

## **Corrosion of plastic pipes – the rôle of disinfectants**

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## **Abstract**

A well made and maintained pipe system will decreased the need of disinfectants. Disinfectants are, however, still added to the water and are known to cause corrosion of the pipes. In plastic pipes made from polyolefins, such as polypropylene and polyethylene which are often used for transportation of water this manifests itself as a brittle surface layer inside the pipes which can lead to premature 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 mainly due to its efficiency in fighting Legionella, 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 - le rôle des désinfectants**

Des canalisations bien faites et bien entretenues réduisent le besoin de désinfectants. Des désinfectants continuent toutefois d'être ajoutés à l'eau alors que l'on sait qu'ils provoquent une corrosion des tuyaux. Dans les tuyaux en plastique à base de polyoléfines, tels que le polypropylène et le polyéthylène, souvent utilisés pour le transport de l'eau, la corrosion se manifeste par la formation à l'intérieur des tuyaux d'une couche superficielle cassante qui peut provoquer une rupture prématurée des tuyaux. La vitesse et le mécanisme de corrosion varient en fonction du type de désinfectant utilisé. Il a été observé que le dioxyde de chlore, de plus en plus utilisé comme désinfectant pour son efficacité contre les légionnelles, semble abîmer les tuyaux plus vite que le chlore (sous forme d'acide hypochloreux). Le mécanisme responsable fait toutefois encore l'objet d'un débat.

## **Korrosion von Kunststoffrohren - die Rolle von Desinfektionsmitteln**

Ein gut konstruiertes und gewartetes Rohrleitungssystem senkt den Bedarf an Desinfektionsmitteln. Obwohl sie als Auslöser von Korrosionen in Rohren bekannt sind, werden Desinfektionsmittel auch weiterhin dem Wasser hinzugefügt. Bei Kunststoffrohren aus Polyolefinen, wie Polypropylen und Polyethylen, die häufig für den Transport von Wasser eingesetzt werden, zeigt sich dieser Effekt in Form einer brüchigen Innenfläche der Rohre, die zu einer frühzeitigen Rohrbruch führen kann. Die Häufigkeit und der Mechanismus einer Korrosion sind abhängig vom Typ des verwendeten Desinfektionsmittels. Es wurde beobachtet, dass Chlordioxid, das vor allem aufgrund seiner Wirksamkeit bei der Bekämpfung von Legionellen immer häufiger als Desinfektionsmittel eingesetzt wird, die Rohre schneller zersetzt als Chlor (in Form von Hypochlorsäure). Der dafür verantwortliche Mechanismus ist allerdings noch Gegenstand von Diskussionen.

## Introduction

By minimising regions of still standing water and by reducing build-up of bio-films on pipe walls the need for disinfectants can be kept very low. However, very often pipe systems in old buildings can have been altered many times over the years which can have resulted in dead ends and other areas where bacteria would thrive. The reality is thus that disinfectants are needed. The problem is that these disinfectants are known to cause corrosion of the plastic pipes and manifests itself as a brittle surface layer inside the pipes which can lead to rupture. The chlorine resistance of plastic pipes can be tested according to e.g. ASTM F2023 (PEX and also used for PP) and ASTM F2263 (PE).

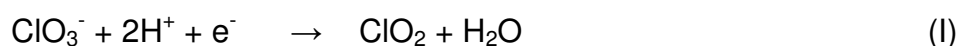
Chlorine dioxide is becoming more and more popular as a disinfectant for drinking water. It has some advantages compared to chlorine (used in the form of hypochlorous acid) which has been the dominating disinfectant in most of Europe and America. Chlorine dioxide is a very effective bacterial disinfectant 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 [2].

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
- Cl<sub>2</sub> activation of aqueous chlorite (Rio Linda Method)
- Cl<sub>2</sub> 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.

## Material and methods

### *Materials*

The ultra high molecular weight polyethylene (UHMWPE) samples were microtomed to slices with a thickness of about 150 μm from a compression moulded block of GUR 1050, produced by Poly Hi Solidur Deutschland. This is a medical grade used

for implants and should not, according to ASTM standard F648, contain any additives [5].

In addition a random polypropylene (PPR) pipe that had been in service for 8 years in a hospital before it had to be taken out of service due to leakage service was also analysed. The hospital was using a chlorine dioxide generator to prevent Legionella in the hot water. The concentration of the chlorine dioxide had been 0.5 mg/l ClO<sub>2</sub> and the temperature around 55 °C.

