Open Journal of Organic Polymer Materials, 2021, 11, 1-50
https://www.scirp.org/journal/ojopm
ISSN Online: 2164-5752
ISSN Print: 2164-5736

Degradation of Polymer & Elastomer Exposed to Chlorinated Water—A Review

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How to cite this paper: Samarth, N.B. and Mahanwar, P.A. (2021) Degradation of Polymer & Elastomer Exposed to Chlorinated Water—A Review. *Open Journal of Organic Polymer Materials*, **11**, 1-50.
https://doi.org/10.4236/ojopm.2021.111001

Received: January 9, 2021
Accepted: January 25, 2021
Published: January 28, 2021

Abstract

In water industry, the chlorine is mostly used as a disinfectant agent. The chlorine present in potable water as a disinfectant has been reported to reduce the lifetime of contact polymeric material. This occurs in polymer pipes and it is now very common in plumbing and other parts of the drinking water distribution system. For more than 50 years, Polymer & Elastomeric materials have been used ubiquitously in drinking water distribution systems. Polymer & Elastomeric materials have successfully been used in a variety of applications ranging from rubber gaskets, to valves, to hydrants, to fittings. Polymer & Elastomers that degrade more quickly than expected create service problems, make it difficult for utilities to cost efficient plan preventive maintenance programs, and negatively affect customer relations. This review paper gives an insight idea to a reader about the selection of proper polymer & elastomer and predicting its performance in chlorinated water. Also the mechanism of degradation of Polymer & elastomer in chlorine environment and some model of life expectancy of in-service of Polymer & elastomer in various conditions and parameter in chlorinated water were discussed.

Keywords

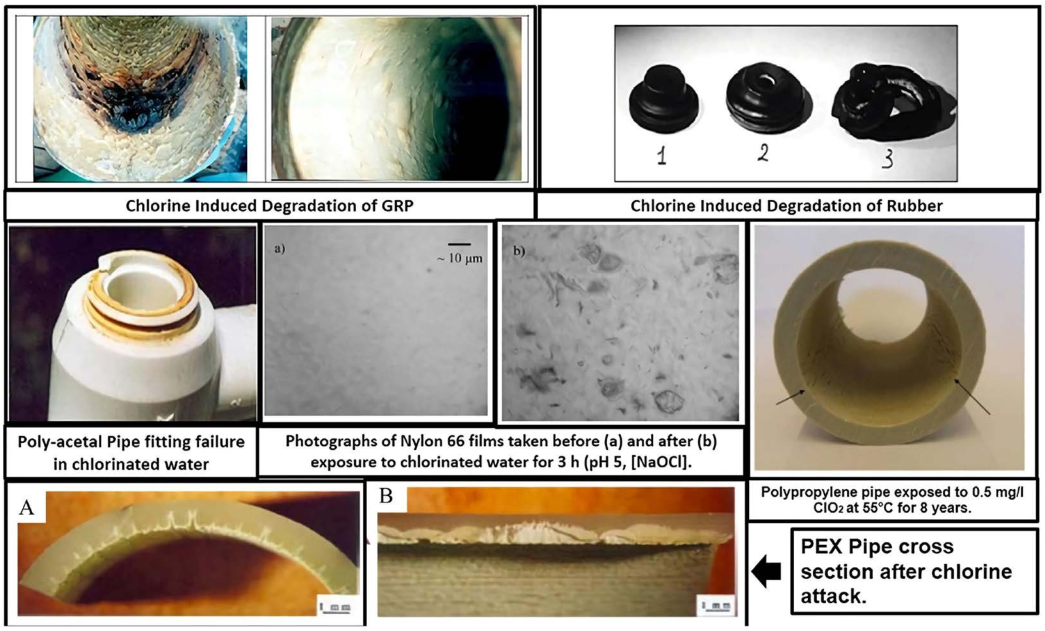
Chlorinated Water, Disinfectants Agent, Life Time Expectancy, Polymeric and Elastomeric Material

1. Introduction

Since the early 1900s, globally water systems have implemented disinfection in their purification process. Originally, free chlorine was the predominant disinfectant used because it was "effective, economical, and easily available" [1] [2] [3] [4]. Chlorinated water remains one of the most significant advancements in public health. This practice dramatically improves our quality of life by giving us the assurance that we get clean, safe drinking water when we turn on the tap in public places, at work and in our homes. For that reason, over 98 % of all water treatment facilities in the U.S. disinfect water with chlorine and chloramine based products as mentioned in **Table 1**. This type of disinfectant offers numerous advantages over other systems, including high germicidal potency, economy and efficiency [5] [6]. The chlorination of water or disinfectant is an acknowledged and often used method by which bacteria can be killed to render the water potable [7]. It is also acknowledged that many polymers exposed to chlorinated water degrade at rates that can adversely influence the properties and, hence, function of the polymer [8] [9] [10]. Thus, polymer-based materials used in the handling of chlorinated water (e.g., purification membranes, pipes, and pump parts) often require frequent replacement due to effects initiated by exposure to chlorinated water. Chlorinated water-induced degradation means any change at the molecular level that ultimately alters the properties of the polymer (e.g., elasticity, permeability). It is well established, however, that even moderate exposure to chlorinated water can result in the readily apparent formation of cracks and the loss of material from a given sample [11]. Very less data are available on the stability of polymers and elastomers in chlorinated media excluding Polyethylene (PE).

Long term exposure to water containing free available chlorine is known to have a deleterious effect on polymer mechanical, surface, and morphological characteristics. Mechanical PE pipe failure in chlorinated media depends on 7 major factors are on material properties, pressure, temperature, water pH, free available chlorine concentration, and exposure time. Specifically, chlorinated water aged PE is signified by a reduction in antioxidant levels, increased crystalline content/amorphous region reduction, chain scission, tie molecule layering, broadening of the molecular weight distribution, increased hydroxyl, carbonyl, and/or vinyl group content, and visible striations and cracking on the surface [10] [12]-[24]. Several researchers report that PE pipe degradation occurs after antioxidants are depleted. This depletion can occur non-uniformly due to natural antioxidant migration from the polymer into water and simultaneous penetration and consumption of chlorine [17] [25] [26]. The three major stages of PE pressure pipe degradation are: 1) chlorinated water attacks the pipe surface leaving a characteristic signature of oxygen, chlorine, hydroxyl, and vinyl components, 2) breakage of interlamellar tie molecules in the degradation region that allow increased chain layering and crystalline content, broader molar mass distribution as large polymer chains are fractured, and 3) micro crack formation which becomes visible, combines, and propagates through the pipe wall until the water pressure exceeds the pipe's mechanical strength and a leak or catastrophic mechanical burst/failure occurs. Differences of opinion exist about the broadening of the molar mass distribution can be determined by gel permeation chromatography while the chemical changes inferred to the polymer as a result of oxidation can be determined from IR spectroscopy [27] [28]; some researchers propose that a statistical cleavage leads in most cases to narrowing of the distribution. Several failure examples of polymeric components during service span time are shown in Figure 1 & Figure 2.

The rate that polymer & elastomers degrade when exposed to potable water is dependent on a number of poorly understood factors. In addition to chlorine concentration, temperature and pH and are believed to play roles, but those have not been adequately defined. Additionally, there is a wide variety of elastomer formulations available to the water industry, ranging from nitriles (NBR), neoprenes, EPDMs, PTFE, PSU, PP, PE and PVC. Each elastomer formulation has a unique reaction when exposed to free chlorine or chloramines; some have been observed to resist degradation, while others degrade rapidly. This field of study is of great importance to understand polymers' behavior under chlorinated environment, new physical phenomena arise because of the synergism between



Chlorine Induced Degradation of GRP

Chlorine Induced Degradation of Rubber

Poly-acetal Pipe fitting failure in chlorinated water

Photographs of Nylon 66 films taken before (a) and after (b) exposure to chlorinated water for 3 h (pH 5, [NaOCl].

Polypropylene pipe exposed to 0.5 mg/l ClO2 at 55°C for 8 years.

PEX Pipe cross section after chlorine attack.

Figure 1. Actual field failure example of polymeric components by Chlorine induced degradation.

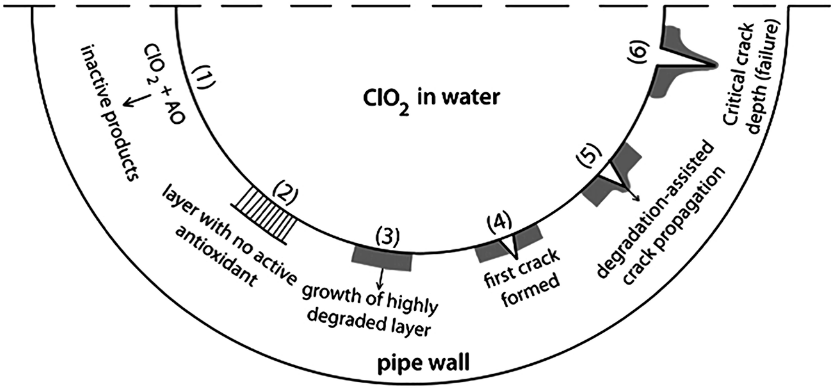


Figure 2. Sketch of mechanisms underlying failure of a pressurized polyethylene pipe exposed to water containing ppm levels of chlorine [Reprinted with Permission] [29].

free chlorine and those of the polymer matrix. In short, this review initiative was intended to clarify the factors that contribute to polymer & elastomer degradation and provide an overview on quantitative method for predicting the performance and life expectancy of in-service polymer & elastomer. The ageing condition and highlighted outcome are given in **Table 7**.

2. Mechanism of Polymer Degradation in Chlorinated Media

Chlorinated aqueous media are intrinsically unstable. They change character with time because many of the chlorinated species are highly oxidative and they undergo reaction. Substances containing chlorine are used at low concentrations in fresh water to avoid the spreading of infections. The benefit is that many human lives are saved. The negative consequence is that essentially all materials in contact with the chlorinated medium degrade relatively rapidly. Many strongly oxidative species can be present in chlorinated water and polymers in contact with such media may deteriorate by oxidation. When chlorine is added to water for disinfection, it transforms to hypochlorous acid tends to chain fracture and chain disentanglement. Chlorine is a strong oxidizer, which is capable of breaking the carbon-to-carbon bonds of the polymer chain, effectively disintegrating it. It is well established that singlet oxygen is a reactive intermediate capable of oxygenating olefins. By extension, singlet oxygen is thus a key reactive intermediate involved in the degradation of many polymeric materials under a variety of conditions. The susceptibility of a given polymer to reaction with singlet oxygen often depends on the structure and thermal history of that particular polymer sample [30] [31]. Specifically, for polymers that have been exposed to high temperatures (e.g., $Tg < T < Tm$), thermal degradation can result in the formation of functional groups (e.g., olefinic residues) that readily react with singlet oxygen. The products of these reactions (e.g., hydroperoxides) can, in turn, initiate chain reactions that ultimately contribute to the further degradation of the polymer [32]. The species in chlorinated media responsible for degradation of polymer are shown in **Figure 3**.

The aim of the current study is to emphasis on the impact of chlorine on the degradation kinetics mechanism. Some studies facilitate the prediction of the degree of polymer embrittlement in chlorinated media since it is this phenomenon that is directly linked to the drop in molar mass during contact with chlorine [35] The experimental results presented by C. Devilliers *et al.* (2011) [36] confirm that the oxidation kinetics are closely related with the chlorine concentration, pH and temperature. This leads to the conclusion that the chlorine solution provides some species which are responsible for initiating the polyethylene oxidation process. These species are then capable of diffusing and reacting further with the polyethylene to give free radicals (P^-). Let us discuss some hypotheses proposed in the literature [35].

As illustrated in **Figure 4**, "chlorinated water" is most accurately described in terms of the pH-dependent concentration profiles of four species: Cl_2, HClO,

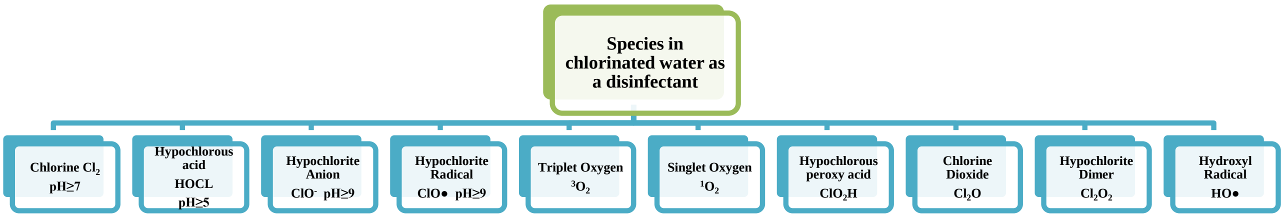


Figure 3. Species in chlorinated media responsible for degradation of polymer and elastomer [14] [23] [33] [34].

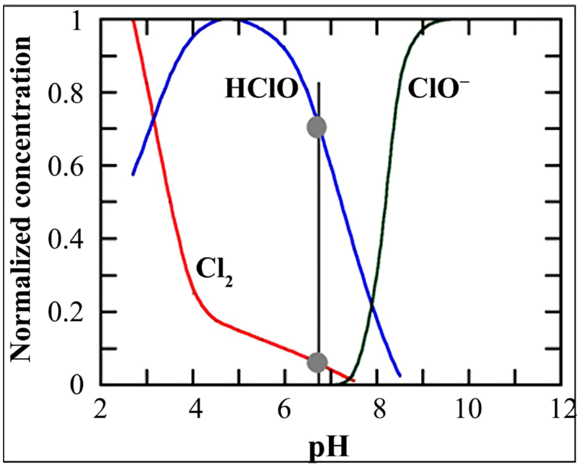


Figure 4. Normalized (with respect to maximum concentration) concentration of Cl_2, HOCl and ClO^- as a function of pH in aquesous solution [4] [18] [26] [Reprinted with permission].

