TRANSPORT OF HYDROGEN WITH POLYETHYLENE NATURAL GAS PIPES

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Summary: This paper concerns the effects of hydrogen transport in polyethylene (PE) gas pipes previously used for transport of natural gas, as well as the effects of reference pipes that have not been exposed, on the chemical and mechanical properties of the PE pipes.

Abstract: As is the case with all fossil energies, natural gas reserves are limited, and it's commonly admitted that the production peak before depletion is expected to be reached during the coming decades.

Research concerning possible alternative sources of energy to natural gas for the future is therefore ongoing; one candidate, offering many advantages, is hydrogen gas.

One question that has risen is whether or not the existing natural gas pipe network could be used also for the distribution of hydrogen gas.

As PE is currently the most popular material worldwide for natural gas distribution, a study of the future possible usage of existing polyethylene PE80 and PE100 natural gas pipes in Denmark has been performed by the Danish Gas Research Centre with analytical support from Borealis AB in Stenungsund. The study has now been in progress for more than four years with pure hydrogen flow in a pilot assembly in Denmark.

An extensive study regarding many mechanical and chemical properties of several different PE80 and PE100 of different production years as well as a pre-use as gas pipes for natural gas transport has been performed. No evidence has been found of any reaction or degradation of the mechanical properties of the PE pipes from coming into contact with hydrogen gas. The possibility of using PE for hydrogen transport, according to this investigation, appears viable.

Introduction:

It has become ever clearer that the resource of natural gas is an energy source which will be less important in the future due to limitations in natural reserves. In order to prepare for the future, the gas industry is looking at alternative fuel gases, one of which is hydrogen.

A dominant part of the natural gas distribution grid today consists of PE pipe due to its excellent track record as a reliable piping material with minimal problems and maintenance (see also References 4 to 6). The reason for this are its inherent properties such as its corrosion free nature, the possibility to create fully weldable systems, its high ductility and excellent low-temperature properties.

In order to prepare for future use of hydrogen as a fuel gas, it became evident to the Danish Gas Research Centre that very little information existed regarding the compatibility between long-term exposure and transport of hydrogen in PE gas pipelines. A programme was

therefore set up to study the transport in a small-scale pilot grid at the research centre in Hörsholm, Denmark.

Borealis, one of the biggest suppliers of raw material from polyethylene for the production of pipes (e.g. pressure pipes for gas distribution), volunteered to provide analytical services for the determination of any compatibility problems between PE pipes and hydrogen under long-term exposure.

Sample programme and materials:

The programme was devised so that part of the grid was to be dug up each year, and an analysis was performed of the pipes. In this way, any form of influence on the integrity of the PE pipe would be detected. The pipes were analysed before exposure to hydrogen, then dug up after 1 year, 2 years, 3 years and 4 years of exposure. Some of the pipes were virgin pipes and some had also previously been used in the Danish natural gas network for 4 years (PE100), 5 years (PE80) and 20 years (PE80), since there was a need to get insight into whether or not the existing pipe lines' previous use as natural gas transport pipes had influenced the use of them for hydrogen gas transport. Lengths of pipes were cut out of the Danish natural gas grid and replaced. The pipes were then fitted into the pilot grid in Hörsholm and subjected to H_2 and, of course, were dug up as described above.

Experiments and evaluations

After each year of exposure to hydrogen gas and its references, the planned experiments was to determine if there had been any 1) Structural changes in the polymer, 2) Consumption of antioxidants, 3) Change of tensile properties, 4) Change of slow crack growth properties of the material, or 5) Change of MFR/FRR. The reason for this choice is that if no influences are detected in these properties, then one can assume that the media and polymer pipe are compatible and can safely be used, as seen from a polymer structure-property-pipe property point of view.

Samples used in the analysis there pre-history and year of making

The samples consist of three distinctly different materials, namely 1) a yellow solid wall s.c. PE80 medium-density polyethylene (PE80 MDPE), 2) An orange solid wall s.c. PE100 high-density polyethylene (PE100 HDPE), hereinafter called PE100 type I, 3) A natural coloured pipe with an orange outer protective layer; the natural coloured material is a s.c. PE100 high-density polyethylene (PE100 HDPE), hereinafter called PE100 type II.

Determination of structural changes:

Pressure pipe PE polymers are high molecular weight materials with a broad molecular weight distribution. The physical properties of the polymer determine, to a large extent, the high molecular weight portion of the material. There are two main ways of determining the structure, molecular weight and molecular weight distribution. It can be determined by Size Exclusion Chromatography (SEC alt GPC) or it can be determined by rheology. Since we are to analyse high molecular weight materials with a broad molecular weight distribution, the choice fell upon rheology since this is more sensitive to changes in the high molecular

portion, and these changes are coupled to physical properties of the material. In these rheological measurements, one can define certain indexes. In this study, we have chosen to use $\eta_{2,7KPa}$ which corresponds to the average molecular weight Mw, $SHI_{2,7/210KPa}$ which corresponds to the molecular weight distribution MWD as well as η_{747Pa} which roughly correspond to the high molecular weight tail Mz (see Reference 1, 2, 3).

Determination of oxidative resistance – consumption of antioxidants:

In order to detect interaction between the transported medium and antioxidant (the pipe grades contain mainly phenolic antioxidants), the so-called Oxygen Induction Time (OIT, acc EN728) was chosen as it gives a quick and reliable measurement of the oxidation power of the additivation in the polymer. This has been determined at two temperatures to increase the accuracy of the determination. However, many gas pipe materials contain UV-stabilisers, and they act also as antioxidants at temperatures below 120°C. Since the analysis is performed at 200°C and 210°C, this capability is not captured. However, the analysis will show an interaction between the antioxidant and transported media, and the antioxidative power will be at least that shown.

Determination of changes in tensile properties:

In order to detect changes in the basic mechanical properties of the pipes, we have chosen to test the pipes according to ISO 527-2/1B and have determined yield point, break point, elongation at break as well as the tensile modulus of the pipe.

Determination of changes in slow crack growth:

In order to be able to use specimens prepared out of the pipes, we have chosen a method called CTL (ISO 6252-1992) fitted with notches according to ASTM 1473 F of 40% notch depth. The test was performed at 5 MPa and 60ºC in a 10% solution of Igepal 720 in water.

Determination of MFR/FRR:

In order to determine any changes in the basic parameters, MFR5 and FRR21/5 measurements according to ISO 1133 were performed (However not referred to in this report, as there was no changes whatsoever).

Further determination:

In order to detect any prior negative influence from the pipe extrusion, a measurement of the carbonyl index (i.e. the surface oxidation of the inner surface of the pipes) was performed. The surface oxidation was measured with the Fourier Transform Infra Red (FTIR) technique.

Results:

Surface oxidation:

All pipes where tested with FTIR in order to check if surface oxidation was present. No sample showed any evidence of surface oxidation.

