

Corrosion of plastic pipes used in contact with chlorinated water

Karin Jacobson, PhD Swerea KIMAB AB, Stockholm, Sweden

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Abstract

Plastic pipes made from polyolefins, such as polypropylene and polyethylene, are often used for transportation of water. Disinfectants added to the water are known to cause corrosion of the pipes and manifests itself as a brittle surface layer inside the pipes which can lead to rupture of the pipes. Depending on the type of disinfectant used, the corrosion rate and mechanism varies. It has been observed that chlorine dioxide, which is becoming more and more popular as disinfectant, seems to be degrading the pipes faster than chlorine (as hypochlorous acid). The mechanism responsible for this is, however, under debate.

Corrosion des tuyaux en plastique utilisés au contact de l'eau chlorée

Les tuyaux en plastique faits de polyoléfines, comme le polypropylène et le polyéthylène, sont souvent utilisés pour transporter l'eau. Les désinfectants ajoutés à l'eau sont connus pour provoquer la corrosion des tuyaux, qui se manifeste elle-même sous la forme d'une couche superficielle fragile à l'intérieur des tuyaux, susceptible de provoquer la rupture des tuyaux. Selon le type de désinfectant utilisé, la vitesse de corrosion et le mécanisme de corrosion varient. Il a été constaté que le dioxyde de chlore, qui devient de plus en plus populaire en tant que désinfectant, semble dégrader les tuyaux plus rapidement que le chlore (sous forme d'acide hypochloreux). Le mécanisme responsable de ce phénomène fait cependant l'objet de débats.

Korrosion von Kunststoffrohren, die in Kontakt mit chloriertem Wasser verwendet werden

Kunststoffrohre aus Polyolefinen wie Polypropylen und Polyethylen werden häufig für die Verteilung von Wasser verwendet. Es ist bekannt, dass Desinfektionsmittel, die dem Wasser beigemengt werden, Korrosion an den Rohren verursachen. Sie zeigt sich an einer spröden Oberfläche in den Rohren, die zu einem Brechen der Rohre führen kann. Je nach Art des verwendeten Desinfektionsmittels schwanken Korrosionsgeschwindigkeit und -mechanismus. Es wurde beobachtet, dass Chlordioxid, das als Desinfektionsmittel immer populärer wird, die Rohre schneller zu schädigen scheint als Chlor (in Form von Hypochlorsäure). Der hierfür verantwortliche Mechanismus wird jedoch noch diskutiert.

Introduction

Light-weight, strength, flexibility and a long service life makes plastic pipes an attractive and cost-effective alternative. Plastic pipe systems are also easy to install and require minimum maintenance. In addition, chemical resistance to many common chemicals such as acids, bases, salts, and oxidants make plastic pipes suitable for a wide range of applications. Plastic pipes made from polyolefins, such as polypropylene, polyethylene and cross linked polyethylene (PEX), are often used for transportation of water. Disinfectants added to the water are known to cause corrosion of the pipes and manifests itself as a brittle surface layer inside the pipes which can lead to rupture of the pipes. The chlorine resistance of the pipes can be tested according to e.g. ASTM F2023 (PEX and also used for PP) and ASTM F2263 (PE).

Chlorine dioxide is becoming more and more popular as a disinfectant for drinking water. It has some advantages compared to chlorine (used in the form of hypochlorous acid) which has been the dominating disinfectant in most of Europe and America. Chlorine dioxide is a very effective bacterial disinfectant and it is even more effective than chlorine for the disinfection of water that contains viruses and it effectively deactivates the chlorine-resistant pathogens *Giardia* and *Cryptosporidium*. Chlorine dioxide also removes and prevents bio film. Disinfection with chlorine dioxide also destroys phenols, which can cause odor and taste problems. In addition chlorine dioxide is more effective for the removal of iron and manganese than chlorine, especially when these are found in complex substances. Another advantage with chlorine dioxide over chlorine is its efficiency in *Legionella* prevention. It has therefore become popular to install small chlorine dioxide generators in hotels and hospitals where there is an increased risk for *Legionella*.

