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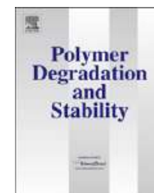

Antioxidant consumption in squalane and polyethylene exposed to chlorinated aqueous media

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ABSTRACT

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 = 6.8) at different temperatures between 30 and 70 °C. The squalane phase was characterized by differential scanning calorimetry (oxidation induction time, OIT) and infrared spectroscopy, and the aqueous media were analysed after concentrating the analytes using liquid–liquid extraction by liquid chromatography, mass spectrometry and infrared spectroscopy. OIT measurements were carried out on the polyethylene samples after exposure to the chlorinated aqueous media. Exposure of the squalane systems to water containing ClO_2 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 mol^{-1}) in the squalane test (no diffusion control) and 21 ± 2 kJ 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 Cl_2-water yielded an activation energy for the loss antioxidant activity of 68 kJ 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. Possible further reactions, in agreement with the observations made, are proposed.

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1. Introduction

Chlorine or chlorine dioxide are added to tap water as disinfectants in order to prevent the spread of infection. Most pipe materials, including polyethylene, are sensitive to chlorinated species with a resulting shortening of their lifetime [1–3]. In earlier studies [4,5] reporting results from exposure of high- and medium-density polyethylene pipes to aqueous phases with 3–4 ppm of ClO_2 or Cl_2 at pH = 6.8 and at different temperatures ranging from 90 to 105 °C, it was shown that ClO_2 and Cl_2 attack the phenolic antioxidant and that, when the antioxidant system is depleted, the polymer is degraded by other chlorinated species in an immediate surface reaction. The polymer degradation reactions are, as expected, confined to the amorphous regions and the reaction products are characteristic of 'conventional' oxidation [4,5]. In these particular chlorinated aqueous media, polymer degradation is digestive; a significant fraction of the amorphous component is degraded into oligomeric oxidation products that are transferred to the water phase leaving a degraded surface layer with high crystallinity and porosity [4,5]. Degradation of the polymer component in a hot water medium (without chlorine) causes a moderate number of amorphous chain scissions but without any essential leakage of oxidized degradation products to the surrounding water medium [6,7]. Hence, the rate of degradation is significantly higher in the chlorinated aqueous media than in chlorine-free hot water. It should be noted that both aqueous media contain dissolved oxygen. The mechanisms involved in the deterioration of the polyethylene pipes are sketched in Fig. 1. The initial stage is the loss of stabilizer protection which, in the case of a hindered phenolic antioxidant, is by a one-electron transfer from the phenol to ClO_2 followed by

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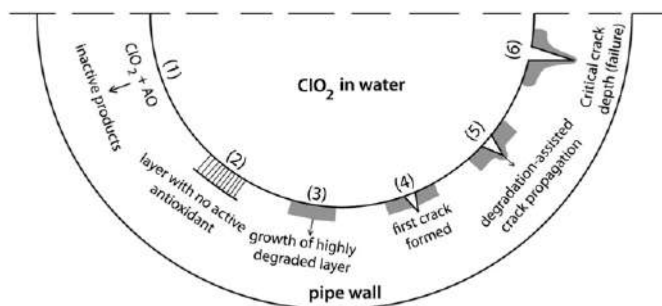

Fig. 1. Sketch of mechanisms underlying the failure of a pressurized polyethylene pipe exposed to water containing ppm levels of chlorine dioxide according to findings presented in Ref. [5]. Phase 1: consumption of phenolic antioxidant by reaction with chlorine dioxide. Phase 2: a significant part of the pipe towards the inner wall has no antioxidant protection. Phase 3: polymer degradation of the unprotected polymer at the inner wall. This immediate surface reaction yields a layer of degraded and porous material. The thickness of the layer increases with increasing exposure time. Phase 4: Cracks are initiated in this layer that stopped to grow in the fresh material beneath. Phase 5: Degradation occurs of the material at the crack walls and at the crack tip, assisting further crack propagation until a critical crack size is reached and pipe failure occurs (phase 6).

other reactions yielding inactive products [5]. When the antioxidant system reaches depletion, highly reactive radicals present in the aqueous phase (e.g. hydroxyl radicals) react in the immediate surface with the polymer by hydrogen abstraction [5]. Hence, a large number of radicals ($R^\cdot$) are formed which react with oxygen to form peroxy radicals which react further according to the Bolland–Gee oxidation scheme [8,9]. Cracks are formed in the degraded surface layer, which blunt in the fresh, undegraded material beneath and the aggressive species present in the aqueous medium can attack the polymer at the crack walls promoting further crack propagation [5].

Thus the overall kinetics underlying pipe failure are complex, including (i) deterioration of the stabilizer by ClO_2 (or Cl_2), (ii) polymer degradation localized to the immediate surface, and (iii) crack initiation and propagation. Processes (ii) and (iii) occur in a 'cyclic' fashion until a critical crack depth is reached and final failure occurs.

This paper deals with two related topics. Firstly, the consumption of phenolic antioxidant was studied. Polyethylene with a known concentration of Irganox 1010 was exposed to water containing 10 ppm ClO_2 (pH = 6.8) at different temperatures between 30 and 70 °C and the antioxidant consumption rate was assessed at different depths from the specimen surface. A second series of experiments was conducted where the only difference was that the polyethylene was replaced by 'stirred' squalane thus minimizing the influence of diffusion on the antioxidant degradation process. This provides details useful for extrapolation and input for gaining further mechanistic insight. Secondly, the antioxidant and its degradation products transferred by migration to the water phase from the squalane phase during exposure to aqueous media containing either 10 ppm ClO_2 or 10 ppm Cl_2 were analysed by liquid chromatography, mass spectrometry and infrared spectroscopy. This provided information about the nature of the degradation products and a basis for understanding the mechanisms involved in the antioxidant degradation.

