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CAN PE AND PVC GAS DISTRIBUTION PIPES WITHSTAND THE IMPACT OF SUSTAINABLE GASES?

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SHORT SUMMARY
The replacement of fossil fuels like natural gas by sustainable gases such as biogas and hydrogen can mitigate global warming. There has been some debate about the impact of sustainable gases on the materials used in the gas grid. An extensive study of the behaviour of PE, PVC, POM and rubber materials was therefore conducted. The most important conclusion from this study is that Dutch gas distribution grids will not be degraded by sustainable gas provided that the gas is dry.

KEYWORDS
Distribution, Renewable, Sustainable, Natural gas, Biogas, Biomethane, PE, PVC, Rubber, Pipe, Joints

ABSTRACT
To evaluate the effects of different types of renewable gases on PE and PVC piping systems in existing gas networks, Kiwa Technology participated in a Dutch research programme, Energy Delta Gas Research (EDGaR). The goal was to determine whether sustainable gases could degrade the PE and PVC pipes, rubber seals and polymeric couplers used in the Dutch gas distribution grid to an unacceptable extent.

A literature survey was first conducted to identify the chemical components in sustainable gases, the concentrations of the components, and the possible effects on the plastic pipe and coupler materials. It was found that some combinations of polymers and gas components could lead to environmental stress cracking (ESC) or an acceleration of known degradation processes.

Extensive exposure tests were then conducted with environmental stress cracking test rigs built and designed for this purpose to study combinations of plastic pipe materials gas components in realistic gas grid conditions such as concentrations and *applied pressure. A total of 1300 polymeric samples were tested using twelve different gas compositions.*

Finally, after two years of exposure, the environmental stress cracking samples were subjected to non-destructive and destructive testing.

This paper presents the results: rubber, PE and PVC pipes can withstand the impact of sustainable gases and POM is degraded by sustainable gases.

INTRODUCTION

The use of renewable gases (such as biomethane, biogas and synthetic natural gas) is increasing worldwide, in particular to reduce greenhouse-gas emissions. Questions have been raised about the impact of these gases on materials in gas grids and about whether the current specification for biomethane is still valid or whether it should be amended. In this context, Kiwa Technology has participated in a Dutch research programme, Energy Delta Gas Research (EDGaR), [1] in order to evaluate the effects of different types of renewable gases on the piping systems used in Dutch gas networks and subsequently to issue recommendations about how to work with sustainable gases in the near future. Although both metallic and polymeric pipe materials were studied, this paper will focus on polymeric materials only.

The composition of sustainable gases can vary depending on the production methods and feeds used and the gases may contain an enormous variety of different chemical components. Gases with these components may lead to unacceptable degradation in PE and PVC pipes, couplers and rubber seals.

The EDGaR research programme was initiated in 2010 to establish a clear understanding of the susceptibility of the grid to these gas components. This paper presents the results of the programme.

EXPERIMENTAL

The research programme consisted of three stages:

1. a literature survey;
2. the exposure of gas grid materials to deleterious gas components;
3. an evaluation of the effects of sustainable gases on gas distribution materials.

The literature survey was conducted to identify the materials in Dutch gas distribution grids, the extent to which they are used, the chemical components present in sustainable gases, the concentrations at which they occur and the effects of the known sustainable gases on the materials used in the grids.

Exposure tests were designed, constructed and initiated [2] [3] to investigate the degradation of the used PE, PVC, coupler and rubber materials by the different chemical compounds found in the literature survey. The impact of sustainable gases on polymeric materials was studied in environmental stress cracking (ESC) experiments. Many different ESC methods have been described in the literature and they have been standardised [5] [6] [7]. Environmental stress cracking methods in which samples were taken from pipes and fittings were designed specifically for the present study: dog bones under constant load (Figure 1), rings in a U-clamp (Figure 2), dog bones in a Marbone clamp (Figure 3) and rubber rings over oversized pipes (Figure 4). Particular attention was paid during the design of the tests to obtaining reproducible and reliable results.