Basic quality level of pipes of different manufacturing years:

During the investigations, we have found that there are basic quality level differences between pipes of different manufacturing years. This leads sometimes to an impression that there might be a certain relation between exposure time to H_2 or previous usage of the pipe as a natural gas pipe. However, as can be seen below, there are basic quality level differences between pipes from different manufacturing years (see Figures 1 and 2). Since pipes of these different manufacturing dates in some diagrams are mixed, in some of the exposure experiment evaluations, we receive a larger scatter than normally would be received.

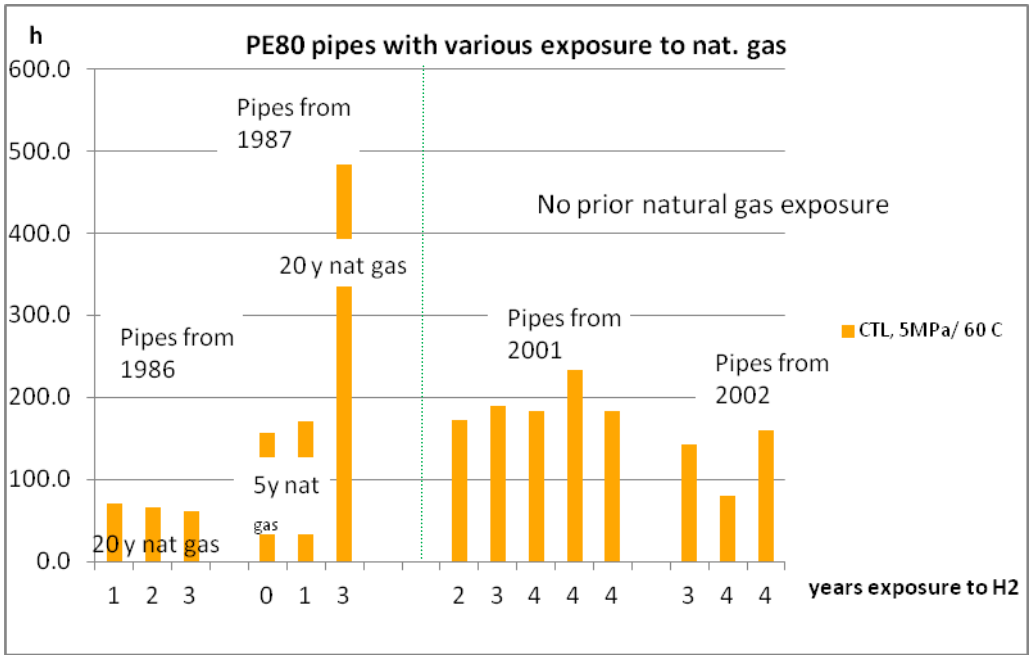


Figure 1: CTL test resistance to slow crack growth of PE80 pipes of different manufacturing years.

This basic variation in quality level is most likely due to the polymer manufacturing process, since no detectable surface oxidation or other quality problems with the pipes can be found. Please also note that there is one outlier in performance among the pipes manufactured in 1987; it has not been possible to determine with a high level of accuracy if this is due to the polymer manufacturing or an unusual variation in testing (however not likely).

Similar variations can also be seen in the rheology (i.e. as previously explained the basic structure of the material).

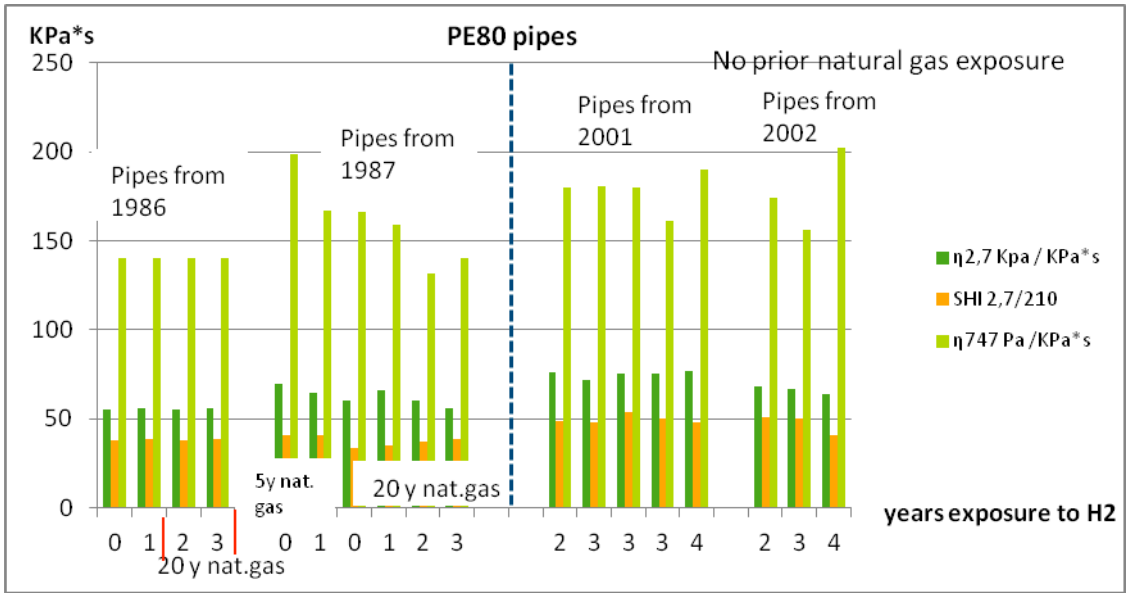


Figure 2: Rheological results of PE80 pipes of different manufacturing years.

So what this diagram reveals is that depending upon the manufacturing year, there are differences in molecular weight, Mw, molecular weight distribution, MWD, and high molecular weight portion. These differences are not very big, however, in the coming text regarding results, it may appear that way, e.g. the contact with hydrogen for prolonged times may increase the Mw ($\eta_{2,7KPa}$) and Mz (η_{747Pa}). This is a mere illusion and depends on the basic quality level difference of the polymer manufactured in different years (see Fig. 3).

This problem has not arisen in the PE100 samples since the number of different manufacturing years are much fewer and closer together, and there are two different kinds of samples, one single wall coloured through orange PE100 and one natural coloured PE100 with an orange protective outer layer. The two PE100 samples have been separated, analysed and reported individually.

PE80 MDPE results

Rheology:

As can be seen in Figures 3 to 5 below, there is no indication of any structural changes in the PE80 samples due to the exposure to hydrogen transport. It is also shown that this is true also if the samples have been previously used as pipes for natural gas transport for five or twenty years (see Figures 4 and 5). What is even more interesting is that pipes that have been used for twenty or five years as natural gas transport pipes show no evidence of any structural changes compared to an unused reference (see Figures 4 and 5). The scatter seen in the diagram can be solely attributed to the difference in manufacturing year/polymer manufacturing differences.

