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Polymer Pipes for Distributing Mixtures of Hydrogen and Natural Gas: Evolution of their Transport and Mechanical Properties after an Ageing under an Hydrogen Environment

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Abstract

With the development of hydrogen as an energy vector, its delivery and transport from the production site to the end user remains an issue. Indeed, the key challenge to overcome is the high hydrogen permeation through existing polymer infrastructures used for natural gas distribution (Polyethylene pipes, components as connecting parts). This high flow rate of hydrogen through polymer has to be taken into account for safety and economical requirements. This 3-year project investigates pure hydrogen gas and mixtures (20% CH_4 - 80% H_2) in pipelines made of engineering polymers to develop and assess material solutions to cope with today problems for H_2 distribution. Materials such as polyethylene (PE100) and polyamide 11 (PA11) have been studied. PE100 is considered as a reference material as it is used today in natural gas distribution pipes. PA11 should allow a higher operating pressure combined with better gas-barrier performances. Test benches and protocols for testing materials in terms of mechanical and barrier properties were first developed. The materials have then been studied in terms of barrier, mechanical properties and on a microstructural point of view. The properties of the raw material and samples after ageing in presence of hydrogen in various conditions were compared to assess the long term behaviour in service. These results as well as the comparison between PA11 and PE are presented.

1 Introduction

The project called PolHYtube is relative to the development and study of innovating materials for hydrogen distribution networks and benefits from a subvention of the French Research Agency.

During this project, several engineering polymers have been characterized to assess if they are compatible with the specifications given by a major hydrogen producer, Air Liquide, set at the beginning of the project. The specifications have taken into account:

- the conditions of service of the pipes (pressure, flow of gas required for the application, temperature, …)
- the level of safety in term of hydrogen permeation through the polymer wall. In a first step, the target hydrogen permeation flow will be set equal or much lower than the

one of methane through polyethylene depending on the application. Polyethylene is indeed the reference polymer material for the distribution of a gaseous fuel

- the durability of the polymer (cost and lifetime).

In the framework of the project, the first two points have been investigated more precisely to assess materials suitable for 3 references scenarios that summarize different distribution pathways of hydrogen produced from a SMR or an electrolyser (higher service pressure) to filling stations, fuelling stations and public areas:

- High pressure (15-30 bars) and a level of hydrogen permeation equivalent to the one of methane through HDPE (high density polyethylene)
- Low pressure (4 bars) and high barrier to hydrogen (50 to 200 times lower than the one of methane through HDPE)
- High pressure (15-30 bars) and high barrier to hydrogen (50 to 200 times lower than the one of methane through HDPE).

2 Evaluation of the Materials Properties

As a technical plastics producer, Arkema participates in this project and has provided some polymer materials. In particular, Arkema shared with the other partners it's experience in developing polyamide 11 pipes for gas distribution in US. This allows the project team to well define the technical targets and specifications of the project (pipe diameter, pipe design (i.e. the thickness to diameter ratio), internal pressure). An important point to be taken into account is the extrudability of the preselected polymers and the long term property of these polymers. The aim of this work is to determine the hydrogen permeability of different polymers that could be used as alternative to PE in target pipeline and to understand their gas transport properties as a function of their structure and their crystalline morphology. The evolution of these properties after an ageing under a hydrogen environment was also studied.

Two polymers were particularly studied: a polyethylene (PE XS10B from Total Petrochemical), that has been taken as the reference material, a polyamide (PA11, Rilsan TL from Arkema).

To be representative of the target pipeline, the PA and PE samples we studied were taken from extruded sheets of 1mm thickness. The crystallinity index of each material was measured by DSC. It was equal to 60% for PE, 20% for PA11.

3 Permeation Measurements

Due to safety requirements, one of the main concerns about polymer pipes is their permeability to hydrogen, which may induce critical leakages of gaseous hydrogen. Permeation measurements were performed by IFP, CEA and INSA Lyon on unaged PE100 and PA11 material samples in various conditions of pressure, hydrogen content and temperature.

The experimental technique developed at IFP concerns gas or gas mixtures permeation through a polymer membrane or a pipe section, in a flowing stream of vector gas and detection by gas chromatography. In that kind of measurement, one or several diffusing species cross the polymer to reach an opened volume swept away by an inert gas stream.

This carrier gas fulfils its purpose by pulling the different molecules towards an appropriate detector measuring the present gas proportion. Then, it is possible to determine the intrinsic transport coefficients of each of the gases constituting the initial mixture. It allows determination of the permeability coefficients of pure gas in numerous polymers but also the permeability coefficients of gas mixtures, such as CH_4-H_2.[1, 2] Practically, many tests of permeability (> 70) were carried out during this study in order to identify the influence of four parameters: temperature (at least 3), pressure (5 and 20 bars), compositions of gases (pure CH_4, 80% H_2 – 20% CH_4, pure H_2) and polymer processing (pipe section and membrane). Most experiments have been carried out twice in order to evaluate the repeatability of the tests.

As mentioned before, some permeation experiments were also carried out on PA and PE at INSA Lyon to validate the use of the experimental device, initially developed for the study of thin films, for these thick samples. Measurements were performed for all samples at different temperatures ranging from 10 to 40°C under a pressure gradient of 5 bars. The experimental values of permeability coefficients obtained for PA11 and PE were in good agreement with those measured by the other partners of the project (IFP, CEA) showing that the INSA equipment could be used for thick samples and that the various methods used to detect and quantify the diffusing molecules through the polymer are reproducible.

