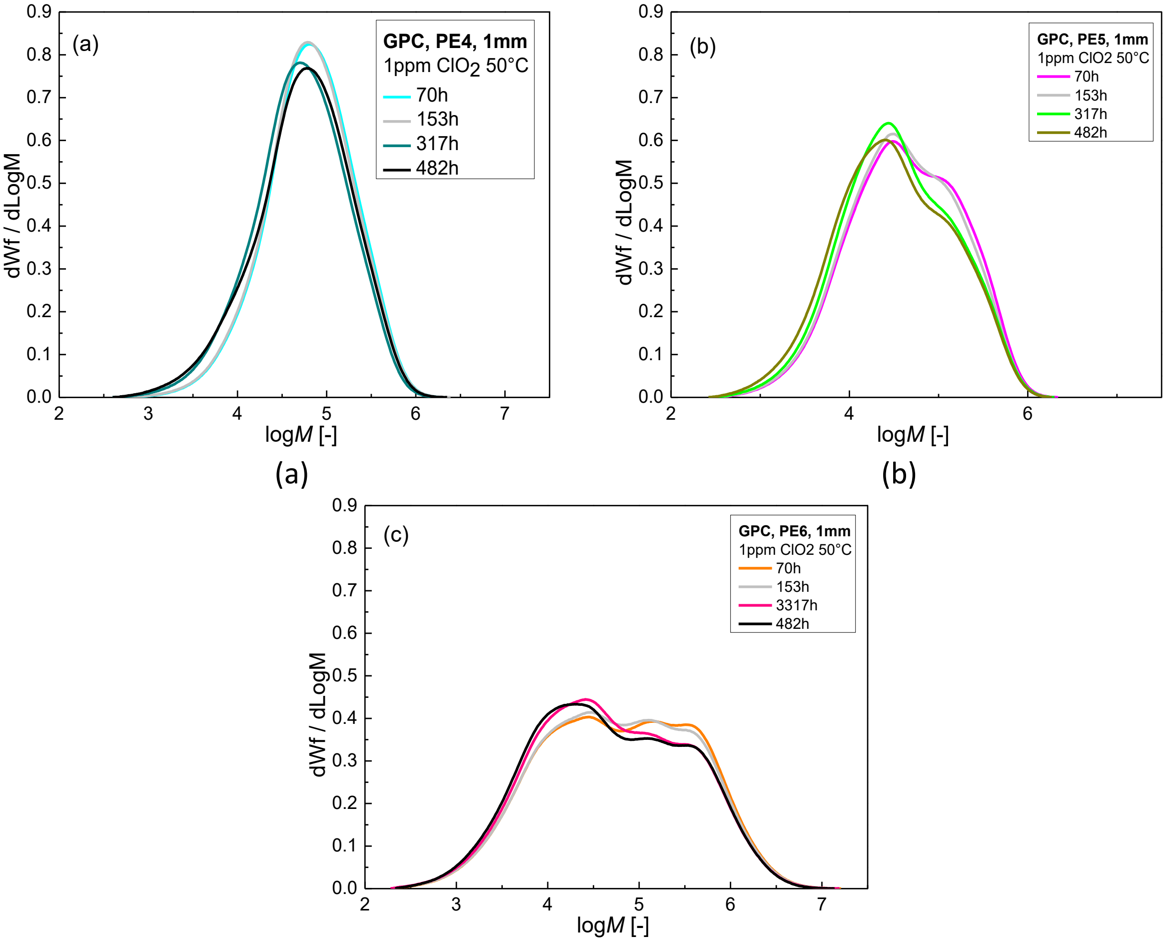
In the case of PE3, PE5 and PE6, almost identical reductions in the $\varepsilon_b$ values were found (Fig. 7.2). The inconsistent material embrittlement recorded for PE1 was probably caused by the scattering of $\varepsilon_b$. Furthermore, the different material classifications observed in Experiment 7, compared to Experiments 4 and 6, are probably caused by the different sampling intervals. An additional sample removal between 237 and 455 h of exposure could lead to the resolution of this contradiction. Considering the different material groups observed based on the $\varepsilon_b$ decline of the six materials, a similar conclusion can be expected from the analysis of molecular weight changes over the exposure time. Therefore, the molecular weight distribution (MWD) curves of Experiments 4 and 1 were analyzed. In Fig. 7.5, the MWD curves plotted over the immersion in 1 ppm $ClO_2$ at 50 °C of PE1, PE2 and PE3 are shown after various sampling intervals. These three materials represent the three different PE grades, as shown in Table 7.1. As far as the PE1 and PE3 weight fraction of longer molecules goes, which has a higher comonomer concentration, they probably decreased due to chain scission process. A slight broadening of the MWD curves can be recognized for PE1 and PE3. In contrast, the exposure of PE2 to $ClO_2$ resulted in more significant MWD broadening, which explains the slower $\varepsilon_b$ decrease of PE2, compared to other materials. The MWD curves of PE4 showed an almost identical change to PE2. In the case of PE5 and PE6 similar changes to PE1 and PE3 were detected, respectively of MWD (see Fig. 7.6). The overall decrease in molecular weight was the most severe for PE5 and PE6, which explains the fastest $\varepsilon_b$ decline in these two samples.