#### *Exposure*

The UHMWPE slices were exposed in pure water and to water with 1 mg/l chlorine dioxide for 9 days at 50 °C.

#### *FTIR*

FTIR scans within the interval 4000-700 cm<sup>-1</sup> were made using a Perkin Elmer System 2000 FT-IR. The resolution was 2 or 4 cm<sup>-1</sup>.

#### *FTIR line-scan*

Thin slices of the cross-section of the PPR pipes were made using a microtome. An FTIR line scan within the interval 4000-700 cm<sup>-1</sup> was then made using a Perkin Elmer System 2000 FT-IR fitted with an *i*-series microscope. Scans were performed every 50 μm over the cross section of the sample unless otherwise specified. The resolution was 2 or 4 cm<sup>-1</sup>.

#### *FTIR imaging*

Thin slices of the cross-section of the PPR pipes were made using a microtome. An FTIR image within the interval 4000-700 cm<sup>-1</sup> was then made using a Perkin Elmer Spotlight 200 FTIR Microscope System. The distribution of carbonyl groups was then calculated by relating the carbonyl absorption at 1720 cm<sup>-1</sup> to an internal standard at 1330 cm<sup>-1</sup>.

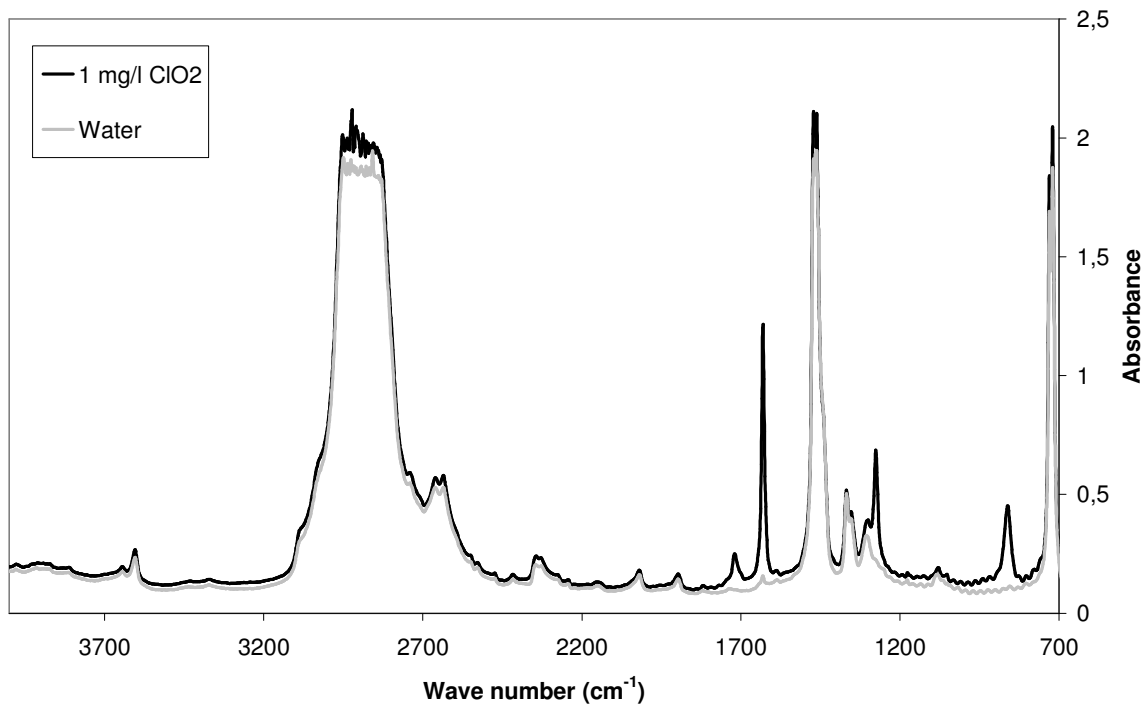
#### *Oxygen induction time (OIT)*

Oxygen induction time was measured at 190 °C using a differential scanning calorimeter, DSC 821-e from Mettler Toledo. The samples were heated from 25 °C to 190 °C (10 °C/min) in nitrogen (80ml/min) and held isothermally at 190 °C for 5 min before the gas flow was changed to oxygen (80ml/min).