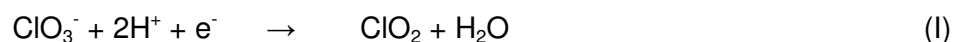
The macroscopic mechanism responsible for ultimate pipe rupture when tested with water containing any of the three disinfectants chlorine, chloramines and chlorine dioxide is considered to be the same i.e. depletion of stabiliser at the inner pipe surface, oxidation of the inner layer, microcracking of the inner layer, crack propagation through the wall with oxidation in advance of the crack front and final rupture of the remaining pipe, resulting in ultimate fracture [1]. There is, however, a difference in the reactivity between the different disinfectants, which is reflected also in their disinfectant properties. It has been observed by scientists that chlorine dioxide is more aggressive than chlorine towards polyolefinic (polyethylene, polypropylene and polybutylene) pipes [1-3]. One explanation to this could be the fact that chlorine dioxide is a dissolved gas which diffuses easier into the polymer. In addition chlorine dioxide easily reacts with phenols. As mentioned above this is one of the advantages with chlorine dioxide as a disinfectant but since the long term stabilisers most often are (hindered) phenols this will lead to a fast depletion of the stabiliser. This will make the material susceptible to oxidative degradation. There is some dispute whether chlorine dioxide can attack the polymer directly or if it is degraded by reaction products from the reaction between the stabiliser and chlorine dioxide.

The main problems with failures of plastic pipes used in contact with chlorine dioxide disinfected water have been on polypropylene pipes for hot water (around 50 °C) applications in hotels and hospitals but failures have also been encountered in municipal water supply pipes of polyethylene. While the failure mechanism in polyethylene exposed to chlorine dioxide has been studied by a few of research groups [1-3] no publications can be found on polypropylene, polybutylene or PEX.

End users, such as cruise ships, hotels, hospitals and municipal water suppliers, might wish to use chlorine dioxide disinfection but cannot risk premature failures which could result in costly water damages. This is a problem not only for the end users but also for the suppliers of chlorine dioxide systems. It is thus important that the service life of the piping system can be predicted and to have the knowledge if more durable materials can be installed, at least in

the most critical positions. Since there are many different ways to produce chlorine dioxide it is also important to understand if the production method makes the chlorine dioxide more or less aggressive.

Chlorine dioxide can be produced from either the reduction of chlorate (reaction I) or the oxidation of chlorite (reaction II) [4]. For large scale production, like for producing chlorine dioxide for bleaching in the pulp and paper industry, chlorate reduction is used almost exclusively. Small scale production, like chlorine dioxide generators for water disinfection, on the other hand, is often based on chlorite chemistry. The cost of chlorite is several times that of chlorate.



For both chlorate and chlorite based chlorine dioxide generation a number of different chemistries exists and the purity of the end product will depend on the chemistry used. For water purification the most common chlorate chemistry is the Purate process (trademark of EKA Chemicals). This comprises a stable mixture of sodium chlorate and hydrogen peroxide which is mixed with sulphuric acid in the generator.

The chlorite reduction can be made by:

- Electrochemical activation
- UV-activation
- Acid (normally HCl)
- Acid cation exchange
- HClO activation
- Cl₂ activation of aqueous chlorite (Rio Linda Method)
- Cl₂ activation of solid chlorite

An important step in understanding the degradation mechanism is to determine if it is the chlorine dioxide itself which is the active specie or if the degradation could be due to, or enhance by, by-products from the generation process. This is very important since this clarify if the production method of chlorine dioxide is an important factor in determining the service life of the pipes.

Investigation of a polypropylene pipe exposed to 0.5 mg/l ClO₂ at 55°C for 8 years.

Figure 1 shows a piece of a pipe from a hot water piping in a hospital having a chlorine dioxide water purification system in order to prevent Legionella. The pipe had to be replaced due to leakage.

