



Chlorine dioxide resistance of different phenolic antioxidants in polyethylene



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ABSTRACT

A series of polyethylene tape samples containing 8 different phenolic antioxidants (concentration = 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 O3 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.

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1. Introduction

Water must be disinfected before human consumption in order to prevent the spread of infections. Chlorine dioxide has become important as a tap water disinfectant due to its high effectiveness in eliminating pathogenic microorganisms such as fungi, bacteria and viruses and also in preventing the formation of biofilm [1–3]. Polyethylene pipes that distribute tap water containing chlorine or chlorine dioxide have been found to degrade at the pipe inner wall, and the lifetime of the pipes is shorter than that of pipes exposed to chlorine-free water [4–8]. Antioxidants are added to polyethylene in order to avoid degradation during processing and to extend the product service life. Models have been developed that make it possible to predict the antioxidant loss by migration to the surrounding media [9]. These models are applicable to the loss of stabilizer in hot-water pipes distributing water free from strongly degrading species like chlorine or chlorine dioxide [7–9]. Chlorine dioxide is, however, a very powerful oxidant that degrades phenolic

antioxidants and the loss of antioxidant by degradation is much greater than by migration to the surrounding media [8,10].

Chlorine dioxide is a one-electron oxidant that attacks the phenolic ring and generates a radical cation with the subsequent formation of a phenoxy radical [10,11]. In phenolic antioxidants, the phenoxy radical favours β -cleavage in the side-chain due to hindered character of the phenolic group [10]. This leads to the formation of yellow-coloured quinoid structures [10]. Pospisil [12,13] has outlined other reactions yielding these compounds. The side chain radical is further oxidized by chlorine dioxide or oxygen to yield carbonyl groups and the antioxidant degradation products are highly polar, low in molar mass and, most importantly, of low antioxidant activity [10]. Oxidation reactions directly between chlorine dioxide and polyethylene is a subject of some controversy. Saturated aliphatic hydrocarbons and aliphatic olefins were reported to be unreactive to chlorine dioxide under typical water conditions [14,15]. Lindgren et al. [16,17] reported the presence of oxidative and chlorinated products from the reactions of chlorine dioxide and some olefins, which they suggested to be due to a mechanism whereby the allylic hydrogen is abstracted by chlorine dioxide giving free radical intermediates. The high stability of saturated hydrocarbons towards chlorine dioxide was further

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supported by data presented by Yu et al. [8] on polyethylene pipes exposed to water containing 4.0 ppm chlorine dioxide at 90 °C and pH = 6.8: the material beneath the degradation layer showed no detectable IR absorption due to carbonyl, hydroxyl or chlorine groups. It should be noted that these authors suggest other reactive species than chlorine dioxide to be responsible for the formation of the degradation layer. Colin et al. [18] exposed 100 µm medium-density polyethylene films to 40 °C water containing 80–90 ppm chlorine dioxide (pH = 2–3 and 6) and they found oxidation products (carbonyl IR band), which gradually increased with increasing exposure time. Furthermore, they detected chlorine grafted to the polymer, which increased in a linear fashion with increasing exposure time [18]. It may be added that the medium-density polyethylene contained some unsaturation (IR spectroscopy: vinyl and *trans*-vinylene bands) [18]. In a later study by Colins et al. [19], which exposed pipes (pipe wall = 4.5 mm) to water containing 66.5 ppm chlorine dioxide at 40 °C, oxidation was shown to be concentrated to the outer 0.5 mm surface layer after 99 days of exposure. These different studies [8,18,19] showed the formation of an oxidized surface layer, more distinct in the case of high temperature and low chlorine dioxide exposure. The presence of grafted chlorine onto polymer chains was only revealed by Colins et al. [18]. This polymer contained some unsaturation, which in view of the early findings of Lindgren et al. [16,17] suggest some reactivity between the polymer and chlorine dioxide.

When the antioxidant system has become totally depleted, a fast but strictly surface-confined degradation of polyethylene occurs [10]. Highly reactive radicals (e.g. hydroxyl radicals) present in the aqueous phase react in the immediate surface with the polymer, and hydrogen abstraction occurs [10]. Many hydrocarbon radicals are formed, peroxy radicals are subsequently formed in the presence of oxygen (O₂) and further oxidation of the polymer occurs according to the Bolland–Gee reaction scheme [20,21]. The oxidation is confined to the amorphous phase of polyethylene and the molecular continuity between adjacent crystals is gradually lost and, when a stress acts on the structure, cracks are formed that stop growing in the fresh material [10]. The aggressive aqueous medium has access to the crack walls and further degradation occurs at the crack tip finally driving the crack to grow further (degradation-assisted crack growth) [10]. A suitable polyethylene material for pipes distributing water containing chlorine dioxide should be stabilized with antioxidants that degrade slowly in the presence of chlorine dioxide and, in addition, the polyethylene should exhibit high fracture toughness in order to retard the degradation-assisted crack growth. This study was concerned with the degradation rates of a series of phenolic antioxidants and the main focus was to establish a relationship between the antioxidant structure and the rate at which the antioxidant degrades in water containing chlorine dioxide.