## **Results and Discussion**

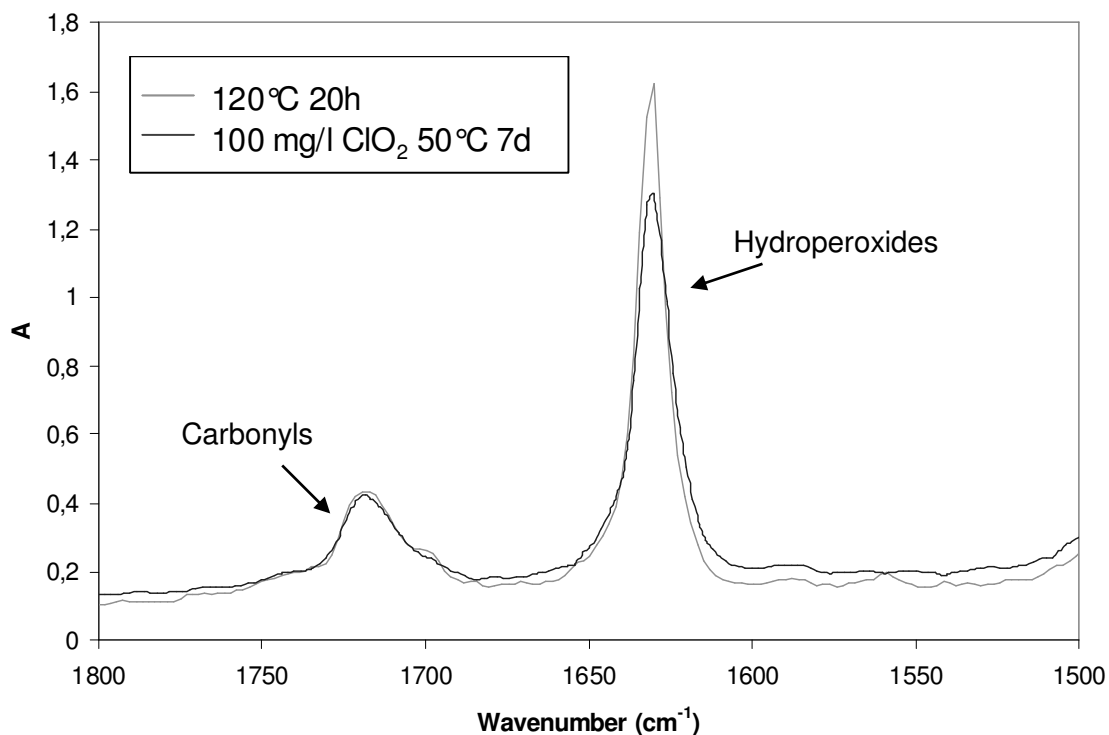
Figure 1 shows FTIR scans of a medical grade of UHMWPE (ultra high molecular weight polyethylene) which does not contain any stabiliser exposed to pure water and to water with 1 mg/l chlorine dioxide after 9 days at 50 °C. The samples have been reacted with NO-gas to mark the hydroperoxides (new peak appears at 1630 cm<sup>-1</sup>) [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.



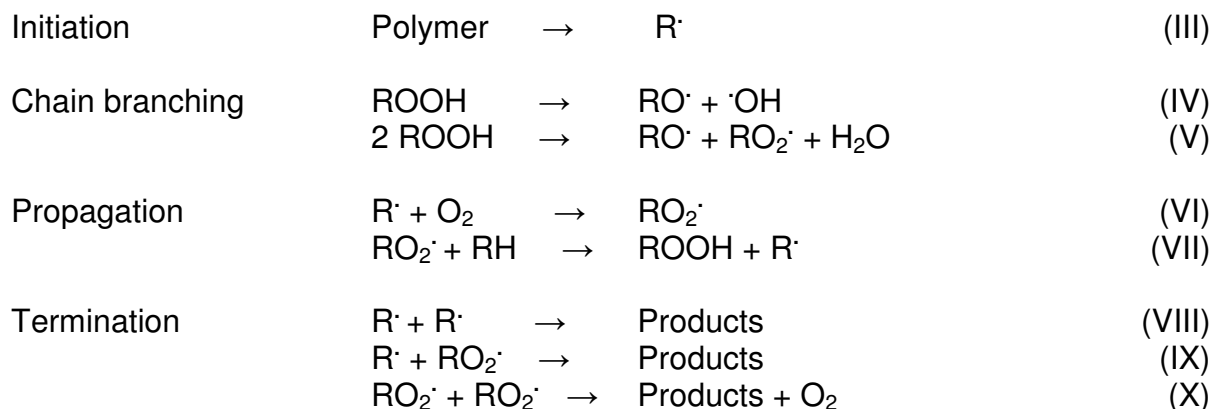
**Figure 1.** Unstabilised UHMWPE exposed to pure water (grey) and 1 mg/l chlorine dioxide (black) for 9 days at 50°C. Oxidation of the latter sample can clearly be seen by the peaks at 1720 cm<sup>-1</sup> (carbonyls) and 1630, 1276 and 860 cm<sup>-1</sup> (hydroperoxides after NO reaction).