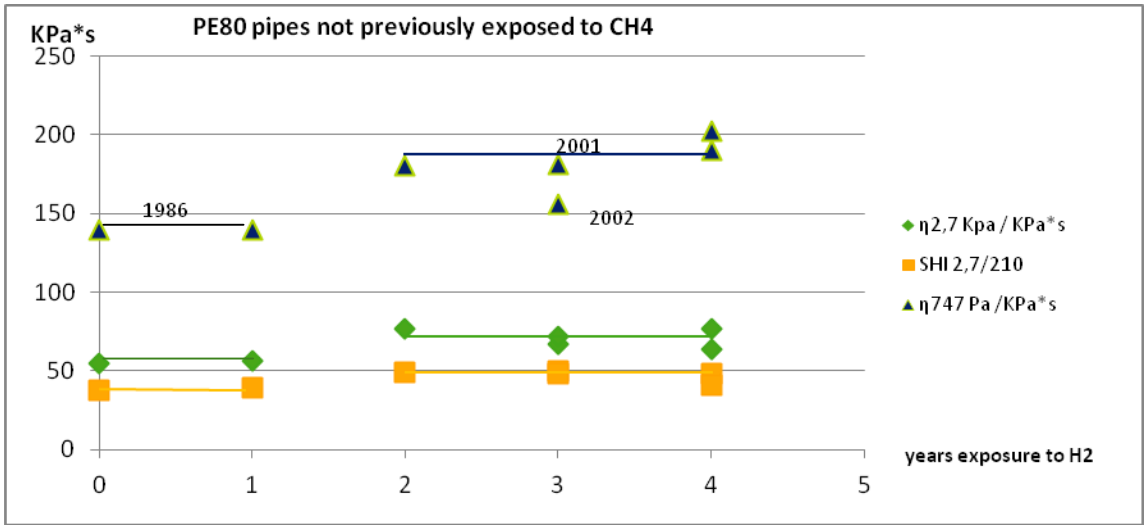


Figure 3: Rheology of PE80 pipes used for transport of H2 in the pilot grid.

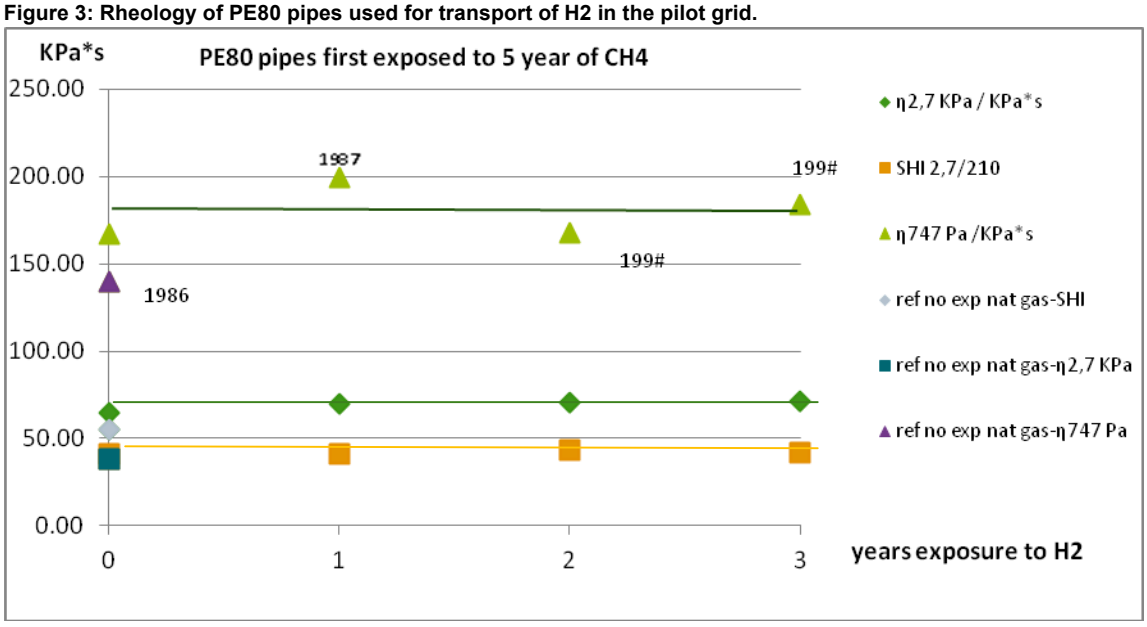


Figure 4: Rheology of material used for transport of H2 in the pilot grid previously used for 5 years of natural gas transport.

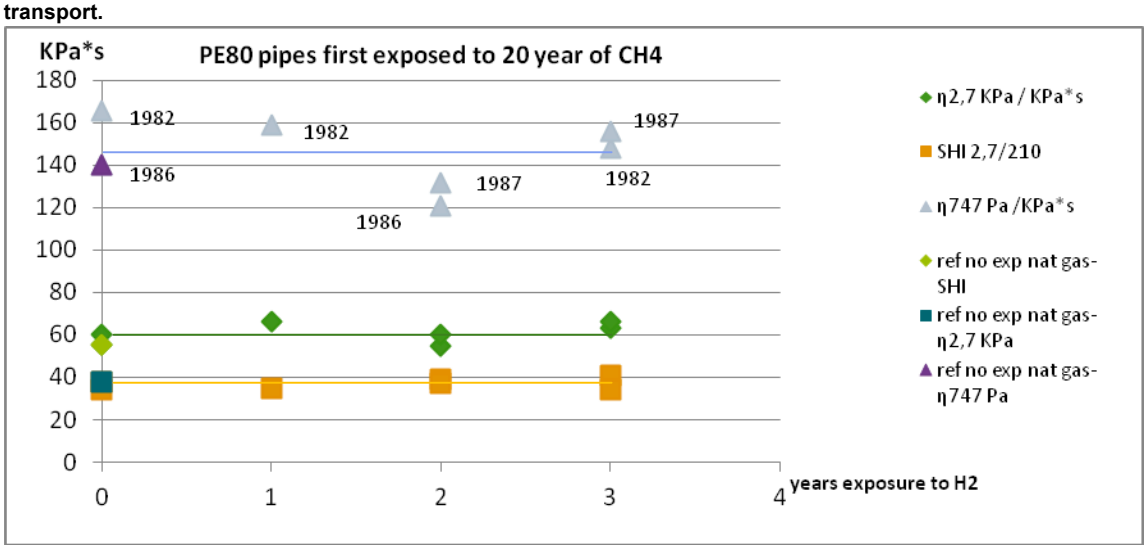


Figure 5: Rheology of material used for transport of H2 in the pilot grid previously used for 20 years of natural gas transport. The manufacturing years is indicated in the diagram.

Oxidation resistance – oxygen induction time:

Also in the case of the measurement of oxygen induction time, there is no indication of any reduction of the oxygen induction time, indicating that the amount of phenolic antioxidant is the same before and after the up to four year exposure to hydrogen (see Figures 6 to 8). What may be somewhat surprising is that the pipes that have been in service for 20 years in the natural gas network in Denmark, before exposure to 3 years of hydrogen, show the same OIT as a sample that has not been in service at all, especially when looking at the inner surface of the pipes (see Figure 8). In conclusion, practically no diffusion has taken place except during extrusion.