(a) (b)

(c)

Fig. 7.5: MWD curves of (a) PE1, (b) PE2 and (c) PE3 after various immersion times in 1 ppm $ClO_2$ at 50 °C.

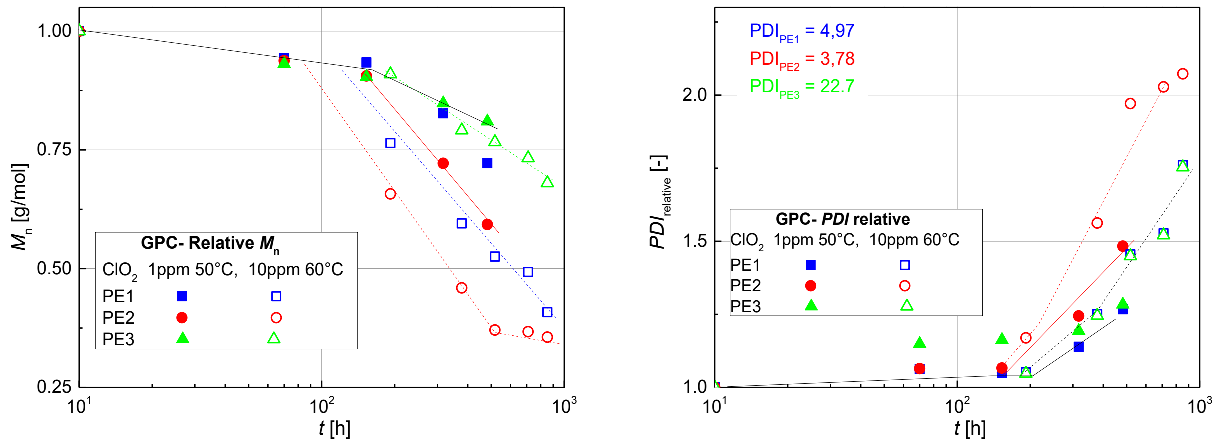


(a) (b)

(c)

Fig. 7.6: MWD curves of (a) PE4, (b) PE5 and (c) PE6 after various immersion times in 0.5 ppm $ClO_2$ at 50 °C.

To interpret the MWD changes more accurately, the molecular weight moments and the polydispersity Index (*PDI*) were examined. The weight average molecular weight values decreased less for PE3 than for PE1 and PE2, although the changes were extremely small. As previously discussed, the degradation process initiated by $ClO_2$ is highly surface-limited. Hence, a significant amount of intact bulk material can be assumed for 1 mm thick specimens, especially in the case of low concentrations. Nonetheless, strong decrease in $\varepsilon_b$ indicates that a significant amount of chain scission reactions took place in the affected material layer and on the immediate contact surface. In Fig. 7.7, normalized $M_n$ and *PDI* values over the aging time represent this process well. Both parameters suggest a more advanced degradation of PE2 compared to PE1 and PE3. The results of the 10 ppm $ClO_2$ aging experiment clearly confirm this difference between the materials.



