DURABILITY EVALUATION TO RESIDUAL CHLORINE ON PLASTIC PIPES FOR HOT WATER SUPPLY - THIRD REPORT

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Abstract
Recently, the polymer electrolyte fuel cells (PEFC) cogeneration systems with plastic pipes for hot water supply has been commercialized in Japan. The pipes for hot water supply are installed with bending from the polymer electrolyte fuel cell to inside a house without using fittings. However, it is expensive and hard to replace these plastic pipes. These pipes which installed with bending were not evaluated in the residual chlorine solutions for long term. Accordingly, it is important to evaluate the durability and to predict the lifetime of these bent pipes.

This study intended to evaluate the bent pipes in the residual chlorine solutions early. The residual chlorine solution immersion test for the bent polybutylene (PB) pipes and the bent double-layer crosslinked polyethylene pipes (PEX2) was conducted at 80 °C, 90 °C and 98 °C. In the residual chlorine solution immersion test, the concentration of the residual chlorine solution is 5 ppm and 10 ppm for 80 °C, 5 ppm for 90 °C and 5 ppm for 98 °C.

As a result, it took much time to get the results back from this immersion test beyond expectation. It was found that the bent polybutylene (PB) pipes had the cracks over for 36,000 hours at 5 ppm in 90 °C, over for 40,000 hours at 10 ppm in 80 °C and over for 44,000 hours at 5 ppm in 80 °C. On the other hand, the bent double-layer crosslinked polyethylene pipes (PEX2) in the residual chlorine solution immersion test did not have the crack at all over for 47,000 hours.

Introduction
In the present day, our life style has become very convenient and comfortable by the advanced technology. The housing and facility systems using hot water pipes have been especially progressed in Japan. For example, the polymer electrolyte fuel cells (PEFC) cogeneration system has been commercialized in Japan. The number of commercialized PEFC residential cogeneration systems have reached over 150,000 units in total in July, 2016. The waste heat can be used for hot water supply and central heating. Hot water distribution pipes connecting a gas cogeneration system with the water heater and terminal appliances are very important. The pipes for hot water supply are installed with bent from the polymer electrolyte fuel cell to inside a house without using fittings. However, as it is hard and expensive to replace plastic pipes for hot water supply if they are damaged, the longer lifetime of the heating and hot water supply system is required for consumers and the reliable plastic pipes have been developed. Moreover, the observation of their damage or degradation of pipes has been difficult since they are less obvious in the early stage. Therefore, some unexpected failures were reported in Japan. In order to prevent field failures and accidents, it is necessary to evaluate the durability and to predict the lifetime of these materials and pipes. Evaluation of long-term performance on plastic pipes for heating and hot water supply should be clarified for their lifetime applications.

In our first study [1-7], two types of plastic pipes; the polybutylene (PB) pipes and the double-layer crosslinked polyethylene pipes (PEX2) for water and hot water supply were immersed in residual chlorine solution of 0 ppm, 5 ppm and 10 ppm at elevated temperatures of 80 °C for 10000 hours. As results, it was found that the elongation at break of the polybutylene (PB) pipes decreased after immersion for 5000 hours in 10 ppm chlorine solution.

In our second study [8-10], the tensile test and the thermal analysis were conducted to evaluate the effect of residual chlorine and the degradation of the polybutylene (PB) pipes and the double-layer crosslinked polyethylene pipes (PEX2) for a long time elapsed since the first report. As results, it was found that the yield stress of the polybutylene (PB) pipes and the double-layer crosslinked polyethylene pipes (PEX2) increased with increasing elapsed time in residual chlorine solution at 80 °C and the heat of fusion of the polybutylene (PB) pipes and the double-layer crosslinked polyethylene pipes (PEX2) also increased with increasing elapsed time in residual chlorine solution until 10000 hours. However, the heat of fusion did not decrease at the 30000 hours in spite of greatly decreasing the yield stress. On the other hand, the elongation at break of PB and PEX2 pipes decreased with increasing the heat of fusion of PB and PEX2 pipes until 10000 hours, and the elongation of break of PB and PEX2 pipes gradually increased at the 30000 hours as compared with that of at 10000 hours. And the oxidation induction time of both of the polybutylene (PB) pipes and the double-layer crosslinked polyethylene pipes (PEX2) dropped under 5 minutes after 15000 hours in every residual chlorine solution immersion.