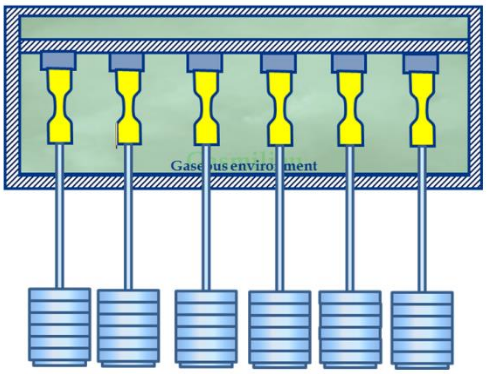

Figure 1 – Schematic view of the constant load equipment for testing PE and PVC samples

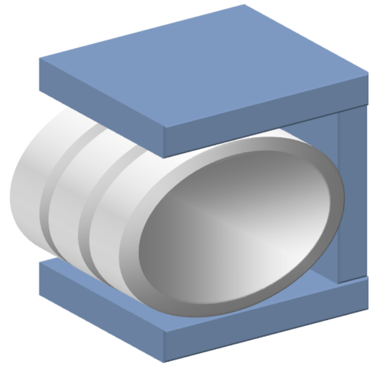

Figure 2 – Principle of a U-clamp test on PE and POM rings

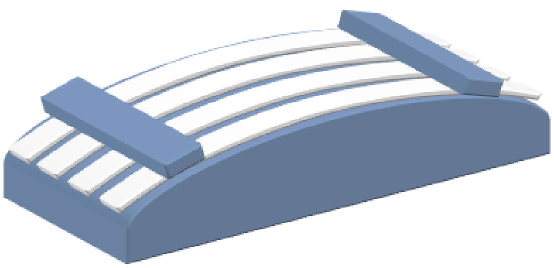

Figure 3 – Principle of a Marbone clamp test on POM tensile test bars

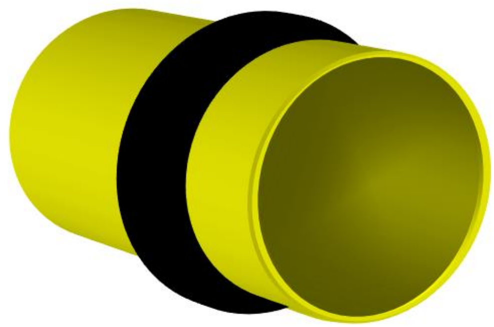

Figure 4 – Set-up for exposing stressed rubber rings to a particular gaseous environment

Table 1 lists all the different polymeric materials used in the Dutch gas distribution grid and the ESC method used. The PE and PVC samples were taken directly from pipes. In the case of old materials (such as first-generation PE and PVC-U pipes), this pipes had to be dug out of the Dutch gas distribution network. New materials were used in the case of other PE and PVC materials. The rubber materials were taken from the sealing rings of new PVC couplers. The POM rings used in the U-clamps were milled from new POM couplers. The POM dog bones for the Marbone clamp were not taken from couplers but punched out of sheets of virgin POM material.

Table 1 –Types of materials studied, condition of the materials and the ESC methods employed

Polymeric materials		**Condition of material**	**ESC methods**
PE	First-generation PE50	Old and used	Constant load & U-clamp
	Second-generation PE80	New	Constant load & U-clamp
	Third-generation PE100	New	Constant load & U-clamp
PVC	PVC-U – type 1	Old and used	Constant load
	PVC-U – type 2	Old and used	Constant load

	PVC-HI – type 1	New	Constant load
	PVC-HI – type 2	New	Constant load
Rubber	SBR	New	Ring over pipe
	NBR	New	Ring over pipe
POM	Homopolymer	New	U-clamp & Marbone clamp
	Copolymer	New	Marbone clamp

Table 2 shows the different materials and the gaseous environments studied. The chemical compositions of the gaseous environments chosen, are based on the "white spots" determined in the literature survey. The concentrations in these gaseous environments are based on the values given for the limiting concentration values for biomethane [7] and on the maximum concentrations found in raw gases/biogases [8]. An explanation of why some concentrations were used can also be found in Table 2. A model gas was used for a group of gaseous components in two cases.