(a) (b)

Fig. 7.7: Evolution of normalized $M_n$ (a) and *PDI* (b) plotted over the aging time of Experiments 4 and 1.

## 7.3 Summary and conclusion

Comparing various aging experiments, some important observations can be made, especially considering the different base polymer and stabilizer packages. In spite of the same stabilizer packages of PE1, PE2 and PE4, variation in the thermal stability and in the AO loss rate can be recognized. This phenomenon clearly originates from the difference in molecular morphology. On the one hand, the combination of a base polymer and a certain AO package provides a given thermal performance. In fact, unaged samples with the same AO showed some slight differences in the *OOT* values (see Table 3.2), which corresponds well to the effect of different base polymers. On the other hand, material properties, such as crystallinity and morphology, have a distinct influence on AO consumption. Compared to PE2 (see Fig. 6.4) in the affected surface layer, the faster crystallinity ratio increases in the PE3 and PE1 samples explain the slower AO consumption of PE3 and PE1 during the aging of 1 mm thick specimens. The immense effect of $ClO_2$ on the consumption of active AO molecules is well illustrated by comparison of the constant *OOT* level of control samples with the clearly decreasing *OOT* of the immersed samples (see Fig. 7.3). In case of short-term exposure to aqueous solutions, physical loss including diffusion of AO molecules are negligible [17, 18]. Thus, the chemical reaction between $ClO_2$ and AO is a dominating mechanism during such immersion tests.

Significantly reduced $\varepsilon_b$ of $ClO_2$-aged samples (Fig. 7.3) compared to the control specimens points out the impact of the oxidizing agent on polymer degradation. These results imply chain scission reactions caused by $ClO_2$. In accordance with reports of Colin et al. [6, 7], $ClO_2$ or its derivatives can initiate radical chain scissions. This initiation of chain scission most likely takes place in competitive reactions between the chain defects and tertiary carbon atoms (see 5.2.2). Moreover, the radical ground state of $ClO_2$ also supports the viability of this explanation. The results presented above further affirm the previously discussed simultaneous AO consumption and polymer degradation reactions. Examining the data points in Fig. 7.3 during Experiment 6 after the first sampling, significant $\varepsilon_b$ reduction prior to complete AO consumption can be observed. One explanation for this phenomenon is the parallel reaction of $ClO_2$ with AO and polymer molecules. It was shown previously that the degraded surface layer based on *OOT* and carbonyl depth profiles is around 250 µm thick after 3 weeks of exposure to 10 ppm $ClO_2$ solution at 60 °C. The significantly lower $ClO_2$ concentration applied in Experiments 4, 6 and 7 probably caused AO consumption to a lesser extent and in a thinner surface layer. Therefore, in the bulk of 1 mm thick samples, a sufficient amount of active AO should be available to prevent degradation of the polymer chains. In spite of this, decreased $\varepsilon_b$ values were recorded. The most logical explanation for this contradiction is that immersion in $ClO_2$ causes simultaneous AO consumption and polymer degradation. Data presented in Fig. 5.10 further validates this interpretation of the PE aging mechanism in $ClO_2$.

Regarding thermal stability, PE3 shows superior behavior. The PE6 and PE3 are formulated from the same base polymer containing different AO packages. The remarkably improved thermal stability of PE3 compared to PE6 represents distinctly increased $ClO_2$ resistance of the AO package *1** combined with *2* (Table 7.1). Therefore, the combination of the PE2 or PE4 base polymer with the stabilizer package of PE3 could provide a better performance overall when it comes to contact with $ClO_2$-containing media. Despite the highest molecular weight and density of PE3 and PE6, their resistance to $ClO_2$ was found to be only moderate compared to the other PE materials, which reflects well the complexity of the aging mechanism induced by $ClO_2$. Confirming material ranking observed, GPC results of Experiments 4 and 1 were investigated. The evolution of $M_n$ and *PDI* values over the aging time corresponds to more advanced degradation of PE2 than PE1 and PE3 based on both immersion tests. The contradiction between the tensile test and GPC results regarding relative material performances draws attention to the importance of a critical data evaluation. Nevertheless, the applied material aging and characterization methodology is applicable for relative material classification based on their $ClO_2$ resistance. The three material classes determined clearly demonstrate the potential of this approach to assist in AO and PE resin development.