2. Experimental

2.1. Materials

Squalane (2,6,10,15,19,23-hexamethyltetracosane) with a purity higher than 95% was purchased from Sigma–Aldrich. Irganox 1010 (pentaerythritol tetrakis (3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate); CAS No. 6683–19–8; molar mass = 1178 g mol^{-1}) was supplied by Ciba Specialty Chemicals, Switzerland. A medium-density pipe-grade polyethylene (density at 23 °C = 951 kg m^{-3}) containing 0.1 wt.% Irganox 1010 was obtained from Borealis AB, Sweden. 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 (product code: Chlorine 2.8 containing less than 5 ppm water).

2.2. Preparation of chlorinated aqueous media

Chlorine gas was bubbled through deionized water at 22 °C for 40 min yielding a stock solution with ca. 10,000 ppm Cl_2. This stock solution was diluted with Milli-Q water to reach a concentration of 12.5 ppm Cl_2 typically giving 500 mL of solution for a single exposure experiment. A buffer solution (67 vol.% 0.1 M KH_2PO_4 solution and 33 vol.% 0.1 M NaOH solution) of 125 mL was added to finally yield a 10 ± 1 ppm Cl_2 solution with pH = 6.8 ± 0.1. The Cl_2 concentration was determined by titration according to Azhdar et al. [10].

A stock solution with 16,000 ppm ClO_2 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 Cl_2, and the ClO_2 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 ClO_2 solution and 125 mL of buffer solution (the same as that used for the Cl_2-water solution) was added to yield a 10 ± 1 ppm ClO_2 solution with pH = 6.8 ± 0.1. The ClO_2 concentration was determined by titration according to Azhdar et al. [10].

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

A solution containing 0.2 wt.% of antioxidant was prepared by adding 40 mg Irganox 1010 to 20 g squalane. The solution was heated to 190 °C and stirred for 30 min under nitrogen, until the resulting solution was clear, which indicated that the antioxidant was properly dissolved in the squalane. The solution was then slowly cooled to 90 °C without any loss of clarity. The squalane solution was divided into 5 mL parts per test tube using a pipette with a heated tip.

The polyethylene plaques (4 mm thick, 10 mm wide and 100 mm long) and polyethylene tapes (0.5 mm thick, 15 mm wide and 200 mm long) were obtained by compression moulding using a Fontijne TP400 press (Fontijne, Netherlands) at 140 °C for 10 min followed by rapid cooling to room temperature.

2.4. Exposure of antioxidant-squalane solution and polyethylene containing antioxidant to chlorinated water media

The experimental set-up included a bottom heater, an enclosing heater controlled by a Eurotherm 914 PID device, a condenser and the test tube equipped with a magnetic stirrer containing the chlorinated water and squalane mixture in accordance with Azhdar et al. [10]. The experiments were carried out in a dark hood. The two-phase-system consisted of 5 mL squalane with antioxidant and 50 mL aqueous phase (Milli-Q water containing 10 ppm either Cl_2 or ClO_2 buffered to pH = 6.8 ± 0.1). The liquids were stirred at

250 rpm using a PTFE-coated magnet bar. The temperature of the tests was varied between 30 ± 3 and 70 ± 3 °C (the latter was the 'standard' temperature). A condenser fed with cold water (ca. 10 °C) was placed on top of the test tube to minimize loss of volatiles. The same set up was used to expose the polyethylene tape samples and the 4 mm thick polyethylene plaques. These tests were performed at different temperatures between 30 ± 3 and 70 ± 3 °C.

2.5. Determination of antioxidant concentration by differential scanning calorimetry

A Mettler-Toledo differential scanning calorimeter (DSC) with Mettler Toledo STARe software V9.2 was used to assess the concentration of effective antioxidant in the squalane phase by determining the oxidation induction time (OIT). Aluminium pans (volume = 100 μL) each filled with either a 35 μL (25 ± 3 mg) squalane phase sample or 3 ± 0.5 mg polyethylene sample (polyethylene tape samples: the whole cross-section; from the polyethylene plaques: sections obtained at different depths using a Jung rotational microtome; thickness of sections: 0.3–0.4 mm) were studied. Three holes were punched in the lid to allow access to oxygen. The aluminium pans sealed with samples were heated from 100 °C to 190 °C at 10 °C min^{-1} in nitrogen (50 mL min^{-1}) and equilibrated at this temperature for 5 min, after which the atmosphere was changed from nitrogen to oxygen maintaining the same gas flow rate. The OIT was obtained as the time elapsing between the onset of the oxygen gas flow and the intersection with the isothermal base line of the tangent at 0.2 W g^{-1} (squalane solutions) or the 1.5 W g^{-1} (polyethylene samples) deviation from the isothermal base line.