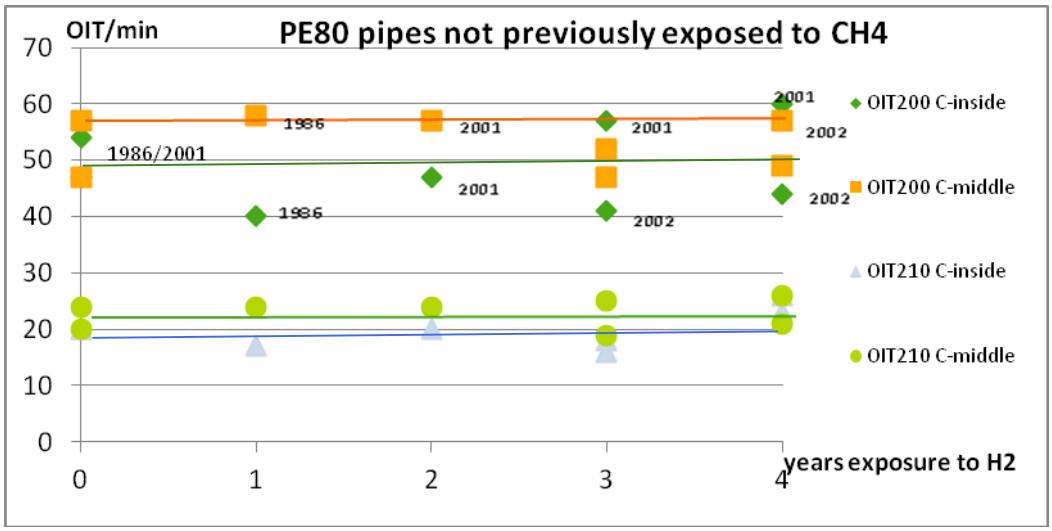


Figure 6: Oxygen Induction Time (OIT) versus years of hydrogen transport in the pilot hydrogen grid. Previously non-used pipes.

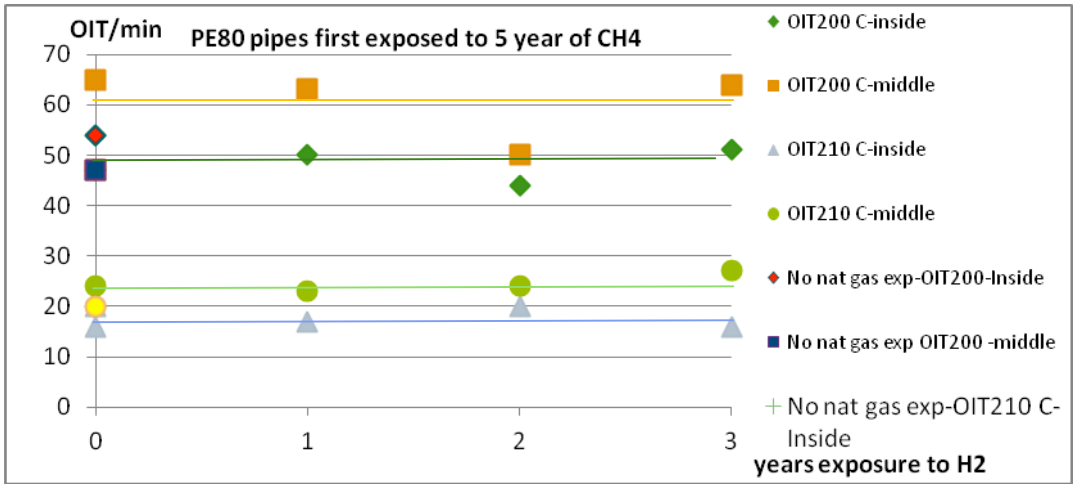


Figure 7: Oxygen Induction Time (OIT) versus years of hydrogen transport in the pilot hydrogen grid. Pipes previously used for 5 years in the natural gas grid in Denmark.

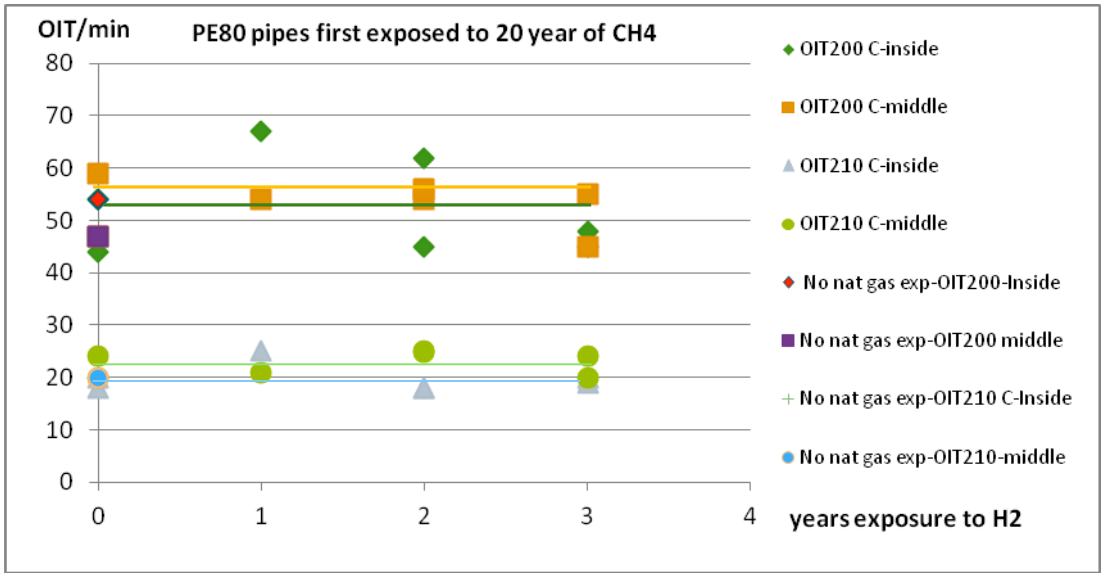


Figure 8: Oxygen Induction Time (OIT) versus years of hydrogen transport in the pilot hydrogen grid. Pipes previously used for 20 years in the natural gas grid in Denmark.

Mechanical properties and slow crack growth:

In regards to elongation and e-modulus (Figures 9 to 11) in the mechanical determination, we can't really see any influence from the use of the pipes in natural gas transport or the additional use for four years of hydrogen transport. There is, however, a tendency that the last points indicate a trend upwards. This may unfortunately be due to a change in equipment set-up leading to a systematic error (i.e. all analysis made in the last year gives higher e-modulus but also elongation at break).

Slow crack growth: As can be seen in Figures 12 to 14, the slow crack growth results on the PE80 samples are unchanged. The drawback that pipes of different manufacturing years are used leads to a bigger scatter but, as can be seen, the manufacturing years are indicated in the diagram.