Figure 2 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.



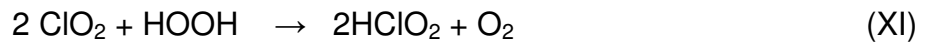
**Figure 2.** Unstabilised UHMWPE exposed in air at 120°C for 20 hours and to 100 mg/l ClO<sub>2</sub> for 7 days. The reaction products are almost identical (carbonyls at 1720 cm<sup>-1</sup> and hydroperoxides after NO reaction at 1630 cm<sup>-1</sup>).

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.

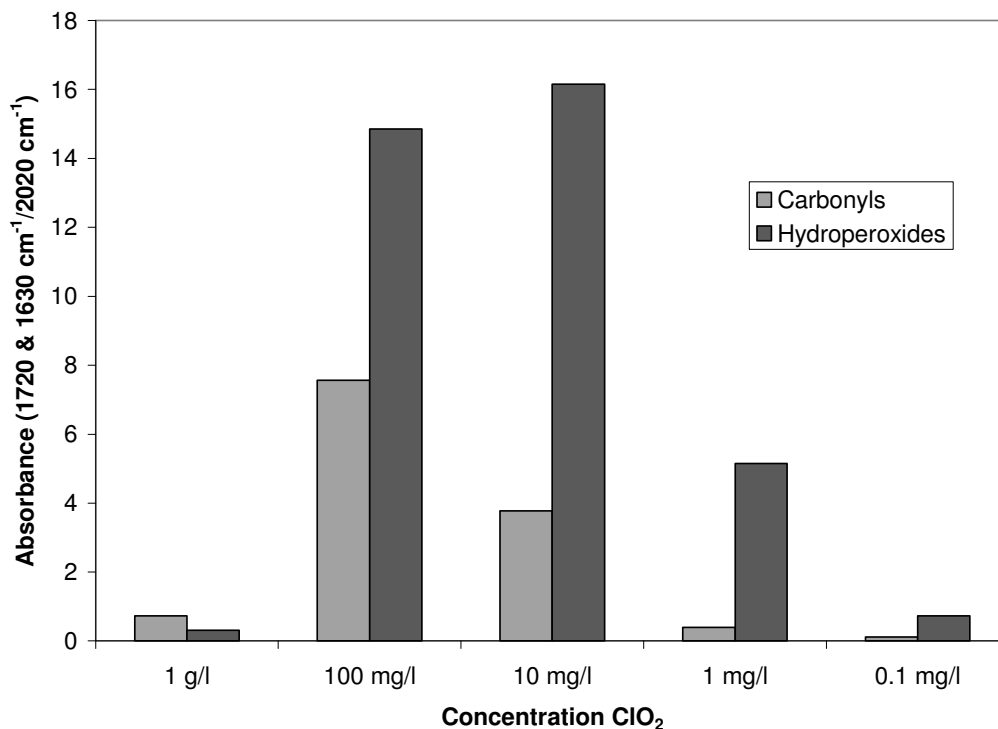
Chlorine dioxide is known to react with hydrogen peroxide



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. Reaction XII could be the reason for the accelerated rate of oxidative degradation in chlorine dioxide. If this reaction is responsible for this increased rate of degradation the effect should be lower at high concentrations of  $\text{ClO}_2$ . As can be seen in Figure 3 there is a very distinct drop in the accelerating effect of the oxidation of UHMWPE at 50°C between 100 mg/l and 1 g/l chlorine dioxide which further supports this mechanism.