2.6. Liquid chromatography and mass spectrometry

The aqueous phase (25 mL) was collected after each 30 min period of exposure up to a total of 300 min exposure time. The 250 mL aqueous phase collected was extracted five times, each time using 5 mL dichloromethane. The dichloromethane phase containing the migration species was concentrated with regard to the analytes by evaporation of the dichloromethane at 50 °C for 4 h in a nitrogen flow. Only ca. 100 μL of liquid, referred to as the concentrated extracted solution, remained and it was diluted in 1 mL acetonitrile before being analysed by high-performance liquid chromatography-electrospray ionization tandem mass spectrometry (HPLC-ESI MS). The chromatograms of these samples were recorded by a LCQ ion trap Surveyor Plus LC System equipped with a Surveyor PDA detector (UV detector recording analytes at 270 nm) provided by Thermo Finnigan Corporation, San Jose, USA. This system used an electron spray ionization system and it was adjusted to reveal ions in the mass range from 600 to 1200 *m/z*. The analyses were run with positive mode and the ion source from LC was operating at 5 kV. The mobile phase consisted of 98.5 wt.% acetonitrile (LC-MS grade, Fisher Scientific, USA) and 2.5 wt.% Milli-Q water and the flow rate was 0.8 mL min^{-1}. A Discovery C18 HPLC column (reversed phase) with 5 μm particle size and 18 nm pore size was used. The thermostat of the column was set to 24 °C. The injection volume was 20 μL.

2.7. Infrared spectroscopy

Samples from both the squalane phase and the concentrated extracted aqueous phase were analysed by attenuated total reflection infrared (ATR-IR) spectroscopy using a Perkin Elmer Spectrum 2000 (Wellesley, MA, USA) equipped with a golden gate single-reflection accessory from Graseby Specac (Kent, UK). Each spectrum was based on eight scans between 500 and 4000 cm^{-1}. All absorbance spectra presented were normalised with respect to the 2950 cm^{-1} band.

3. Results and discussion

3.1. Structural changes within the squalane phase

After 300 min of exposure to water containing ClO_2, the squalane phase turned dark yellow and hazy whereas, after the corresponding exposure to water containing Cl_2, the squalane solution remained transparent and colourless. The discolouration in the former case is suggested to be due to ClO_2-initiated degradation of the antioxidant yielding quinoid structures (further details are presented in Section 3.4). The reaction between Cl_2 and the antioxidant occurs according to a different mechanism leading to colourless products (Section 3.4). Despite these differences in absorption in the visible spectral range, infrared spectroscopy revealed no changes induced in the squalane phases by exposure to the different chlorinated aqueous media. The concentrations of antioxidant and its degradation products were low in the squalane phases after both types of exposure and it is not surprising that the infrared spectra of the squalane samples were similar. The absence of carbonyl absorption confirmed that the antioxidant protected the squalane phase during the 300 min of exposure. Note that antioxidant protection remained in the squalane phases after 300 min of exposure to the aqueous media containing Cl_2 and ClO_2 (Fig. 2).

The gradual decrease in concentration of effective antioxidant in the squalane phase is displayed in Fig. 2. It has been established that the oxidation induction time (OIT) is proportional to the concentration of effective antioxidant (i.e. dissolved antioxidant) for hindered phenolic antioxidants [11,12]. A limitation of this method to assess antioxidant concentration was more recently pointed out by Pospisil et al. [13]; the degradation products of the antioxidant can accelerate the further consumption of the hindered phenol. The small loss of antioxidant from the squalane phase exposed to pure water, ca. 10% during 300 min of exposure, was due to migration of antioxidant to the aqueous phase [10]. The faster

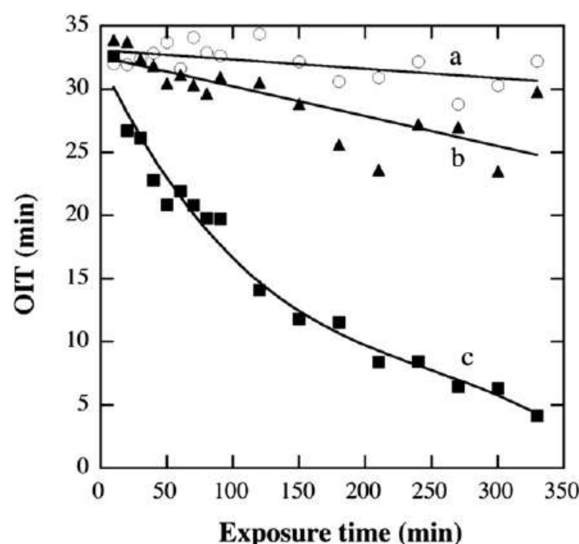

Fig. 2. Exposure time dependence of the oxidation induction time (OIT) of squalane (initial concentration of Irganox 1010 = 0.2 wt.%) after exposure to water (○ line a), water containing 10 ppm Cl_2 (▲ line b) and water containing 10 ppm ClO_2 (■ line c). All exposures were at 70 °C. The curves are either linear (water and Cl_2-water) or a third degree polynomial (ClO_2-water) fits to the experimental data.

loss of antioxidant in the squalane phase on exposure to the chlorinated aqueous media was due to chemical reactions [2–5]. The remaining concentrations of the active antioxidant after 300 min of exposure were thus ca. 10% of the initial concentration (ClO_2) and ca. 75% (Cl_2). The reactions between the phenolic antioxidant and Cl_2 and ClO_2 respectively are fundamentally different, leading to modifications in the former case that are still active as antioxidants and in the latter case structures of less value as antioxidants (details are presented in Section 3.4).