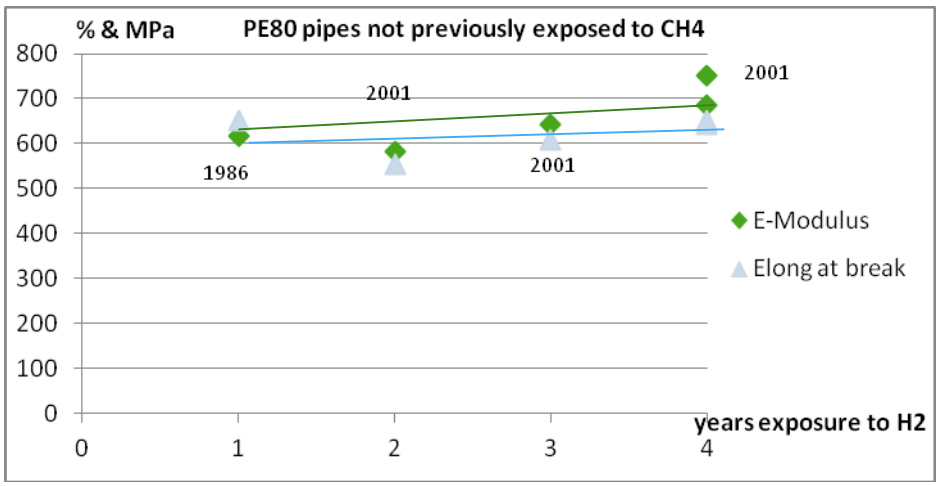


Figure 9: Elongation at break and tensile modulus versus years of exposure to hydrogen of pipes previously not used.

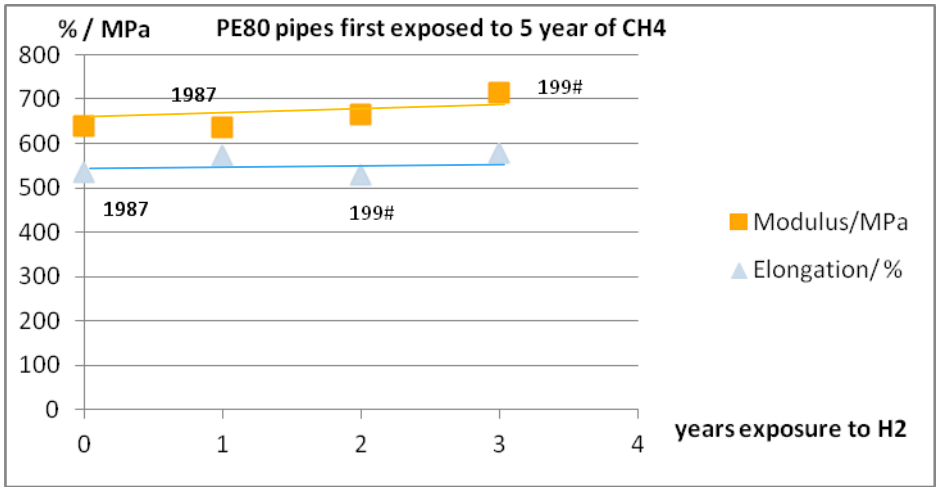


Figure 10: Elongation at break and tensile modulus versus years of exposure to hydrogen of pipes previously used for 5 years in the natural gas grid.

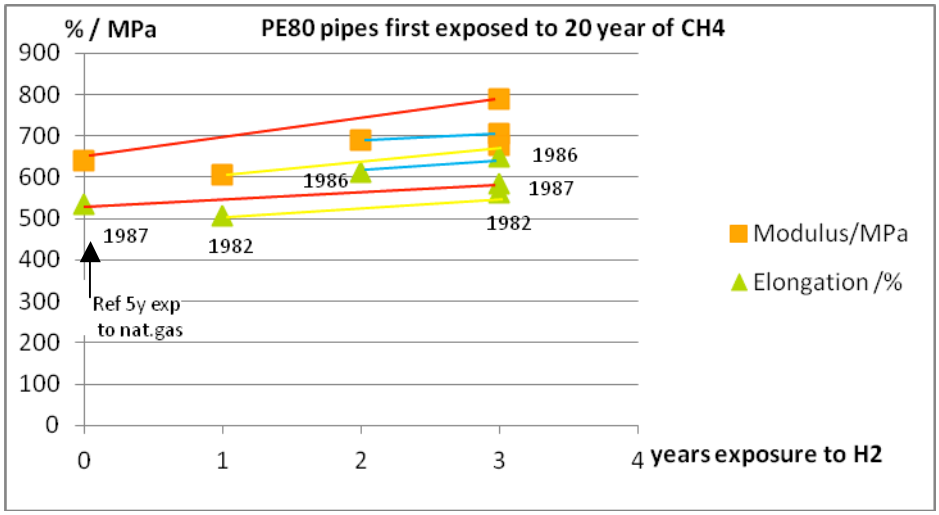


Figure 11: Elongation at break and tensile modulus versus years of exposure to hydrogen of pipes previously used for 20 years in the natural gas grid.

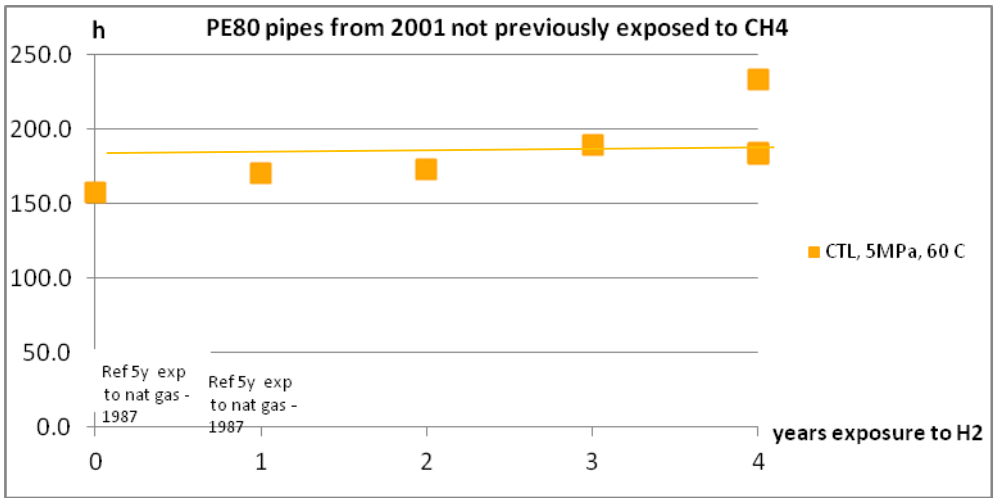


Figure 12: ESCR-CTL at 5MPa /60 C versus years of exposure to hydrogen of pipes previously not used.