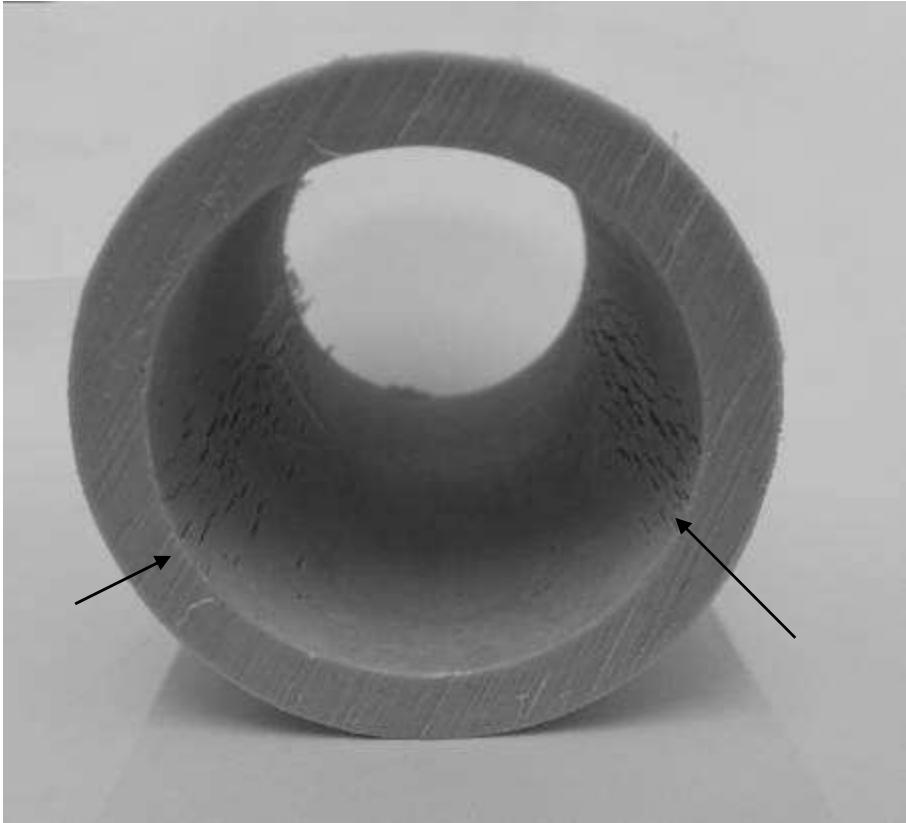


**Figure 3.** Concentration of hydroperoxides and carbonyls in UHMWPE after exposure to different concentrations of chlorine dioxide at 50°C for 24 hours

### Investigation of a polypropylene pipe exposed to 0.5 mg/l $\text{ClO}_2$ at 55°C for 8 years.

Figure 4 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 4.** A piece of pipe from a hot water supply in a hospital using chlorine dioxide disinfection. The arrows are pointing to two bands of small cracks running in the direction of the pipe.

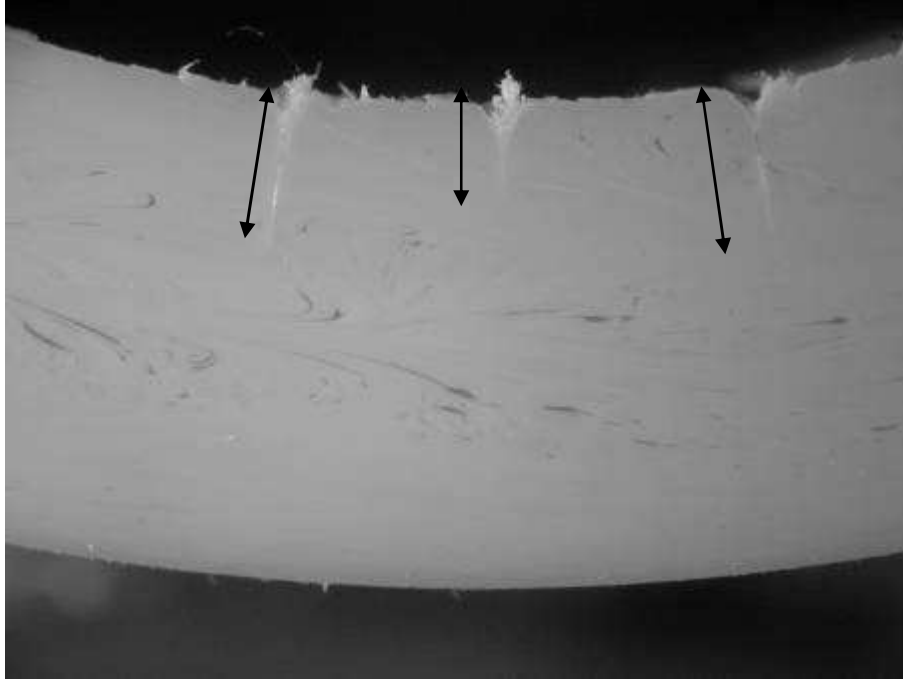
As can be seen in the figure there are two bands of small cracks running in the direction of the pipe. Figure 5 shows a close up of the cracks.