3.2. Temperature dependence of the consumption of phenolic antioxidant on exposure to chlorinated aqueous media

Fig. 3 shows that the rate of consumption of antioxidant in squalane exposed to the aqueous ClO_2-phase was essentially independent of temperature between 30 and 70 °C. All the data taken at the different temperatures fell within a narrow OIT range (typically ± 2 min) at each exposure time. The stirring of the solutions during the exposure minimized concentration gradients in the squalane phase. Hence, the effective activation energy of the reaction leading to the formation of inactive products should be very low (<10 kJ mol^{-1}). Grimley and Gordon [14] reported an activation energy for the reaction between ClO_2 and phenol in acidic water of 48 kJ mol^{-1}. Ganiev et al. [15] studied oxidation with ClO_2 of a variety of phenolic compounds dissolved in acetonitrile and reported activation energy values in the range 40–50 kJ mol^{-1}. Colin et al. [16,17], on the other hand, presented experimental data that was verified in modelling of OIT data suggesting a very low activation energy (close to zero) for the reaction between ClO_2 and hindered phenolic antioxidant in a hydrocarbon medium. The results obtained in squalane were thus markedly different from the reported values obtained for oxidation rates of phenolic substances in more polar solvents (water and acetonitrile). Furthermore, the low activation energy obtained for ClO_2-induced oxidation of Irganox 1010 in squalane was in accordance with the OIT data for polyethylene samples displayed in Figs. 4 and 5 and with data reported by Colin et al. [18] on Irganox 1010-stabilized polyethylene.

Fig. 4 shows that the rate of antioxidant consumption in the polyethylene tape samples was higher at the higher exposure temperatures. The consumption rate showed a moderate temperature dependence corresponding to an activation energy of the order of 10 kJ mol^{-1}. The antioxidant consumption rate (expressed as the decrease in OIT over the 300 min exposure period) was calculated at different depths in a 4 mm thick polyethylene specimen after exposure at either 30 °C or 70 °C. The activation energy increased with increasing distance from the specimen surface reaching an almost constant value in the specimen centre of 21 ± 2 kJ mol^{-1} (Fig. 5), which is in accordance with data of Colin et al. [18] reporting an activation energy of 26 kJ mol^{-1} from data of polyethylene stabilized with Irganox 1010. The activation energy for the diffusion of similar sized molecules (carbon dioxide) in polyethylene is according to Flaconnèche et al. [19] of ca. 30 kJ mol^{-1}. Hence, the results obtained suggested that the antioxidant consumption rate was largely controlled by the diffusion of chlorine dioxide.

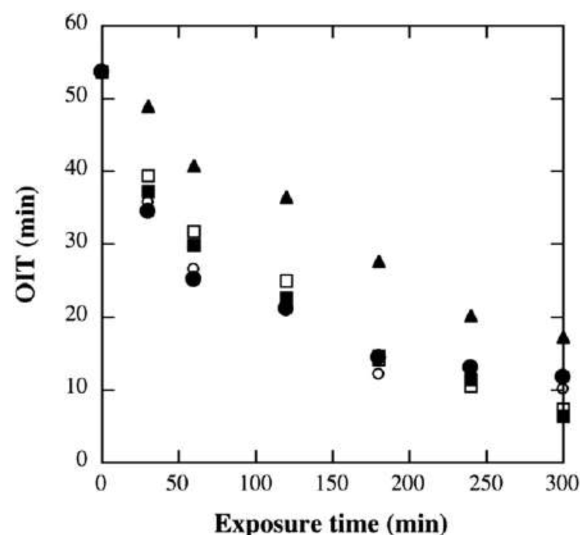

Fig. 4. Exposure time dependence of the oxidation induction time (OIT) of polyethylene tape samples (initial concentration of Irganox 1010 = 0.1 wt.%) exposed to water containing 10 ppm chlorine dioxide at the following temperatures: 30 °C (▲), 40 °C (□), 50 °C (■), 60 °C (○), 70 °C (●).

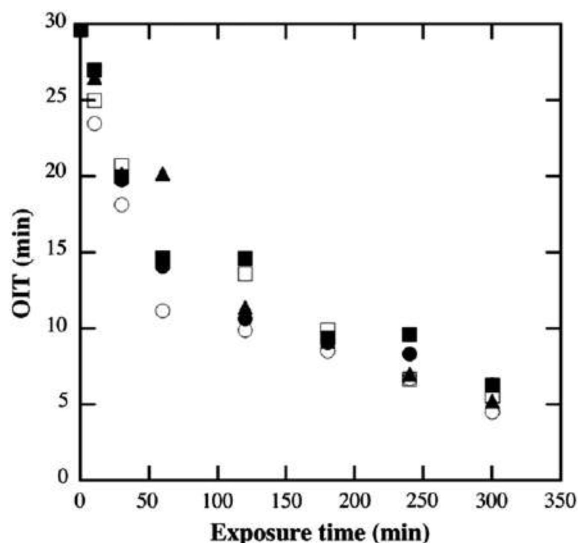

Fig. 3. Exposure time dependence of the oxidation induction time (OIT) of squalane (initial concentration of Irganox 1010 = 0.2 wt.%) exposed to water containing 10 ppm chlorine dioxide at the following temperatures: 30 °C (▲), 40 °C (□), 50 °C (■), 60 °C(○) and 70 °C (●).

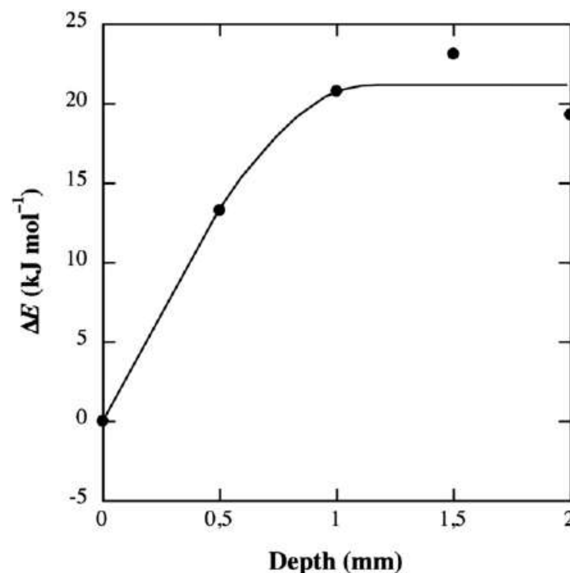

Fig. 5. Activation energy of the antioxidant consumption rate (30–70 °C in water with 10 ppm ClO_2) plotted as a function of depth (i.e. distance from the sample surface).