Of all the components containing chlorine and fluorine that may be present in the different gases, dichloromethane (DCM) is known to be one of the most aggressive halogenated organics in terms of its effect on PVC [9]. It was therefore decided to use DCM as the model gas (worst case) for all gases containing halogen.
Sulphur-containing components may also be present in a wide variety of gases. H_2S is considered to be the most aggressive of these components and the one associated with the highest risk of adverse effects on polymeric materials. It was therefore decided to use H_2S as the model gas for all gases containing sulphur and to investigate the effects of this gas only.

Table 2 – Polymeric materials, the investigated gaseous environments and explanation of these concentrations

Polymeric materials	**Gaseous environments**	**Explanation of the concentrations**
PE, PVC, rubber, POM	100 vol% N_2	Nitrogen was selected as the matrix gas and 100 vol% N_2 is therefore needed for reference purposes.
Rubber	5 ppm H_2S	The maximum allowed concentration of H_2S in biomethane is 5 ppm [7].
PE, PVC, Rubber, POM	160 ppm H_2S	This concentration of 160 ppm H_2S for raw gas/biogas was selected by the Dutch Distribution System Operators (DSO) as being acceptable (= five times the MAC value for eight hours). The Dutch DSOs have decided that it is not safe to operate the grid above these concentrations [8] .
Rubber	80 ppm H_2S	This concentration is between those in biomethane and raw gases/biogases.
PE, PVC, Rubber, POM	75 mg/m^3 DCM	The maximum allowed concentration of halogen-containing compounds in biomethane is 75 mg/m^3 [7].
PE, PVC, Rubber,	1000 mg/m^3 DCM	The maximum concentration of halogen-containing chemicals in raw gas/biogas is 1000 mg/m^3 [8].

POM		
Rubber	550 mg/m^3 DCM	This concentration is between those in biomethane and raw gases/biogases.
PE, PVC, Rubber, POM	100 ppm NH_3	The maximum concentration of NH_3 found in raw gas/biogas is 100 ppm [8].
PVC, Rubber, POM	59 vol% CO_2	The maximum concentration of CO_2 found in raw gas/biogas is 59 vol% [8].
POM	3 ppm HCl	The maximum allowed concentration of HCl in biomethane is 1 ppm * [7].
POM	62 vol% H_2	The maximum concentration of H_2 found in raw gas/biogas is 62 vol% [8].
Rubber	Natural gas	G-gas** is needed for reference purposes.
Rubber	2 vol% propene	The maximum concentration of propene found in raw gas/biogas is 2 vol% [8].

* *Several gas mixture producers stated that it is impossible (with current techniques) to produce a constant gas mixture of 1 ppm HCl. A concentration of 3 ppm was therefore used.*

** *G-gas: the natural gas currently used in the Netherlands.*

The gas pressures used in the Dutch gas distribution grid are predominantly between 30 and 100 mbar(g) and between 4 and 8 bar(g). It was therefore decided to perform the experiments at gas pressures of 30 mbar(g) and 8 bar(g). After two years of exposure, the environmental stress cracking samples were subjected to non-destructive (visual and dimensional changes) and destructive testing. Table 3 provides an overview of the destructive tests performed on the polymeric samples.

Table 3 – Destructive tests performed on the polymeric materials after exposure to components of sustainable gases for a period of two years

Material	**Samples**	**Destructive testing**
PE	Dog-bone samples	Tensile testing in accordance with ISO 6259-3
	Ring samples	Ring tensile testing in accordance with ISO 8496
PVC	Dog-bone samples	Impact testing in accordance with ISO 8256, but over a temperature range from -27˚C to +50˚C [10].
Rubber	Ring samples	Tensile test ISO 37
		Hardness test ISO 48
POM	Ring samples	Ring tensile testing in accordance with ISO 8496
	Dog-bone samples	Tensile test in accordance with ISO 527

Fusibility after the possible absorption of certain gaseous components by PE materials was also tested. Two principal gas components were investigated:

- A mixture of 59 vol% CO_2 in a matrix of N_2
  PE can absorb large amounts of CO_2. This can have a negative impact during welding.
- A mixture of different siloxanes (L1, D4 and D5)
  PE does not absorb siloxanes well. However, the siloxanes can form a layer on the pipe wall. It is known that these siloxanes are hard to remove from the welding zone and that they can have a negative impact during welding [9].