**Figure 5.** A close up of the surface with the cracks.

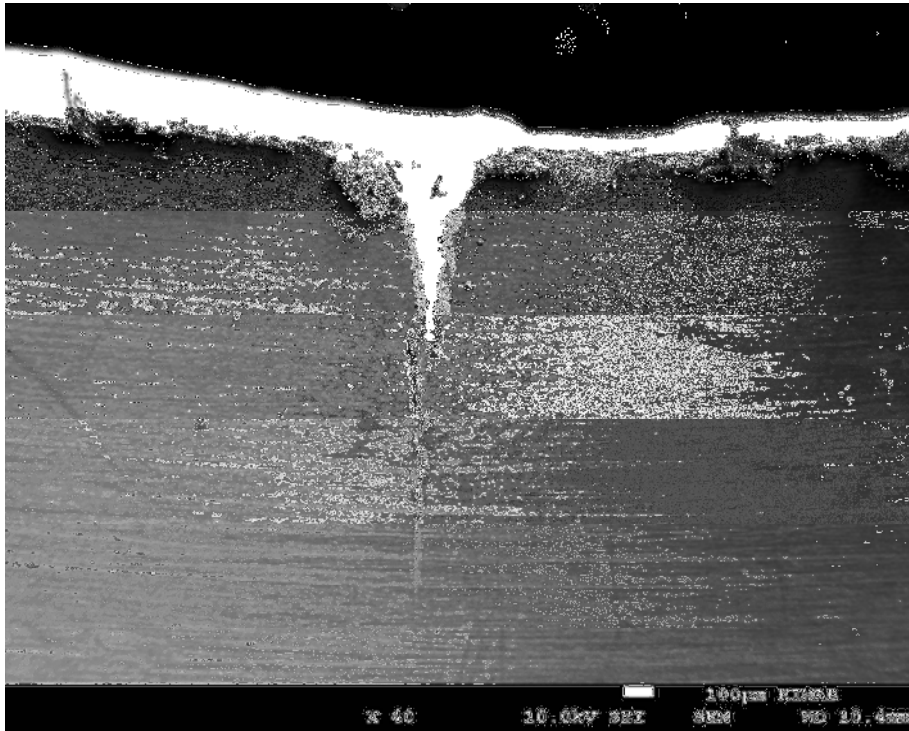
In Figure 5 it can also be seen that the inside surface of the pipe has a powdered layer that is easily scratched off.

Figure 6 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 6.** Cross section of the pipe wall. The arrows are indicating the penetration depth of the cracks.

Figure 7 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 7.** SEM picture in 40 times enlargement of one of the cracks.