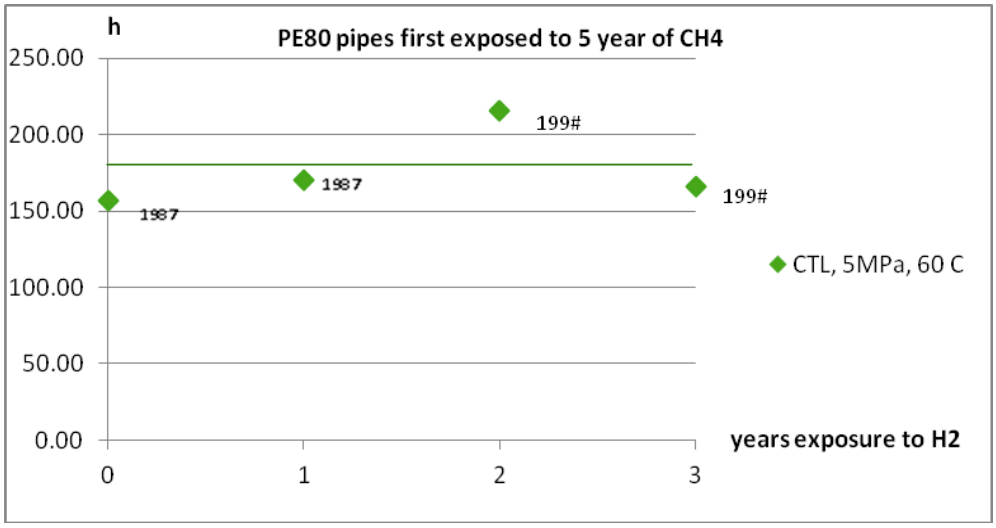


Figure 13: ESCR-CTL at 5MPa /60 C versus years of exposure to hydrogen of pipes previously used for 5 years in the natural gas grid.

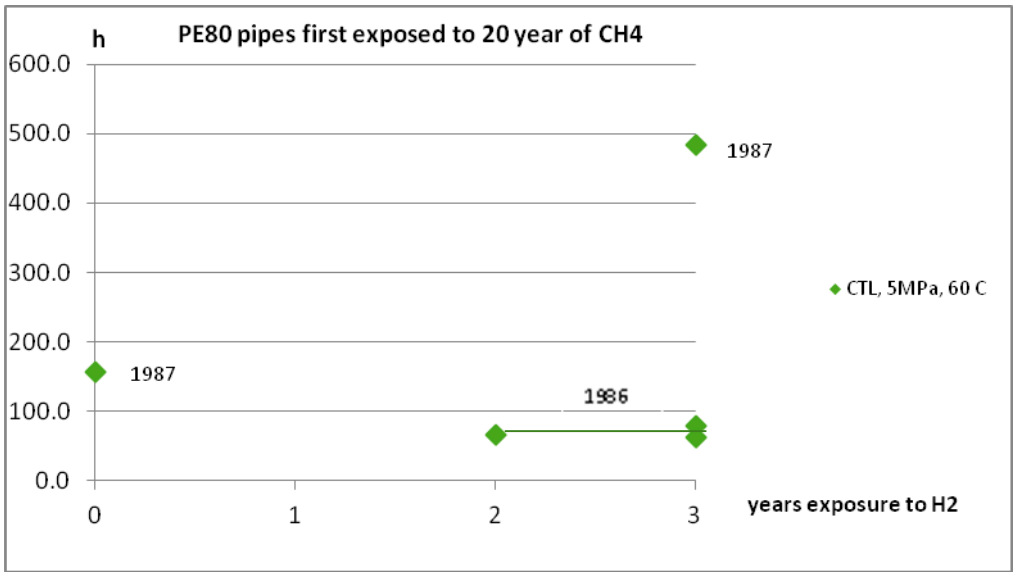


Figure 14: ESCR-CTL at 5MPa /60 C versus years of exposure to hydrogen of pipes previously used for 20 years in the natural gas grid.

PE100:

Also in the case of the two PE100 materials, type I being a solid wall orange pipe and type II being a natural PE100 with an orange outer protective cap, it is clear that no changes take place during the four years of hydrogen exposure. The material is the same in terms of oxidation resistance, basic polymer structure measured with rheology, mechanical properties measured as e-modulus and elongation at break as well as slow crack growth measurement with CTL at 60 C (see Figures 15 to 22 below).

The scatter seen in the diagram is attributed to different manufacturing years and in the case of e-modulus, also a systematic error caused by the analysis set-up in the last year of analysis.

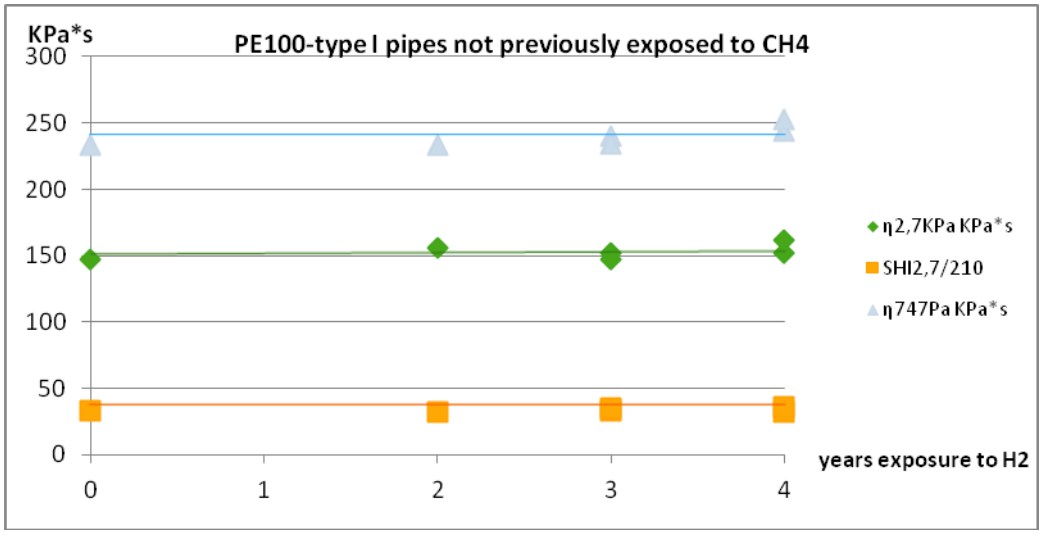


Figure 15: Rheology of PE100 type I pipes used for transport of H2 in the pilot grid.