The effects of CO_2 absorption were tested by exposing the PE pipes to the CO_2 and N_2 mixtures at a slight overpressure at room temperature for a period of two years. After two years of exposure, the PE pipes were welded. The quality of the welds were tested destructively.

In order to investigate the formation of siloxane layers and the effect that this has on the fusibility of PE pipes, the pipes were exposed to a mixture of pure siloxanes. The PE pipes were sprinkled with a mixture of organo-silicons (L1, D4 and D5) on each working day for a total of 90 days. The pipes were then taken out and welded together. The quality of the joints was tested destructively and non-destructively.

The tests described above require specially-designed test rigs. This was a challenging operation. The test rigs needed to be able to hold a large number of samples and required special safety measures due to the severe toxicity of some of the gases and the elevated pressures of up to 8 bar (see Figure 8). The concentrations of the chemical components had to be maintained at very constant levels throughout the test period of two years. This was in itself challenging. Figure 5 shows a detail of the test rig for the samples under constant load and constant strain Figure 7 and Figure 6 shows the complete installation used for testing.

Figure 5 – Constant load experiments on PVC samples

Figure 6 – Full-scale set-up (30 mbar(g)) used to determine the effects of sustainable gases on polymeric materials

Figure 7 – Opened test rig with several ESC samples of PE and rubber

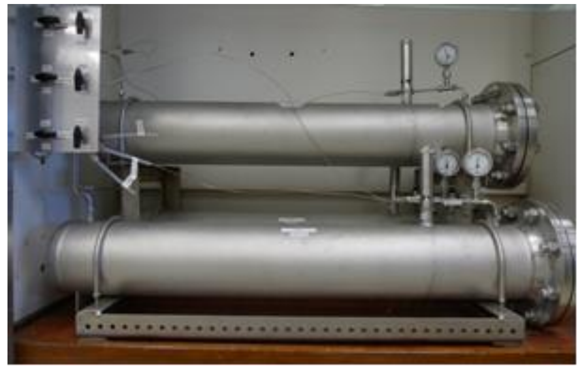

Figure 8 – Test rig configuration for high pressure applications (up to 8 bars)

Field experiments were conducted in addition to the laboratory tests to determine whether biomethane has any unforeseen adverse effect. The field experiments involved inserting two rigs in the Dutch distribution grid, one directly after a biomethane feed (Figure 9) and the other in a pipeline transporting G-gas quality only (Figure 10). The G-gas test rig was installed for reference purposes. The test rigs were filled with the same materials as used in the laboratory experiments, where applicable under the same applied stresses. After exposure for two years, the materials exposed to G-gas and biomethane were tested using a method similar to the protocol for the lab samples to identify any degradation in quality.