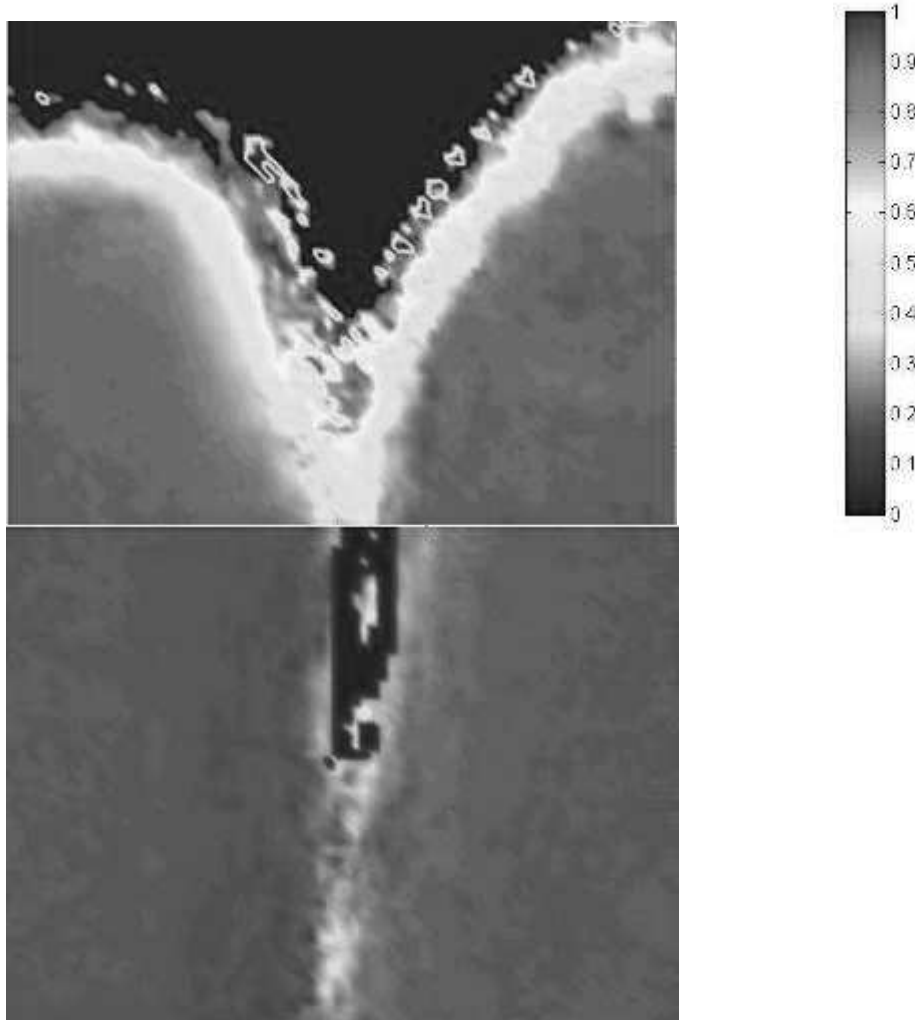
SO<sub>2</sub> can be used to stain polyolefins to visualise hydroperoxides (which are normally the primary oxidation product) [8]. In Figure 8 the cross section of the pipe wall after reaction with SO<sub>2</sub> is shown. As can be seen hydroperoxides are present but localised to the surface of the pipe wall and on the inside of the wide part of the crack.



**Figure 8.** The cross section of the pipe wall after reaction with SO<sub>2</sub> to visualise the hydroperoxides.

With FTIR imaging it is possible to get a picture of the distribution of oxidation products over an area.

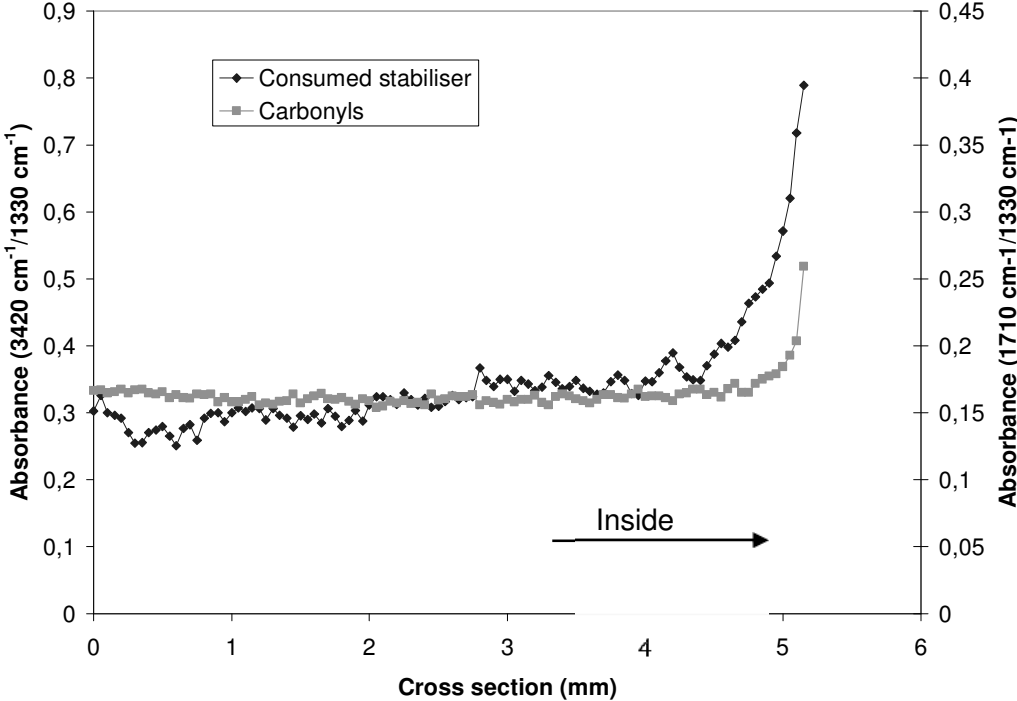
Figure 9 shows the FTIR image of the carbonyl distribution ( $1720\text{ cm}^{-1}/1330\text{ cm}^{-1}$ ) of one of the cracks. As can be seen in the figure the oxidation is limited to the outermost surface and only in the wide part of the crack. The degree and depth of oxidation seems to be the same at the surface of the crack as in the wide part of the crack. The propagating crack tip does not show any signs of oxidation.