ClO^-, and singlet molecular oxygen, O_2. Alkaline systems with a pH greater than 9 are characterized by a high concentration of ClO^-. Upon acidification with HCl, the concentration of HClO correspondingly increases, reaching a maximum at a pH of 5. At the same time, one must consider the equilibrium shown in Equation (1) in which molecular chlorine, Cl_2, is formed [37] [38]

$$HClO + HCL = Cl_2 + H_2O \tag{1}$$

Upon progressive acidification of ClO^-, the concentration of Cl_2 increases slowly, beginning at a pH of 7. Upon continued acidification, and at pH values below 5, the equilibrium of Equation (1) shifts to the right and the decrease in HClO concentration is accompanied by a pronounced and steady increase in the concentration of Cl_2. In 1994, Khan and Kasha [39] established that singlet oxygen is produced simply upon acidifying aqueous solutions of NaClO. In this process, the yield of singlet oxygen roughly correlates with the pH dependent concentration profile of HClO (**Figure 2**). Thus, the latter is implicated as the precursor to singlet oxygen under these conditions [40].

Chorine speciation depends on the pH thereby influencing the degree of polymer oxidation. Potable water in the USA commonly has a pH between 6.5 and 8.5 in accordance with Federal Regulation [41] and this pH range is common for most drinking waters worldwide. Drinking water pH values from 5 to 10 can occur but are not as common. Maximum rates of polymer degradation are reported to occur at pH values less than 7.5 [42] [43] [44] which indicated that the HOCl species would dominate in the drinking water pH between 6.5 and 7.5.

Several methodologies for assessing a material's resistance to chlorine (or chloramines) have been proposed as shown in **Table 4** and **Table 5** [45] [46] [47]. ASTM Standard D6284 provides a test method for evaluating the ability of rubber materials to withstand the effects of aqueous chlorine and chloramine solutions. Testing is conducted at slightly elevated temperatures (recommend 70˚C) in aqueous solutions with high concentration of chlorine (50 mg/L (ppm)). Samples are immersed in aqueous chlorine or chloramine solutions at the test temperature with the test solutions being changed daily. Material properties are measured before and after exposure. The procedure provides a relative indication of a material's susceptibility to chlorine or chloramines but does not provide a means of estimating a performance lifetime in the field. Both ASTM F2023 and the NSF Protocol for Chlorine Resistance of Plastic Piping Materials, involve testing of end use product under pressure in a flowing system. The continuous flow of water ensures that a constant and controlled level of chlorine is used in the test water throughout testing. Samples were tested under aggressive water quality conditions that are intended to represent the potential worst case water quality that might be seen in service. Elevated temperatures are used to accelerate failures. Testing was conducted at multiple temperatures and pressures. Multiple linear regression is then used to fit the experimental data to the Rate Process Model to allow determination of an extrapolated test lifetime under end use conditions [48].

Chlorine is a very reactive oxidising agent, which will react instantly with almost anything organic and most inorganic materials. It is because of this powerful oxidising property that chlorine is such an effective sterilising agent. It is important to understand, however, that chlorine will react not only with the chemicals in water, but also with any organic material in the tank. Chemically, chlorine is a halogen, and always wants to add an electron to its outer electron shell. This electron must be taken from another material, with which the chlorine reacts. The chlorine dosed in water will always, when correctly dosed, first react with materials in the water, then with the materials in contact with the water (like a liner).

When chlorine is dissolved in water, the following equilibrium reactions occur [32] [49] [50].

$$\mathrm{Cl_2 + H_2O \leftrightharpoons HOCL + H^+ + Cl^-}\ (\mathrm{pKa} \approx 3.4)$$

$$\mathrm{HOCl \leftrightharpoons H^+ + ClO^-}\ (\mathrm{pKa} \approx 7.4)$$

The relative amount of the three oxidizing chlorine species, Cl_2, HOCl and ClO^-, are determined by the pH of the aqueous environment. **Figure 4** shows the relative concentrations of these substances as a function of pH. At pH 6.8, Cl_2 is a maximum of 5.5% and the rest species are HOCl, which means that the concentration of the hypochlorous anion (ClO^-) is essentially zero (**Figure 4**). In acidic solutions (pH < 7), singlet oxygen is also present. However, the comprehensive study by Zebger *et al.* [32] showed that neither singlet oxygen nor HOCl was responsible for the degradation of polystyrene and poly (styrene-*co*-butadiene).

It is suggested, based on these reports, that chemical consumption reaching far into the pipe wall is due to Cl_2. The latter is soluble in the polymer, which is a necessary prerequisite for migration into the pipe wall. The polymer degradation, which is an immediate surface reaction, must be due to other species ("superoxidants") of ionic and/or radical character, e.g., the chloridyl radical $Cl_2\cdot^-$. This water-bound radical is predominantly a strong one-electron oxidant ($e$red = 2.3 V vs. NHE) and under the chosen reaction conditions it may even oxidize water and give rise to hydroxyl radical formation:

$$Cl_2\cdot^- + H_2O \leftrightharpoons \cdot OH + H^+ + 2Cl^- \text{ [51]}$$

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

$$Cl_2 + O_2\cdot^- \rightarrow Cl_2\cdot^- + O_2 \text{ [52]}$$

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

$$HOCl + O_2\cdot^- \rightarrow \cdot OH + Cl^- + O_2$$

Molecular chlorine present in aqueous solutions will cause a gradual reduction in laminate thickness (see **Figure 5** & **Figure 6**) and mechanical properties. The active form of chlorine in an aqueous solution depends on the pH of the solution, which is controlled by the following reactions:

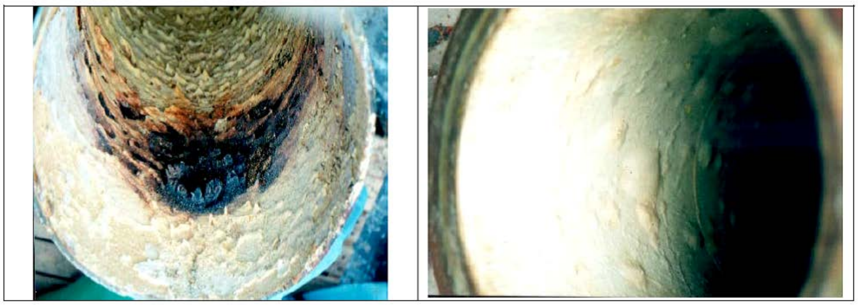


Figure 5. Chlorine degradation (left) and hydrogen chloride induced blistering (right) of a GRP pipe.

Figure 6. Example of chloramines induced elastomer degradation of a rubber components from the appliances industry.

$$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^-$$

$$HClO \rightarrow H^+ + ClO$$

Historically, already in 1954 the first study that dealt with chlorine degradation proposed the following scheme as that occurring in the chlorine solution [53]:

$$HOCL + ClO^- => ClO\cdot + Cl^- + OH\cdot$$

$$OH\cdot + ClO^- => ClO\cdot + OH^-$$

$$ClO\cdot + ClO^- + OH^- => 2Cl^- + O_2 + OH\cdot$$

Based on this scheme, it is proposed that the ClO^- and OH^- radicals are susceptible to attacking polyethylene to give P^-. More recently, using Electron Spin Resonance Utsumi *et al.* showed that OH^- radicals are present in chlorine solution [54]. However, due to their high reactivity, these radicals are unlikely to diffuse to any great extent deep into the polyethylene [14]. Indeed, the correlation length (l*) of these species is determined by the scaling law (D/k*) 1/2 where D is the diffusion coefficient for the radical and k* their reactivity with PE. A rough assessment of l* leads to the conclusion that ClO^- and OH^- can only diffuse into polyethylene over a short distance (smaller than 1 mm). Knowing that the degradation is homogeneous for the 100 mm films in this study, it is more than likely that another less reactive species exists that is responsible for homogeneous degradation observed. The radical species such HO· and ClO· are non selective, highly reactive and can abstract hydrogen from polymers initiating auto oxidation whereas less reactive radicals (*i.e.* the peroxyl radical HOO·, ClO·, $^3O_2$) would favor abstraction of tertiary hydrogen, with lesser reactivity towards secondary and primary hydrogen, lessening the likelihood that they would be HDPE degradation initiators [55] [56] [57] [58].

Following a similar argument, Khatua *et al.* proposed that the other reactive species could be a hydroperoxide such as Cl_2OOH which is formed according to the following scheme [34].

Factors Which Influence Degradation

Chlorine is extremely reactive and will react with all materials. However, four factors significantly influence the degree of attack on the liner material: (**Figure 7** & **Table 1**).

3. Overview on Degradation Study of Various Polymers under Chlorinated Environment

The reported literature data with conditions of testing and finding are shown in

Table 1. Normal chlorine concentration in water (Typical dosing levels are).

Tap Water	**0.1 - 0.4 mg/l (ppm)**
Swimming Pools	0.5 - 5.0 mg/l (ppm)
Disinfection, max	500 mg/l (ppm)

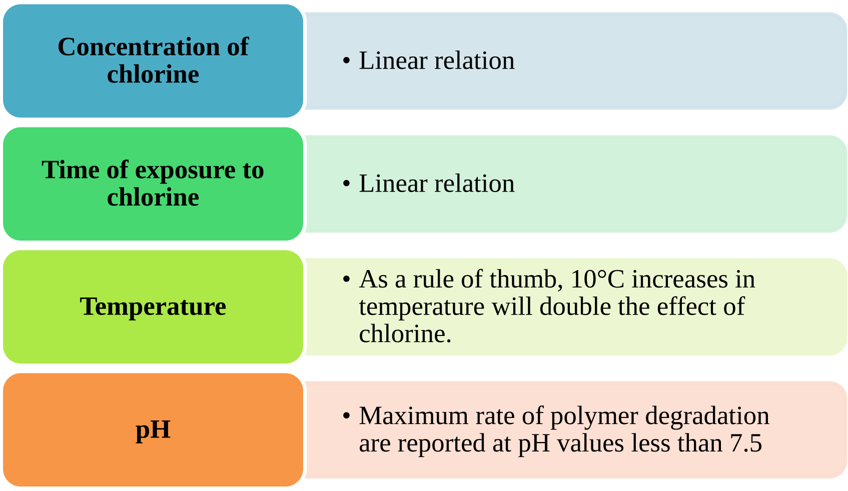


Figure 7. Factors influence the degree of attack on the linear material.

Table 4 and **Table 5**. Ingo Zebger (2003) *et al.*, stated that during exposure of many polymers to chlorinated water, the degradation rates can adversely influence the properties and, hence, function of the polymer. Polymer-based materials used in the handling of chlorinated water (e.g., purification membranes, pipes, and pump parts) often require frequent replacement due to effects initiated by exposure to chlorinated water. It is well established that even moderate exposure to chlorinated water can result in the readily apparent formation of cracks and the loss of material from a given sample [32]. Because it is known that singlet oxygen is produced in chlorinated water [39]. In the late 1960s, the plumbing industry began to use polyacetal resin, primarily in plumbing fittings, because of the material's reasonable hydrolytic stability at moderate temperatures, high crystallinity, low creep and relatively low water absorption. By the mid 1970s, however, it became apparent that some problems existed with using polyacetal resin in chlorine environments. Despite this information, millions of homes were constructed by the end of the decade that used polyacetal fittings to connect polybutylene pipe. Within a few years, many of these homes had leakage problems caused by the failure of the polyacetal fittings. Although polyacetal has some limitations, other plastics have enjoyed many years of success in plumbing applications. For example, polyvinylchloride (PVC) has been used for over 40 years in cold water applications such as water distribution, DWV (drain, waste and vent), sewer and irrigation systems. Chlorinated polyvinylchloride (CPVC) is well-suited for both hot and cold water delivery systems. Since its introduction in 1960, over 2 billion feet of CPVC pipe have been installed in single-family dwellings, condominiums, buildings, apartments and hotels. CPVC has proven that a potable water delivery system made completely from plastic can be both viable and reliable. A notable limitation of CPVC is that it is a rigid system that requires solvent welding of fittings and joints. Cross-linked polyethylene (PEX) is another viable choice for all-plastic hot and cold potable water systems. PEX systems have been thoroughly tested in aggressive chlorinated water environments and delivered an outstanding performance. In Europe, PEX has been used successfully for 25 years in radiant floor heating and plumbing systems. A significant advantage of a PEX system over other piping systems is that it is a flexible tubing delivery system that does not require heat or solvents for assembly. Historically, PEX systems were assembled using brass or copper fittings. More recently, many of these systems have been assembled using fittings made from sulfone polymers, providing a reliable all-plastic alternative to CPVC systems [59].