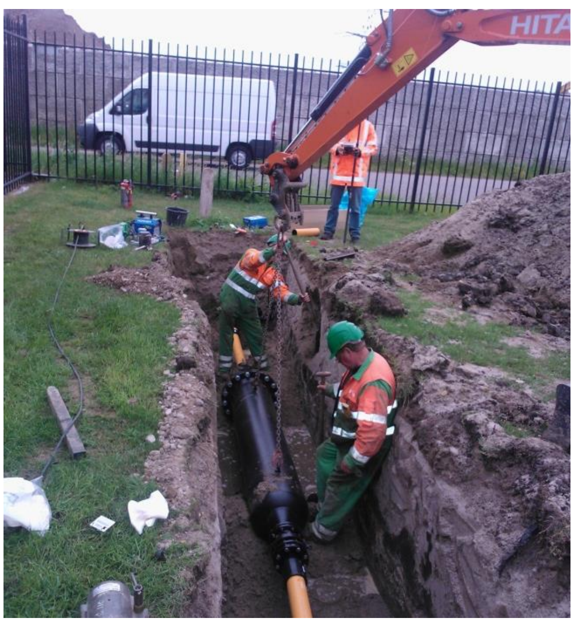

Figure 9 – Test rig for biomethane

Figure 10 – Test rig for G-gas

RESULTS AND DISCUSSION

The literature review revealed that some combinations of polymers and gas components may lead to environmental stress cracking (ESC) or an acceleration of the known degradation processes [12] [8] [13]. No data was available for other combinations of polymers and gas components, which were therefore prioritised in the selection for the experimental part of the study.

The tests demonstrated that ESC does not lead to failure after two years of exposure to gas component concentrations comparable to those measured in sustainable gases in the Netherlands.

There was no acceleration in the known degradation processes in almost all polymers (with the exception of POM) [14] [15] [16].

The results for POM were the exception: the combination of hydrochloric acid (HCl) and water (H_2O) resulted in severe degradation. The concentration of hydrochloric acid in the test gas was 3 ppm, which is very low. Some of the results for this test are shown in Figure 11 and Figure 12. POM is found in full-end-load resistant mechanical fittings used in gas service lines and for sprocket wheels and spindles in domestic gas meters and in service regulators.

Problems caused by sustainable gases containing hydrochloric acid can be avoided by removing the water to a dew point of approximately -40 ˚C.

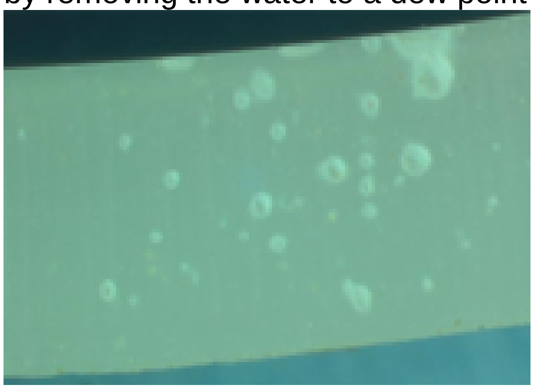

Figure 11 –Degradation of POM by HCl/H_2O

Figure 12 – Magnification showing degradation of POM by HCl/H_2O

The results of this study (both the literature review and the experimental work) are summarised in Table 4. The first row shows the gas components present in sustainable gases and the first column lists the most important polymeric materials used in the Dutch gas distribution grid. The results for the polymeric materials (PVC, PE and POM) and the rubber materials (SBR and NBR) are shown in green. They demonstrate that these materials are almost always safe for use with sustainable gases, with the exception of the combination of POM and hydrochloric acid and water referred to above.

Joints

In addition to the literature review and the experiments performed with pipe materials, this study also included an investigation of the effects of sustainable gases on both existing and new joints. The latter are particularly important in terms of maintaining the pipe system, and particularly for leak repairs. Commonly-used joints were therefore studied. The results showed that leaks in electro-fusion joints can also be repaired in pipe systems with sustainable gases. Furthermore, no degradation was observed on butt fusion joints made of PE pipes exposed to a mixture of pure siloxanes and PE pipes exposed to CO_2/N_2 gas mixtures.

It is important to note that several gas components (hydrogen cyanide (HCN) and carbon monoxide (CO)) were not tested or were not tested at high concentrations (> 160 ppm hydrogen sulphide) because these gases are toxic for humans, making laboratory experiments dangerous. It is therefore not known what effect these toxic gases have on polymeric materials.

Table 4 shows that the answer to the research question depends on the presence of water in the gas distribution grid. This was also one of the main outcomes of the study of metal materials. In the absence of water, there is no degradation of the polymeric and metal materials used.

Only a few restrictions on the maximum allowable concentrations of gas components in sustainable gases are needed in preparation for the transportation of future sustainable gases in the gas distribution grid.