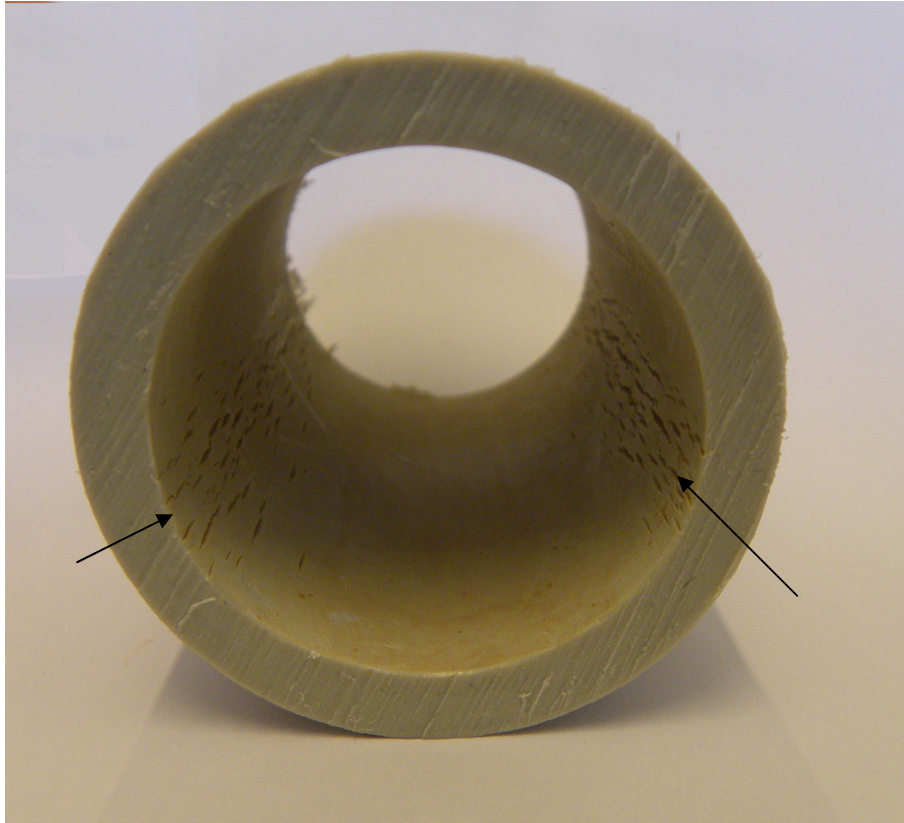


Figure 1. A piece of pipe from a hot water supply in a hospital using chlorine dioxide disinfection.

As can be seen in the figure there are two bands of small cracks running in the direction of the pipe. Figure 2 shows a close up of the cracks.



Figure 2. A close up of the surface with the cracks.

In Figure 2 it can also be seen that the inside surface of the pipe has a powdered layer that is easily scratched off.

Figure 3 shows a cross section of the pipe wall. It is quite clear in this picture that the polymer in the pipe is not well mixed. It is quite possible that the mechanical properties of this pipe have been badly affected by poor processing. In addition, the cross section of some of the cracks can be seen. The cracks have here penetrated up to about 1.6 mm into the pipe wall.

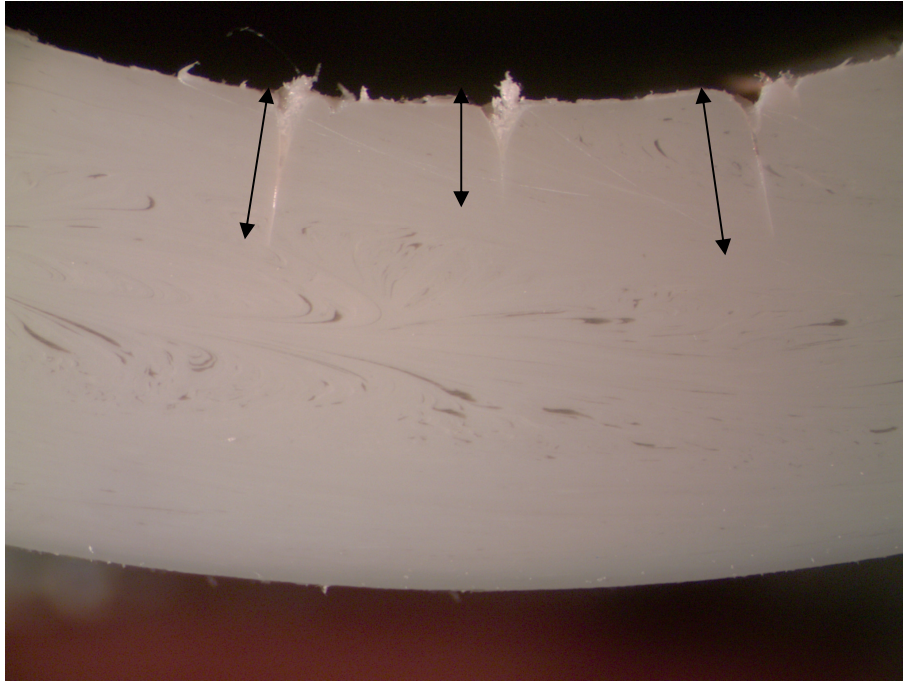


Figure 3. Cross section of the pipe wall. The arrows are indicating the penetration depth of the cracks.