High density polyethylene (HDPE) pipes are approved by several United States and European standards organization for potable water transport (25˚C or less) [60]. These pipes are flexible and operate well above their glass-transition temperature and below their melting temperature. Breaking of the carbon-hydrogen or carbon-carbon bonds, disruption of polymer backbone, and reduction of molecular weight decreases the tensile strength of the polymer, which can lead to pipe rupture. The accepted preamble to HDPE pipe crack formation is characteristic oxygen, chlorine, hydroxyl, and vinyl functional group formation on pipe surfaces. J. Hassinen *et al.* [2004], examined the effect of chlorinated water on high-density polyethylene pipes stabilised with a combination of phenolic and phosphite antioxidants. Antioxidant concentration profiles in exposed pipes have been used to reveal the mechanism of loss of stabiliser. The results show that chlorinated water rapidly degraded the antioxidants. Polymer degradation started when the antioxidant system was depleted at the inner wall and it was strictly confined to the surface [25] [26] [51] [61] [62]. The degradation front propagated at an approximately constant rate. Degradation was confined to the amorphous component and it was digestive in a fashion similar to the action of fuming nitric acid on polyethylene [14]. W. Yu *et al.* [2011], examined the effect on polyethylene pipes of water containing chlorine dioxide. Medium-density polyethylene pipes stabilized with hindered phenol and phosphite antioxidants were pressure tested with water containing 4 ppm chlorine dioxide at 90˚C and pH 1/4 6.8 as internal medium. The stabilizers were rapidly consumed towards the inner pipe wall; the rate of consumption was four times greater than in chlorinated water (4 ppm, pH 1/4 6.8) at the same temperature. The depletion of stabilizer occurred far into the pipe wall. A supplementary study on a polymer analogue (squalane) containing the same stabilizer package showed that the consumption of the phenolic antioxidant was 2.5 times faster when exposed water containing chlorine dioxide than on exposure to chlorinated water. The subsequent polymer degradation was an immediate surface reaction. It was confirmed by differential scanning calorimetry, infrared spectroscopy and size exclusion chromatography that in the surface layer which came into contact with the oxidising medium, the amorphous component of the polymer was heavily oxidized leaving a highly crystalline powder with many carboxylic acid chain ends in extended and once-folded chains. Scanning electron microscopy showed that propagation of cracks through the pipe wall was assisted by polymer degradation [4]. S. Damodaran *et al.* [2015], investigated the effect of hot water and chlorinated water at 95˚C on differently nucleated random polypropylene pipes. Infrared microscopy (mFT-IR) was used to monitor the loss of the AOs as well as to identify their degradation products during ageing. For the quantification of the primary

AO,1,3,5-Tris(3,5-di-tertbutyl-4-hydroxybenzyl)-2,4,6-methylbenzene (AO-13) in a mixture with Pentaerythritol tetrakis (3-3,5-di-tert-butyl-4-hydroxyphenyl) propionate (AO-18) and the processing stabiliser tris(2,4-di-tertbutylphenyl) phosphate (PS-2) in PP-R, a new mFT-IR method has been developed and the results were supported by extraction/HPLC [63]. Oxidative induction time (OIT) measurements of mechanically prepared samples across the pipe wall also validate the bilateral and unidirectional loss profiles of AOs [64] [65]. The loss in average molar mass of the polymer as a result of chain scission was analysed by gel permeation chromatography. The linear relations drawn for molar mass against the relative content of AOs explain that the deterioration of the pipes was accelerated with chlorinated water. From the substantial differences in the AO loss coefficients which were calculated using mFT-IR, it can be speculated that nucleation of the PP-R exerts an influence on the depletion of AOs [66]. W. Yu *et al.* [2013], reported the method assesses the stability of the antioxidants towards these aqueous chlorinated media by determining the oxidation induction time through differential scanning calorimetry. A 0.3 mm thick polyethylene tape replaced the squalane phase and the supply of fresh water containing chlorine dioxide (10 ppm at pH 1/4 6.8) was continuous; this required minimum attention from the operator over the longer exposure time periods used. Tapes of medium-density polyethylene containing 0.1 wt% of six different phenolic antioxidants were studied. A linear relationship was established between the times to reach antioxidant depletion in the polyethylene tape samples and the times in the squalane samples (with the same antioxidants at the same concentration). A linear relationship was also found between the initial antioxidant consumption rates in polyethylene and squalane. Infrared spectroscopy and scanning electron microscopy of drawn samples revealed the onset of surface oxidation and surface embrittlement in tape samples exposed beyond the time for antioxidant depletion [67]. Donald Duvall *et al.* [2014], this study presents the results of testing of the resistance of random copolymer polypropylene pipe to chlorinated water and the failure mechanisms observed in the tests. A group of commercially available pipe products manufactured from a polypropylene random copolymer material (PP-R) were tested for resistance to an aqueous solution of a chlorine disinfectant widely used in potable water. Samples of pipe that were made in both an unreinforced PP-R and a glass fiber-reinforced (GFR) form were tested. Test results obtained at 115 C and 60 psig on the unreinforced 20 mm DR 6 pipe and the GFRP 25 mm DR 7.3 pipe yielded essentially the same failure times, in spite of the glass fiber reinforcement layer in the GFRP pipe. It appears that, insofar as chlorine resistance is concerned, the reinforcing layer in the GFRP pipe construction does little to prolong pipe life [68]. Polypropylene is particularly susceptible to oxidative degradation. Ezrin [69] has noted, “Oxidative degradation occurs readily for both polymers [PE & PP], possibly more so for PP. Contributing to degradation of PP is the fact that every other carbon atom is a tertiary carbon atom where both a hydrogen [atom] and a methyl group (CH_3) are located. Aggravating the degradation of PP is the fact that it degrades primarily by chain scission [70]. PE experiences a combination of crosslinking and chain scission reactions during degradation [71]. On balance, in PP degradation is more likely to occur than PE because of its much higher tertiary carbon content and the adverse effects manifest sooner with chain scission as the primary degradation result. For these reasons, PP has to be stabilized against oxidation even more so than does PE. Scheirs [72] notes that polypropylene is among the most easily oxidized polymers. Andrew J. Whelton *et al.* [2011] [73], Author reported the aging of polyethylene (HDPE, PEX-A and PEX-B) water pipes by exposure to chlorinated water altered polar and nonpolar contaminant diffusivity and solubility by analyzing new, laboratory-aged, and exhumed water distribution system polyethylene (PE) pipes. After 141 days of aging in pH 6.5 water with 45 mg/L free chlorine, the surface chemistry and bulk properties of PEX-A pipe were unaffected. Carbonyl bonds (σ 1/4 1713 cm^{-1}) were detected on the surfaces of HDPE and PEX-B pipe, and these oxygenated surfaces became more hydrophilic, resulting in statistically significant increases in diffusion rates. All 10 contaminant and four pipe material combinations had diffusivity increases on average of 50% for polar contaminants and 5% for nonpolar contaminants. Contaminant solubility was slightly increased for aged PEX-A and slightly decreased for PEX-B pipes. Toluene and trichloromethane diffusivity and solubility values for 7- to 25-year-old buried water utility pipes were similar to values for new and laboratory-aged HDPE-based materials. Because chlorinated water exposure alters how polar contaminants interact with aged PE pipes, results of this work should be considered in future health risk assessments, water quality modeling, pipe performance, and service-life considerations [31] [73]. Most PMCs will absorb small, but potentially damaging amounts of moisture from the surrounding environments with the degree of degradation that occurs being linked directly with the amount of moisture absorbed. The absorbed water may adversely affect the material in a number of ways:

- Dimensional changes (swelling);
- Reduction in mechanical and physical properties (*i.e.* stiffness, strength and hardness).

The rate of moisture uptake by a composite laminate is dependent on the temperature, relative humidity, exposure time and mechanical load. At elevated temperatures, the rate of moisture uptake and material property degradation is accelerated. The presence of water in aged PE water pipe could impact material properties such as mechanical strength by influencing chain rotation and/or by plasticization. The three accepted water-polymer interactions are: 1) polymer/polymer whereby water penetrates and is located within layered chain cavities, 2) polymer/water where water is hydrogen bonded to additives such as carbon black, antioxidants, and oxygenated backbone or branches, and 3) water/water where water molecules within cavities hydrogen bond with one another forming "clusters".

Andrew J. Whelton *et al.* (2009), Earlier water penetration has been reported in LDPE and MDPE films at temperatures greater than 50˚C and oxidized PE sorbed more water than unoxidized PE [74] [75] [76]. Marshall reported one of the few investigations designed to examine water sorption in PE and concluded that 0.6 - 0.8 g of water sorbed per gram of PE (when immersed in 168 - 2000 h at 90˚C). The type of PE and the extent of oxidation were not specified. More recently, aged PEX water pipe with a hoop stress of 2.62 MPa, 110˚C, 17,136 h exposure (chlorine free water but pH not reported) and concluded that infrared spectroscopy bands detected between 1680 and 1500 cm^{-1} were not related to double bonding, but were due to water sorbed into the oxidized PEX pipewall because water absorbs near 1600 cm^{-1} Smith *et al.* "speculated" and Viebke and Gedde proposed that water molecules were sorbed into the wall of MDPE pipe during accelerated ageing because results of their antioxidant diffusion model for the internal pipe wall and external pipe wall were two orders of magnitude different (ageing conditions: 80˚C, 95˚C, 110˚C, 0.84 - 2.51 MPa hoop stress, chlorine free water, pH not reported). In summary, the literature shows a precedent for water sorption in LDPE and MDPE at temperatures > 50˚C. No quantitative data were found for water penetration into PE during accelerated ageing experiments for HDPE resin or potable water pipe at temperatures equal to or less than 37˚C [77].

Table 2 describe the Solvay Specialty Polymers contracted one such study that tested a variety of polymers at 0, 10, 20 and 30 ppm levels of chlorine at 60˚C (140˚F), which is the typical operating temperature of residential hot water systems. The chlorine levels were elevated above the normal potable water levels of 1 ppm to 2 ppm in order to accelerate the effect of chlorine and to enable the use of regression analysis to predict reaction rates at various chlorine levels [78].

X. Colin *et al.* (2009), studied the aging of unfilled polyethylene (PE) films in concentrated (80 - 100 ppm) chlorine dioxide (DOC) solutions at 20˚C and 40 by IR spectrophotometry, melt rheometry, chlorine titration, and tensile testing to establish the mechanisms of PE degradation induced by DOC, to determine some important kinetic parameters, to identify the embrittlement mechanism,

Table 2. Weight loss of various after 1500 Hours of exposure to flowing water at 90˚C.

	Weight loss [%]	
	0 PPM Chlorine	**5 PPM Chlorine**
Udel PSU, Unfilled	0.0	0.1
Udel PSU, 20% glass-filled	0.0	0.0
Radel PPSU	0.5	0.2
Acudel Modified PPSU	0.3	−0.1
CPVC	−0.6	1.2

and to examine the possibility to predict non empirically embrittlement from a kinetic model [79] [80] [81] [82]. A similar study by Brocca *et al.* (2002) made impressive advancements in detecting 20 to 30 organic chemicals that could potentially be released by polyethylene pipe materials (PEX, PEM, PEL, cross-linked, medium density and low density respectively). The pipe materials used were all available on the Danish market for use in drinking water distribution systems. For analysis the pipe samples were filled with test water for 24 hours, flushed with tap water for 60 min and finally rinsed with test water for 2 min. Liquid-liquid extractions followed by GC-MS were the methods employed for chemical analysis. This work added needed data to understanding leaching of PE materials. More recent studies done, using the leaching protocol EN 1420, showed that HD-PE leached 2,4-di-tert-butyl-phenol (2,4-DTBP), and 2,6-di-tert-butyl benzoquinone (2,6-DTBQ), known degradation products of the antioxidant Irgafos 168® and Irganox 1010® and Irganox 1076® respectively. In addition several esters, aldehydes, ketones, aromatics and terpenoids were detected. Cross-bonded polyethylene (PEX) leached methyl-tert butyl ether (MTBE), tert-butanol, 4-butoxy phenol while polyvinyl chloride (PVC) leached hexanal, octanal, nonanal, decanal. The T&O identified in leachate samples were quantified using the threshold flavor number (TFN) and the threshold odor number (TON). TFN/TON represents the highest dilution of a sample in which a perceptible flavor or odor is detected by the panelists. A TON > 3 represents an undesirable odor [83].

Villberg *et al.* (1997) investigated the off-flavor and off-odor compounds in high density polyethylene resin (HD-PE) used for pipe manufacturing. The volatile organic compounds from polyethylene were identified using gas chromatography-mass spectrometry-sniffing system and gas chromatography-fourier transform infrared spectroscopy-sniffing system. Two experimental conditions were analyzed in an attempt to identify volatile organic compounds from HDPE; pure samples of high density polyethylene granule and odor free water in which granules had been shaken for 4 h. Further characterization of the odors was carried out by a trained panel. Panel members analyzed 5 ml of leachate water for T&O using individual descriptors. GC work identified several organic compounds that contributed T&O in samples analyzed. These include: 2-propanal—putrid, glue; ethyl propanate—sweet, candy; C6-ketone—solvent, plastic; methylpentenone. plastic; toluene. model glue; hexanal. leafy; 2,4-heptadienal . aldehydic; C7-ketone. chemical; ethylcyclohexanone. bitter; butyl acrylate. glue; C8-ketone. solvent; methylhexanal. pungent green; 2 octenal. mushroom; pentamethylheptane. stony, dusty; nonanal. bad, aldehyde; undecadienal. pungent [84].

Several studies have revealed the potential of VOCs to leach from pipes and linings and directly contribute tastes and odors to drinking water. Plasticizers, antioxidants and application solvents used in association with synthetic materials can contribute to off-flavors and odors in drinking water. Antioxidants are sacrificial coatings that protect the underlying polymer material from oxidation reactions. The dissolution of antioxidant as a mechanism that destroys the quality of drinking water has been studied in France as early as 1985 [85] [86].

Similar case studies were reported by Rigal *et al.* (1999) that depicted T&O episodes resulting from the use of synthetic materials. In one case, a newly refurbished water tower leached styrene at 230 µg/L which resulted in a .chemical. odor in drinking water. The problem was attributed to the rehabilitation of the water tower with a composite coating made of fiber glass reinforced polyester resin. In another instance solvent and petroleum odors were detected in cheese and butter. The chemicals contributing to these odors were leached from a vinyl-based coating applied to the dairy water tower. Several chemicals such as styrene, acetone and methyl isobutylketone were identified. Another case involved a taste episode that occurred following the rehabilitation of a reservoir in Rennes. Consumers complained of a very strong medicinal taste in the water. Investigation revealed that a vinyl polychloride net added to the cement used to renew the reservoir leached triphenylphosphate which is a known plasticizer. Triphenylphosphate hydrolyzed in the presence of chlorine and formed mono-, di- and trichlorophenols that contributed the medicinal taste [87]. Khiari *et al.* (1999) presented case studies which portrayed these phenomena. The sensory method employed was flavor profile analysis (FPA) and the chemical methods were closed loop stripping analysis or liquid-liquid extraction coupled with gas chromatography and mass spectrometry. In one case which occurred in eastern France in May 1994, phenol leached from an acrylic coating used to line a water storage reservoir and resulted in phenol/styrene Type odors. This case study further illustrated the production of medicinal smelling bromophenols and bromodichloro-iodomethane as a result of the reaction of phenol with chlorine in bromide containing water. Another medicinal odor was reported in Barcelona Spain in 1995. It was suspected that the odors were produced when residual disinfectant reacted with natural organic matter forming branched aldehydes such as 2-methyl propanal and 3-methyl propanal. In yet another case, installation of a new main in the distribution system resulted in oil-base paint. And paint/putty type of taste and odor. Chemical analysis of water samples revealed substituted benzenes and naphthalene suspected to be leached from bituminous coating on the inside of the pipes [88].