The mains steps to reduce the risk of water entering the gas distribution grid include:

- Raising the distribution pressure to 100 mbar(g).
  The risk of groundwater entering the gas grid (water ingress) is significantly lower at 100 mbar(g) gas pressure than at 30 mbar(g) gas pressure.
- Reducing the water dew point of the gas at gas entry points. In other words, the gas must be dried before it enters the gas distribution grid. This solution should be given a prominent role in the processing of sustainable gases.

In addition to drying the gas to remove water, it is also important to remove any liquid hydrocarbons and aromatic hydrocarbons that may be present. The literature study showed that high gas concentrations and liquid aromatic hydrocarbons are known to have a negative effect on the mechanical properties of polymeric materials. At present, only traces of aromatic hydrocarbons are found in sustainable gases. The concentration of aromatic hydrocarbons should be limited to 800 ppm to prevent future extremes. The maximum concentration measured in G-gas in the Dutch gas distribution grid in the last ten years was 800 ppm and it did not lead to any material degradation.

If the presence of water cannot be ruled out, the concentration of certain gas components should be limited. The maximum allowable concentrations of HCl should to be limited to less than 0.1 ppm.

The highest concentration of hydrogen investigated was 20 mol%. It is not yet known what effect higher concentrations may have and they should therefore be avoided.

As described above, limiting values for carbon monoxide and hydrogen cyanide should be as low as possible due to the toxicity of these components.

The final reports [16] [17] [18] for these studies are available on the Kiwa Technology website.

CONCLUSIONS

The effect of various components in sustainable gases on the plastic materials used in the Dutch gas distribution grid is summarised in Table 4

Table 4 - Results of the experiments (including the results of the literature review)

<table>
<tr><th></th><th>Components containing sulphur</th><th>H_2S</th><th>Mercaptans</th><th>Odorant</th><th>Ammonia</th><th>Components containing chlorine</th><th>Components containing fluorine</th><th>HCl</th><th>HCN</th><th>CO</th><th>CO_2</th><th>Hydro-carbons</th><th>Aromatic hydro-carbons</th><th>O_2</th><th>H_2</th></tr>
<tr><td>PVC</td><td colspan="2">none
(up to 160 ppm)</td><td colspan="2">probably none</td><td colspan="3">None</td><td colspan="2">probably none</td><td>unknown</td><td>none</td><td colspan="2">none, unless liquid</td><td>none</td><td>none (up to 20 mol%)</td></tr>
<tr><td>PE</td><td colspan="2">none
(up to 160 ppm)</td><td colspan="2">probably none</td><td colspan="3">None</td><td colspan="2">probably none</td><td>unknown</td><td>none</td><td colspan="2">none,
unless liquid</td><td>none</td><td>none (up to 20 mol%)</td></tr>
<tr><td>POM</td><td colspan="2">none
(up to 160 ppm)</td><td colspan="2">probably none</td><td colspan="3">None</td><td>water</td><td colspan="2">unknown</td><td>none</td><td colspan="3">probably none</td><td>none</td></tr>
<tr><td>N BR</td><td colspan="2">none
(up to 160 ppm)</td><td colspan="2">probably none</td><td colspan="3">None</td><td colspan="2">probably none</td><td colspan="2">none</td><td colspan="2">none,
unless liquid</td><td colspan="2">none</td></tr>
<tr><td>SBR</td><td colspan="2">none
(up to 160 ppm)</td><td colspan="2">probably none</td><td colspan="3">None</td><td colspan="2">probably none</td><td colspan="2">none</td><td colspan="2">none,
unless liquid</td><td colspan="2">none</td></tr>
</table>

legend

	=	The effect is not known, but is expected to be very small or non-existent.
	=	This component in wide-band gas has no effect on materials.
	=	The effect is not known.
	=	Deleterious effects are to be expected in some conditions.

The most important conclusion from this study is that Dutch gas distribution grids will not be degraded by sustainable gas provided that the gas is dry.

ACKNOWLEDGMENTS

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