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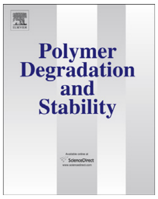

Reaction mechanism for oxidation and degradation of high density polyethylene in chlorinated water

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ABSTRACT

Polyethylene is increasingly used for potable water pipe even though polyethylene is susceptible to oxidative degradation. Accelerated aging conditions with chlorinated water solutions which minimized variations in solution chemistry were used in a 160-day (3840 h) immersion study of high density polyethylene (HDPE) pipe and HDPE resin. Samples were periodically characterized for changes in visual appearance and surface chemistry using infrared spectroscopy. Surface carbonyl bonds were detected for both HDPE pipe and HDPE resin samples. Experiments with isotopic $^{18}O_2$ gas demonstrated that molecular oxygen is partly responsible for formation of the carbonyl oxygen. Both HDPE pipe and HDPE resin samples were demonstrated to form 4-chloro-2-methylbutan-2-ol and 2,3-dichloro-2-methylbutane as novel HDPE breakdown products which leached into chlorinated water. From these data, reactive species involved in the breakdown of HDPE pipe have been identified. A proposed mechanism for the breakdown of HDPE is Cl• or HO• initiated H-abstraction to produce a carbon-center radical that reacts with triplet oxygen to form a peroxyl, which upon decomposition yields a carbonyl and further propagates the formation of radicals.

1. Introduction

Globally, polyethylene (PE) pipes are increasingly being utilized as a means of potable water transport for industrial and residential applications. High density polyethylene (HDPE) pipes are approved by several United States and European standards organization for potable water transport (25 °C or less) [1,2]. These pipes are flexible and operate well above their glass-transition temperature and below their melting temperature. The flexibility of these materials is underscored by the performance of buried HDPE pipe during a 6.9 magnitude Kobe, Japan earthquake in1995; while many steel pipes mechanically fractured, HDPE pipes remained intact [3]. When used for potable water applications, polyethylene pipes contact water that typically contains 0.1–4 mg/L aqueous free chlorine or chloramines. Under these typical conditions, polyethylene pipes are observed to release volatile and odorous molecules [4]. Potable water pipes are also exposed to up to 500 mg/L free chlorine when "superchlorinated" for disinfection during installation or after a water main break. While far too high of a value to exemplify typical drinking water conditions, such a value is at the low end for accelerated aging studies. In such studies, free chlorine concentrations up to 10,000 mg/L Cl_2 are typically applied at temperatures >25 °C to accelerate aging so that test results are obtained within a few months time for extrapolation to a life expectancy [1].

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 [1,5–8]. 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 [3] initiated at the internal pipe surface [7,8]. HDPE is a long chain high molecular weight polyolefin with very little branching and a density of 0.94–0.96 g/mL [9]. 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

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Abbreviations: HDPE, high density polyethylene; Resin, HDPE resin (no antioxidants); DCM-HDPE, HDPE pipe treated with dichloromethane to extract antioxidants; OIT, oxidation induction time; 500-Cl_2, aqueous solution with 500 mg/L chlorine as Cl_2; 250-Cl_2, aqueous solution with 250 mg/L chlorine as Cl_2; 50-Cl_2, aqueous solution with 50 mg/L chlorine as Cl_2.

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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 FT-IR absorbance at 1715 cm^{-1} [1,10]. 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 [3,8,10–12]. 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 – or what mechanisms control – 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 [5,6,8,11,13]. 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 [5,6,8,11,14]. 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 [1]. A follow-up review to this same literature revealed that chlorine (Cl_2), chlorine oxide (Cl_2O), hypochlorite dimer (Cl_2O_2) hypochlorous peroxy acid (ClO_2H), hypochlorous acid (HOCl), the hypochlorite anion (ClO^-), the hypochlorite radical (ClO•), the hydroxyl radical (HO•), triplet oxygen ($^3O_2$), and singlet oxygen ($^1O_2$) have been proposed as polymer degradation agents [8,15–21]; 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 [8,13], while others argue that diffusion of oxidants into the pipe cause further degradation [10].