Some researcher performed the experiments were in an attempt to identify the reactive intermediate(s) involved in the degradation of a polyamide, Nylon 66, in chlorinated water [89]. N-chlorination is certainly one reaction that ultimately contributes to polyamide degradation [44] [90]. The intermediates involved could either be Cl_2 or HClO. Available information also indicates that, for many polymers, singlet molecular oxygen chemically generated from HClO, could likewise be involved as an intermediate in a degradation reaction. The degradation of Nylon 66 was monitored under a variety of conditions by FT-IR spectroscopy. The rate of degradation was pH-dependent, and degradation was most pronounced at pH < 5. Characteristic tests for the intermediacy of singlet oxygen, however, were negative. Rather, the data strongly pointed to Cl_2 as the key intermediate in the degradation. The presence of compounds capable of being oxidized by Cl_2 arrested the degradation reaction. These results should be pertinent in an attempt to stabilize polymers exposed, e.g., to water that has been chlorinated to kill bacteria (*i.e.*, drinking water) [11]. Several experiments were performed to identify the reactive intermediate(s) involved in the degradation of a heat-pressed polyamide (Nylon 66) in chlorinated water. As stated above studies indicated that N-chlorination was one reaction that contributed to the degradation of polyamides, and that either Cl_2 and/or HClO were the pertinent reactive intermediates. The data now recorded, however, clearly indicate that singlet oxygen is not involved as an intermediate in this degradation reaction. FT-IR Spectra recorded from the polyamide samples are consistent with N-chlorination as the initial step in the degradation of the polymer. A correlation between the pH dependence of the degradation rate and the pH-dependent Cl_2 concentration profile implicate Cl_2 as the principal reactive intermediate in this process. An amine added to the system effectively competes with the amide moiety for the chlorinating agent and, as a consequence, arrests the degradation of the polyamide.

A series of polyethylene tape samples containing 8 different phenolic antioxidants (concentration 1/4 0.1 ± 0.01 wt%) were exposed to water containing 10 ppm chlorine dioxide buffered to pH 6.8 at 70˚C for different periods of time. The degradation rate and depletion time of the antioxidants in the polyethylene were obtained by oxidation induction time measurements using DSC. The majority of the tape samples (6 out of 8) showed a simple behaviour: the rate of antioxidant loss decreased and the antioxidant depletion time increased in linear fashion with increasing initial molar concentration of phenolic groups in the polymer. The tape that contained Hostanox O_3 had a high initial phenolic concentration but it exhibited a short antioxidant depletion time due to the limited solubility of this antioxidant in polyethylene. Tapes containing Irganox 1330 and Cyanox 1790 showed antioxidant depletion times that were almost twice that of the other antioxidants with the same initial molar concentration of phenolic groups [91] [92].

Polymer materials considered for use in domestic hot water heating systems must maintain mechanical properties in the working fluid over their target lifetimes. In potable water, chlorine and pH combine to create an oxidative environment, commonly characterized by the oxidative reduction potential (ORP), that can chemically attack a polymer, resulting in permanent loss of mechanical strength and stiffness. Water absorption and hydrolysis can also impact polymer properties [93]. In the present study, experiments were conducted to evaluate the mechanical performance of polysulfone, polybutylene, and polyamide 6/6 immersed for up to 1100 h in water at ORP levels of 550 and 825 mV at 60 and 80˚C. Mechanical performance was evaluated by measuring creep compliance and the change in tensile strength and molecular weight after exposure. Surface morphology of the exposed materials was examined using scanning electron microscopy. Polyamide 6/6 showed significant degradation in strength and creep compliance in all environments. Despite some variability in measured properties, the blend of polybutylene, which has additives to prolong life, did not degrade. Polysulfone performed the best of the three materials with no discernable change in properties over the duration of the experiments [94].

Recent studies on membrane stated that Crosslinked (C-ESFx-BP) and non-crosslinked (N-ESFx-BP) sulfonated poly(arylene ether) (SPAE) membranes displayed the long-term stability longer than 30 days during the operation condition under high acidic chlorine concentration of NaOCl 4000 ppm unlike commercial PA membranes which are unstable under the chlorine treatment [95]. The polyimide thin film composite, reverse osmosis membranes prepared from MPD [m-phenylene diamine], BTC [1,2,4,5-benzene tetracarbonyl chloride] and TMC [trimesoyl chloride] showed significantly enhanced chlorine resistance due to the elimination of chlorine-sensitive sites by the replacement of amide linkage with imide linkage [96]. Julius *et al.* (1994) [8] studied the a variety of aromatic model compounds containing amide, urea, and ester linkages were exposed to sodium hypochlorite solutions at pH 4.5 and 10. Following are significant conclusions generated from their results: Chlorine sensitivity is pH dependent. Most model compounds in this study were more reactive at pH 4.5. Chlorine sensitivity is greatly enhanced when the aromatic group is linked to nitrogen in amides or ureas. Ureas were shown to be more chlorine sensitive than amides. Ester linkages were generally chlorine resistant. Model compounds containing tertiary substituted nitrogen showed the highest levels of chlorine resistance.

The study of Solvay was undertaken to demonstrate the suitability of Ryton® PPS (polyphenylene sulfide) for such service. The performance of Ryton® PPS compounds compared to other high temperature engineering thermoplastics was also evaluated. Elevated temperature immersion tests have shown that PPS polymer is not attacked by hot water. These tests involved total immersion of standard test specimens in hot water for a period of time, and stress testing after exposure to determine retention of mechanical strength. For example, after exposure to 93˚C (200˚F) water for twelve months, unfilled Ryton® PPS retained over 90% of original tensile strength. The slight drop in tensile strength was likely due to thermal aging rather than chemical attack, and similar retention of mechanical strength after hot water exposure was observed at temperatures up to 149˚C (300˚F). Many other polymers, such as polyamides (nylons) and polyesters, will actually be hydrolyzed in hot water; the polymer chain is broken down and the plastic material is degraded (**Figure 8**).

Ryton meets the requirements of NSF Standard 61 and BS 6920 for use in potable water systems. This makes Ryton an excellent choice for components of hot potable water systems [97]. Water-distributing pipes made of polyethylene undergo degradation due to disinfectant in the water. Chlorine (Cl_2) and chlorine dioxide (ClO_2) are the most common water treatments [98] [99] and they

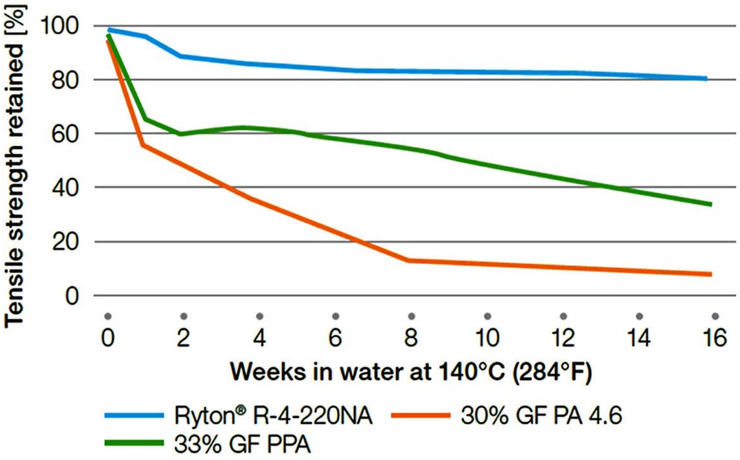


Figure 8. Tensile strength retained after 16 week iimersion in hot chlorinated water (140˚C) [Solvey Bulletin 2002].

are strong oxidants even at a very low concentration. Polyethylene is chosen for piping materials due to its chemical stability and it performs equally well for buried, trenchless, floating and marine installations. In spite of all the advantages, polyethylene pipe degradation is unavoidable and visible cracks can be observed on the inner wall of the pipe with time. The deterioration of polyethylene pipes with internal chlorinated media has been studied [32] [85] [94] [100] [101] [102] [103]. Due to the unstable nature of chlorine and chlorine dioxide, the strict definition of the pH and concentration of the chlorinated species in water is essential in any study of the degradation mechanism [37]. Usually the degradation of polyethylene needs a long period of time and earlier attempts have been made to accelerate aging using empirical methods (mechanical loading, hydrostatic pressure, UV exposure thermal degradation) [26] [49] [50] [104] [105] [106].

Commercial polyethylene products are stabilized to reduce oxidation during processing [107]. With added antioxidants, polyethylene pipes had a 12% longer lifetime in regime III in the hotwater distribution systems [62]. Hassinen *et al.* [14] have observed that antioxidant consumed rapidly even far into the pipe wall, which may be caused by the diffusion of chlorine species into the solid plastic material. Colin *et al.* [79] showed a rapid consumption of a phenolic antioxidant in a 1.2 mm thick layer near the inner pipe wall, after which essentially no propagation of the antioxidant-free layer occurred. These authors suggested that chlorine dioxide reacts not only with the antioxidant but also with polyethylene, but at a considerable lower rate. However, Stevens and Seeger [108] provided evidence that the reactivity of saturated hydrocarbons to chlorine dioxide is strictly zero. Dear and Mason [100] found that chlorine can penetrate polyethylene in amorphous regions without reacting with the polymer chains. In 1957, Russell [109] reported the autoxidation of aralkyl hydrocarbons and peroxy radicals was a cause of the failure of polymer materials. Hence, the deterioration of polyethylene may be due not to the disinfectant but to the by-products (radicals) of chlorine or chlorine dioxide dissolving in water.

The chlorine present in potable water as a disinfectant has been reported to reduce the lifetime of some plumbing system components. In this study the nature of the failure mechanism of a commercial cross-linked polyethylene (PEX) pipe material exposed in the laboratory to chlorinated potable water is examined. The observed failure mechanism for laboratory tested PEX pipe materials is seen to be similar to the failure mechanism observed for field failures of polybutylene (PB) pipe materials, indicating that laboratory testing can replicate potential failure mechanisms in service. Water quality, or more specifically, chlorine level, is seen to have a significant impact on material performance.

Test lifetimes are seen to be noticeably lower for chlorinated potable water, even at chlorine levels as low as 0.1 mg/L (ppm), than for non-chlorinated water. Through accelerated testing at multiple temperature and pressure conditions and the use of the Rate Process Model, a model to estimate the test lifetime of the PEX pipe material at end use conditions is developed. Based on this analysis the PEX pipe material examined in this study appears to have good resistance to chlorinated potable water. Chlorine in potable water is seen to accelerate the brittle oxidative failure of a PEX pipe material. The failure mechanism observed in laboratory generated failures for PEX pipe exposed to chlorinated water is consistent with that observed for a field failure of PB pipe. The effects of chlorine on lifetime reduction are observed even at very low levels of chlorine. The Rate Process Model is seen to provide a good fit to experimental data generated by testing to failure at multiple temperatures and pressure conditions. An indication of material performance can then be obtained by extrapolation to end use conditions. Based on this analysis, the PEX pipe material examined appears to have good resistance to chlorinated water [110].

Bulletin focuses on the effects of chloroamines on a variety of different plastics in a hot water environment. Additional bulletins are available from Solvay that compare the performance of sulfone polymers, CPC and polyacetals in chlorinated environments: Also the following materials were evaluated. PVDF (Solef® 1010), ECTFE (Halar® 350 LC), PPSU (Radel® R-5000), PSU (Udel® P-1700), PEX-b (Polidan® T-A/SL), PA12. Test specimens were aged at 70˚C (160˚F) for 8 weeks (1344 hours) in a 50-ppm monochloramine (NH_2Cl) solution prepared according to ASTM D6284a. The solution was replaced every 2 to 4 days to ensure that enough reactive chloramine was present throughout the study. The performance of the material were evaluated from the mechanical properties were shown in **Table 3**.

The weight loss evident in PA12 may be an indication of oxidation. DSC is typically used as a quick screening tool to check any structural changes in the material when heating up the sample. For semi-crystalline materials, this is used to measure the amount of energy needed to crystallize. No changes are seen for the materials except for PA12 whereas a slight shift in crystallization temperature is seen after ageing. This is an indication that the crystalline structure from the material is somewhat changed. FT-IR is used to evaluate potential chemical

Table 3. Mechanical properties before and after ageing [97].

Initial Properties	PVDF	ECTFE	PPSU	PSU	PEX-b	PA12
E-Modulus [Mpa]	2027	1645	2000	2200	920	1035
Tensile Strength [Mpa]	56.9	31.9	78.8	79.6	26.6	38.1
Elongation at yield [%]	7	6.5	6.5	6.5	6	8.5
Changes in properties after ageing						
E-Modulus [Mpa]	−6	−4	0	0	−7	−33
Tensile Strength [Mpa]	4	8	−2	0	−1	−9
Elongation at yield [%]	11	4	−3	−16	6	96

organic changes in a material. The right section of the graph is used as a fingerprint area from a material and can be used to identify a material. There are some minor changes visible for PA12 around 1120 cm^{-1} which is an indication of oxidation. No changes are seen for the other materials.

Castagnetti *et al.* (2011) [111], studied the effect of disinfectants on the mechanical and chemical resistance of high-density polyethylene pipes. A fully monitored test plant was built that was able to simultaneously expose both pipe sections and pre-cut dumbbell specimens to chlorinated and non-chlorinated water. Polyethylene pipes were tested in two sets of experiments involving both chlorine dioxide (at a constant concentration of 5 ppm), and sodium hypochlorite (at a constant concentration of 2.5 ppm).

