Resistance of PVC pipes against Disinfectants

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1. Background

Drinking water contains usually a small amount of disinfecting agent in order to guarantee the requested bacteriological quality. The influence of this disinfectant should be negligible on the pipe material. Nevertheless during the summer of 2003 some premature failures of plastics pipes for drinking water occurred in France.

The studies showed that these events were related to the conjunction of some elements :

- The use of a particular disinfectant : ClO_2
- A high level of this disinfectant
- High environment temperatures (hot summer)

The bursting of these PE pipes occurred with normal service pressure before the pipes reached the requested minimum of 50 years lifetime.
The PVC4Pipes organisation wished to check if PVC pipes could resist strong oxidising conditions.

The most common disinfectant used for drinking water is the $NaClO + Cl_2$ system.
It is efficient as disinfectant agent but presents the disadvantage of an unpleasant smell and taste at high levels (≥ 0.5 ppm).
Another disinfectant agent is ClO_2 : it is highly efficient, it does not give unpleasant smell to the drinking water even at high levels. But it is a very strong oxidising agent and this gas can not be stored or transported, it has to be generated on site.

1. Testing method

It is generally known that PVC has a very good resistance to oxidation at room temperature but the literature is poor on the topic of the action of disinfectants and PVC pipes (no mention in **ISO/TR 10358** and the existing papers we found only deal with exposure at 90°C). This is why this study was realised.
The resistance of pipes was assessed on tensile testing specimens according to the mechanical testing of the **ISO 4433.**

Requirements of ISO 4433

ISO 4433 expresses the following requirements to assess the resistance of a pipe material : The degree of swelling of the material in the presence of the liquid (not relevant in this case) and the residual mechanical properties after 3 months exposure (ratio = Q : see table 1) :

Pipe material	Residual property	Satisfactory if	Limited if	non-satisfactory if
PE, PE-X, PP	E_modulus Elong @ rupture	Q_E ≥ 38% 200% ≥ Q_R ≥ 50%	38% ≥ Q_E ≥ 31% 50% ≥ Q_R ≥ 30%	Q_E < 31% Q_R < 30%
PVC	E_modulus Elong @ rupture	Q_E ≥ 83% 125% ≥ Q_R ≥ 50%	83% ≥ Q_E ≥ 46% 50% ≥ Q_R ≥ 30%	Q_E < 46% Q_R < 30%

Samples : 4 pipes have been investigated :

- « **1 PVC** **Ca-Zn stabilised**
- « **1 PVC** **OBS stab**
- « **1 PVC** **Tin stab**
- « **1 PE80** **as reference material**

The PVC pipes were chosen with slightly different compositions in order to check if some compositions could be more sensitive to oxidation.
Table 2 gives the elemental composition of the PVC pipes measured by X-Ray fluorescence. The gelation level of these pipes was checked by DSC (Differential Scanning Calorimetry).

Element (%)	PVC Sn-stab	PVC OBS	PVC Ca-Zn
Na	0.02	0.1	0.1
Al	0	0.1	0.09
Si	0.03	0.1	0.1
S	0.02	0.01	0.01
Ca	2.8	1.3	1.7
Ti	0	0.07	0.2
Zn	0	0	0.1
Sn	0.01	0	0.0
DSC - analysis			
Tb (°C)	186	184	183
ΔHa (J/g)	2.8	2.5	2.3
Gelation %	73%	70%	63%

We confirm also that the filler level is very low in all pipes (below 3 phr).