Chlorine speciation depends on the pH, which directly affects the degree of polymer oxidation. For typical drinking water conditions using free chlorine, the pH of water is near 7.0 and HOCl is the dominant species. Bradley reported that oxygen is formed from the decomposition of HOCl, and this species is the responsible agent for degradation (Scheme 1) [18]. The oxygen produced can then directly interact with the pipe material.

From a thorough review of water chlorination chemistry [1,10], radical species such as HO• and ClO• and closed-shell oxygen compounds have been implicated in chlorinated water induced polymer degradation. These agents are nonselective, highly reactive, and can abstract hydrogen from polymers initiating autooxidation. Extremely reactive radicals, such as HO• and Cl•, would be expected to show little to no selectivity, 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 [22–25].

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl \rightleftharpoons 2H^+ + Cl^- + ClO^-$$

$$2HClO \longrightarrow 2HCl + O_2$$

Scheme 1. HOCl degradation to HCl and O_2.

With extensive need for new and replacement pipe in water distribution systems, as well as increased reliance on polyethylene pipe for potable water transport in society, a full scientific understanding must be developed to thoroughly understand PE degradation under chlorinated drinking water conditions. Knowledge of which agents are responsible for HDPE degradation in chlorinated water is fundamental to understanding the mechanistic breakdown of these pipes and designing more sustainable materials. The research goal of the present study was to identify the species and mechanism(s) behind the oxidative breakdown of HDPE under conditions that more closely resemble conditions of potable drinking water distribution and superchlorination. The specific objectives were to: (1) differentiate between oxidation of HDPE pipe (containing additives) and an antioxidant free HDPE resin (2) decipher the source of oxygen leading to the initiation of the carbonyl functionality and identify any additional HDPE degradation products and (3) provide a mechanism for initial stages of HDPE degradation.

2. Experimental

2.1. Polymer samples

Three different types of HDPE were used in this study. HDPE resin devoid of antioxidants (Resin), HDPE pipe, and HDPE pipe treated with dichloromethane to extract antioxidants (DCM-HDPE). Resin was CPChem HDPE obtained from Chevron-Phillips Chemical Company LP with a reported density of 0.955 g/cm^3, molecular weight (M_w) = 317.48 kg/mol, and number average molecular weight (M_n) = 9.37 kg/mol. Resin was obtained as a powder and melt pressed under argon into 0.58 mm sheets (5.0 cm × 5.0 cm) at 135 °C for approximately 3 min at a pressure of 15,000 pounds. HDPE pipe was obtained from a commercial source, with an outer diameter of 19 mm (SIDR 9), a reported density of 0.954 g/cm^3 and thickness of 2.6 mm. To ensure uniform shape, dog-bone shaped samples were cut from the Resin sheets and HDPE pipe using a microtensile die Dewes Gumbs Die Company, Inc. (Long Island City, NY). All samples were 2.0 cm in length.

Fifty HDPE microtensile samples then underwent a pre-treatment Soxhlet extraction reflux treatment with dichloromethane (12 h, 40 °C) to remove additives prior to aging (DCM-HDPE). (Note: dichloromethane was chosen as the solvent for the extraction, as it is able to dissolve many organic compounds and can be refluxed at a low temperature (boiling point = 40 °C) to limit degradation of the polymer and extracted materials). The oxidation induction time (OIT) was determined from these samples and compared to HDPE samples using a TA Instruments Q1000 Differential Scanning Calorimeter (see Figure A-1 in Supporting Information).

Treatment with dichloromethane reduced the oxidation induction time from 117.7 (±0.6; $n = 3$) minutes to 102.7 (±2.5; $n = 3$) minutes indicating that the oxidative stability of the high density polyethylene pipe samples was reduced, ostensibly through the loss of antioxidants at the superficial layer of the pipe that was contacted with dichloromethane. Analysis of the extract through GC/MS corroborated this theory, as 2,6-di-*tert*-butylphenol and 2,4-di-*tert*-butylphenol were found to be the main products of the extraction through GC/MS library search match (while authentic samples were unavailable for comparison, library matches were found with >90% accuracy). These deciphered hindered phenols are likely remnants of larger deteriorated antioxidants commonly used in pipe material. Before the DCM-HDPE materials were characterized and used in aging experiments, the samples were thrice