Figure 4 shows an SEM picture in 40 times enlargement of one of the cracks. As can be seen it consists of two parts. One wide crack and one thin which has propagated from the tip of the wide one.

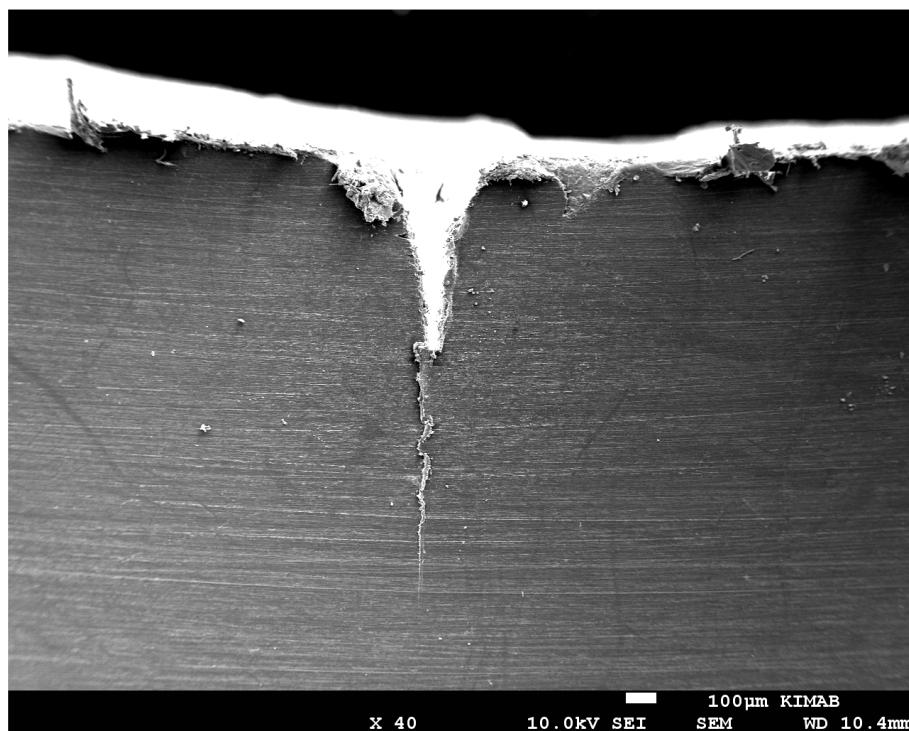


Figure 4. SEM picture in 40 times enlargement of one of the cracks.

SO₂ can be used to stain polyolefins to visualise hydroperoxides (which are normally the primary oxidation product) [5]. In Figure 5 the cross section of the pipe wall after reaction with SO₂ is shown. As can be seen hydroperoxides are present but localised to the surface of the pipe wall and on the inside of the wide part of the crack.