In this study, the cracked time was studied in the residual chlorine solution immersion test for the bent polybutylene (PB) pipes and the bent double-layer crosslinked polyethylene pipes (PEX2) at 5 ppm and 10 ppm for 80 °C, at 5 ppm for 90 °C and at 5 ppm for 98 °C.

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And the cracked surface of the pipes was observed.

**Experimental**

**Test Materials**

Plastic pipes used in the study were polybutene (PB) pipe and double-layer crosslinked polyethylene (PEX2) pipe which are commercially available for hot water supply in Japan. The nominal 13 mm PB pipes and PEX2 pipes were used for the residual chlorine solution immersion test. Figure 1 shows the photographs of (a) polybutylene (PB) pipe and (b) double-layer crosslinked polyethylene (PEX2) pipes used in the experiment. The PEX2 pipe is composed of two layers as per Figure 2. Figure 3 shows the dimension of polybutene (PB) pipe and double-layer crosslinked polyethylene (PEX2) pipe.

![Figure 1. Plastic pipe photographs of (a) polybutylene (PB) pipe and (b) double-layer crosslinked polyethylene (PEX2) pipe for the residual chlorine solution immersion test.](image)

![Figure 2. The cross-section diagram of the double-layer crosslinked polyethylene (PEX2) pipe.](image)

![Table 1. The dimension of polybutene (PB) pipe and double-layer crosslinked polyethylene (PEX2) pipe.](table)

<table>
<thead>
<tr>
<th></th>
<th>PB pipe</th>
<th>PEX2 pipe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outer diameter</td>
<td>17 mm</td>
<td>17 mm</td>
</tr>
<tr>
<td>Thickness</td>
<td>2.1 mm</td>
<td>Outer : 0.3 mm (Non crosslinked) Inner : 2.1 mm (Crosslinked)</td>
</tr>
</tbody>
</table>

![Figure 3. The photograph of bent polybutylene (PB) pipe for residual chlorine solution immersion test (Six times the radius of the diameter of the pipe).](image)

![Figure 4. The photograph of the residual chlorine solution immersion test by using electric pots.](image)

![Table 2. The condition of residual chlorine solution immersion test and the bent radius of polybutylene (PB) pipe and double-layer crosslinked polyethylene (PEX2).](table)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Concentration of chlorine</th>
<th>Bent radius</th>
<th>Number of pipes</th>
</tr>
</thead>
<tbody>
<tr>
<td>80 °C</td>
<td>5 ppm</td>
<td>6 x OD</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>10 ppm</td>
<td>10 x OD</td>
<td>10</td>
</tr>
<tr>
<td>90 °C</td>
<td>5 ppm</td>
<td>6 x OD</td>
<td>10</td>
</tr>
<tr>
<td>98 °C</td>
<td>5 ppm</td>
<td>6 x OD</td>
<td>10</td>
</tr>
</tbody>
</table>

**Immersion tests**

The polybutylene (PB) pipes and the double-layer crosslinked polyethylene pipes (PEX2) were cut in predefined length. These pipes were bent in the middle of the pipe and secure the ends of the pipes for keeping the bent state. The stainless steel wire was used for holding the pipe bend. The bent radius was six times and ten times the radius of the diameter of the pipe. Figure 3 shows the photographs of the bent polybutylene (PB) pipe (In case of six times the radius of the diameter of the pipe). Table 2 shows the condition of the residual chlorine solution immersion test for the bent polybutylene (PB) pipes and the bent double-layer crosslinked polyethylene pipes (PEX2) at 5 ppm and 10 ppm for 80 °C, at 5 ppm for 90 °C and at 5 ppm for 98 °C.

![Figure 4. The photograph of the residual chlorine solution immersion test by using electric pots.](image)
Inner surface of the pipes and cracked surface was examined visually by using digital microscope, KEYENCE DIGITAL MICROSCOPE VHX-900.