Based on the result from Chapter 4, an optimized ranking approach was applied to conduct three accelerated aging experiments in 1 and 0.5 ppm of $ClO_2$ at 50 and 60 °C on six various PE pipe grades. The accuracy of the exposure device is clearly illustrated by the highly stable disinfectant concentrations over the complete testing series. This well-defined conditioning led to a better differentiation between the six PE grades. The parallel reduction of $\varepsilon_b$ with the consumption of active AO observed suggests that the $ClO_2$-induced aging mechanism differs from the commonly known auto-oxidative degradation of polyolefin materials. Applying the material ranking methodology introduced, a fast evaluation of the different PE grades in $ClO_2$-containing medium was performed. The testing methodology presented shows great potential to analyze and evaluate the relative disinfectant resistance of PE materials in a timeframe of a few weeks. It must be noted that this approach does not provide absolute $ClO_2$ resistance. However, it points out relative differences between various material formulations. Furthermore, a critical evaluation of the aging dataset is crucial to identify higher and lower performing material classes in $ClO_2$, because of the complex interaction of PE, AO and disinfectants.

## 7.4 References

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# 8 Summary

Secondary disinfection creates the risk of premature failure of PE pipes in the water distribution system. The strong oxidizing nature of $ClO_2$ and HOCl leads to an accelerated material embrittlement, decreasing the overall lifetime expectancy dramatically. To assist the progress of the material development with improved disinfectant resistance, a comprehensive understanding of relevant material degradation is crucial. In this dissertation the following major goals were set:

**A: Method development and optimization of accelerated aging in $ClO_2$ and HOCl solutions for PE pipe grades under constant conditions.**

**B: Determination of the aging mechanisms of PE in $ClO_2$ and HOCl solutions applying immersion tests without mechanical loading.**

**C: Development and application of material screening methods in order to identify the relative $ClO_2$ resistance of different PE pipe grades.**

Considering the fast oxidative and decomposition reactions of HOCl and $ClO_2$, studying the effect of disinfectants on polyolefin pipe grades stable exposure conditions are necessary. Moreover, safety measures regarding the production and handling of $ClO_2$ accelerated aging experiments in a laboratory environment can be challenging. Therefore, a new exposure device has been developed and implemented, which can accommodate safe and well-controlled immersion tests in HOCl and $ClO_2$. Applying this exposure device, the aging mechanism and material ranking of PE grades in HOCl and $ClO_2$ including the optimization of aging conditions were studied. Based on the collected data the following conclusions were drawn regarding the three major objectives of this dissertation.

**A:**

In order to precisely study the aging behavior of PE pipe grades an optimization process of the immersion conditions, specimen geometries and material characterization methods were performed. Exposure of 1 mm thick tensile specimens to 1 ppm $ClO_2$ at 50 °C or at lower concentrations and temperatures was found suitable to observe material degradation in accelerated aging experiments. Material characterization with SEM, tensile tests, oxidation tests and FTIR-ATR analyses were found applicable to detect material aging comprehensively. Furthermore, the OOT measurements showed significantly higher sensitivity to active AO consumption the than OIT analyses. Since the degradation process in HOCl solution is substantially slower and more surface-limited than in $ClO_2$, the immersion of 0.3 mm thick specimens in 100 ppm HOCl at 60 °C was found to be optimal.