The temperature dependence of the antioxidant consumption in high-density polyethylene pipes exposed to Cl_2-water was assessed from data of the time to reach depletion of the phenolic antioxidant (Irganox 1010, originally present at 0.1 wt.%) at 0.4 mm from the inner wall of the pipe during pressure testing at 25 and 95 °C [4]. The inner medium was circulating water with 3 ppm Cl_2 (pH = 6.5) and the outer medium was air [4]. The activation energy obtained was 68 kJ mol^{-1}.

3.3. Analyses of the aqueous phase by liquid chromatography, mass spectrometry and infrared spectroscopy

Pristine Irganox 1010 displayed a single peak at a retention time of 15.3 min in the standard solution liquid chromatogram. Figs. 6 and 7 present chromatograms of extracts obtained from the aqueous phases after exposure to the two different chlorinated aqueous media. Both chromatograms show the presence of intact Irganox 1010 (marked with a in the graphs), which confirmed that a fraction of the antioxidant had migrated from the squalane phase to the water phase without undergoing any reaction. The peaks that appeared at other retention times are marked with b–i in Fig. 6 and with b–h in Fig. 7. The mass spectra associated with each peak in the liquid chromatograms are displayed in Figs. 8 and 9. The extract obtained from the aqueous medium after exposure to water containing Cl_2 displayed peaks associated with antioxidant degradation products that were small and well resolved at the following retention times (Fig. 6): 5.1 min, 6.8 min, 7.3 min, 7.7 min, 8.3 min, 9.5 min, 16.4 min and 18.3 min. The extract obtained from the aqueous phase after exposure to water containing ClO_2 showed only a small Irganox 1010 peak and stronger peaks associated with the degradation products of the antioxidant at the following retention times: 5.0, 6.1, 6.6 and 7.3 min and a broad shoulder between 7.5 and 11 min (Fig. 7). The higher relative concentration of intact Irganox 1010 in the aqueous phase after exposure to Cl_2-water than after exposure to ClO_2-water is consistent with the significantly higher OIT of the squalane phase after 300 min of exposure to Cl_2-water (ca. 25 min) than after a similar exposure to ClO_2-water (ca. 5 min). The retention time scale in this type of chromatography essentially probes the polarity of the compounds; the retention time increases with decreasing polarity [20]. The fact that the retention times of the degradation compounds in the extract from the ClO_2-water exposure were generally shorter than those after Cl_2-water exposure showed that the degradation products found after ClO_2-water exposure were more polar than those obtained after exposure to Cl_2-water.

The mass spectra presented in Figs. 8 and 9 reveal that the mass distribution peaks for the degradation products were different in the two cases suggesting a difference in antioxidant degradation mechanism depending on the aqueous phase (containing either Cl_2 or ClO_2). Peak a showed a mass of ca. 1200 m/z, which is 23 m/z higher than the mass of pristine Irganox 1010 (1177 Da), suggesting that adducts between the mother substance and sodium were formed. Sodiation is commonly seen in mass spectrometry. It is also believed that other substances, including the degradation products, formed such adducts. The molecular mass values presented in the figures and text are all gross values, the actual mass values for the mother substances are 23 m/z lower. Most of the degraded species found in the extract from the Cl_2-water exposure were in mass range 930–1020 m/z (Fig. 8). The most prominent peaks as judged from the UV-absorbance and the intensity of the peaks in the mass spectra were peaks d–g (Fig. 6). The mass spectra revealed the following mass values of the material in these peaks: 955 (d), 955 and 1020 (e), 940 and 956 (f), and 931 and 953 (g) m/z (Fig. 8). Two of the peaks from this extract appeared at 1–2 min longer retention times than pristine Irganox 1010 (Fig. 6) and these species showed essentially the same mass as pristine Irganox 1010, i.e. 1195 ± 5 m/z (Fig. 8). The scission of one ester bond in Irganox 1010 would result in a three-arm molecule with a mass of 887 m/z. The scission of the bond adjacent to the phenolic group would yield a molecule with a mass of 973 m/z. The dominating species had masses between these limiting values. Oxidation by the introduction of oxygen would cause an increase in mass by 16 m/z for each added oxygen atom; note the tendency for a decrease in molar mass with increasing retention time (i.e. decrease in polarity). Thus, oxygen uptake should result in an increase in polarity and a decrease in retention time.

The degraded species present in the extract after exposure to the ClO_2 aqueous medium were in two different mass ranges (Figs. 7 and 9): 700–800 m/z (prominent peaks were b and c with masses 704 and 743 m/z) and 970–1050 m/z (prominent peaks were e/f (1040 ± 10 m/z), g (1004 m/z) and h (972 m/z)). The presence of light molecules suggests that two chain scissions occurred in some antioxidant molecules. A two-arm moiety without aliphatic cilia would have a mass of 596 m/z and with full-length aliphatic cilia, 768 m/z. The high polarity of this extract suggests that these species were more oxidized, adding more mass (16 m/z per added oxygen atom) than the molecules exposed to water containing Cl_2.