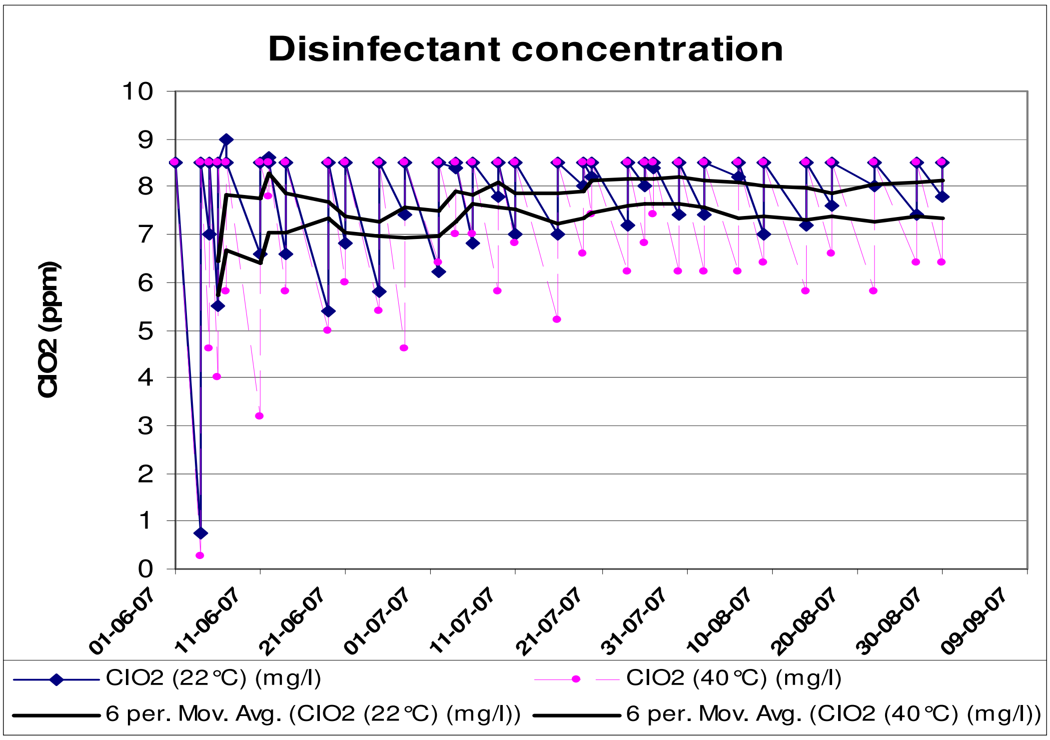
2. Exposure to ClO_2 Disinfectant

ClO_2 disinfectant is not stable and can not be purchased as such. It has to be generated on site and this can be produced according to the following equation :

$2\ NaClO_2 + \ NaOCl + 2\ HCl \rightarrow 2\ ClO_2 + 3\ NaCl + H_2O$

ClO_2 Disinfectant was introduced using a commercial kit (Accepta ®)
Concentration

The concentration of ClO_2 in the exposure vessels is decreasing with time (decay of ClO_2) and was kept approximately constant by regular analysis and addition of the missing amount of ClO_2
(see fig. 1 for the high concentration case).



The pipe specimens are immersed in a solution of ClO_2, in black tanks (protected from daylight), at specified temperature (respectively at 40°C and at 22°C).

3. Testing of the exposed samples

Tensile test specimens (ISO-2) have been cut out of the pipes (pipes of DN 110 mm except the Tin-stab pipe which was DN 160). Samples were exposed for 2000 h for each series. After exposure, samples and blanks were sent to the Austrian Institute TGM for measurement of :

- Tensile testing
- Residual stability (OIT or DHC)
- Molecular weight measurements
- Micrographs of exposed surface