**B:**

Different aging mechanisms of PE in the two disinfectant solutions were identified and described for the first time based on a thorough experimental approach. Distinct aging characteristics of PE in $ClO_2$ and HOCl were found by differences in the surface aging process, AO consumption, diffusion of reactive disinfectant molecules, molecular weight decreases and degradation products. Beside the appearance of surface cracks and an embrittled surface layer, simultaneous chemical attacks on the AO and polymer molecules were identified, as an effect of $ClO_2$. As a reactive species, which can diffuse into the bulk, $ClO_2$ molecules are the most probable candidates. In fact, chlorine molecules were detected in the degraded surface layer with a thickness between 100 – 300 µm. Chain scission reactions most likely occurs in a competitive way on tertiary carbon atoms and on oxidized or chain defect points of the polymer molecules. An inverse evaluation approach of the surface functional groups caused by immersion in $ClO_2$ suggests that the dominating chain scission reaction follows the α-keto-hydroperoxide decomposition reaction path. Exposure to HOCl led to surface voids and cavities and an overall surface erosion process, without any indication of an embrittled surface layer. Degradation was found to be highly surface limited and follows the auto-oxidative degradation process in an accelerated fashion. Presumably, $Cl_2$ and HOCl molecules are able to diffuse into the bulk and react with active AO. The analysis of molecular weight moments implies that HOCl leads to a quasi-selective chain scission process on tertiary carbon atoms. Surface degradation products indicate that decomposition of allylic hydroperoxides dominates the chain scission reactions on the immediate contact surface. Degradation products probably originate predominantly from polymer oxidation, considering the material properties compared over the aging period. The differences observed in the PE aging mechanisms caused by $ClO_2$ and HOCl are summarized in Table 8.1. Conclusions concerning PE degradation in disinfected aqueous solutions are of high importance for the further development of PE grades and AO packages. Preventing the above-mentioned aging processes would lead to an improved disinfectant resistance of the polymer composition and consequently to a higher lifetime expectancy of PE pipes.

**C:**

Fundamental studies on the performance of PE pipe grades in aqueous solution with high and low amounts of $ClO_2$-containing media were already discussed above. Concerning the PE performance screening, these investigations indicate that the AO consumption and degradation product profile of three different PE grades can be used to differentiate between PE grades. Moreover, data collected, including the crystallinity ratio profiles, suggests that the rate determining process is the diffusion speed of $ClO_2$. The AO consumption rate is mainly determined by the polymer density and by the gradual increase in the crystallinity ratio in the affected surface layer. Furthermore, these material property profiles are applicable to evaluate the thermal stability of a given PE matrix and AO package in contact with $ClO_2$ disinfected water. For accelerated material ranking, aging experiments with low concentration of $ClO_2$, applying 1 mm thick tensile specimens were performed. Due to the long testing times in HOCl, material ranking was not realized. Immersion tests conducted in 1 and 0.5 ppm $ClO_2$ with six selected PE grades resulted in three distinct material groups based on embrittlement and the AO consumption rate. These relative differences were confirmed by three separate immersion tests. Considering the knowledge presented in the literature overview chapter, this is the first material ranking data, based on the few-weeks-long immersion tests in $ClO_2$. Moreover, the applicability of this testing methodology draws attention to the importance of stable, precisely controlled aging conditions. It should be noted that the material classification method applied must be critically evaluated. With additional material characterization data, such as GPC, absolute differences between the $ClO_2$ resistance of PE materials can be assessed.

Overall, the presented work points out the detrimental effects and major differences between the aging mechanisms of PE in $ClO_2$ and HOCl. Including relative material ranking data, the determined results are highly advantageous in order to assist and promote the development of PE grades with improved disinfectant resistance.

Table 8.1: Observed and deduced differences of PE aging mechanisms caused by $ClO_2$ and HOCl solutions. Conclusions are based on accelerated laboratory aging experiments.

| | **$ClO_2$** | **HOCl** |
|---|---|---|
| **Surface** | → Cracks<br>→ Degraded layer, up to 300 µm | → Cavities and voids, erosion<br>→ No degraded surface layer |
| **Cl atoms in the bulk** | → Detected both on the surface and in the degraded layer | → Detected only on the surface, but diffusion into the bulk is assumed |
| **Oxidation process** | → Simultaneous oxidative reaction with AO and polymer | → Accelerated auto-oxidative aging |
| **Chain scission reaction** | → Competitive reaction with the tertiary C atoms defect and oxidized polymer atoms<br>→ Predominantly α-keto-hydroperoxide decomposition | → Quasi-selective reactions with tertiary C atoms<br>→ Predominantly allylic hydroperoxide decomposition |
| **Reactive molecules** | → $ClO_2$ and radicals derived from $ClO_2$<br>→ Diffusion of $ClO_2$ | → HOCl and radicals derived from HOCl<br>→ Diffusion of $Cl_2$ and in lower extent HOCl |