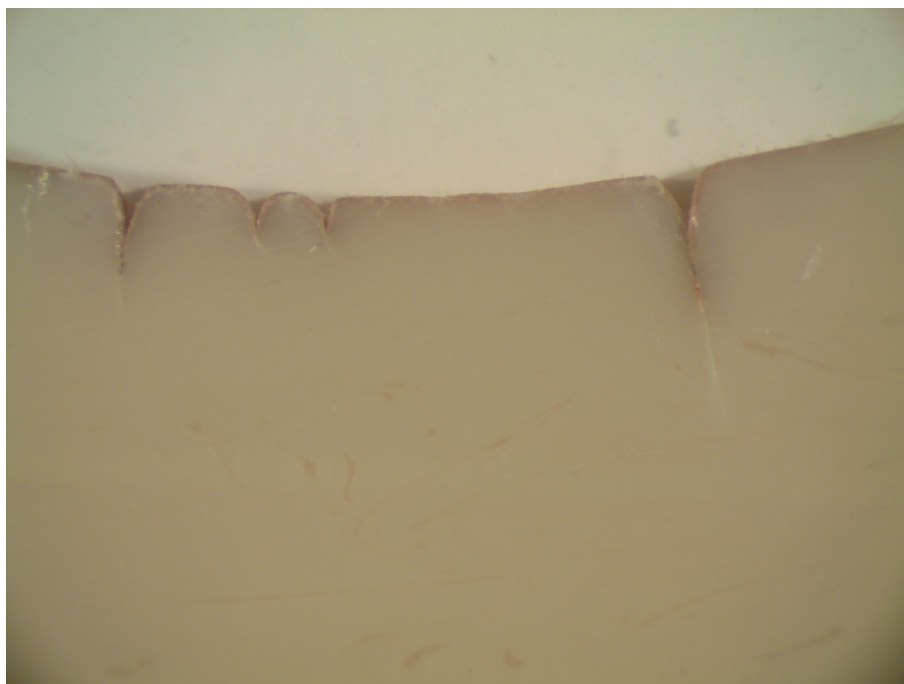


Figure 5. The cross section of the pipe wall after reaction with SO₂ to visualise the hydroperoxides.

Discussion

Figure 6 shows FTIR scans of a medical grade of UHMWPE (ultra high molecular weight polyethylene) which does not contain any stabiliser exposed to pure water and to water with 1 mg/l chlorine dioxide after 9 days at 50°C. The samples have been reacted with NO-gas to mark the hydroperoxides (new peak appears at 1630 cm⁻¹) [6]. It shows that addition of chlorine dioxide changes the rate of oxidation compared to pure water. This means that chlorine dioxide on its own can initiate and/or accelerate polyethylene oxidation. This contradicts the mechanism proposed by Yu et al [2] who propose that it is a reaction product from the degradation of the stabiliser which will promote the degradation of the polymer. Colin et al [3] propose that it is only the initiation and one termination step that involves chlorine dioxide. The initiation is believed to be due to hydrogen abstraction from the polymer (polyethylene) and by this initiate the radical chain reaction. Chlorine dioxide has an unpaired electron but others have reported that it is not reactive enough to abstract a hydrogen from a hydrocarbon [2, 7]. Polymers are, however, most often not as perfect as a hydrocarbon but will contain sites that are more susceptible to oxidation. It is thus quite possible that the chlorine dioxide is not initiating the oxidation *per se* but accelerates the oxidation that has already been initiated but normally proceeds very slowly. It thus accelerates the auto-oxidation. The oxidation reaction has also been found to involve both hydroperoxides and carbonyls much in the same way as thermally induced oxidation of polyethylene.