It should be noted that single phenolic units with short aliphatic groups must have been present in the water phase but these were cut off at 600 m/z in the mass spectra. The presence of squalane in the concentrated extracts was revealed by infrared spectroscopy,

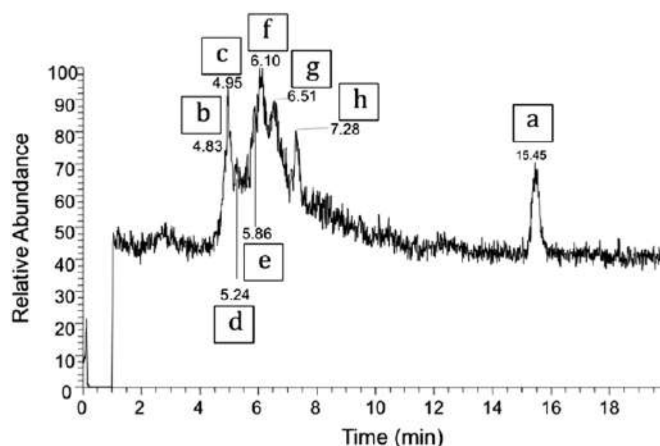

Fig. 7. Liquid chromatogram of extracted solution obtained from the aqueous phase sampled during 330 min of exposure to water containing 10 ppm ClO_2 at 70 °C.

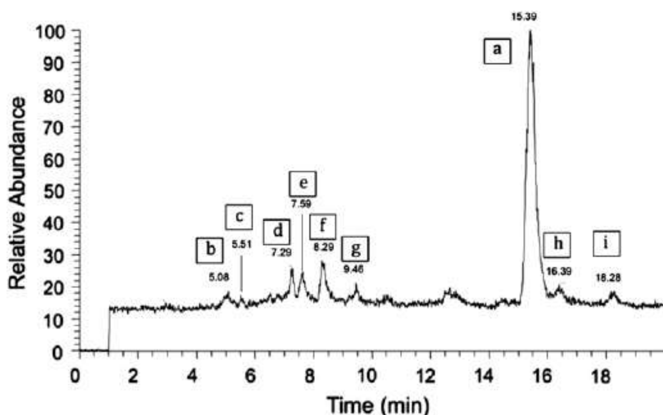

Fig. 6. Liquid chromatogram of solution extracted solution from the aqueous phase sampled during 330 min of exposure to water containing 10 ppm Cl_2 at 70 °C.

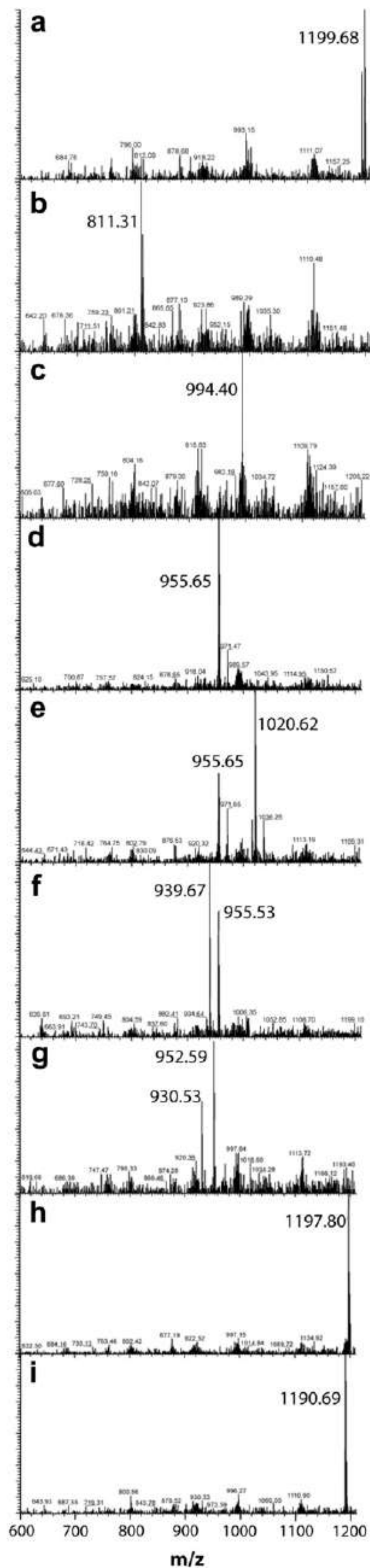

Fig. 8. Mass spectra of the peaks marked a–j in Fig. 6.