**Figure 9.** FTIR image of one of the cracks which have propagated

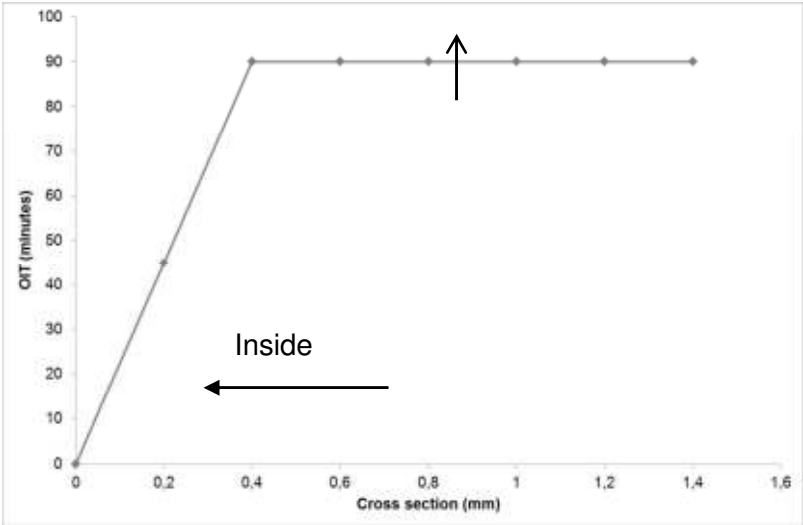
As mentioned in the introduction, chlorine dioxide easily reacts with phenols and due to this the hindered phenol stabilisers are quickly destroyed when exposed to  $\text{ClO}_2$ . When exposing a polyolefin which contains a hindered phenol stabiliser to a water solution with chlorine dioxide there is an initial large water absorption found in the sample which can be studied with FTIR. This disappears slowly when the sample is removed from the water but it can be seen again once the sample is exposed in pure water. This phenomenon is believed to be due to water being bonded to reaction products formed by the reaction between the hindered phenol and chlorine dioxide. By treating the cross section of the polypropylene pipe wall with pure water (at  $50^\circ\text{C}$  for 18 hours) a clear water absorption could be found in the part of the wall closest to the inside of the pipe, Figure 10. This indicates that the hindered phenol in this part of the pipe has been attacked by chlorine dioxide which has diffused into the pipe. As can be seen in Figure 10, which also shows the carbonyl index over the cross section, it seems as if the stabiliser is consumed just ahead of the oxidation front.

The water only indicates the part of the stabiliser which has been reacted and does not tell anything if stabiliser has also been lost due to physical loss, i.e migration. Since the stabiliser in this pipe seems to be Irganox 1330, it is very difficult to detect the stabiliser with FTIR in the same way as is possible with Irganox 1010 which has an easily detected ester group [9].



**Figure 10.** FTIR line scans through the cross section of the pipe wall showing the distribution of carbonyl groups and water. The water absorption is a result of reaction products from the degraded stabiliser and can thus be used as a measure of consumed stabiliser.

The results from OIT measurements on samples microtomed stepwise from the surface and into the bulk of the pipe are shown in Figure 11. These results indicates that the stabiliser is completely lost at the surface, slightly reduced further in but that the rest of the pipe still has a large quantity of active stabiliser.



**Figure 11.** OIT of samples cut from the inner surface and into the bulk of the same sample as shown in Figure 10. The OIT of all the samples except for the two closest to the surface was more than 90

minutes.

## Conclusions

It is clear that chlorine dioxide will accelerate the oxidative degradation of polyolefins such as polyethylene and polypropylene. The degradation mechanism is believed not to be by a direct attack of the chlorine dioxide on the polymer but rather a chain branching reaction in the propagation stage of the oxidation accelerating the degradation.

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