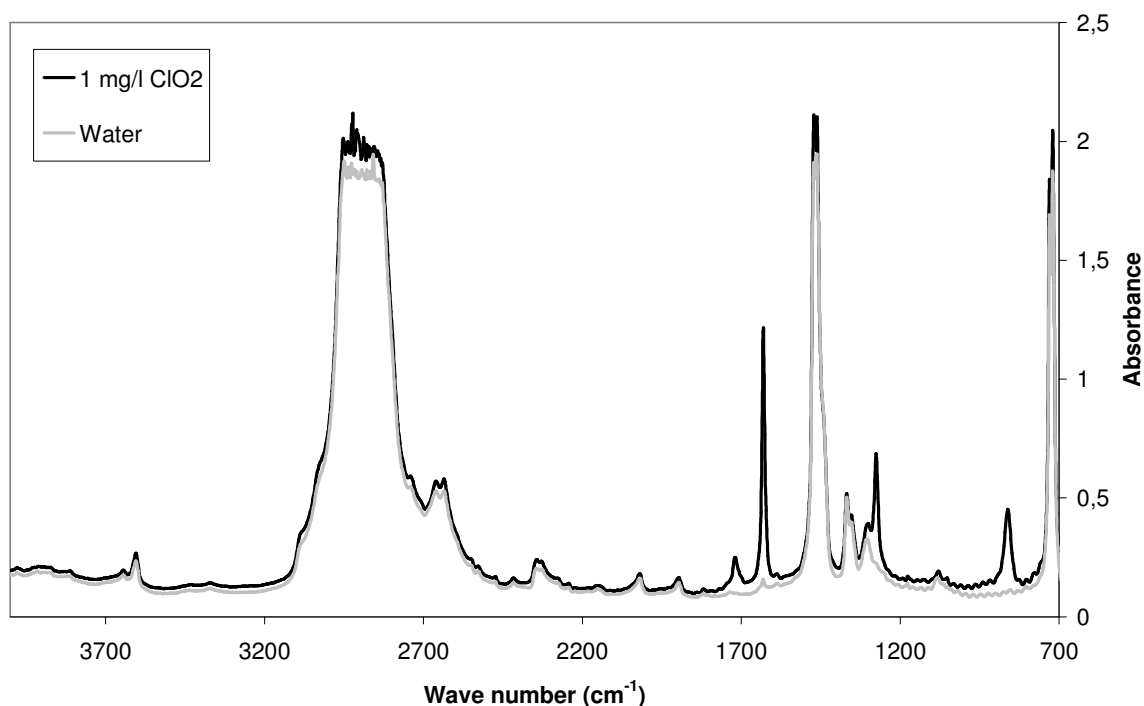


Figure 6. Unstabilised UHMWPE exposed to pure water (gray) and 1 mg/l chlorine dioxide (black) for 9 days at 50°C. Oxidation of the latter sample can clearly be seen by the peaks at 1720 cm⁻¹ (carbonyls) and 1630, 1276 and 860 cm⁻¹ (hydroperoxides after NO reaction).

Figure 7 shows FTIR scans of one UHMWPE sample oxidised in air at 120°C for 20 hours and one which had been exposed to 100 mg/l chlorine dioxide at 50°C for 7 days after reaction with NO-gas to mark the hydroperoxides. As can be seen in the figure the oxidation products are about the same in the two samples.

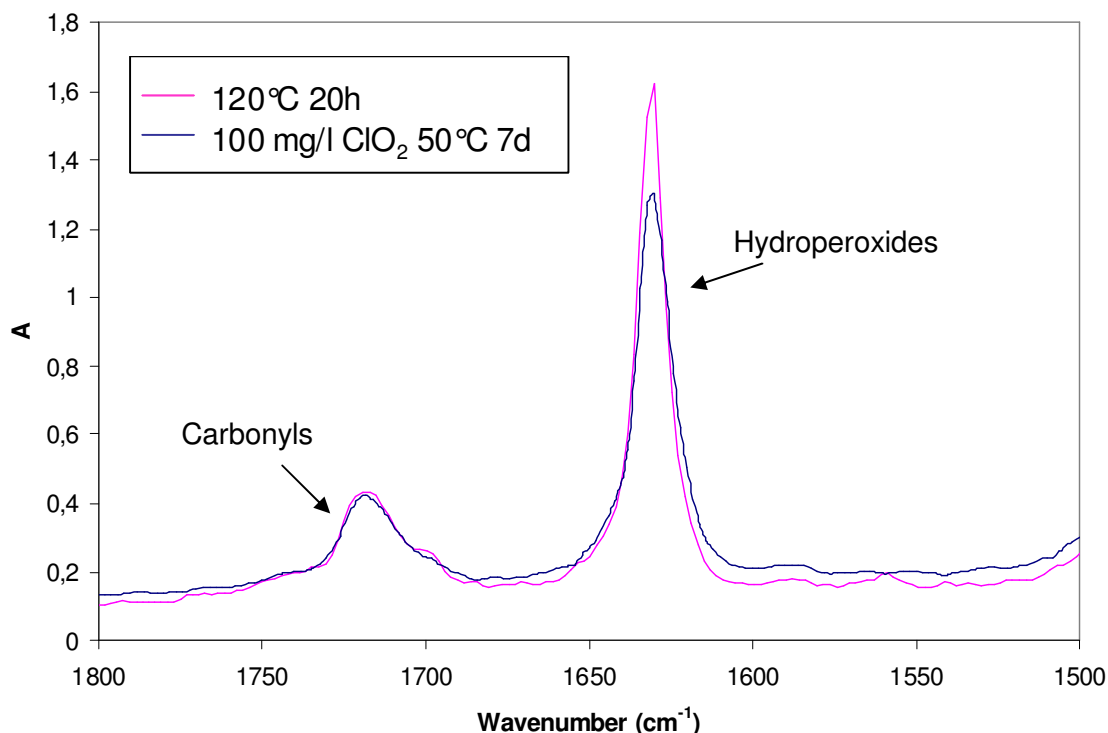
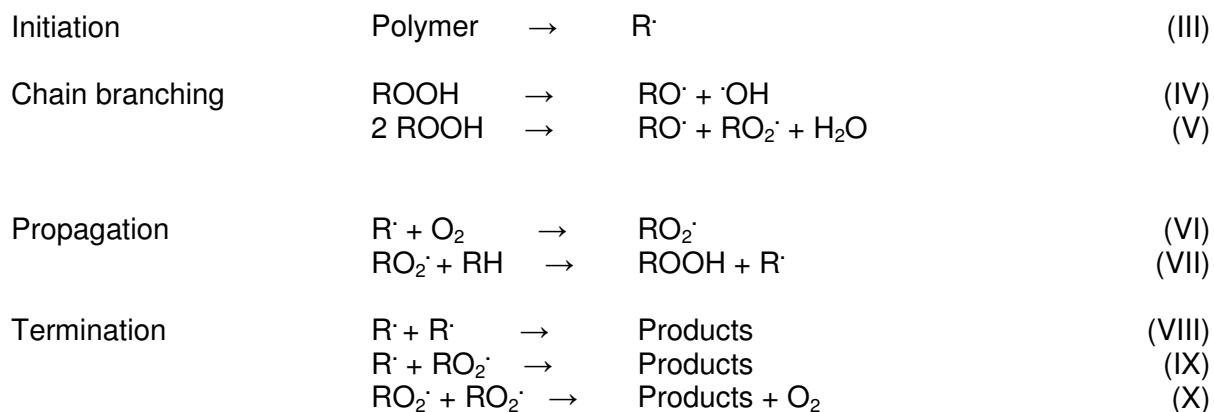