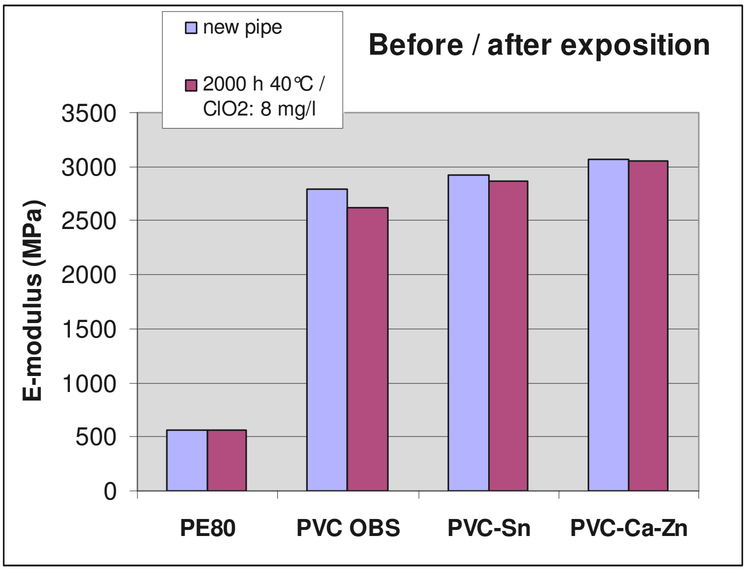
4. First series : hard conditions

As a preliminary test and in order to get results in a protocol of acceptable duration, we used very hard conditions in order to check if some oxidation could be induced in PVC pipes :

« **Very high oxidant concentration : 8 ppm ClO_2**
« **High temperature** : 40 °C

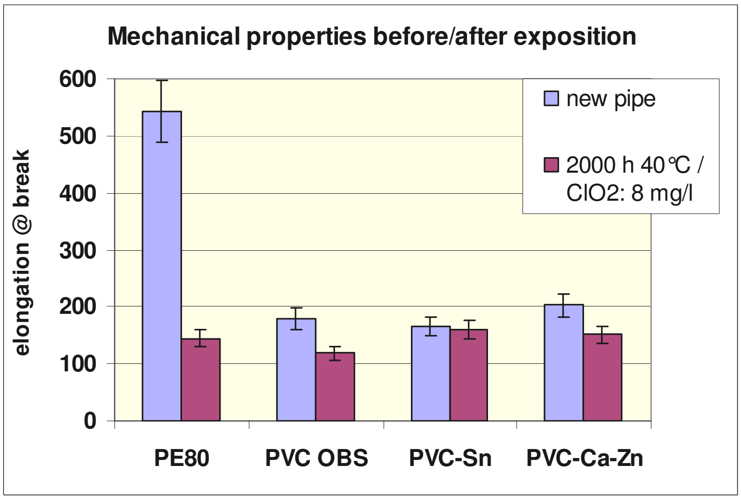
Results after exposure in hard conditions

The E-modulus was measured before and after exposure (fig. 2)



No significant changes were registered for any type of pipe and all residual values of E-modulue are > 83 % of initial value (= satisfactory according to the requirements of ISO 4433).

The Elongation at break was also measured for these conditions (fig. 3)



With these very hard conditions, the elongation at break shows that PE becomes brittle (Residual elongation at break : $Q_B < 30\%$ of the initial value) but the PVC does not undergo significant modification ($Q_B >> 50\%$ = inside the limit-levels of ISO 4433).

