CHLORINE DIOXIDE RESISTANT HDPE

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SHORT SUMMARY

The use of chlorine dioxide to disinfect drinking water is associated with accelerated degradation of polyethylene pipes. Through careful evaluation of the effects of chlorine dioxide on polyethylene samples and the development of a small scale test method based upon those findings, a screening method was developed that revealed a number of candidates with enhanced performance in presence of this disinfectant. In subsequent long-term pipe tests a number of recipes performed successfully under accelerated conditions against chlorine dioxide exposure, thereby providing a safe and long-term solution for (drinking) water pipe applications in contact with chlorine dioxide.

KEYWORDS

PE100, chlorine dioxide, disinfectants, bimodal HDPE

INTRODUCTION

High Density Polyethylene (HDPE) is well accepted as a material for standard pressurized water pipes, offering an excellent solution for safe transport of (drinking) water. The HDPE pipe market is growing globally. Especially in countries that suffer from water scarcity, surface water and water from rivers has to be used for drinking water supply. To guarantee a safe drinking water supply, the water has to be disinfected properly, and various disinfecting agents or treatments are available. One of the most efficient disinfecting agents is chlorine dioxide. It has advantages over chlorine, since it does not affect taste or smell of water. The disadvantage of this disinfecting agent is the associated accelerated degradation in water pipe systems in combination with temperature, for both traditional materials as well as for high density polyethylene.

In this paper, work done to gain further insight into the mode of failure and the route to validate potential solutions is highlighted. The route taken consists of two stages, one small-scale evaluation to perform a screening of potential solutions and a second stage of a long-term evaluation of pipe performance. The small-scale evaluation method was developed after close examination of both pipe and small-scale aged specimen.

DISCUSSION ON FAILURE MODE

Open Literature

A number of groups have researched the effects of chlorine dioxide on polyethylene pipe resins, with most of them focusing on the chemistry between chlorine dioxide and the pipe additive package and less on the direct or indirect effect of chlorine dioxide on the polymer chains. Although providing insights in the mechanism at work, these efforts have not been conclusive. [1-3] The use of different temperatures and chlorine dioxide concentrations for accelerated tests make comparison between results challenging. One common observation seems to be the propensity of the phenoxyl-OH group of commonly used antioxidants to react with chlorine dioxide, rendering the antioxidants useless and ultimately resulting in oxidation of the polymer chain. Whether chlorine dioxide directly or indirectly degrades the polymer chains has been a topic of debate.

Observations

To take a closer look, compression moulded plaques of standard PE100 pipe material were exposed to 40 °C, 1 ppm chlorine dioxide and evaluated after 0, 20, 39 and 60 days. Evaluation of the samples before and after exposure was performed using microscopy, infrared spectroscopy for additive mapping, molecular weight evaluation and evaluation of chlorination (Figure 1). These observations confirmed the depletion of the anti-oxidant in a 50-100 micron range near the surface, coinciding with degradation of the polymer chains of the material near the surface and, ultimately crack formation and propagation.

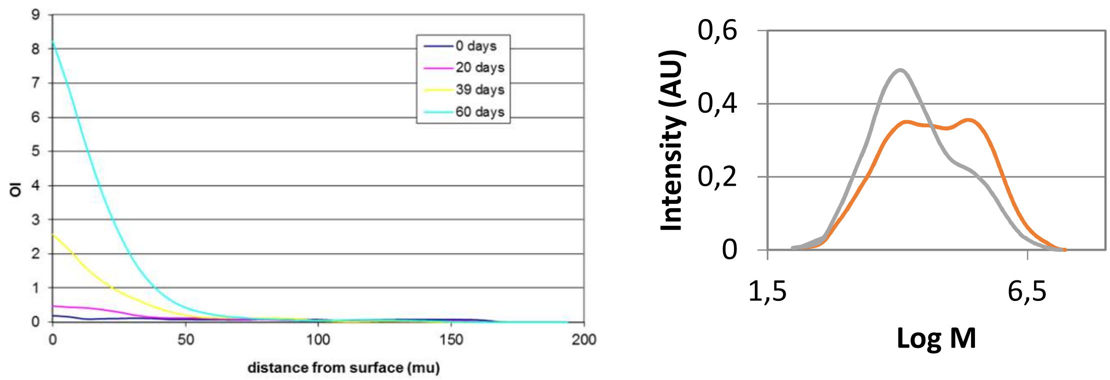

Figure 1. Oxidation index of the resin as function of the distance from the surface (left) and gel permeation chromatogram of resin taken directly from the surface before (orange trace) and after 42 days of exposure (grey trace) to chlorine dioxide.