An accelerated ageing method with an auto-refreshing water phase system that makes it possible to monitor the chlorine dioxide concentration, pH and temperature was recently developed to assess the loss of antioxidant activity in polyethylene exposed to water containing chlorine dioxide [22]. The consumption of antioxidant was assessed by DSC determining the oxidation induction time (OIT) of tape samples exposed to the medium for different periods of time. The method is however applicable only to phenolic antioxidants, and the proportionality between antioxidant concentration in the polymer and the OIT requires that the antioxidant is soluble in the polymer [23,24]. Hence, the OIT method assesses the accessible fraction of the antioxidant and not the antioxidant present as a separate phase in crystals [25] or strongly adsorbed onto nanoparticle surfaces [26]. This study shows that the primary factor that controls the depletion time is the molar fraction of soluble phenolic groups in the polymer; a few of the antioxidants

(Irganox 1330 and Cyanox 1790) showed greater stability towards chlorine dioxide (normalized with respect to the molar concentration of phenolic groups in the polymer) than the other phenolic antioxidants.

2. Experimental

2.1. Materials

Irganox 1010 (pentaerythritol tetrakis (3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionate; CAS Registry No. 6683-19-8) Irganox MD 1024 (1,2-bis(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamoyl)hydrazine, CAS Registry No. 32687-78-8), Naugard XL1 (2,2'-oxamido-bis[ethyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionate]; CAS Registry No. 70331-94-1), Irganox 1330 (1,3,5-tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)-2,4,6-methylbenzene, CAS Registry No. 1709-70-2), Cyanox 1076 (octadecyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionate, CAS Registry No. 2082-79-3), Cyanox 1790 (1,3,5-tris(4-*tert*-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione, CAS Registry No. 040601-76-1), and Cyasorb UV-2908 (hexadecyl 3,5-di-*tert*-butyl-4-hydroxybenzoate, CAS Registry No. 067845-93-6) were supplied by Ciba Specialty Chemicals, Switzerland). All the antioxidants used are listed in Table 1. Chemicals used for titration, i.e. sulphuric acid, potassium iodide, sodium thiosulfate and starch were purchased from VWR International. Sodium chlorite, monopotassium phosphate and sodium hydroxide used for the preparation of the aqueous phase were obtained from Sigma–Aldrich. AGA Gas AB, Sweden supplied the chlorine gas (Chlorine 2.8, which contained less than 5 ppm water).

Before compounding, the medium-density polyethylene (density at 23 °C: 951 kg m⁻³) powder (2 kg) together with antioxidant (0.1 wt.%) was dry mixed to obtain a good dispersion of the antioxidant. After dry mixing, the material was added to a Prism TSE 24 TC pilot scale extruder (Thermo Electron GmbH, Germany) with the following temperature settings: 110 °C (zone 1) and 150 °C (zones 2–6). The extruder operated at 238 rpm, a 6.5 MPa pressure and an output rate of 6 kg h⁻¹. The pelletized compound was extruded into a tape (thickness = 0.3 ± 0.01 mm, width = 10 mm) using a Collin Teach-Line E 20T extruder (Dr. Collin GmbH, Germany; settings: 180 °C (zone 1), 190 °C (zone 2), 210 °C (zone 3) and 30 rpm). The antioxidant concentrations of the different tapes were 0.10 ± 0.01 wt.%. One of the supplied tapes, which had only 0.02 wt.% Irganox 1076, was produced by dry mixing using ca. 10 g of polymer powder. The antioxidant was dissolved in 6 mL *n*-heptane, added to the polymer powder, dry mixed using a Vortex Genie 2 shaker (G560E, Scientific Industries) at 25 °C for 1 h after which the powder was dried to constant mass, compounded in a twin-screw micro compounder (Xplore MC5, Xplore Instrument BV, Geleen, the Netherlands; temperature setting = 115 °C, screw angular velocity = 100 rpm, residence time = 6 min) and finally compression-moulded at 120 °C into 0.3 mm thick film using a LabEcon press TP400, Fontijne Grotnes BV, the Netherlands.

2.2. Preparation of chlorinated aqueous media

A stock solution with 16,000 ppm ClO₂ was prepared by a two-stage method. First, 210 g sodium chlorite was dissolved in 7 L water and chlorine gas was bubbled through the system for 4 h. Nitrogen gas was then gently bubbled through the solution for 8 h and the gas stream was led through a column with sodium chlorite to eliminate residual Cl₂, and the ClO₂ formed was transferred to a dark flask filled with pure water. The stock solution was diluted with Milli-Q water to obtain 500 mL of 12.5 ppm ClO₂ solution, and 125 mL of buffer solution (67 vol.% 0.1 M KH₂PO₄ solution and 33

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