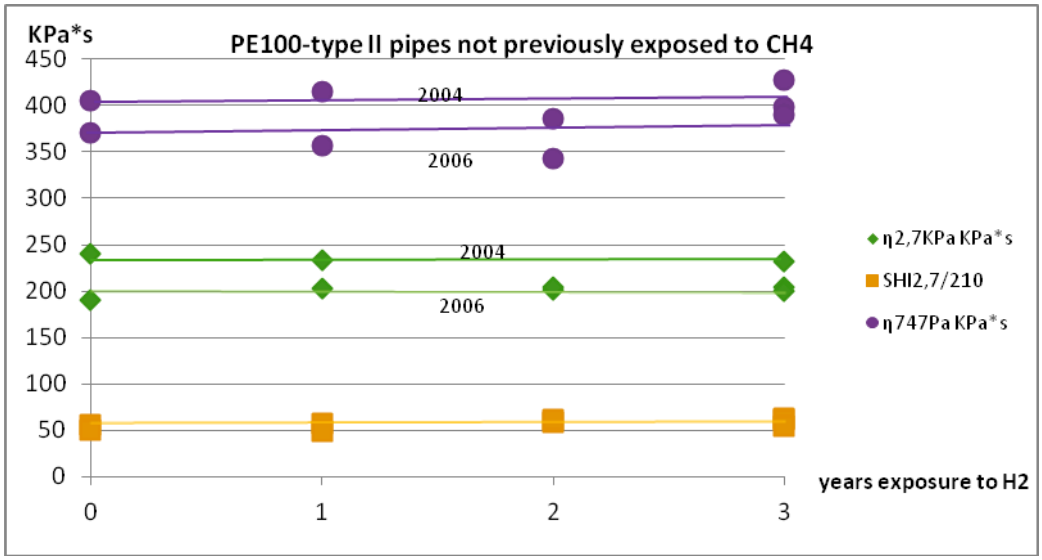
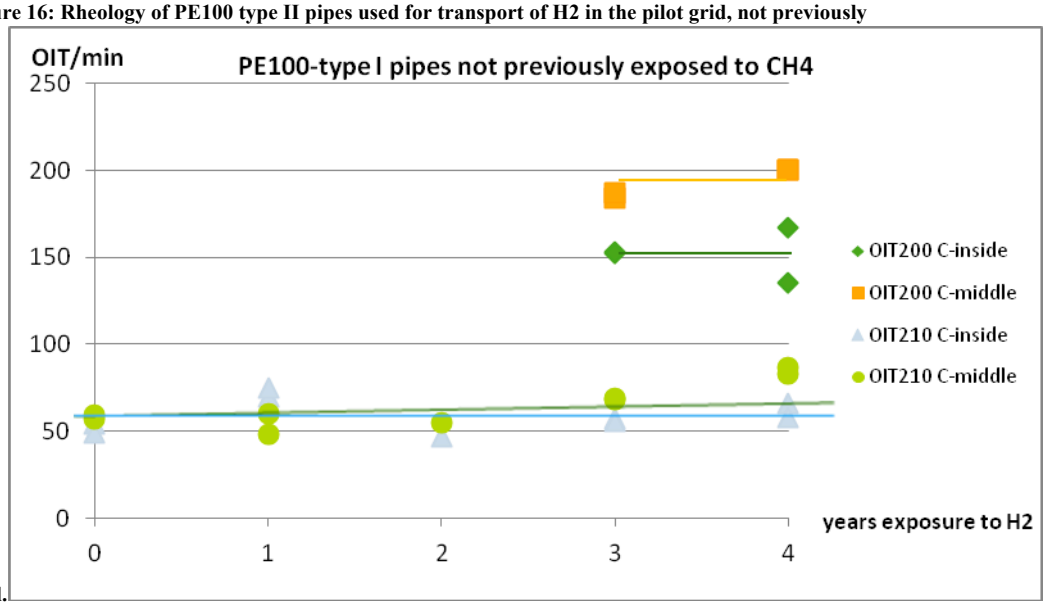


Figure 16: Rheology of PE100 type II pipes used for transport of H2 in the pilot grid, not previously



used.

Figure 17: Oxygen Induction Time (OIT) versus years of hydrogen transport in the pilot hydrogen grid. Pipes previously not used.

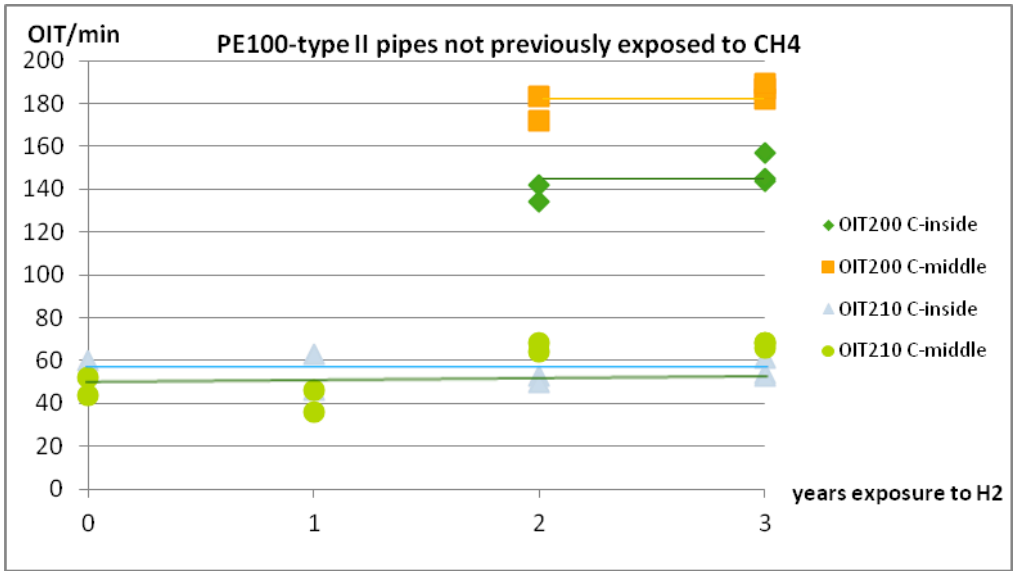


Figure 18: Oxygen Induction Time (OIT) versus years of hydrogen transport in the pilot hydrogen grid. Pipes previously not used.

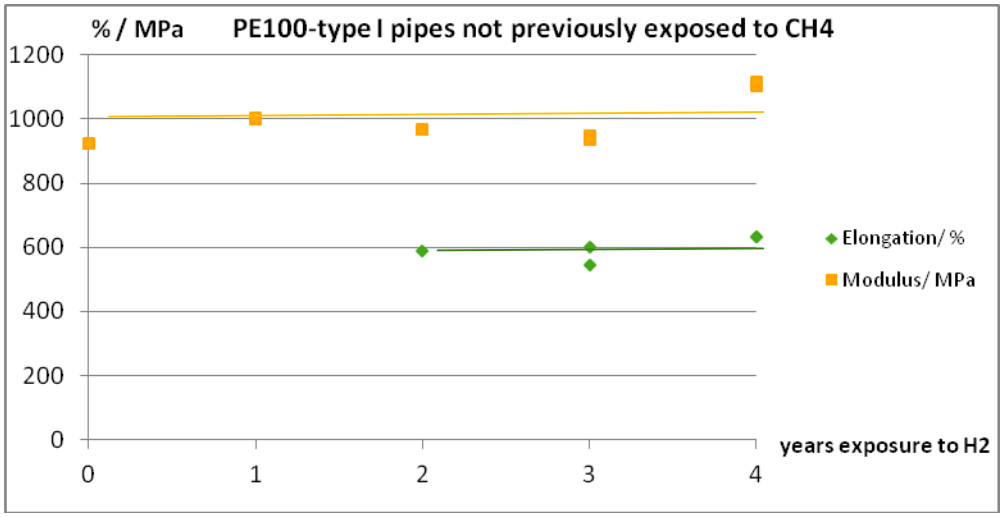


Figure 19: Elongation at break and tensile modulus versus years of exposure to hydrogen of pipes previously not used.