# 9 Outlook: effect of disinfectants on PE pipe lifetime

Complex chemistry and the aging process of PE pipe degradation in contact with disinfected water makes it difficult to estimate the lifetime of such materials. Applying different temperatures during pipe pressure tests, in accordance with ATSM 2023 [1] and ASTM 2263 [2], Arrhenius equation based extrapolation of the pipe failure time to application temperature can be performed. Although the available standardized test methods, are applicable for lifetime assessment in HOCl, there are some critical arguments. Beside the fact that these tests could take up to 5000 h at 95 °C [3, 4], the costs are also considerably high. On the one hand, most modern PE pipe grades are likely to pass these tests without failure; hence, the data collected supports neither the extrapolation of failure times to application conditions nor the comparison of non-failed PE grades. On the other hand, high testing temperatures (above 100 °C) may initiate the melting of thin crystallite lamellae. This process is illustrated well in Fig. 9.1, where the onset of melting already takes place below 100 °C. This thermal effect draws attention to the following important considerations:

- First, failure times of experiments conducted over the onset temperature of melting cannot be used for Arrhenius equation-based extrapolation [5], since this data represent the molten physical state and not the rubbery physical state.
- Secondly, the Arrhenius concept is only applicable in a given temperature range, in which the polymer stays in the same physical state and the dominating reaction mechanism is unchanged.

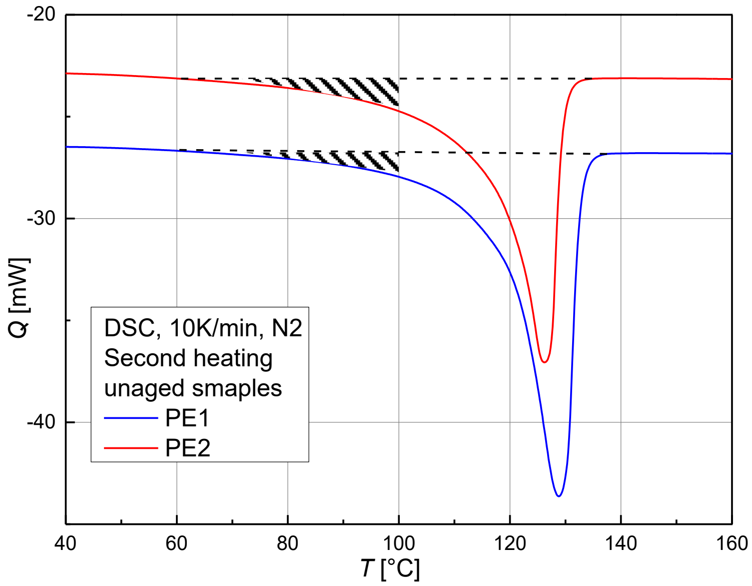


Fig. 9.1: Melting curves of unaged PE1 and PE2.

These criteria reflect the fact that the rate of reaction follows the Arrhenius reaction rate functions. In other words, a 10 °C increase doubles the reaction rate. Preceding the calculation of pipe lifetime on application temperature, the above-mentioned criteria and assumptions must be considered. In fact nonlinearities and the limited application of Arrhenius lifetime extrapolation have been reported based on standardized pressure tests [6]. The authors report that the Arrhenius model is not applicable for PE pipes in contact with $ClO_2$, since the complex aging process does not follow the Arrhenius reaction rate function. The physical states change of semi-crystalline polymers (e.g. melting leads to abrupt change in properties such as free volume and chain mobility) effects substantially the material properties, leading to a modified dominating reaction mechanism. Consequently, different reaction rate functions must be considered for each physical state. Moreover, the high scattering of failure times obtained from the pipe pressure tests [7], according to [8], raises further questions about the reliability and applicability of this testing method. These considerations point out the need for a better approach to estimating the effect of $ClO_2$ on the lifetime of PE pipe grades. This section focuses on the introduction of a theoretical model combining the disinfectants that caused enhanced surface aging and the fracture mechanical pipe lifetime prediction method. In the following section, at first the fracture mechanical based PE pipe lifetime prediction is discussed. Secondly, a theoretical concept is presented, which would allow the incorporation of advanced surface aging effects in the lifetime prediction concept.