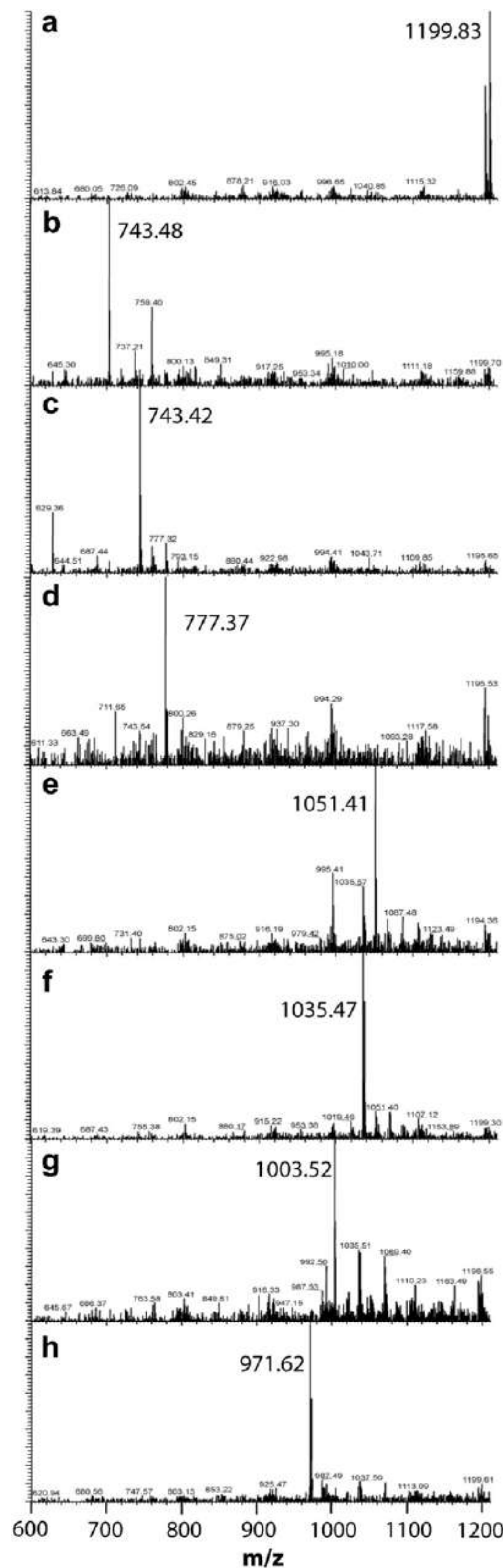

Fig. 9. Mass spectra of the peaks marked a–h in Fig. 7.

but these species were not detected in the chromatograms because hydrophobic substances have very long retention times.

Fig. 10 shows the presence of carbonyl absorption peaks (centring at 1745 cm^{-1}) in the concentrated extracts after exposure to the chlorinated aqueous media. The extract obtained from the exposure to the aqueous ClO_2 medium showed the strongest carbonyl peak. The concentrated extracts contained a certain fraction of squalane and the question was whether the carbonyl peak originated from oxidized squalane species or from the antioxidant. Oxidized medium-density polyethylene showed a maximum in carbonyl absorption at 1715 cm^{-1} [21,22], precisely matching the absorption peak of ketonic carbonyls [23,24]. The position of the absorbance peak at 1745 cm^{-1} in the case of the concentrated extracts indicated that ester groups were present to a great extent in the concentrates [23,24]. Both the intact form and a substantial fraction of the degradation products of the antioxidant should contain ester groups and hence, based on these arguments, the observed carbonyl absorption originated from the antioxidant species. Importantly, a small peak associated with a stretching vibration of the chlorine-carbon bond at ca. 760 cm^{-1} was observed only in the system exposed to the aqueous ClO_2 medium (Fig. 10). This is one of few indications that chlorine possibly was to some extent covalently bonded to the degraded antioxidant species.

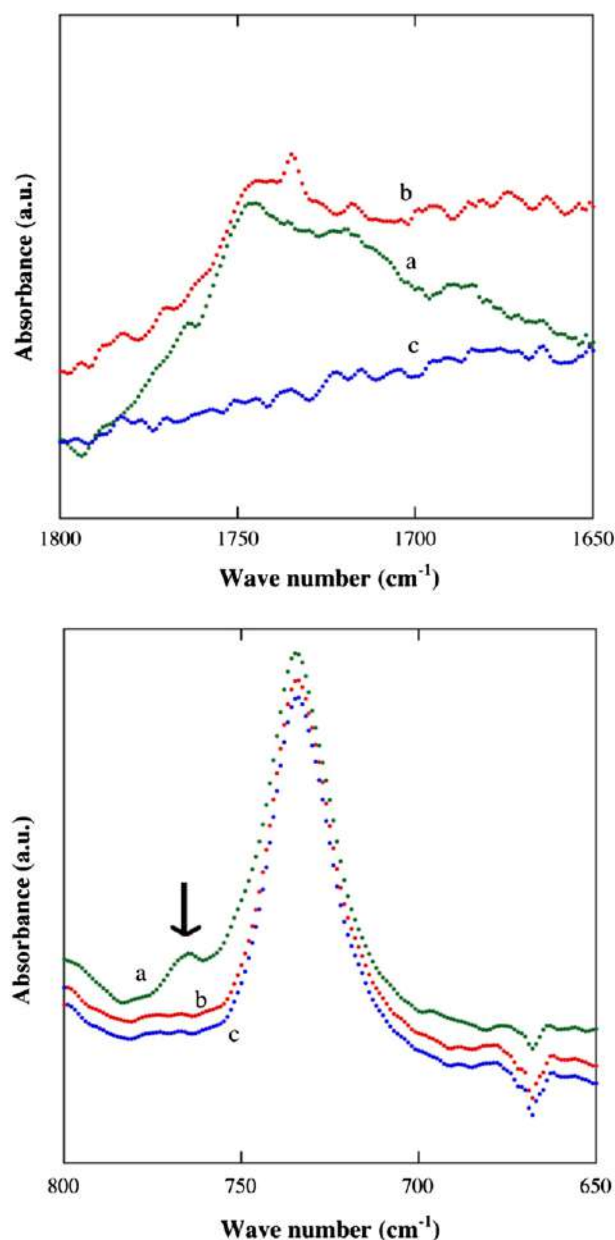

Fig. 10. Infrared absorbance (ATR) spectra of extracts obtained from the aqueous phase from 300 min of exposure of squalane containing 0.2 wt.% Irganox 1010 to the following aqueous phases: (a) water containing 10 ppm ClO_2; (b) water containing 10 ppm Cl_2 and (c) Milli-Q water. The upper graphs shows the carbonyl stretching region and the lower graph the carbon-chlorine vibration region.