**SEM examination**

Inner surfaces of the pipes and cracked surface was investigated with the SEM, JEOL JSM-6010LA.

**Thermal analysis**

The oxidation induction time (OIT) measurements were performed using a SHIMADZU DSC-60A differential scanning calorimeter (DSC). The OIT measurements were performed in the temperature range from 40 °C to 200 °C at a ramp of 50 °C/min under nitrogen atmosphere and the cell atmosphere was changed to oxygen at 200 °C. The four test samples were cut out from the cross section of the pipes. These samples were used for the OIT measurements performed as described in Figure 5 to evaluate the degree of their oxidative degradation.

**Results and Discussions**

**Immersion test**

Table 3 shows the cracked time and cracked number of the bent polybutylene (PB) pipes in the residual chlorine solution immersion test. It was found that the bent polybutylene (PB) pipes were cracked over for 36,000 hours at 5 ppm in 90 °C, over for 40,000 hours at 10 ppm in 80 °C and over for 44,000 hours at 5 ppm in 80 °C. Only the bent polybutylene (PB) pipes with six times radius the diameter of the pipe was cracked. The bent polybutylene (PB) pipes with ten times radius the diameter of the pipe at 80 °C was not cracked. And also the bent polybutylene (PB) pipes with even six times radius the diameter of the pipe at 98 °C were not cracked.

On the other hand, the bent double-layer crosslinked polyethylene pipes (PEX2) in the residual chlorine solution immersion test were not cracked at all over for 47,000.

**Observation**

Figure 6 shows the photograph of the bent polybutylene (PB) pipes in residual chlorine solution of 5 ppm at 80 °C. Figure 7 shows the photograph of cracked surface of the polybutylene (PB) pipes in residual chlorine solution of 5 ppm at 80 °C. Figure 8 shows the photograph of cracked surface of the polybutylene (PB) pipes in residual chlorine solution of 10 ppm at 80 °C. Several cracks were observed outside surface of the polybutylene (PB) pipes. Figure 9 shows the photograph of the bent double-layer crosslinked polyethylene pipes (PEX2) in residual chlorine solution of 5 ppm at 80 °C. Figure 10 shows the photograph of the bent surface of the double-layer crosslinked polyethylene pipes (PEX2) in residual chlorine solution of 5 ppm at 80 °C.

**Table 3.** The cracked time and cracked number of PB pipes in the residual chlorine solution immersion test.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Concentration of chlorine</th>
<th>Bent radius</th>
<th>Number of fracture</th>
<th>Time of fracture</th>
</tr>
</thead>
<tbody>
<tr>
<td>80 °C</td>
<td>5ppm</td>
<td>6 x OD</td>
<td>1</td>
<td>45,504</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10 x OD</td>
<td>1</td>
<td>44,064</td>
</tr>
<tr>
<td>10 ppm</td>
<td></td>
<td>6 x OD</td>
<td>3</td>
<td>40,008</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10 x OD</td>
<td>1</td>
<td>44,064</td>
</tr>
<tr>
<td>90 °C</td>
<td>5ppm</td>
<td>6 x OD</td>
<td>1</td>
<td>36,480</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10 x OD</td>
<td>1</td>
<td>44,880</td>
</tr>
<tr>
<td>98 °C</td>
<td>5ppm</td>
<td>6 x OD</td>
<td>0</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 5. Schematic illustrations OIT measurement.
Figure 9. The photograph of the bent double-layer crosslinked polyethylene pipes (PEX2) in residual chlorine solution of 5 ppm at 80 °C.

Figure 10. The photograph of the bent surface of the double-layer crosslinked polyethylene pipes (PEX2) in residual chlorine solution of 5 ppm at 80 °C.