SMALL SCALE SCREENING TEST

Test set-up

As ultimately the pipe performance is at stake, also the mechanical performance of the test specimen demands attention as an indication of the material resistance to the effects of the disinfectant. Since production and testing of pipes requires significant amounts of resin and long testing times, for screening purposes a small scale screening test is desired. Therefore, ISO 527 tensile bars were prepared of 4 mm thickness. The bars were exposed to 40 °C, 1 ppm chlorine-dioxide for different durations. The chlorine dioxide was continuously freshly generated and circulated through the test bath (200 L/h). The elongation at break of the tensile bars before and after exposure was compared as a measure of loss of mechanical properties. Next to their mechanical properties the specimens were also investigated for other properties, as mentioned under 1.2 (Figure 2).

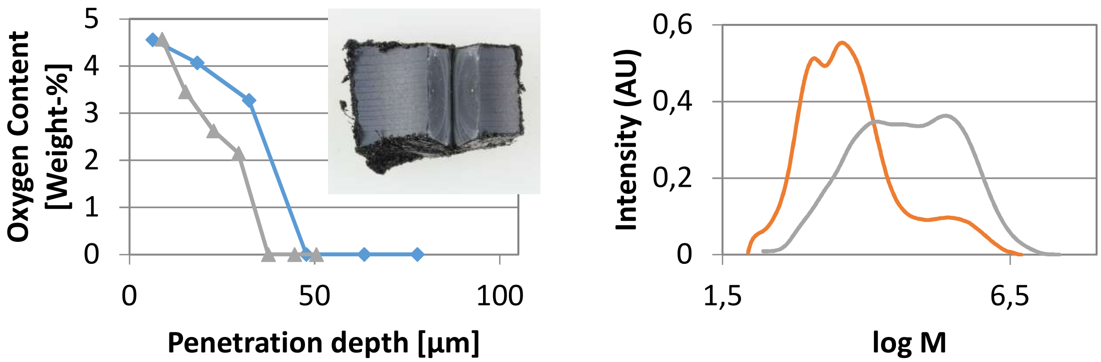

Figure 2. FEG-SEM analysis of depth of oxidation from the exposed surface of a tensile bar (grey) and a pipe (blue) of the same resin after 1500 h of exposure (left) and gel permeation chromatograms of resin taken directly from the surface of the pipe before (grey) and after (orange) exposure (1500 h). The inset of the left figure is an opened crack in a failed pipe.

The results from the exposed tensile bars were shown to correlate well with the exposed pipe results on the same resins.

Next, a number of potential material formulations was prepared on kilogram scale and submitted for the small scale test.

Results of small scale screening

The evaluation of retention at break after exposure of series of tensile bars led to the identification of a number of promising leads (Figure 3).

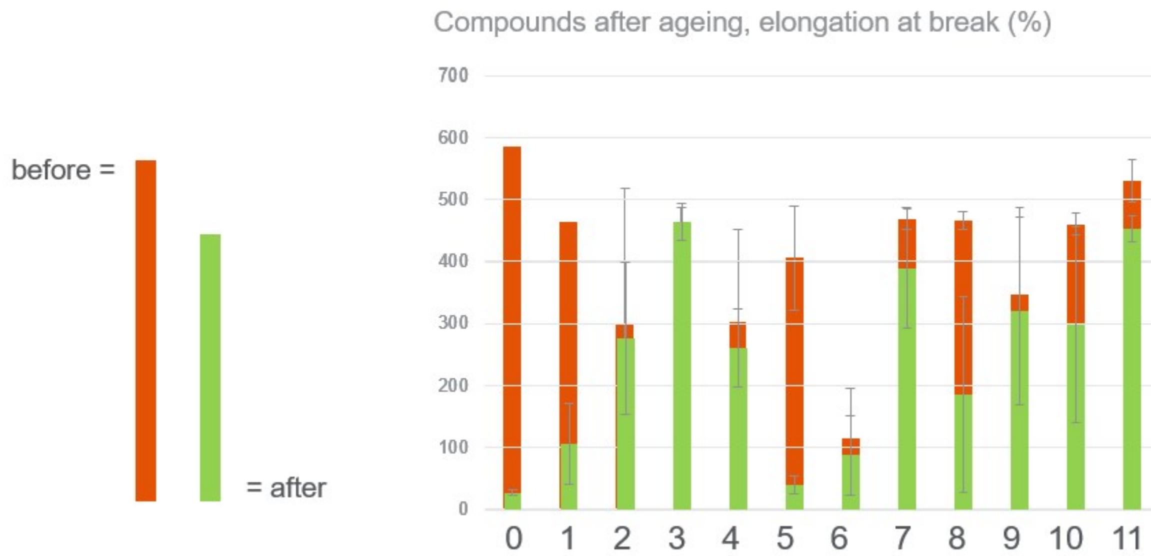

Figure 3. Elongation at break (%) as measured before and after ageing of one series of 4 mm thick tensile bars for 1000 h (40 °C, 1 ppm chlorine-dioxide) for various material formulations. From this particular series, formulations 3, 7 and 11 were selected for further evaluation.