3.4. Antioxidant degradation mechanisms

The principal chemical difference between ClO_2 and Cl_2 is the fact that ClO_2 is a one-electron oxidant ($E^{\circ} = 934$ mV [25]) whereas Cl_2 preferentially reacts by hydrogen substitution [26]. This paradox reflects that, although Cl_2 is generally recognized as being a very strong oxidant, its first reduction step, i.e. $Cl_2 + e^- \rightarrow Cl_2^{\bullet -}$, is associated with a reduction potential of only about 0.4 V [25]. Hence, direct electron transfer from substrate to Cl_2 is much less efficient than for ClO_2 and electrophilic hydrogen atom substitution predominates in most cases. It should be noted that the major chlorinated component in water with dissolved Cl_2 at pH = 6.8 is hypochlorous acid [27], but this substance is not efficient in oxidizing the phenolic antioxidant [5]. Chlorine (Cl_2) only present at a low concentration (5.5% of the maximum value) is the most likely compound to attack the phenolic antioxidant.

A one-electron oxidation of a phenol, in this case by ClO_2, leads to radical-cation formation and, by prompt proton elimination, to the formation of a phenoxyl radical. The addition of another ClO_2 to a resonant radical site in the aromatic ring leads to the formation of a chlorite ester and this can undergo hydrolysis and ring opening, resulting in formation of muconic acid derivatives [28]. However, in Irganox 1010 this reaction mode is 'hindered' by the *tert*-butyl groups and it is more likely that a β-cleavage in the side chain is induced. This would result in the formation of yellow-coloured quinoid structures (see results presented in Section 3.1) and ClO_2 or O_2 further oxidizes the remaining side chain radical to carbonyl sites or even chlorine-containing products. Chlorination of the antioxidant (traces found by infrared spectroscopy) may also occur by reaction between the antioxidant and $ClOH/ClO^-$ and Cl_2 (formed by reduction of ClO_2).

This is in sharp contrast to the product pattern resulting from the action of Cl_2. In this case, the initial reaction is a substitution of hydrogen atoms, both in the aromatic ring and in side chains, by chlorine atoms. These may in turn be replaced by hydrolysis into OH-groups. As a result, Cl_2 mostly modifies only the original Irganox 1010 structure and these modifications may still act as efficient antioxidants, whereas ClO_2 degrades the original structure into more or less coloured products of less value as antioxidants. This clearly demonstrates that ClO_2 has a much more deleterious effect on phenolic antioxidants than Cl_2.

4. Conclusions

Squalane containing Irganox 1010 exposed to two different chlorinated aqueous media at 70 °C and pH = 6.8 showed distinct differences in behaviour depending on the aqueous medium. Exposure to an aqueous medium containing 10 ppm ClO_2 caused distinct yellowing, and a fast loss of antioxidant activity and of degradation products of the antioxidant, where the latter were highly polar and a substantial fraction were of low molar mass. Chlorine dioxide-water exposures of squalane containing Irganox 1010 at different temperatures (30–70 °C) using OIT data suggested a surprisingly low activation energy (<10 kJ mol^{-1}) in systems with

no diffusion barrier. Similar experiments conducted on polyethylene stabilized with Irganox 1010 revealed an activation energy of 21 kJ mol^{-1}, which is in accordance with data of Colin et al. [18]. This value is of the same order of magnitude as the activation energy for diffusion of a similar sized penetrant molecule in polyethylene. Exposure to an aqueous medium containing 10 ppm Cl_2 had no impact on the colour of the squalane phase, and caused a loss of antioxidant activity that was slower than in the case of ClO_2-water exposure but faster than in the case of pristine water exposure (with the same concentration of oxygen). This led to a slower generation of antioxidant degradation products than in the case of ClO_2-water exposure, the degradation products being less polar and of higher molar mass than in the case of ClO_2-water exposure. The activation energy for antioxidant activity loss on exposure of a HDPE pipe (0.4 mm from the inner pipe wall) to Cl_2-water was calculated from earlier published OIT data to 68 kJ mol^{-1} confirming that the mechanisms for antioxidant consumption in Cl_2-water is different from those in ClO_2-water.

As a one-electron oxidant, chlorine (Cl_2) affords only about half the reduction potential shown by chlorine dioxide (ClO_2). For this reason, electron transfer from substrate to Cl_2 is much less efficient than for ClO_2 and electrophilic hydrogen atom substitution predominates in most cases. In these reactions, the original structure of Irganox 1010 is basically preserved and chlorine atoms have substituted hydrogen atoms in the aromatic unit and possibly also in side groups. Under the prevailing experimental conditions, hydrolysis has probably replaced most of the chlorine substitution by hydroxyl groups. These modifications are fairly 'innocent'; they lead to no colour change and the loss of antioxidant activity is probably less pronounced.

The great antioxidant degrading capacity of ClO_2 can therefore be related to the fact that ClO_2 is a one-electron oxidant. One-electron oxidation of a phenol leads to formation of a radical cation and subsequent formation of a phenoxyl radical. In Irganox 1010, the corresponding phenoxyl radical, due to the hindered character of the phenolic unity (*tert*-butyl structures), favours a β-cleavage in the side chain and the formation of yellow-coloured quinoid structures. Further oxidation of the side chain radical (by O_2 or ClO_2) is expected to yield carbonyl groups or even chlorine-containing products. The expected products formed are highly polar and lower in molar mass than the antioxidant and also of low antioxidant activity. All these characteristics are in accordance with the reported experimental findings.

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