Figure 11 shows the photograph of inner cracked surface of the polybutylene (PB) pipes after 44,064 hours in residual chlorine solution of 5 ppm at 80 °C. Figure 12 shows the photograph of opposite side cracked surface of the polybutylene (PB) pipes after 44,064 hours in residual chlorine solution of 5 ppm at 80 °C. These surfaces were wiped with ethyl alcohol for removing scale. Figure 13 shows the photograph of inner cracked surface of the polybutylene (PB) pipes after 40,008 hours in residual chlorine solution of 10 ppm at 80 °C. Figure 14 shows the photograph of opposite side cracked surface of the polybutylene (PB) pipes after 40,008 hours in residual chlorine solution of 10 ppm at 80 °C. These surfaces were not wiped with ethyl alcohol.

Figure 15 shows the photograph of cracked section and inner surface of the polybutylene (PB) pipes after 40,008 hours in residual chlorine solution of 10 ppm at 80 °C. These surfaces were not wiped with ethyl alcohol.

Figure 16 shows the photograph of inner surface of the outside curve of bent double-layer crosslinked polyethylene pipes (PEX2) after 47,000 hours in residual chlorine solution of 5 ppm at 80 °C. Figure 17 shows the photograph of opposite side of the outside curve of bent double-layer crosslinked polyethylene pipes (PEX2) after 47,000 hours in residual chlorine solution of 5 ppm at 80 °C. These surfaces were wiped with ethyl alcohol for removing scale.

The inner of the polybutylene (PB) pipe had many cracks at the cracked side and no cracks at the opposite the cracked side. This indicated that the outside curve of the bent polybutylene (PB) pipes was applied high load for polybutylene. It was considered that the cracked was caused by connecting a crack with another crack.

It was found that the bent polybutylene (PB) pipes were cracked at 5 ppm in 80 °C, at 10 ppm in 80 °C and at 5 ppm in 90 °C and the pipe had many small and large circumferential cracks. On the other hand, the bent double-layer crosslinked polyethylene pipes (PEX2) in the residual chlorine solution immersion test did not have the crack at all over for 47,000 hours.
Figure 16. The photograph of inner surface of the outside curve of bent double-layer crosslinked polyethylene pipes (PEX2) after 47,000 hours in residual chlorine solution of 5 ppm at 80 °C.

Figure 17. The photograph of opposite side of the outside curve of bent double-layer crosslinked polyethylene pipes (PEX2) after 47,000 hours in residual chlorine solution of 5 ppm at 80 °C.

Figure 18 shows the photograph of the SEM image of inner surface without scale of the outside curve of bent double-layer crosslinked polyethylene pipes (PEX2) after 47,000 hours in residual chlorine solution of 5 ppm at 80 °C. The scale was covered whole inner surface of the pipe. It was found that the scale surface on the inner surface of the pipe was cracked and the inner surface without scale was not cracked of the bent double-layer crosslinked polyethylene pipes (PEX2).

Figure 19. The photograph of the SEM image of inner surface with scale of the outside curve of bent double-layer crosslinked polyethylene pipes (PEX2) after 47,000 hours in residual chlorine solution of 5 ppm at 80 °C.

The strain $\varepsilon$ was subjected on the bent pipes as can be seen in Figure 20. The strain $\varepsilon$ was approximated by the following formula.

$$\varepsilon = \frac{(R + D/2)\theta - R\theta}{R\theta} = \frac{D}{2R}$$

Therefore,

- In case of six times the radius of the diameter of the pipe, $\varepsilon_{6\times OD} = 0.083$
- In case of ten times the radius of the diameter of the pipe, $\varepsilon_{10\times OD} = 0.05$

The stress $\sigma$ was able to get from the stress-strain diagram of the polybutylene (PB) at 23 °C. Each stress as follows.

- In case of six times the radius of the diameter of the pipe, $\sigma_{6\times OD} = 9.24$ MPa
- In case of ten times the radius of the diameter of the pipe, $\sigma_{10\times OD} = 2.52$ MPa

After the immersion test, the bent radius was changed to eight times the radius of the diameter from six times the radius of the diameter by stress relaxation. As a result, the following residual stress was generated on this bent polybutylene (PB) pipes.