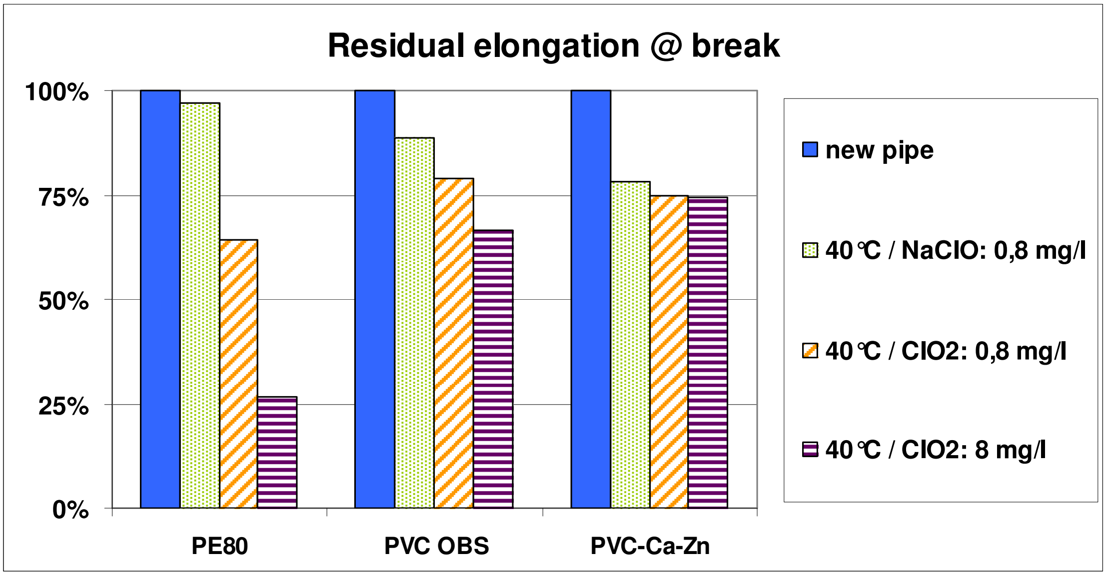
5. Other exposure conditions

More realistic testing conditions were also investigated for some of the pipes :

- Use of the common NaClO-Cl_2 system, with T = 40°C
- Concentration of 0.8 ppm ClO_2 ; with T = 40 °C

The mechanical properties and especially the elongation at break were also assessed for these exposures.

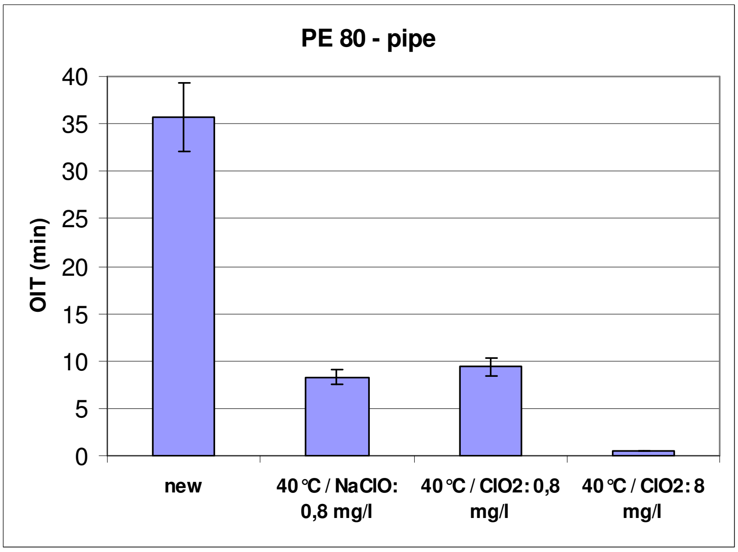
The ratios of remaining elongation at break (Q_B) after different types of exposures were established, they are given in fig. 4 :



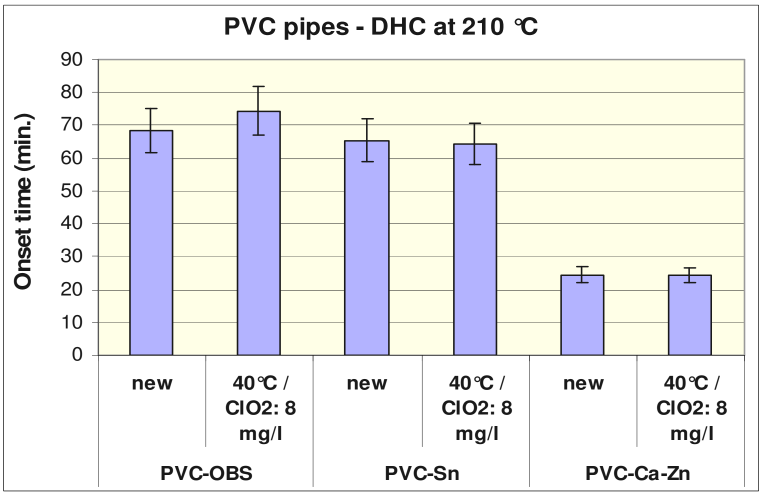
The PE pipe exposed to the high concentration of disinfectant (8 ppm) show an important reduction compared to the initial elongation at break. For the PVC pipes the elongation at break is not strongly reduced (always > 60% of initial value) and is still considered as suitable according to ISO 4433.