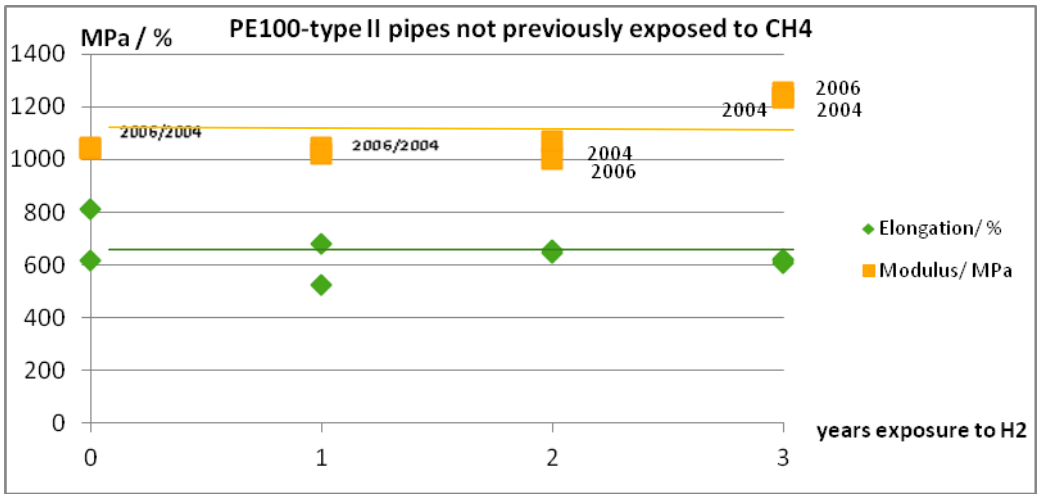


Figure 20: Elongation at break and tensile modulus versus years of exposure to hydrogen of pipes previously not used.

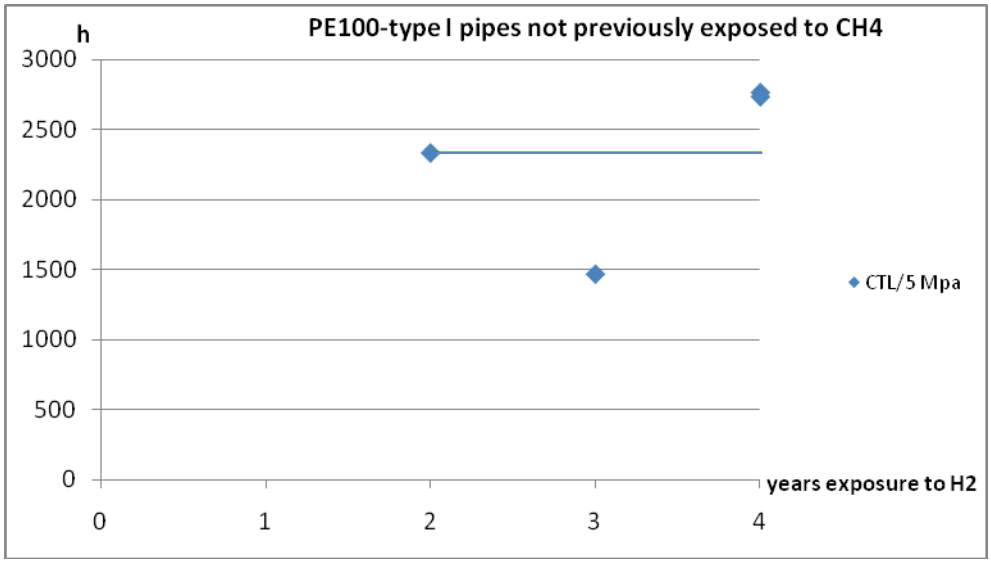


Figure 21: ESCR-CTL at 5MPa /60 C versus years of exposure to hydrogen of pipes previously not used.

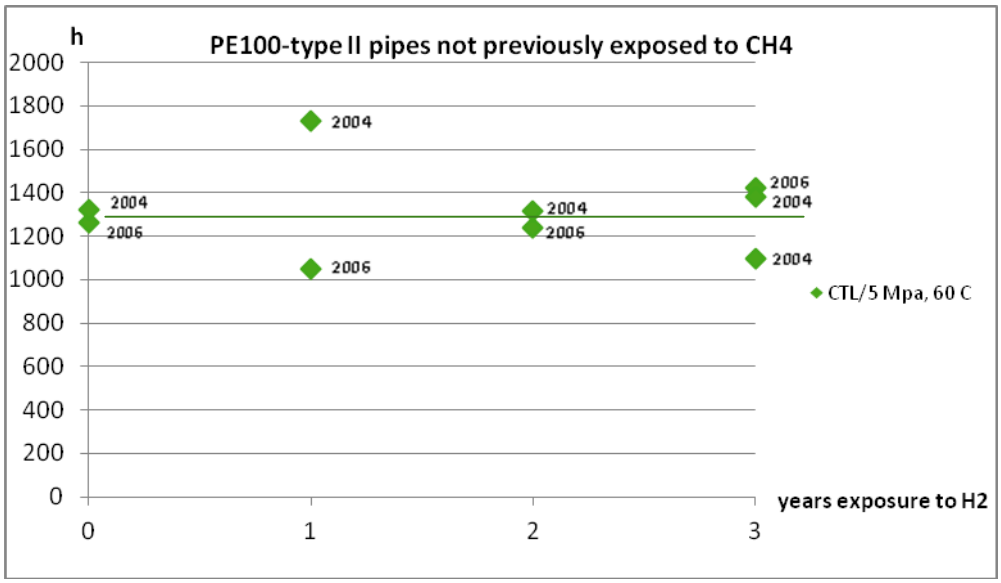


Figure 22: ESCR-CTL at 5MPa /60 C versus years of exposure to hydrogen of pipes previously not used.

Possible future work

An interesting way of further strengthening this investigation could be to make some pressure testing at 80 C, especially in the brittle region, on the pipes that have first been 20 years in the natural pipe grid and another 4 years in the hydrogen pilot. This investigation could give a clear indication of the remaining lifetime of these pipes and thereby provide further insight into the aging of PE when used for gaseous transport.

Conclusions

We can see from the four years of exposure to hydrogen in the pilot grid in Denmark that.

- No adverse effect is found on either PE80 pipes or on two types of PE100 in terms of its:

- Oxidative resistance measured with oxygen induction time;
- Mechanical properties measured as e-modulus and elongation at break;
- Slow crack growth resistance measured with CTL at 60 C;
- We see no reason why MDPE PE80 or HDPE PE100 can't be used as media pipes for hydrogen transport.

We have also found that:

- There is no adverse effect if the pipes have previously been used for natural gas transport, still no effect on the above-mentioned properties;
- The pipes that have been exposed to 20 years of usage as natural gas transport pipes show the same properties as unused pipes in the above-mentioned properties;
- Pipes with a total of 24 years of usage, natural gas transport + hydrogen transport show the same properties as virgin pipes.

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