- In case of eight times the radius of the diameter of the pipe, $\sigma_{8\times OD} = 7.20$ MPa
- In case of six times the radius of the diameter of the pipe, $\sigma_{6\times OD} - \sigma_{8\times OD} = 9.24 - 7.20 = 2.04$ MPa

When the bent radius was six times the radius of the diameter, the high stress was generated on the bent polybutylene (PB) pipes and the bent double-layer crosslinked polyethylene pipes (PEX2). It was found that the bent polybutylene (PB) pipes were cracked earlier than the bent double-layer crosslinked polyethylene pipes (PEX2), because the polybutylene (PB) pipes more...
affected by the chlorine solution than the crosslinked polyethylene pipes.

Seven of the bent polybutylene (PB) pipes were cracked at 10 ppm in 80 °C and the three-bent polybutylene (PB) pipes were cracked at 5 ppm in 80 °C. It was considered the effect of the concentration of chlorine solution.

![Figure 20. The strain model of bent pipe.](image)

And it was considered no effect of the temperature, because that the only two-bent polybutylene (PB) pipes were cracked at 5 ppm in 90 °C. No bent polybutylene (PB) pipes were fractured at 5 ppm in 98 °C. This is because that the concentration of chlorine solution at 98 °C decreased about four times rapidly than 80 °C. Figure 21 shows the result of residual chlorine concentration measurement.

These results showed that the cracked of the bent polybutylene (PB) pipes was affected by the content of chlorine solution than the high temperature.

![Figure 21. Result of residual chlorine concentration measurement.](image)

As a result, it was found that the three-bent polybutylene (PB) pipes were cracked over for 44,000 hours at 5 ppm in 80 °C, seven of the bent polybutylene (PB) pipes were cracked over for 40,000 hours at 10 ppm in 80 °C and the 2-bent polybutylene (PB) pipes were cracked over for 36,000 hours at 5 ppm in 90 °C. Only the bent polybutylene (PB) pipes with six times radius the diameter of the pipe was cracked. The bent polybutylene (PB) pipes with ten times radius the diameter of the pipe at 80 °C was not cracked. And the bent polybutylene (PB) pipes with even six times radius the diameter of the pipe at 98 °C was not cracked. On the other hand, the bent double-layer crosslinked polyethylene pipes (PEX2) in the residual chlorine solution immersion test at all temperature were not cracked at all over for 47,000.

In our second study, the oxidation induction time of both of the polybutylene (PB) pipes and the double-layer crosslinked polyethylene pipes (PEX2) dropped under 5 minutes after 15,000 hours in every residual chlorine solution immersion. Figure 22 shows the OIT of polybutylene (PB) and double-layer crosslinked polyethylene pipes (PEX2) pipes with the elapsed time after residual chlorine solution, hot water immersion at 80 °C. At this period, the antioxidants did not work well enough to be used to extend the lifetime.

![Figure 22. OIT plots of (a) PB pipes and (b) PEX2 pipes for elapsed time at various chlorine concentration.](image)

Conclusions

In this study, the residual chlorine solution immersion test for the bent polybutylene (PB) pipes and the bent double-layer crosslinked polyethylene pipes (PEX2) was conducted at 80 °C, 90 °C and 98 °C. In the residual chlorine solution immersion test, the concentration of the residual choline solution is 5 ppm and 10 ppm for 80 °C, 5 ppm for 90 °C and 5 ppm for 98 °C.
The bent polybutylene (PB) pipes were cracked under the chlorine solution in 21,000 hours and 25,000 hours after loss of effect of antioxidants.

On the other hand, the double-layer crosslinked polyethylene (PEX2) pipes were not cracked in 32,000 hours after loss of effect of antioxidants. The double-layer crosslinked polyethylene pipes (PEX2) was thought to be less affected by the chlorine and temperature.

At the beginning of this study, we thought that the residual chlorine solution immersion test using bent pipes was able to accelerate the deterioration could be the easy evaluation method. But it took much time to get the results back from this immersion test beyond expectation. As the future study, we are going to consider the easy accelerated evaluation method for resistance property of the plastic pipes for residual chlorine solution and the effect of scale on the pipes for lifetime of the plastic pipes.

References