To assess the lifetime of PE pipes under static loading based on fracture mechanics, the following three phenomena have to be considered.

1. Inherent defects in PE pipes derived from impurities, polymer agglomerates, inhomogeneity and shrinkage cavities usually have a size between 50 µm and 250 µm [9].
2. Time to crack initiation ($t_{ini}$) depends on
   a. the inherent defect size,
   b. the stress intensity factor and hence on the crack size, geometry and applied hoop stress in pipes, as shown in Equation 15, and
   c. the temperature.
3. Slow crack growth (SCG) resistance, which is described by Equation 16.

Moreover, the SCG rate increase with increasing crack length, as it is displayed by Equation 1 and 2 [10, 11], where $K_I$ is the stress intensity factor of loading mode I, $\sigma$ is global loading, $a$ is crack length, $Y$ is a geometry factor and $A$ and $m$ are material parameters. Equation 2 was suggested by Paris and Erdogan [12] to describe the linear crack growth.

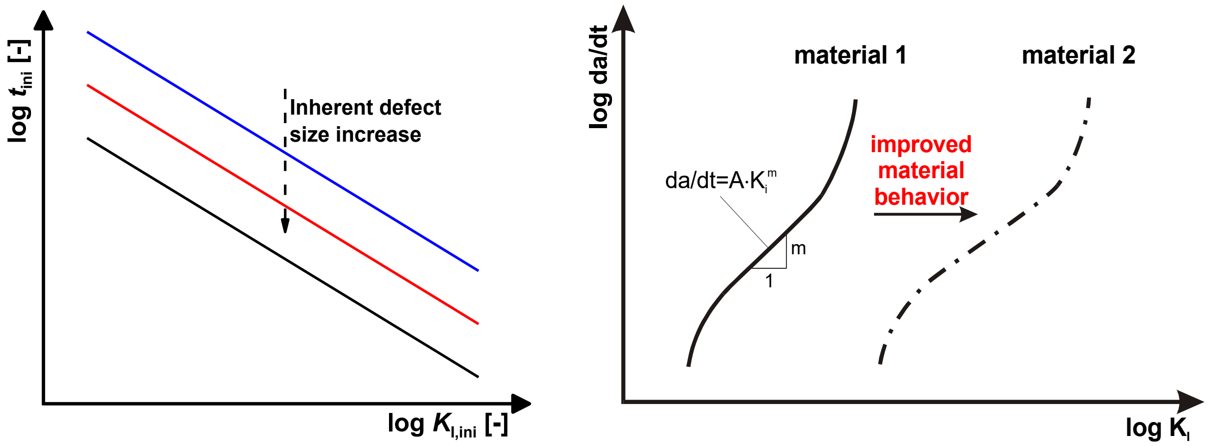
$$K_I = \sigma * \sqrt{a} * Y \tag{15}$$

$$\frac{da}{dt} = A * K_I^m \quad 16)$$

In non-disinfected water $t_{ini}$ depends on the inherent defect size and on $K_I$ (see Equation 17). This correlation is schematically illustrated in Fig. 9.2 (a). Assuming a constant $K_I$ value, bigger inherent defect sizes will lead to shorter $t_{ini}$. The total time to pipe failure is the sum of $t_{ini}$, and the time of SCG ($t_{SCG}$) as it is presented in Equation 17. Solving Equation 16 in the interval between $a_{ini}$ and $a_f$, which is the pipe wall thickness, $t_{SCG}$ can be calculated (see Equation 18) [13, 14]. In Fig. 9.2 (b) the determination of material parameters is illustrated.

$$t_f = t_{ini} + t_{SCG} \tag{17}$$

$$t_{SCG} = \frac{1}{A} * \int_{a_{ini}}^{a_f} \frac{1}{K_I^m} * da \qquad (18)$$



(a) (b)

Fig. 9.2: Schematic illustration of inherent defect size effect on crack initiation time – stress intensity factor function (a) and Paris law for the determination of material parameters *K* and *m* (b).