These leads were found to originate from different conceptual approaches, either from molecular architecture, from crack arresting additives, from more classical additives as well as from sacrificial additives, or combinations thereof. From these the most promising candidates were selected for further evaluation as pipes in the long-term bench set-up.

LONG-TERM EVALUATION OF PIPE PERFORMANCE

Pipe preparation

The selected recipes were produced using a two stage twin-screw extruder (Coperion NT configuration) and processed on a Kraus-Maffei pipe extrusion line (KME 1-45-30/KMBE 1-30-25D) to yield 25 x 2.3 mm SDR 11 pipes.

Pipe evaluation

Pipes were exposed to chlorine dioxide (1 ppm, 40 °C, 6 bar, hoop stress 3.75 MPa) in a long-term ageing bench (Figure 4). The chlorine-dioxide was continuously freshly generated and circulated through the loop (200 L/h).

Figure 4. Accelerated ageing installation used for small scale screening test and pipe performance long-term test.

The results are depicted in Figure 5. As references incumbent commercial standard PE100 and PE80 pipes were taken. PEX references were also included as they are often used in applications featuring chlorinated disinfectants. The different samples tested contain a tailored molecular architecture combined with special additive packages.

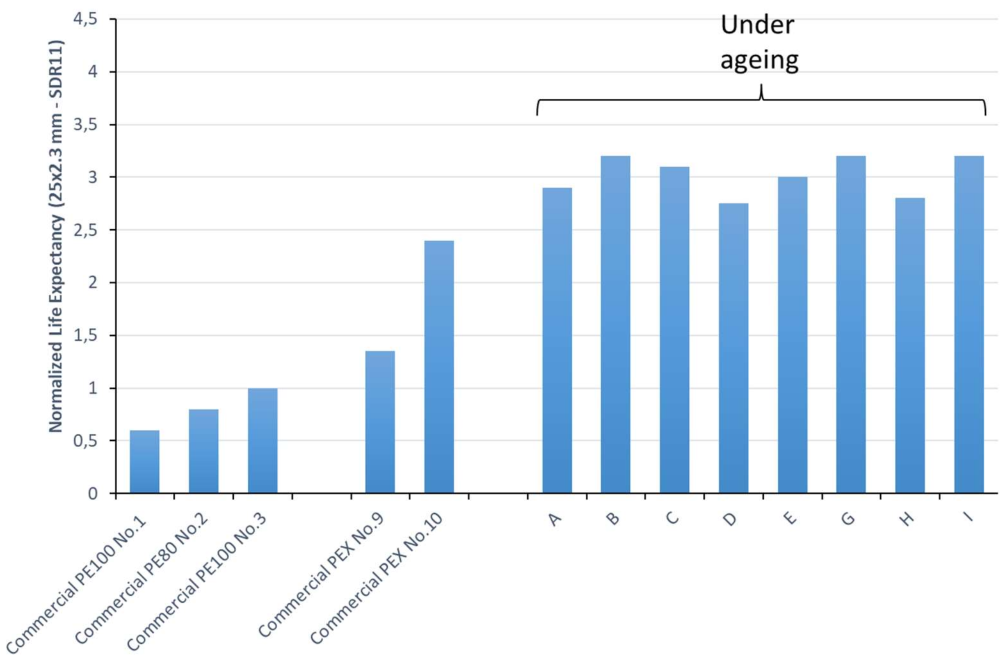

Figure 5. Normalized life expectancies of the tailored chlorine dioxide resistant HDPE compared to standard commercial products.

CONCLUSIONS

In conclusion, through careful evaluation of the effects of chlorine dioxide on polyethylene samples and the development of a small scale test method based upon those findings, a screening method was developed that revealed a number of candidates for upscaling and, subsequently, pipe testing. In the long-term pipe test a number of recipes performed successfully under accelerated conditions against chlorine dioxide exposure, thereby providing a safe and long-term solution for (drinking) water pipe applications in contact with chlorine dioxide.

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