The effect of disinfectants on high-density polyethylene (HDPE) pipes, commonly used in modern urban networks for water conveyance, has been examined experimentally. The first programme investigated the effect of chlorine dioxide at a constant concentration of 5 ppm, the second investigated the effect of sodium hypochlorite at a constant concentration of 2.5 ppm. These different concentrations of disinfectants were chosen so as to produce the same concentration (5 ppm) of free chlorine in the exposure line. The pipes were exposed both in the form of pre-cut dumbbells immersed in still water and as pipe sections exposed to running water. Chlorine dioxide appeared to be the most aggressive disinfectant since it led to a drastic reduction in elongation at failure of the pre-cut dumbbell specimens, together with dramatic antioxidant consumption after a few weeks of exposure. In contrast, in the case of sodium hypochlorite, the monotonic tensile tests up to failure highlighted no substantial influence on the mechanical behaviour of PE. This is in accordance with the slight antioxidant consumption testified by the OIT tests [112]. Oner and White (1993) [113] investigated the degradation of commercial polyoxymethylene copolymer in water service applications, it can be said that chlorine (or hypochlorite) at any level may react with acetal copolymer and ultimately adversely affect properties. It can be said that an increase in crystallinity was observed for the inner layer of used samples. An increase of carbonyl groups in the polymer molecule with degradation was confirmed by infrared spectroscopy [114] [115]. B. Azhdar *et al.*

(2009) [116] developed a new method which assesses the protection efficiency of phenolic antioxidants in polyolefins on exposure to chlorinated water media (water containing Cl_2 or ClO_2, each at a concentration of 10 ppm). The method uses a liquid hydrocarbon analogue, squalane, in which antioxidants are dissolved. The organic phase was dispersed in the aqueous chlorinated phase (containing 10 ppm of either Cl_2 or ClO_2; pH = 6.8) at 70˚C by intense stirring.

W. Yu *et al.* (2011) [4] examined Medium-density polyethylene pipes stabilized with hindered phenol and phosphite antioxidants were pressure tested with water containing 4 ppm chlorine dioxide at 90˚C and pH ¼ 6.8 as internal medium. The stabilizers were rapidly consumed towards the inner pipe wall; the rate of consumption was four times greater than in chlorinated water (4 ppm, pH - 6.8) at the same temperature. The depletion of stabilizer occurred far into the pipe wall. The depletion of the antioxidant system occurred more rapidly with internal water containing chlorine dioxide than with chlorinated water; the factorial difference between the two cases amounted to 4. Similar factorial differences (2.5) were found in the squalane experiments. The chemical complexity of these aqueous systems is considerable. However, chlorine dioxide itself is the most probable attacking candidate for the rapid consumption of antioxidant. Chlorine dioxide does not attack the polymer chain itself but targets the antioxidant molecules. This initial reaction should lead to formation of chlorite, ClO_2 which by subsequent proton and electron transfer processes involving another phenolic antioxidant may generate hydrogen abstracting radical species such as chlorine monoxide, ClO^-. Several direct indications of a digestive degradation of the amorphous component occurring at the water/polymer interface were obtained. Several direct indications of a digestive degradation of the amorphous component occurring at the water/polymer interface were obtained leading to a significant increase in the degree of crystallinity of the degraded surface layer. Size exclusion chromatography indicated degradation near the crystale amorphous interface, leaving extended and once-folded crystal chains intact. Scanning electron microscopy confirmed that degradation-assisted crack propagation. Although polymer degradation in this case is an immediate surface reaction, the chemical damage propagates through a pipe wall with the aid of the cracks.

J. Castillo Montes *et al.* (2012) [117] studied the influence of sodium hypochlorite concentration on PERT/Al/PERT (PolyEthylene Raised Temperature) pipe degradation. Pipe samples were filled with chlorinated water solutions (concentrations ranging between 0 and 100 ppm) and maintained in static conditions during 270 days at 70˚C. The antioxidant depletion profile through a PERT wall was monitored using the oxidation induction time (OIT) method, which is a conventional technique of Differential Scanning Calorimetry. Chemical changes on the aged polymer were checked by Infrared Spectrometry. OIT change showed that the PERT stabilizing system was rapidly chemically consumed by the action of chlorinated water at 25 and 100 ppm concentrations. However, PERT degradation was strictly confined to the immediate inner wall. Only a 0.3 mm thick layer (inner part of the pipe) showed significant antioxidant depletion. An increase of the OH and C-O-C infrared bands was also observed on inner part of any samples during ageing which characterize the oxidation of the PERT on the inner wall. W. Yu *et al.* (2012) [29] reported that Squalane stabilized with 0.2 wt% of Irganox 1010 and a medium-density polyethylene containing 0.1 wt% of the same antioxidant were exposed to two different aqueous media (water solutions containing either 10 ppm Cl_2 or 10 ppm ClO_2, both buffered to pH 1/4 6.8) at different temperatures between 30˚C and 70˚C. OIT measurements were carried out on the polyethylene samples after exposure to the chlorinated aqueous media. Exposure of the squalane systems to water containing ClO2 resulted in discolouration by the formation of quinoid structures and a faster depletion of the antioxidant than exposure to water containing Cl_2. The activation energy for the loss of antioxidant activity on exposure to ClO_2 water was very low (<10 $kJ\cdot mol^{-1}$) in the squalane test (no diffusion control) and 21 - 2 $kJ\cdot mol^{-1}$ at a depth of 1 - 2 mm from the surface of polyethylene plaques (diffusion control). Calculation from earlier published OIT data from a HDPE exposed to Cl2-water yielded an activation energy for the loss antioxidant activity of 68 $kJ\cdot mol^{-1}$. The antioxidant degradation products obtained from the exposure to the ClO_2 aqueous medium were found at a higher concentration, were more polar and exhibited a higher proportion of low molar mass species than those obtained after exposure to the Cl_2 aqueous medium. The important chemical difference between ClO_2 and Cl_2 is that the former is a one-electron oxidant whereas the latter preferentially reacts by hydrogen substitution.

Kirchhain *et al.* (2015) [118] studied commonly used phenolic antioxidants can extend the service life of the polymer but the expected lifetime is still much shorter than desired (50 years) due to depletion of the antioxidant in the surface zone exposed to the aqueous solution. In search for better stabilizers for the pipes, we have tested an organotellurium compound, 4-(N, N-dimethylamino) phenyl 3-phenoxypropyl telluride (1), as well as its corresponding selenium and sulphur analogues and a series of organotellurium compounds where the electron density at the heteroatom was varied. Stabilizers were dissolved in squalane, which is a liquid hydrocarbon that could serve as a model for a polyolefin. The oxidation induction time (OIT), determined after exposure of the squalane solution to an aqueous solution of 10 ppm of chlorine dioxide for various times was determined by DSC to indicate the loss of antioxidant protection. Whereas Irganox 1010 was only effective as a stabilizer for a few hours, many of the organochalcogen compounds were considerably more resistant (>91 h for compound 1) towards chlorine dioxide. Thermogravimetric analyses of antioxidants indicated insignificant decomposition below 200 ˚C and increasing stability for the lighter chalcogen compounds (telluride < selenide < sulfide). Among organotelluriums, stability increases with increasing electron density at the heteroatom. Oxidation potentials of stabilizers as determined by cyclic voltammetry correlated fairly well with their protective effect in squalane (OIT-values). We therefore hypothesize that these compounds act primarily as electron donors towards peroxyl radicals. As determined by NMR-spectroscopy, organotellurium compound 1 in the presence of an excess of chlorine dioxide failed to produce an oxidation product. This may be the clue to its long-lasting protective effect in the squalane-assay.

Gill *et al.* (1999) [10] studied the effect of degradation of crosslinked polyethylene tubing subjected to pressurised, hot chlorinated water in flow through systems (e.g. home plumbing) and to estimate its service lifetime. Crosslinked polyethylene tubing was subjected to pressure testing with flowing hot, chlorinated water at elevated temperatures from 90˚C to 120˚C, with chlorine levels between 0 and 5 ppm. The combined effects of free chlorine, pH, and metal ion content on the time to failure were found to correlate better with the oxidation–reduction potential than with the free chlorine content directly. Flow through systems, which continuously replenish their chlorine, give shorter times to failure at 115˚C and at 105˚C than do recirculating systems without chlorine additions. The effect of chlorine is better indicated by the oxidation–reduction potential than by the amount of free chlorine alone. The antioxidant as measured by the oxidation induction time at 200˚C was fully consumed by 40% of the lifetime of the crosslinked polyethylene pipe at 115˚C.

S. Chung *et al.* (2003) [119] examined the impact of chlorinated potable water on four polysulfone materials (PPSU, PSU, a PPSU/PSU blend and a glass-reinforced PSU). It is shown that the materials were found to have excellent oxidative resistance to the chlorinated potable water at the test condition. Testing was performed in three phases. The first phase involved exposing specimens to chlorinated water at 115˚C (239˚F) for approximately twice the test lifetime, at the same condition, of a commercial ASTM F876 1/2” SDR 9 PEX pipe material listed by NSF International to the NSF P171 Protocol6 for hot water Continuous Recirculation applications. At the test condition, all polysulfone formulations showed excellent oxidative resistance to the chlorinated potable water at the tested condition. The exposure appears to have not affected the mechanical strength of the fittings when compared to the application pipe. Optical analysis has lead to the following ranking, in order of resistance to chlorinated potable water, of the formulations at the test condition:

PPSU > PPSU/PSU Blend > Reinforced PSU > PSU

The long term performance of isotactic polybutene-1 pipes exposed to hot water has been reported in several paper. The state of art pipe grades show very high fracture toughness and pipe fracture initiated from an oxidized (degraded) layer [120] [121] [122].

4. Predicting Performance Lifetime in Chlorinated Potable Water

Given the significant impact of chlorine on a material’s brittle oxidative lifetime and reported failures of materials in potable water applications [113] the ability to validate a material's performance prior to field installation is essential. Further, plumbing system materials are often installed in applications requiring service lifetimes of 50 years or more. An accelerated means of assessing field performance is, therefore, required. In some cases, [47] experiments performed at elevated temperatures to accelerate failure times while testing with a single aggressive water quality to provide a "worst case" scenario. Testing were conducted at multiple temperatures and pressures and the Rate Process Model is used to model the experimental data. Extrapolation to anticipated end use conditions can then be performed to predict material performance. This approach was applied to a commercial PEX pipe material, intended for both hot and cold potable water applications [17]. Testing was conducted at eight different temperature and pressure conditions with a total of 16 failure points generated. The experimental data was fitted to the Rate Process Model:

$$\log(\text{failure time}) = A + B/T + C/T * \log(\text{hoop stress}) \tag{1}$$

Using multiple linear regression to solve for the coefficients A, B and C. The resulting equation for predicting failure time as a function of temperature and pressure is:

$$\log(\text{failure time}) = -16.45 + 8367.2/T - 372.2/T * \log(\text{hoop stress}) \tag{2}$$

Polymer & Elastomer materials installed in water distribution systems are expected to have design lives similar to their surrounding materials. For diaphragms a reasonable design life may be several months to years, but for gaskets and valves, the design life may be 50 or 100 years. It would be impractical to obtain examples of all parts now in service, and unrealistic to test materials over a period of many years. Therefore, researchers selected un-aged samples of elastomer formulations that were representative of components currently in use. They established a systematic testing program that would duplicate field conditions in a condensed (or accelerated) time period. Using increased temperatures and increased concentrations of chlorine and chloramines, these accelerated-aging tests were conducted in the lab on un-aged samples. The results were then compared to actual field samples. By overlaying the degradation curves, the researchers could build a reliable method for predicting the performance of in-service parts [123].

According to the model explained by Devilliers *et al.* (2011) [36], it is now possible to simulate the molar mass drop as a function of the chlorine concentration at 20˚C. In order to predict mechanical behaviour changes during long-term ageing, the coupling between the chemical degradation and the mechanical properties is needed. For this purpose, it has been proposed that the chemical degradation induced by chlorine is responsible for the embrittlement mechanisms occurring at the inner surface [124]. In the case of polyethylene films, it is well known that polyethylene is brittle since Mw is below the critical molar mass (M'*c*) value; close to 40 kg·mol^{-1} [126]. More precisely, it has been shown that this critical molar mass value is intimately linked with the chemi-crystallization process leading to reduce amorphous layer thickness. Once the amorphous layer thickness is below a specific critical value (≈6 nm for polyethylene), the mechanical behaviour starts to exhibit a brittle behaviour [35]. In a preliminary approach, considerate can be assumed that the time to embrittlement (for films or oxidized layers) is closely associated with any Mw decrease lower than 40 kg·mol^{-1}. According to **Figure 5(a)**, **Figure 5(b)**, the time to embrittlement for both stabilized and unstabilized polyethylene is roughly 5 days and 15 weeks for 4000 and 400 mg/l ageing conditions, respectively. These data are plotted in **Figure 9** where the x-axis is the chlorine concentration using a log scale. The curve corresponds to the simulation resulting from a combination of the kinetic model and the selected embrittlement criterion M'C, for a chlorine concentration range from 0.01 to 10,000 mg/l as applied to an unstabilized polyethylene. Thanks to this curve, one can observe two domains: the first domain is where the chlorine concentration is below 0.01 mg/l and corresponds to the situation in which oxidation is mainly controlled by intrinsic polyethylene thermal oxidation, *i.e.* hydroperoxide decomposition (no chlorine effect). The second domain corresponds to the 10 - 1000 mg/l range where the oxidation kinetics are governed by the chlorine concentration. This is most probably why no stabilizer impact has been observed in the latter case. In other words, the oxidative species generated by the chlorine concentration is higher than any generated by the stabilizers. Experimental results at 70 mg/l confirm this trend (see **Figure 9**). For both situations (0.01 - 10 mg/l), the oxidation kinetics are controlled by the initiation processes: hydroperoxide decomposition and chlorine initiation. As a result, it is to be expected that the stabilizer efficiency in this 0.01 - 10 mg/range, which is the usual range observed in drinking water supply, is in operation.