Applying the above-presented correlations, pipe lifetimes can be calculated under the given application conditions (transported fluid, temperature, hoop stress, pipe geometry). Naturally, if the transported fluid contains strong oxidizing agents, like disinfected water, the effect of these substances on the pipe lifetime is a matter of interest. Considering the highly surface-limited aging effects of disinfectants [15–18], the effect of these oxidizing agents is presumably limited to the crack initiation part of the total pipe lifetime. In order to describe the dependence of the surface embrittlement rate of PE pipe grades on the aging conditions (disinfectant concentration and temperature), the correlation illustrated in Fig. 9.3 has to be determined experimentally. As it was discussed thoroughly in this dissertation, the thickness of the embrittled surface layer converges to a constant value. Hence, a saturation-like correlation can be assumed. It is assumed that the embrittled surface layer acts as the initial defect and dominates the crack initiation times. After crack initiation, crack growth is mainly dominated by the crack growth resistance of the base material, with only a limited effect of the disinfectant on it.

The combination of a stabilization system and molecular structure fundamentally determines the disinfectant resistance of a given PE pipe grade. Different PE pipe grades probably have distinct aging behaviors and surface embrittlement rates under the chosen aging conditions. In other words, PE_A has a thicker aged surface layer than PE_B (see Fig. 9.3) at a given point in the aging process. First, this knowledge would provide an improved material ranking. Secondly, if the asymptotic embrittled surface thickness ($a_{\text{ini, chem}}$) can be determined experimentally under different aging conditions, then for a chosen PE, the $a_{\text{ini, chem}}$ and embrittlement rate function can be extrapolated to the service conditions. Combining such information with the fracture mechanical lifetime prediction method would allow the integration of disinfectant caused degradation into the predicted pipe lifetimes. It should be noted that for such a model, several further aspects have to be investigated, such as the relationship of the inherent defect size and

$a_{\text{ini, chem}}$, the effect of $a_{\text{ini, chem}}$ on $t_{\text{ini}}$ and the influence of $K_I$ on $a_{\text{ini, chem}}$. The precise analysis of these relationships and incorporation of $a_{\text{ini, chem}}$ and embrittlement rate into the fracture mechanical lifetime prediction is a matter of further scientific work.

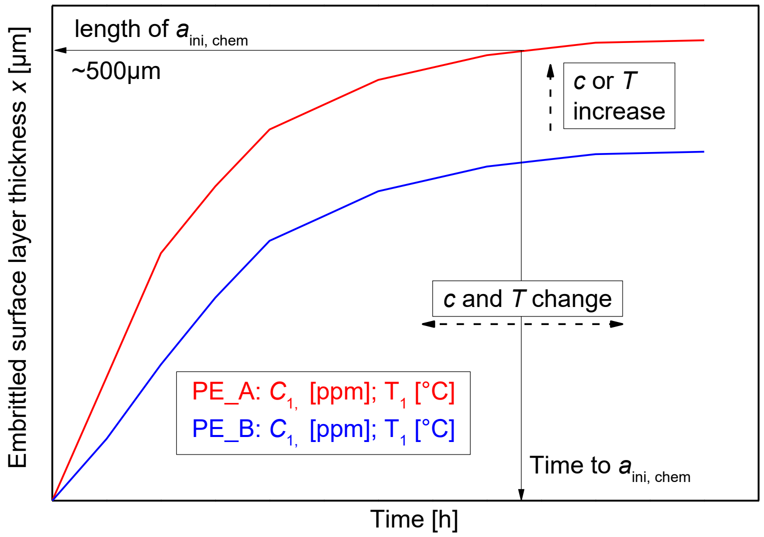


Fig. 9.3: Schematic illustration for the determination of surface embrittlement rate.

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