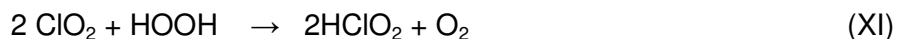
Figure 7. Unstabilised UHMWPE exposed in air at 120°C for 20 hours and to 100 mg/l ClO₂ for 7 days. The reaction products are almost identical (carbonyls at 1720 cm⁻¹ and hydroperoxides after NO reaction at 1630 cm⁻¹).

From this it can be speculated that the chlorine dioxide will accelerate the oxidation similar to an increase in temperature, i.e. by decomposing the hydroperoxides into reactive radicals, reaction IV and V in the oxidation scheme shown below:

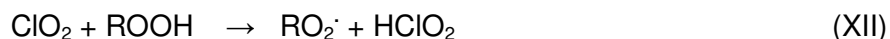


Reactions (IV) and (V) are referred to as chain branching reactions. Reaction (IV) has higher activation energy than (V) and is favoured at higher temperatures, whereas the bimolecular decomposition (V) is favoured in the accumulation of hydroperoxides. The hydroperoxides are accumulated during the first part of the oxidation and will then decrease in number, when they decompose to radicals forming carbonyls as end products. Hydroperoxides are thus only an intermediate in the oxidative degradation of polymers, but since they are formed first their detection is of great interest to follow oxidation at an early stage.

Chlorine dioxide is known to react with hydrogen peroxide



It can thus most probably also react with polymeric hydroperoxides



Reaction XII will thus also be a chain branching reaction just as reaction VI and VII and the peroxy radical formed is reactive enough to abstract a hydrogen from the polymer chain according to reaction VII.

New project

Due to a number of open questions a new project is being launched. This aims at determining the suitability of different types of plastic pipe materials in contact with chlorine dioxide, to predict their service life and possibly also finding ways to improve their performance in this environment. To achieve this it is important to understand the mechanism responsible for the deterioration of the materials.

The project will comprise the following:

- Failure analysis of pipes that have failed during service
- Collection of samples which have been in service for different times (samples for collection with service lives up to 10 years are available)
- Building a test loop at one of the facilities that are now installing a chlorine dioxide generator. This will enable testing of pipes in real service conditions.
- Laboratory exposures which will include systematic studies at different temperatures and concentrations of chlorine dioxide at different pH values

The concentration of chlorine dioxide in water when used as a disinfectant is maximum 0.8 mg/l but normally between 0.2 and 0.4 mg/l. The main focus of the work will thus be this concentration range but also higher concentrations (up to 10 g/l) will be of interest to look at since they are relevant to the piping system at the feed from the chlorine dioxide generator.

The possible influence of the pH value of the water pipes will also be investigated. Possible under deposit corrosion due to a localised decrease of the pH value originating from H^+ production from bacteria, will also be considered.

The main polymeric materials to be investigated will be the polyolefins (polypropylene, polyethylene and polybutylene) but also PVC and CPVC and other thermoplastics could be included if considered relevant to the participants.

End-users of pipes, pipe manufacturers, polymer producers and manufacturers of chlorine dioxide generators are invited to participate in the project.

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