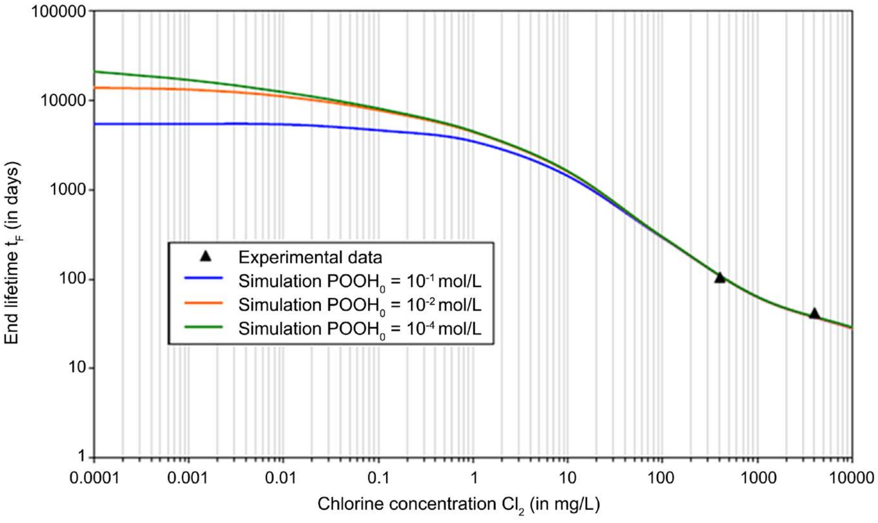


Figure 9. Evolution of time to embrittlement of polyethylene surface in contact with water as a function of chlorine concentration the curve corresponds to simulation by kinetic modelling for unstabilized polyethylene [Reprinted with permission].

There are several ways to check the validity of the kinetic model. As an example, one can calculate the profiles in the pipe wall of [126]:

- Antioxidants concentration (determined by differential calorimetry, assuming that the oxidation induction time (OIT) is directly proportional to the remaining antioxidants concentration [13] [112];
- Carbonyl groups build-up (determined by IR spectrophotometry);
- Chlorine grafted to polymer (determined by elemental analysis);
- Weight average molar masses (determined by rheometry in molten state);

One can also determine the lifetimes of pipes naturally aged in the drinking water distribution networks. Of course, the predictions are as good as the input data of the kinetic model are. In practice, the main unknown parameters are:

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

The exposure conditions of the pipes (concentration of disinfectant in water, water temperature and pressure, water oxygenation, and their respective seasonal fluctuations) in the drinking water distribution network. This model has been successfully applied to chlorine dioxide (DOC). In general, the water temperature and the DOC concentration range respectively between 9˚C and 24˚C and 0.1 ppm and 0.3 ppm (milligram per litre of water) from one site (of drinking water network) to another. For the sake of simplicity, in a first approach, the simulations have been made for the average values of 15˚C and 0.15 ppm in water (*i.e.* for a concentration of DOC of $[Y^\circ]_{z=0} = 2.3 \times 10^{-6}$ mol·l^{-1} in PE) [127] [128]. The lifetimes have been calculated for a virtual pipe of 40 mm diameter and 4.5 mm thickness, made in a PE generation anterior to the PE 80 one, having an initial average molar mass of MW = 150 kg·mol^{-1}, and containing an initial Irganox 1010 ($n_{AH} = 4$) concentration equals to its equilibrium value ($[AH]_{t=0} = 1.8 \times 10^{-5}$ mol·l^{-1}). Examples of simulations are given in **Figure 10** and **Figure 11**. In each case, one observes a satisfying agreement between theory and experiment.

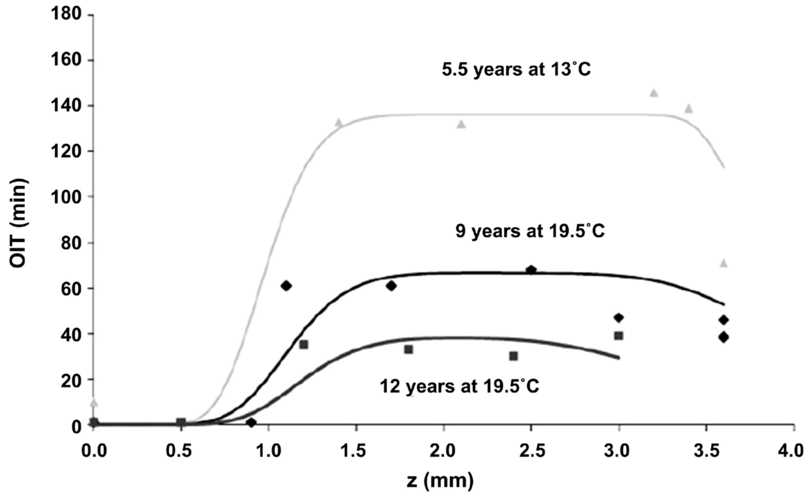


Figure 10. Example of simulations of oxidation induction time profiles (continues line). Comparison to experimental ones determined by differential at 190˚C in pure oxygen on pipes naturally aged in the presence of DOC.

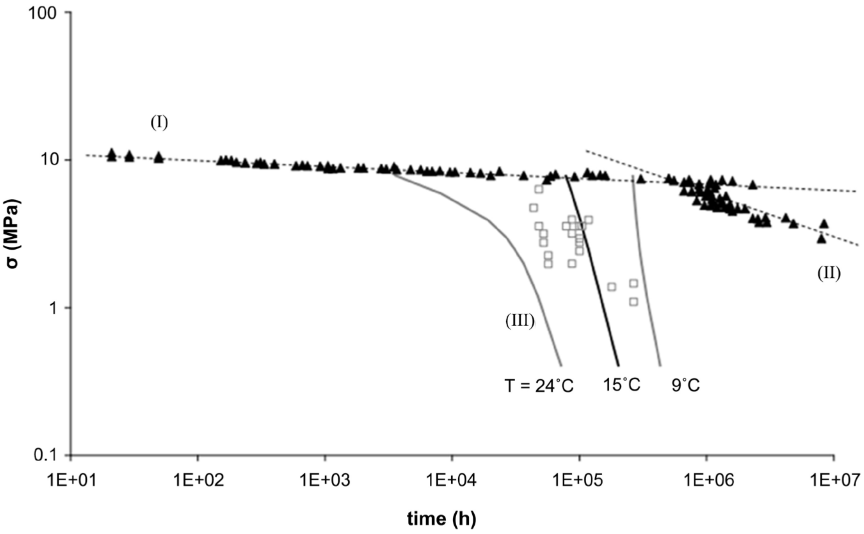


Figure 11. Simulation of regime (III) at three different water temperature (continues line). Comparison to lifetimes of Pipes naturally aged in the presence of DOC. The regression plot in pure water (without disinfectant) at 15˚C (Δ) has been determined from experimental results.

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

With the implementation of NSF protocol P171 in 1999 [129], and subsequent adoption of ASTM F 2023 in 2000 [130], Miner's rule has been used extensively in developing estimations of cross-linked polyethylene (PEX) pipe lifetimes when exposed to varying system conditions in the presence of chlorinated water [131]. Past work reported in this area demonstrated that Miner's rule can be effectively used and validated for some polyolefins under standard hydrostatic test conditions [132] [133]. Studies by Tanaka *et al.* [134] have investigated the influence of residual chlorine on the durability of PEX, using the full notch, creep test method. A relationship between time to failure, applied stress, and chlorine concentration was developed, based on tensile testing of samples. Long term studies performed by Gedde and Ifwarson [135] concluded that the best method for estimating the lifetime for plastic tubing carrying hot, chlorinated water is by extrapolation of the shorter time to failure from long term pressure testing at elevated temperature to lower service temperature with a much longer time to failure. X. Colin *et al.* (2009) [79] reported the kinetic model which is composed of differential equations corresponding to the reactive species, plus the equations allowing to compute the measurable quantities such as concentration of carbonyl groups, the number of chain scissions, the number of crosslinks, the number of chlorine atoms grafted to the polymer, and the whole oxygen quantity grafted to the polymer [136].

5. Selection of Material

Selection of material for targeted application is an important task for the material specialist engineer. During material selection several point need to be consider with counting cost factor. The polymer material selection for chlorine resistant application depends upon its chemical stability, lifetime, structure cost and end use application. The material which contain long chain structure and having unsaturation in the main backbone are more susceptible to chlorine attack. From several year olefin polymer was used and also lot of work carried on its stabilization by addition of antioxidant. In this point emphasis will be given on to cover the selection factor of widely used material for chlorine resistant application. Polyethylene is a popular material for water distribution application for example cold and/hot water, buried and premise potable water pipes due its low cost, easy processing, absences of corrosion related problem and long term service life up to 50 to 100 year service life.

Poly-olefins

PP is a highly versatile thermoplastic used for both short term and durable applications. A very important one in the latter category is pipes and fittings which are used to transport diverse liquid media. Transportation of water through polyolefin pipes spans a history of more than fifty years. Depending on the final application of the transported water various disinfection methods have been used which can be classified as physical (UV radiation, solar disinfection, thermal etc.) and chemical (chlorine, chlorine dioxide, ozone etc.). A widely used disinfectant to treat both drinking water and waste water is chlorine because of its strong oxidising effect, widespread availability, and storability. However, the chlorinated water has the potential to initiate the degradation of polyolefins. Studies on the degradation of polyolefins by chlorinated water were mainly carried out on polyethylene (PE) using moulded plates, dog bones or thin films as test specimen, and immersing them in chlorinated water. Sealed PE pipes containing pressurized chlorinated water as inner medium were aged as described by WIS 4-32-08. Even though, control of crucial testing parameters such as pH, chlorine concentration and temperature of the ageing medium throughout the experiments was not maintained. As a rule, polyolefins can only be used in durable applications when compounded with stabilisers which ensure the longevity in different environmental conditions where oxidation of the polymer accompanied by chain scission is the typical process reducing the life time. The loss of AO activity which can be the result of either extraction into the inner medium or chemical consumption by reaction with various active species formed in the ageing medium is a prevalent step during ageing. Subsequently the polymer undergoes chain scission which then leads to a loss in mechanical strength and ultimately a reduction in the life time of pipes as shown for PE pipes exposed to chlorinated water. From an analytical point of view the effect of chlorine on the deterioration of PE pipes was assessed by studying the AO depletion. For this purpose the AO content across the pipewall was profiled by measuring the oxidative induction time (OIT) of samples mechanically prepared. In the same sense the reduction in average molar mass was studied by analysing material scraped from the inner surface of the pipes. Also there are several theoretical models to determine the loss of AOs [137] [138] [139].

When pipes are exposed to liquid media from the inside the degradation of the polymer initiates from the inner surface and then progresses into the wall. In order to understand the effects of ageing media on pipes in a quantitative manner it is therefore stringently necessary to analyse the changes occurring with a high spatial resolution. The molar mass distribution can be determined by gel permeation chromatography while the chemical changes inferred to the polymer as a result of oxidation can be determined from IR spectroscopy. However, a quasi-spatial resolution can only be achieved by mechanical preparation of samples and analysing them individually. IR microscopy (mFT-IR) which combines the optical information available from light microscopy with the chemical information from IR-spectroscopy has found entrance into material science in the early 1980s. The high spatial resolution and reproducibility of results make mFT-IR an attractive analytical technique to study the effect of inner media on polyolefin pipes, and its scope in compiling information such as the distribution of additives or spectral crystallinity across the wall of PP pipes with high spatial resolution has been demonstrated recently [66] [140]. Although PE pipes have a projected service life of 50 - 100 years, long-term exposure to water containing free available chlorine has a deleterious effect on PE pipe mechanical, surface, and morphological characteristics, drastically reducing this lifetime by several decades [25] [141]. Mechanical pipe failure depends on the polymer's chemical structure (e.g., the presence of reactive unsaturated sites), temperature, water pH, free available chlorine concentration, and exposure time and conditions. At low internal stresses, which represent conditions indicative of potable water transport, mechanical failure is due to slow crack growth [142] initiated at the internal pipe surface. The accepted preamble to HDPE pipe crack Although PE pipes have a projected service life of 50 - 100 years, long-term exposure to water containing free available chlorine has a deleterious effect on PE pipe mechanical, surface, and morphological characteristics, drastically reducing this lifetime by several decades [143]. Mechanical pipe failure depends on the polymer's chemical structure (e.g., the presence of reactive unsaturated sites), temperature, water pH, free available chlorine concentration, and exposure time and conditions. At low internal stresses, which represent conditions indicative of potable water transport, mechanical failure is due to slow crack growth initiated at the internal pipe surface. The accepted preamble to HDPE pipe crack formation is characteristic oxygen, chlorine, hydroxyl, and vinyl functional group formation on pipe surfaces. Previous work has established that when HDPE pipe samples are subjected to consistent chlorinated water accelerated aging conditions, the first functionality to appear is a carbonyl group, typically noted by an FTIR absorbance at 1715 cm^{-1}. Carbonyl functional groups on the pipe's inner surface are thought to be precursors to the formation of microcracks, and these cracks may then propagate through the pipe wall until the internal pipe pressure exceeds the pipe's hydrostatic strength, leading to pipe rupture. While these moieties are characteristic of most HDPE pipe accelerated aging studies, there is no fully accepted consensus of either what chemical species are involved in e or what mechanisms control e this process.