6. Physical evaluation

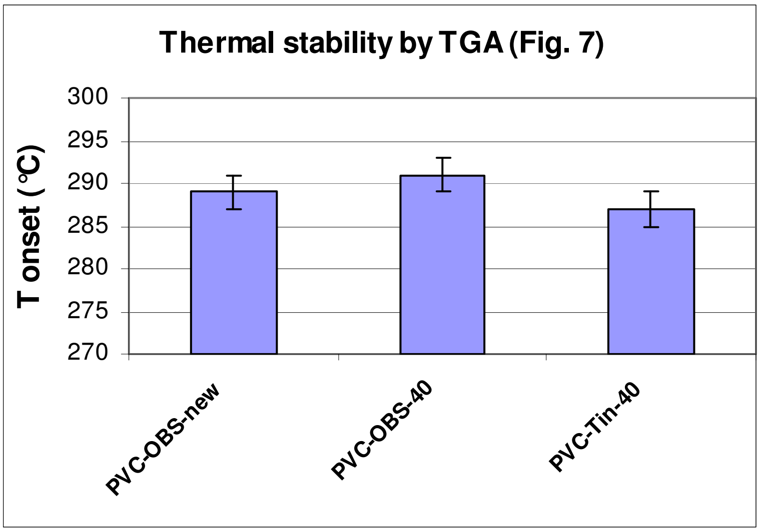
The thermal stability of the samples was investigated in order to check the cause of the loss of mechanical properties of some of the pipes.



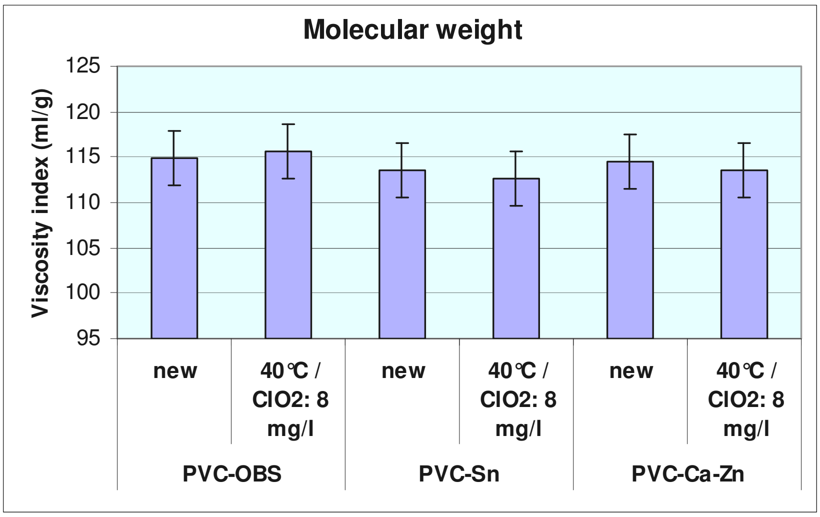
- For PE : we confirm that oxidation is the main cause of the loss of properties since the OIT (Oxygen Induction Time) is strongly reduced for exposures to high concentrations of ClO_2 (fig. 5)
- For PVC : The overall thermal stability by DHC is related to the stabiliser system but the exposure to disinfectant does not lead to any loss in stability (fig. 6).



§ The thermal stability by TGA (Thermo Gravimetric Analysis Fig. 7) as alternative method confirms that there is no significant difference in degradation temperature or oxidation ability for the exposed or unexposed samples (exposures at 40°C and concentr. 8 ppm ClO_2).

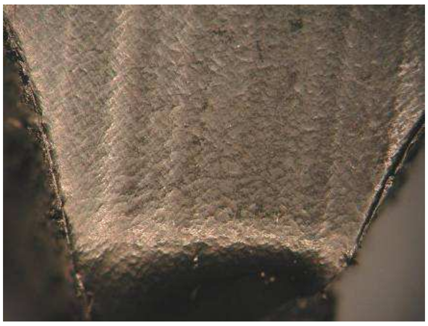


Molecular weight



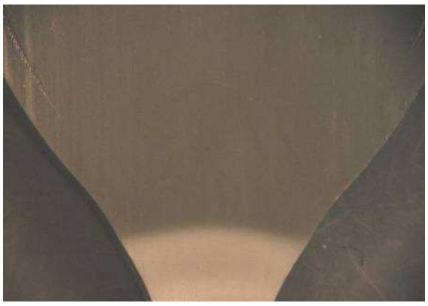
- For PVC pipes : Viscosity index shows no reduction in Mw (fig. 7).

