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Assessing the long-term performance of polyethylene stabilised with phenolic antioxidants exposed to water containing chlorine dioxide



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ABSTRACT

The addition of chlorine dioxide disinfectant to tap water prevents the spread of infection but has a serious drawback in that it degrades materials used in piping, including pipes made of polyethylene. Efficient methods are required to assess the long-term performance of different combinations of antioxidants and polyethylene grades. We have previously presented a screening method which exposes solutions of phenolic antioxidants in squalane (a liquid, low molar mass analogue of polyethylene) to 70 °C water containing either chlorine dioxide or chlorine. This method assesses the stability of the antioxidants towards these aqueous chlorinated media by determining the oxidation induction time through differential scanning calorimetry. The same experimental set-up with two modifications was used in developing a new method. A 0.3 mm thick polyethylene tape replaced the squalane phase and the supply of fresh water containing chlorine dioxide (10 ppm at pH = 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.

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1. Introduction

Chlorinated compounds (e.g. chlorine dioxide) are added to tap water as disinfectants in order to prevent the spread of infection. These substances are, however, strong oxidants that cause material degradation, which shortens the lifespan of structural components such as pipes and

containers [1–4]. This includes polyethylene pipes, which on exposure to water containing chlorine dioxide (4 ppm, pH = 6.8 and 90 °C) rapidly lose their antioxidant protection far into the pipe wall, and the unprotected polymer degrades extensively by a reaction confined to the immediate surface [5]. Cracks formed in the brittle surface layer end in the fresh material beneath, and further crack propagation is assisted by degradation of the material at the crack tip (degradation-assisted crack growth) until a crack of critical size is formed leading to pipe failure [5]. Chlorine

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dioxide selectively attacks phenolic antioxidants by a one-electron transfer from the phenolic unit to chlorine dioxide and further reactions yielding coloured products of little value as antioxidants [5,6].

Efficient methods are required to assess the efficiency of antioxidants in polyethylene exposed to chlorinated aqueous media. Azhdar et al. [7] presented a method using a low molecular analogue (squalane) instead of polyethylene. The stability of phenolic antioxidants dissolved in squalane (typical antioxidant concentrations were 0.1 wt.%) was assessed during 300 min exposures by determining the oxidation induction time using differential scanning calorimetry [7]. This method is applicable to phenolic antioxidants, because the oxidation induction time is proportional to the concentration of efficient antioxidant [8,9]. The assessment of other antioxidants, such as hindered amines and secondary antioxidants, requires more time-consuming methods such as extraction followed by liquid chromatography. The conditions prevailing in the squalane phase are different from those in polyethylene: (i) Stirring causes convective transport within the squalane phase that largely eliminates concentration gradients of chlorine dioxide and antioxidant within this phase. During exposure of polyethylene to water containing chlorine dioxide, concentration gradients for both chlorine dioxide and antioxidant develop [5]. (ii) At the testing temperature, squalane is an amorphous liquid whereas polyethylene is semicrystalline; the polymer used in the current study has a mass crystallinity at room temperature close to 60%.

This paper presents a new method to assess the efficiency of phenolic antioxidants in semicrystalline polyethylene exposed to water containing chlorine dioxide. The method is based on the same basic equipment used in the squalane test but with some important modifications. A 0.3 mm thick polyethylene tape replaces the squalane phase and the supply of fresh water with chlorine dioxide (10 ppm at pH = 6.8) is continuous, which means that it requires minimum attention from the operator over the longer exposure times used. In addition, sampling from the tapes makes it possible to assess the state of oxidation and brittleness of the surface layer. The results obtained with the tape test include a wide range of different phenolic antioxidants and they are critically compared with those obtained from the squalane test. The phenolic antioxidants are denoted AO1 to AO6. The relationship between phenolic antioxidant structure and their efficiency is the topic for a coming scientific paper. However, the present paper has a clear focus on the methodology comparing results obtained by squalane testing and tape testing.

2. Experimental

2.1. Materials

The phenolic antioxidants used in this study are all commercially available and are denoted AO1 to AO6. The initial concentrations of phenolic groups in moles per gram polyethylene or squalane for the different antioxidants ranged within a factor of almost 2.5. All studied systems contained 0.1 wt.% of phenolic antioxidant. Squalane (2,6,10,15,19,23-hexamethyltetracosane) with a purity

higher than 95% was purchased from Sigma-Aldrich. Tapes (thickness = 0.3 ± 0.01 mm; width = 10 mm) based on a medium-density polyethylene stabilised with 0.1 ± 0.01 wt.% of antioxidant were supplied by Borealis AB, Stenungsund, Sweden. The room temperature density of the material was 951 kg m^{-3} . The 0.1 wt.% antioxidant solutions in squalane were prepared by adding 20 mg antioxidant to 20 g squalane. The solution was heated to 190°C and stirred for 30 min under nitrogen. The resulting solution was clear, indicating that the antioxidant was completely 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 before exposure to water containing 10 ppm chlorine dioxide.

The 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 aqueous phase preparation were obtained from Sigma-Aldrich. AGA Gas AB, Sweden supplied the chlorine gas.

2.2. Preparation of the aqueous chlorine dioxide solution

A stock solution with 16 000 ppm chlorine dioxide was prepared by a two-stage method. 210 g sodium chlorite was first dissolved in 7 L water and chlorine was bubbled through the system for 4 h. Nitrogen was then gently bubbled through the solution for 8 h. The gas stream was led through a column with sodium chlorite to eliminate residual chlorine (Cl_2). This transferred the chlorine dioxide formed 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 chlorine dioxide solution, and 125 mL of buffer solution was added to yield a 10 ± 1 ppm chlorine dioxide solution with pH = 6.8 ± 0.1 . The concentration of chlorine dioxide was determined by titration according to Azhdar et al. [7].

2.3. Exposure of squalane or polyethylene samples to aqueous media containing chlorine dioxide

The experimental set-up included a bottom heater, an enclosing heater controlled by a Eurotherm 914 PID device, a condenser (10°C) and the test tube equipped with a magnetic stirrer containing the aqueous solution of chlorine dioxide (volume = 50 mL; Milli-Q water containing 10 ppm chlorine dioxide with pH = 6.8 ± 0.1) and the squalane-antioxidant solution (volume = 5 mL) or the polyethylene tape sample. The liquids were stirred at 250 rpm using a PTFE-coated magnet bar. The temperature was controlled at $70 \pm 3^\circ\text{C}$. Azhdar et al. [7] have presented further details about the squalane testing. The chlorine dioxide solution was renewed by two different methods: (i) 25 mL of the aqueous phase was replaced every 30 min, which is referred to as the intermittent method carried out as described by Azhdar et al. [7]. (ii) Fresh 10 ppm chlorine dioxide solution at pH = 6.8 was added continuously to the test tube which was equipped with an overflow system (flow rate = 1 mL min^{-1} ; L/S PTFE Tubing Pump equipped with a variable speed drive model 7524-40, a pump head model 77800-60 and PTFE tubing (96412-13) supplied by

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