To prevent chemical degradation of the pipe during use, manufacturers incorporate additives into PE such as phosphites, hindered phenol antioxidants, and stabilizers during manufacture. These compounds are designed to inhibit oxidation that accompanies chlorinated water exposure and extend the life of the pipe; manufacturers also control for slow crack growth. It is generally reported that PE surface oxidation and chain scission does not occur in highly chlorinated water (e.g., in excess of 500 mg/L) until antioxidants have been depleted. It would be expected that similar phenomena would occur under more mild drinking water conditions but over longer time periods. Antioxidants are expended due to repeated exposure to chlorinated water, leaving the polyolefin open to oxidative attack. While autooxidation is thought to play a key role in initiating and promoting slow-crack growth, the exact mechanism(s) and species behind this process are unknown. A recent review of the literature on HDPE pipe accelerated aging uncovered an expansive variation in reported aging conditions [55]. However, detailed mechanistic studies have not been performed, and as a consequence, there is no fully accepted consensus regarding the initiating degradation mechanisms. Some have argued that the oxidants responsible for polymer degradation only react at the surface and do not diffuse into the polymer, while others argue that diffusion of oxidants into the pipe cause further degradation.

While Resin and HDPE samples show an increase in carbonyl intensity over time, there are only slight differences at any given point in time within 10-fold differing Cl_2 concentrations. This increase in carbonyl formation over time mirrors previous work by Devilliers *et al.* who saw the same phenomena occur with a more notable effect of chlorine concentration [36] Despite the distinct loss of chlorine in the 500-Cl_2 solution, carbonyl formation remains similar to the 50-Cl_2 solution samples. Likewise, Castillo Montes *et al.* found that loss of OIT was the same for PE pipe exposed to 25 or 100 mg/L Cl_2 solutions at 70 C; the researchers concluded that disinfectant concentration was not the limiting factor for pipe degradation above a certain concentration. This chlorine decrease is also seen when either pipe or resin polymer samples are present, indicating that the loss of chlorine is not primarily due to interaction with the HDPE samples or antioxidants. Thus, while chlorine and chlorine concentration certainly affect

HDPE degradation, it is certainly not the only species involved in the degradation mechanism.

Whelton *et al.* [77] investigated very well data on the aging of HDPE, PEX-A and PEX-B water pipes by exposer to chlorinated water. The result shows that MDPE based PEX-A pipe was generally resistant to chlorinated water induced degradation under the chlorination conditions.

But HDPE based materials were markedly affected by aging during their 141 day exposure. Author reported very good data on summary of polyethylene property and chemical performance changes due to chlorinated water aging as shown in Table 4.

The effect of exposing the polyamide Nylon 66 to chlorinated water also reported arlier. In which, a correlation between the pH-dependent rate of polymer degradation and the pH-dependent Cl_2 concentration profile implicated Cl_2 as the key reactive intermediate responsible for polyamide degradation in chlorinated water. FTIR spectral data indicated that N-chlorination was most likely the initial reactive step involved in this process. Moreover, we specifically established that singlet oxygen was not involved in polyamide degradation under these conditions [11]. The effect of very large increase in Oxidation-reduction potential (ORP) with increasing chlorine content from 0.1 to 1 ppm. In which time to failure in polybutylene (PB) pipe decreses sharply, but with a much more modest further decline in lifetime as the chlorine content is increased from 1 to 5 ppm [144].

Elastomer

For more than 50 years, elastomeric materials have been used ubiquitously in drinking water distribution systems. Elastomeric materials have successfully been utilized in a variety of applications ranging from rubber gaskets, to valves, to hydrants, to fittings—and have been equally suitable to a wide variety of piping materials, including cast iron, ductile iron, steel, copper, and PVC. In general,

Table 4. Effect of chlorinated water aging on the performance changes in property of HDPE, PEX-A and PEX-B.

Polymer Property and performance	Name of Polymer			
	HDPE (Resin)	HDPE pipe	PEX-A Pipe (MDPE)	PEX-B Pipe (MDPE)
Surface Chemistry	Carbonyls formed	Carbonyls formed	Unchanged	Carbonyls formed
OIT	40% reduction	95% Reduction	Unchanged	65% reduction
Bulk density	Unchanged	Slight increase	Unchanged	Unchanged
Mechanical Strength	Unchanged	Unchanged	Unchanged	32% reduction and 60% reduction in elongation at break
Non polar contaminants	Solubility unchanged Diffusivity unchanged	Solubility unchanged Diffusivity unchanged		Solubility unchanged Diffusivity unchanged
Polar contaminants	Solubility unchanged Diffusivity increased by 40%	Solubility unchanged Diffusivity increased by 30%	Solubility slightly increased Diffusivity unchanged	Solubility slightly decreased, Diffusivity increased 20%

[1] PEX-A correspondence to Polyethylene cross linked by peroxide and PEX-B correspondence to Polyethylene cross linked by Silane.

elastomers have performed well in the water distribution system. One of the limitations of the disinfection process in general is that the free chlorine is believed to attack the elastomer matrix. While both free chlorine and chloramines contribute to elastomer degradation, chloramines appear to attack elastomer components much more aggressively than free chlorine [4] [5]. In some situations, the chloramine residual has had significant negative impacts on the water distribution infrastructure and plumbing systems. In some southern cities, the chloramine ion is believed to be responsible for reducing the usable life of rubber components from five or six years to six months. In several Midwestern cities, the increased degradation rate was observed four and ten years after switching to the chloramine system [4] [5]. For the public water utility, chloramine-induced elastomer degradation may cause:

- Increased leaks and line losses
- Increased maintenance and repair
- More expensive replacement parts
- Budget planning difficulties
- Customer dissatisfaction

The rate that elastomers degrade when exposed to potable water is dependent on a number of poorly understood factors. In addition to chlorine/chloramines concentration, temperature and pH and are believed to play roles, but those have not been adequately defined.

Poly(ethylene-co-propylene-co-5-ethylidene-2-norbornene) (EPDM) has superior water repellency, chemical resistance, and ozone resistance due to its nonpolar nature and saturated backbone structure compared with other unsaturated rubbers such as isoprene rubber, nitrile butadiene rubber, and so on. Consequently, EPDM has been widely adopted to prepare rubber seals in water supply systems [145]. In practice, EPDM seals have some issues; for instance, EPDM seals degrade with extended use in water supply systems due to the presence of residual chlorine, which is used as a disinfectant, and metal ions. Additionally, we have found that radicals, which are generated by a reaction between rubber and chlorine, are a major factor in the degradation of EPDM seals [146] [147].

Nagistty *et al.* (2014) [148] investigate long-term drinking water quality concerns, accelerated degradation tests were performed for three of the most commonly used elastomers (natural rubber, styrene butadiene rubber, and sulfur-cured ethylene propylene diene monomer). Test solutions were then analyzed for suspended solids and organic compounds. Most of the organic compounds identified were associated with leaching of compounds from the elastomers; the exception was chloroform, which is thought to be a reaction by-product. The presence of these organic compounds is considered to be long term because they are continually added to the system as the elastomeric compounds degrade over time.

As chloramination has become more widespread, several utilities that switched from free chlorine to monochloramine-based systems have reported problems with substantially higher rates of elastomer failure within their distribution networks [149] [150] [151]. Reiber Steve (1993) [151] evaluated elastomer degradation involved an accelerated life cycle testing protocol whereby sets of tension mounted coupons were exposed to specific chlorine and ammonia concentration at elevated temperature. The coupons were inspected regularly for evidence of oxidative degradation and cracking. After a set exposure period, the coupons were assessed for tensile performance, swelling and surface characterization. With few exceptions, solutions of chloramines produced greater elastomer swelling, deeper and denser surface cracking, more rapid loss of elasticity and greater loss of tensile strength than equivalent concentration of free chlorine. Elastomers most susceptible to attack were those formulated with natural or synthetic isoprene's. the elastomer types commonly used in the water utility field fall into nine categories that reflect diffrenet base polymers. Table 5 lists elastomer that are common to distribution system, some of their typical application and their attributes.

Many companies are modifying the manufacturing process of existing products to improve the performance of elastomers for water utility applications. For example, slightly increasing the ratios of sulfur and accelerator will result in a compound with greater cross-link density. A secondary accelerator added to the formulation will improve oxidation resistance. Adding microcrystalline paraffin wax will reduce oxidation and ozonation as it migrates to the surface of the gasket after cure to act as a barrier. And finally, a strong chemical antioxidant/antiozonant may be added to the formulation to meet the gasket-aging requirements set by the AWWA C111 standard (AWWA 2000). Thus, a variety of additives or modifications to the curing process can significantly affect the behavior of the finished elastomer product.

Several new EPDM-based products are available that have been formulated

Table 5. Elastomer uses in the distribution system.

Polymer Type	Usage	Attributes
Natural (NR)	Flapper valves, large pipeline gaskets	Abrasion Resistance
Synthetic Rubber (SBR)	large gaskets	Abrasion Resistance, inexpensive
Buna-N (NBR)	O-rings, valves seats, pump impellers, check balls	Resistance to petroleum solvents
Ethylene-propylene (EPDM)	O-rings, valves seats, flat gaskets, pond liners, check balls	Chemical resistance, inexpensive
Isobutylene Isoprene (IIR)	Diaphragms	Oxidant resistance
Fluorocarbon (FKM)	O-ring, chemical feed pumps	Superior chemical resistance
Neoprene (CR)	Pump impellers, valve seats, chemical feed pumps	Excellent weathering character, resistance to gas and oils
Hyplon (CSM)	Reservoir liners	Ultraviolet resistance
Silastic (Si)	High temperature applications	

specifically for chloramine resistance in aggressive water utility applications. These new products are designed to work effectively in high-flow conditions with either hot or cold water. Typical applications for these new materials include faucets, showerheads, aerators, water-filtration components, irrigation systems, ice makers, water meters, valves, fittings, and many other uses (Parker Hannifin Corporation 2006). One of the newest materials available to the water industry is *Santoprene* (*PP* + *EPDM*), an advanced, cross-linked thermoplastic elastomer produced by Exxon Mobil Chemicals. It is processed as a plastic, yet performs with the flexibility and durability of rubber (ExxonMobile Chemical 2004). EPDM is a relatively new elastomer product formulated by ExxonMobile Chemical in 1988 (ExxonMobil Chemical 2007). EPDM rubber is ideal for outdoor applications because of its excellent resistance to ozone, oxidants, and severe weather conditions. Its primary limitations are its susceptibility to hydrocarbons and its cost. Within the water industry, EPDM is widely used for O-rings, valve seats, flat gaskets, and pond liners. More recently, peroxide-cured EPDM is being used where chloramines resistance is important. The degradation of elastomers is believed to be caused primarily by chemical cross-link breakages. It is believed that chloramines attack the cross-linking bonds, and the rate of degradation is related to the type of chemical bond. Cross-link bonds that break easily have a low “bond disassociation energy”, and cross-link bonds that are difficult to break have a high “bond disassociation energy”. The chemical attack is likely to be more severe in elastomers with cross-links that have lower bond disassociation energy. The type of cross-link bonds that are formed depends upon the base elastomer polymer and on the curing agent. Natural rubber and most synthetic elastomer materials are sulfur-cured. However, some specialized elastomers (some formulated for chloramines resistance) may be cured with peroxide. The selection of curing agent has a significant effect on the formation of cross-link bonds. In all rubbers, cross-links are formed when the excess curing sulfur attaches to the doublebonded carbon in adjacent polymer chains to form a bridge. The bridge, or cross-link, can be short and of the form C-S-C, or relatively long and of the form C-SX-C, where “x” is the number of sulfur nodes present in the cross-link. The longer cross-link chains are more susceptible to change as the relatively weak sulfur bonds may break and move to new bonding sites. Another commonly used elastomer curing agent is peroxide. While significantly more expensive than sulfur, the peroxide curing agent forces a C-C cross-link bridge between adjacent polymer chains. As the C-C bond has a much higher bond disassociation energy, the peroxide cured elastomers are less susceptible to change. The natural rubber, SBR, nitrile (NBR) and neoprene backbone polymer chains all contain double-bonded carbon atoms that are available to form cross-links during curing. However, not all of the available sites form cross-linkages, and ultimately only a small number of cross-linkages are completed. Thus, the chlorine and chloramine ions attack both the weak cross-link bonds and the available carbon sites (open sulfur bond locations) on the backbone polymer chain. In addition to removing the cross-linkages, the backbone chain length is reduced, which further reduces polymer entanglement to the point that parts of the network break away.