7. Stereo-microscopy pipe-surface

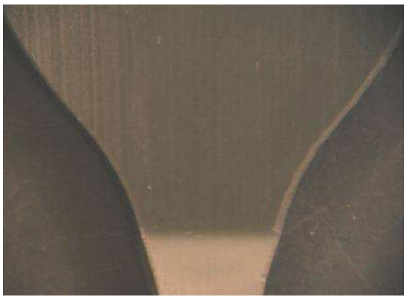


PE 80 new (fig. 8)

PE80 exposed (fig. 9)

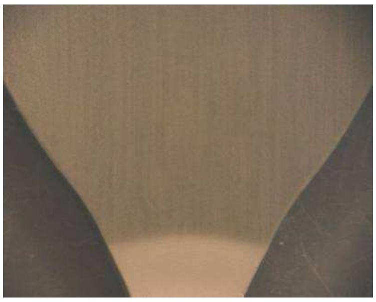


PVC (OBS) new (fig. 10)



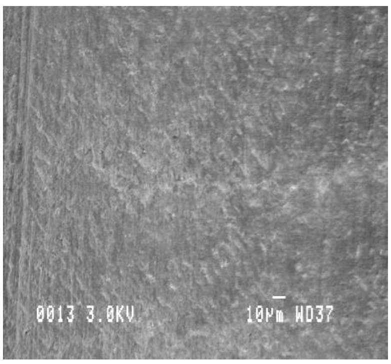
PVC (OBS) exposed (fig. 11)

PVC (Ca-Zn) new (fig. 12)

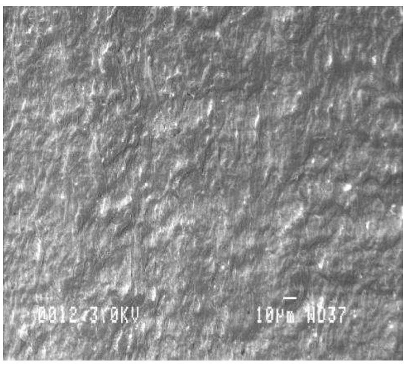


PVC (Ca-Zn) exposed (fig. 13)

8. SEM pipe-surface



PVC (Ca-Zn) new (fig. 14)



PVC (Ca-Zn) exposed 40°C/ClO2: 8 mg/l (fig. 15)

The optical microscopy does not show any degradation of the PVC surface after exposure to the hardest conditions.

The SEM scanning of the PVC surface exposed to the hardest conditions shows only a limited alteration of the surface. These SEM microscopy examinations were only realised on the PVC pipes exposed to the hardest conditions since no significant change in mechanical properties could be registered for the PVC pipes exposed to milder conditions.

9. Conclusions

- With normal concentration conditions (Concentr. ≤ 0.8 ppm),
  no attack of the PVC pipe was registered neither with ClO_2 nor with NaClO.
- In very hard (and unrealistic) conditions : (Temp = 40°C, very high concentration, ...)
  we could only induce a limited attack of the PVC surface.
- This limited attack does not bring a sufficient change in mechanical properties to bring it beyond the limit levels required by ISO 4433 for non acceptance of a pipe material.
- We could not register significant differences in oxidation behaviour between the different stabilising systems examined.
- These results confirm the very low sensitivity of rigid PVC to oxidising agents.

Literature

1. A study of the effects of of chlorinated water on engineering thermoplastics at elevated temperatures. S. Bradley AMOCO - ANTEC 2000.
2. Property changes in polymer materials due to ozone and disinfectants.
D. Rogalla, G. Menges ANTEC 1981.
3. An examination of the relative impact of common potable water disinfectants (chlorine, chloramines and chlorine dioxide) on plastic piping system components. S. Chung, PPXIII 2006

Acknowledgement

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