Due to its chemical composition, EPDM has proved to be a very durable elastomer material. Unlike many elastomers, the double-bonded carbon atoms within EPDM elastomers are not contained within the polymer "backbone" chain. Rather, the double-bonded carbon atoms hang off the polymer chain as a pendant. Thus, the sites available for cross-linkage are offset from the backbone, and chemical or physical attack of the cross-linkage chain does not affect the base polymer backbone or the molecular chain length. Therefore, the material properties derived from chain entanglement will not be altered by chemical or physical attack (Sartomer Company 2002). In addition to selecting the base polymer material and curing agents, elastomer compounders tailor products to meet specific needs by adding vulcanizing agents, antidegradants, accelerators, retarders, pigments, plasticizers, processing aids, and fillers—all of which affect the cross-links. Degradation also is related to elastomer permeability and fluid absorption. Any fluids in contact with the elastomer will permeate the material, and in time, the elastomer swells. The presence of absorbed fluid can weaken the elastomer as the fluid molecules push apart the polymer molecules (plasticization). Additionally, the contacting fluid may leach out soluble elements from the elastomer structure. Or, the fluid may be chemically aggressive, first attacking the elastomer surface, and after absorption, attacking from the inside, causing further deterioration in properties and performance of the component (Loadman 2005, Nagdi 1993) [6] [7]. Till date no has reported data on effect of chlorine on polymeric blend. In our previous work [152] we prepared a blend of PP-R with elastomer and its chlorine resistance were examined. Mechanical, thermal, and morphological properties of the blend systems have been investigated as a function of two different elastomer, chlorine concentration and temperature of test condition. The prepared PP-R/EBC and PP-R/EPDM blend were exposed to chlorine with varying concentration of 50 ppm, 500 ppm and 5000 ppm at different temperature. Mass changes was found for all composition was below statistical limit of 0.5%. The tensile strength of PP-R increases with increase in chlorine concentration with decrease in percent elongation and in PP-R/EBC and PP-R/EPDM blends no significant changes was found. Thermograms obtained from differential scanning calorimetric studies reveal that blends have lower percent crystallinity values compared to pure PP-R and after exposure also no increase in crystallinity was found [122] [153], which confirms excellent resistant of blends to chlorinated water. Optical microscopic observations on surface indicate formation of black domain and increase in surface roughness in PP-R after exposed to 5000 ppm of chlorine and in PP-R/EBC and PP-R/EPDM no changed was observed indicates the better resistant of blends to hot and cold chlorinated water. Mio Gonokami *et al.* (2014) [146] investigated a suitable antioxidant for a poly(ethylene-co-propylene-co-5-ethylidene-2-norbornene) (EPDM) seal in tap water applications was determined with respect to volatilization and decomposition of the antioxidants. Seals were prepared by mixing

EPDM with 1 phr antioxidant and other ingredients followed by vulcanizing the mixture at 433 K for 20 min. The resulting EPDM seals were immersed into chlorinated water to investigate accelerated degradation. The change in antioxidant content was measured by gas chromatography/mass spectroscopy (GC/MS) and high-performance liquid chromatography (HPLC). The weight loss of amine antioxidants during vulcanization was quite low due to their low volatility and decomposition. Antioxidant weight loss during accelerated degradation depended on both the antioxidant's ability to trap radicals and solubility in chlorinated water. TMDQ (2,2,4-tri-methyl-1,2-dihydroquinoline) and ETMDQ (6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline) are the most suitable antioxidants for EPDM seals in a tap water system. Neoprene is one of the best all-purpose elastomers for unique conditions where resistance to sunlight, oxidation, heat and many petroleum derivatives are of prime importance. It has a high degree of flame resistance because of its chlorine content it provides excellent resistance to many oils, chemicals, water acids, and alkalis. It is generally attacked by strong oxidizing acids, esters, and ketones as well as chlorinated, aromatic and nitro hydrocarbons. It is used in a wide variety of environments, such as in wetsuits, electrical insulation, and car fan belts. Its chemical inertness makes it well suited for industrial applications such as gaskets, hoses, and corrosion-resistant coatings. It can also be used as a base for adhesives [8].

Reported Standard and testing methods for Polymer & Elastomer

Table 6 gives an idea about available testing Standard and respective parameter related to Chlorine assisted degradation of polymer. Many elastomer compounders are acutely aware of the water industry's desire to identify an elastomeric material resistant to chloramines degradation. Several compounders have developed their own testing protocol to demonstrate that their products are, not

Table 6. Standard testing methods available for chlorine/chloramines/carbon dioxide resistant test.

Reference	Standard	Title	Year	Finding
[154] [155]	ASTM F 2263 & ASTM F 2023	Chlorine resistance test method for PEX pipes	2003 and 2004	PE (2263) and PEX (2023) pipe exposed to pressurized test-fluid until failure. Air is the external environment. Min. pipe length is 12 - 18 in. Test solution oxidation reduction potential (ORP) should be 825 mV. Flow velocity _0.04 m/s. Conduct at 3 temperature and 2 pressure/temperature Record time-to-failure for each specimen.
[129]	NSF International	NSF Protocol – Chlorine resistant of plastic piping materials.	1999	Ageing solution is continuously pumped around a closed pressurized pipe circulation loop or once through and not recirculated. Air is the external environment. Initial TDS _ 20 mg/L. Flow rate of 0.227 m^3/hr. Conduct at 3 temperature and 2 Pressure/temperature Condition pipe using 66_ C test water for 2 h. Hourly record temperature, pressure, chlorine level, pH, ORP, and flow rate
[156]	ASTM D 6284	Standard test method for rubber-property effect of aqueous solutions with available chlorine and chloramines	1998	Rubber-like materials are immersed in bottles that contain a chlorinated water solution. Air is the external environment. Immersion periods range from 22 - 4366 h. Solutions must be changed every 48 h or more frequent

Continued

[157]	ASTM D 1599	Standard test method for resistance to short-time hydraulic pressure of plastic pipe, tubing, and fittings; 1999	1999	Loading a pipe specimen to failure in a short-time interval by continuously increasing internal hydraulic-pressure. Air or water is the external environment. Increase the pressure uniformly until the specimen fails. The specimen should burst between 60 and 70 s.
	Plastic Pipe Institute Statement A	PPI-Statement-A Relative Oxidative Aggressiveness of Chloramines and Free Chlorine Disinfectants Used in Treated Potable Water on Cross-linked Polyethylene (PEX) Pipe	2013	After the testing was completed, failure times of the PEX pipe specimens tested with the free chlorine test fluid were compared to failure times of the PEX pipe specimens tested with the chloramines test fluid. The results showed pipe failure times approximately 40% longer when tested with chloramines, compared to testing with free chlorine in otherwise identical test conditions.
	ASTM F876	ASTM F876 has four categories for chlorine resistance, as part of the Material Designation Code: 0: Not tested or not rated 1: 25% of time at 140˚F, 75% of time at 73.4˚F 3: 50% of time at 140˚F, 50% of time at 73.4˚F 5: 100% of time at 140˚F, 0% of time at 73.4˚F		ASTM F876 contains the actual performance requirements, in Section 6.10: "PEX tubing intended for use in the transport of potable water shall have a minimum extrapolated time-to-time failure of 50 years when tested and evaluated in accordance with"

Table 7. Aging conditions used to estimate the effect of disinfectants on polymer & elastomeric material.

Source	Title	Year	Material	Temp.	pH	Time	Disinfectant Conc.	Finding
Vibien *et al.*	Chlorine resistance testing of cross linked	2001	PEX	115	6.5 - 6.6	702 - 5890 Hrs	Chlorine	PEX plumbing pipe is subjected to 4 - 3 ppm chlorine at elevated temperature and experience rapid oxidation of inner wall and subsequent britlle fracture of pipe, but extrapolated results of this accelerated aging indicate acceptable life at service temperatures.
Andrew J. Whelton [73]	Critical consideration for the accelerated ageing of high density polyethylene potable water materials.	2009	HDPE	23˚C and 37˚C	6.5	72 Hr	50 ppm, 5000 ppm Cl_2	Of the ten condtions tested, three condtins with an alkalinity concentration of 50 ppm as $CaCO_3$
Hassinen *et al.* [14]	Deterioration polyethylene pipes exposed to chlorinated water	2004	HDPE	95 - 105	6.45	0 - 809 Hrs	Chlorine	Antioxidant were raplildy consumed by relatively low chlorine concentration (3 ppm). Polymer degradation appeared to be confined to the inner surface and strated when the antioxidant system was depleted at the inner pipe wall.
Lundback [15]	Long Term Performance of Polyolefins in different enviorment including chlorinated water antioxidant consumption and migration and polymer degradation	2005	HDPE	90 - 115	6.1 - 6.7	29 - 318 days	Chlorine	Chemical stabilizer were rapidly consumed by relatively low chlorine concentration (0.5 - 1.5 ppm)

Continued

Colin *et al.*	Kinetic Modeling of the aging of PE pipes for the Transport of water containing Disinfectants	2006	MDPE	20 - 40	NR	2 - 99 days/5 - 18 years	ClO_2	PE antioxidant is quickly consumed uniformly in presence of chlorine dioxide to the −1 mm depth; examined filed pipe shows same results; ClO_2 reactions with PE and antioxidant are identified.
Dear and Mason [13]	Effect of chlorine on Polyethylene Pipes in water distribution networks	2006	MDPE	60 - 80	NR	200 - 10,752 Hrs	Chlorine	Observation of failed PE pipes and laboratory work at high Cl concentrations (3000 - 10,000 mg/l) shows that failure occurs by slow crack growth due to creep after initial inner layer of pipe is degraded by chain scission/oxidation; PE in plants can see 3000 mg/l Cl and life is expected to be <10 years.
Castegnetti *et al.* [111]	Effect of chlorinated water on the oxidative resistance and the mechanical strength of PE pipes	2007	HDPE	25 - 80	6.5 - 7.5	0 - 19 weeks	chlorine, and chlorine dioxide	HDPE degrades in the prsences of chlorine dioxide and chlorine under pressure conditions; elongation at fracture after 2 weeks is 50% versus > 700% for control.
Chung *et al.* [158]	An examination of the realative impact of common poatable water disinfectants (chlorine, chloramines and chlorine dioxide) on plastic piping system components	2007	PEX	ASTM F 2023	6.8	ASTM F 2023	chlorine, chloramines and chlorine dioxide	PEX fails in the presence of various disinfectants with inner wall degradation followed by mid and outer wall crack propagation in sample under pressure; chlorine and chlorine dioxide diffusiuon may make these disinfectants more aggressive in polymer degrdation
Audouin *et al.*	Durability of PE Piper Trasporting Chlorine Dioxide Disinfected water-kinetics modeling of embrittlement process	2007	MDPE	20 - 40	2 - 6	1200 Hr	Chlorine Dioxide	Laboratory work confirms dioxide attack on PE resulting in chian scission of PE chains leading to "end of life" embrittlemnt due to free radical kinetics; embrittlment at 400 Hr at 40 degree C; predictive modeling in process.
Montes *et al.*, [117]	Ageing of PE at raised temperature in contact with chlorinated sanitary hot water.	2012	PE	70	9.4 - 8.8	270 days	Chlorine (0, 1, 25, 100 ppm)	Results showed that the degradation rate was almost equivalent for 25 and 100ppm conc ageing.
Damodaran *et al.* [66]	Monitoring the effect of Chlorine on the ageing of PP pipes by infrared microscopy	2015	PP	95	6.8	500 Hrs	Chlorine (4 mg/L)	The effect of hot water at 95˚C on differently nucleated random PP pipes was analyzed with respect to the chemical changes occurring to the polymer and antioxidant.
Zebger *et al.* [43]	Degradation of poly (1,4-phenylene sulfide) on exposer to chlorinated water	2005	PPS	-	2 - 8	1 week	Chlorine (0 - 0.09 M)	Results suugested that upon exposer to chlorinated water, PPS under goes a series of reaction that 1) oxidize the sulfide to the sulfoxide and sulfone, 2) alter and disrupt the phenyl ring, and 3) apparently cleave the polymer such that material loss was observed. This data indicate that Cl_2 and HOCL are species that initiate reaction. In comparison to other (polyamide PA66, Poly(styrene-co-butadiene), and polystyrene), PPS is more sensitive to the effect of chlorinated water.

Continued

Ingo Zebger, *et al.* [32]	Degradation of vinyl polymer films upon exposure to chlorinated water: the pronounced effect of a sample's thermal history	2003	polystyrene and poly(styrene-co-butadiene)				0.2 to 0.08 M in NaClO	Poly(styrene-cobutadiene) was more reactive than polystyrene upon exposure to chlorinated water and the data clearly indicate that olefinic residues are an important reactive functional group under these conditions.
M. Lundback *et al.* [50]	Polybutene-1 pipes exposed to pressurized chlorinated water: Lifetime and antioxidant consumption	2006	Isotactic polybutene-1	95˚C to 115˚C	(6.5G0.1),		≤3 ppm	The lifetime shortening in the isotactic poly(butene-1) pipes exposed to chlorinated water (0.5 - 3 ppm) was approximately by a factor of 10 with respect to that obtained in pure water. The lifetime shortening was significant even at low chlorine concentrations (0.5 ppm Cl) and a further increase in chlorine content led only to a moderate additional increase in the lifetime shortening.
Khatua S, Hsieh Y-L.	Chlorine degradation of polyether-based polyurethane	1997	PU	NA	7		Conc. Clorox 5 to 40,000 ppm	
X. Colin, *et al.* [79]	Aging of Polyethylene Pipes Transporting Drinking Water Disinfected by Chlorine Dioxide. I. Chemical Aspects	2009	PE Pipe	20˚C to 40˚C		(80 - 100 ppm)	chlorine dioxide (DOC)	Aging of polyethylene (PE) films in highly concentrated (80 - 100 ppm) chlorine dioxide (DOC) solutions at 20 and 408C for durations up to 1200 h has been studied by IR spectrophotometry, tensile testing, melt rheometry, and grafted chlorine titration. IR revealed a carbonyl growth indicating that DOC induces PE oxidation. Rheometry revealed the predominance of chain scissions, presumably linked to hydroperoxide decomposition. Tensile testing revealed an embrittlement process when the weight average molar mass MW approaches a critical value of 70 kg mol21, which agrees with a previous study of PE thermooxidation.

only resistant to the degradation caused by chloramine attack, but superior to other products. One such study, Resistance to Aqueous Solution performed by ExxonMobil Chemical, used temperature and concentration to accelerate aging. Three grades of Santoprene were compared to EPDM, NBR, and silicone thermoset rubbers for hardness, tensile strength, ultimate elongation, 100 percent modulus, and weight before and after accelerated-aging tests. The accelerated–aging test specifications were reported to involve immersion of these seven elastomers in an aqueous solution with a chloramines concentration of 1000 ppm at an elevated temperature of 70˚C and two pH values (5.5, slightly acidic, and 8.5, slightly alkaline). These conditions were maintained over 180 days with testing occurring at 14, 30, 60, 90, 120, and 180 days. While many testing details are unavailable, it was reported that Santoprene has a resistance to chloramine attack (ExxonMobile Chemical 2007) (**Table 7**).

6. Conclusion

This review demonstrated the impact that different types of disinfectants can have on polymeric material during service application. It also demonstrated that during chlorine exposure, the solution pH, chorine concentration or free available chlorine, temperature, alkalinity and exposure time must be carefully monitored during study. The results overview are important with respect to the development of polymers that can better resist exposure to water that has been chlorinated to kill bacteria (e.g., drinking water). This work also attempts to be made to covers the steps in building a kinetic model with a view to predicting the lifetime of polymer under operational conditions. This area of research warrants further studies.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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