As expected, permeability coefficients increase with temperature and are well represented by an Arrhenius law, that is to say that the plot of the logarithm of the permeability coefficient as a function of 1/T defined a straight line for each polymer. This is quite normal, because, in the temperature range studied, no transition temperature is associated either to the polymer or to the gases[3-5].

The H_2 permeability coefficients decreased going from PE to polyamide. These results were closely related to the cohesive energy density of the amorphous phase in each polymer. Indeed, and as previously underlined, the crystallinity was higher for PE than for PA11 whereas the barrier properties were higher for PA11 than for PE. By comparing the behaviour of the two single gases, one can see that the permeability of H_2 is larger than that of CH_4 whatever the considered temperature is and whatever the polymer is. On the other hand, no influence of the applied pressure could be detected in the studied range (5 to 20 bars). Moreover, in the case of mixtures of H_2-CH_4 either with PE or PA11, no particular interaction could be noticed that is to say no mixture effect. Consequently, for a given temperature, each gas (either H_2 or CH_4) keeps its intrinsic permeability coefficient whatever the composition of the feed mixture is.

4 Evolution of Permeability Coefficients with Ageing

CEA-Grenoble was in charge of the ageing of polymer samples under various experimental conditions, which includes the following tasks:

- ageing of polymer membranes and tubes by contact with hydrogen or with a hydrogen-methane (80-20%) mixture under controlled pressure (5 to 20 bars) and temperature (20 to 80°C) conditions,
- monitoring of the permeation coefficient during ageing of the samples,
- analysis of its variation in time.

The ageing cells have been designed to allow periodical permeation measurements during the ageing process. They comprise an upstream chamber that is continuously kept under the desired gas pressure and a downstream chamber that is normally open to the atmosphere – the sample, membrane or tube, being sandwiched between the two chambers. Permeation measurements are made on an average every second month. Whenever they are required, the downstream chamber is flushed with a neutral gas (helium or nitrogen) that transports the permeated gases to a gas chromatograph allowing detection and quantification of the hydrogen or methane flux through the sample. This technique is basically the same as the one used for the permeation measurements (previous section). It allows in situ measurement of the permeation coefficients without having to remove the samples from the ageing cells and to disrupt the experimental conditions[6]. Since the permeation coefficient has been found to be independent of pressure and gas composition, and its variation with temperature has been shown to follow Arrhenius's law, the measurements are all converted to an equivalent of pure hydrogen at 20°C to allow comparison in spite of the various experimental conditions.

A total of 17 membrane samples have been submitted to ageing and periodic monitoring for 1 year. Eight small-diameter (8 mm) and eight large-diameter (32 mm) tubes are currently under study, with the objective of also reaching a duration of 1 year.

Exploitation of the measurements on membranes has been made. The most important result is that the permeation coefficient is equal to 2.10^{-17} $Nm^3.m^{-1}.s^{-1}.Pa^{-1}$ for the PE membranes and 8.10^{-18} $Nm^3.m^{-1}.s^{-1}.Pa^{-1}$ for the PA11 membranes (at 20°C under pure H_2), and that it is unaffected by one year of ageing, whatever the experimental conditions (see Figures 1 and 2 relative respectively to PE100 and to PA11). Analysis of the available results for tube samples suggests that the same ratio exists between the permeation coefficients of PE and PA11 tubes and that they are also essentially unaltered by ageing.

5 Mechanical Measurements and Evolution during Ageing

Coupling between gas sorption and mechanics in polymers is bound to modify their mechanical properties and in-situ experiments are needed to characterize such a phenomenon and provide data for the design of industrial parts. However, when dealing with a hydrogen atmosphere, very few experimental works have been reported. Two possible effects of a hydrogen atmosphere on the tensile properties of polymers have been investigated in the present study, in polyethylene (PE), polyamide 11 (PA11): (i) a coupling effect between pressurized gas sorption and several aspects of the mechanical behaviour (tension, creep and ductile fracture), and (ii) the influence of long-term exposure to hydrogen on the tensile properties. Tensile, creep and ductile fracture tests have been carried out in a tensile testing machine fitted with a pressurized-hydrogen chamber displaying pressures from the ambient up to 400 bars. The gas chamber could be filled by nitrogen or hydrogen. Most tests were carried out at 30 bars, after thermal equilibration and gas saturation of the sample.

It can be reasonably concluded that tensile properties are not affected by H_2 diffusion into PE, even up to 100 bars. The same result stands for PA11 materials, for which the room temperature scatter appears of first importance compared to a possible hydrogen effect.

Static properties (modulus and yield stress) obviously depend on the nature of constitutive materials, but no more hydrogen effect is observed. The same conclusion stands for the creep behaviour of as-received PE and PA11. Creep tests performed at different temperatures show that the time-temperature superposition principle can be applied with similar shift factors, both in ambient air and pressurized hydrogen. In the same way, hydrogen environment was shown to have no noticeable effect on the ductile fracture of as-received PE and PA11, as estimated from a short series of tensile tests in double-notched samples.

After long-term aging up to 13 months in hydrogen atmosphere at various pressures (5 or 20 bars) and temperatures (20°C, 50°C and 80°C) ranging below and above the glass transition of PA11 and the alpha-c transition for PE, no deleterious effect was observed on the mechanical properties of PE and PA11. Differences observed for PA11 essentially result from testing temperature variability close to the glass transition temperature. Consistently with the tensile properties, no significant evolution of the crystalline microstructure after ageing into hydrogen arises from DSC experiments. Again, the clearer effect is associated with the annealing temperature in PA11.

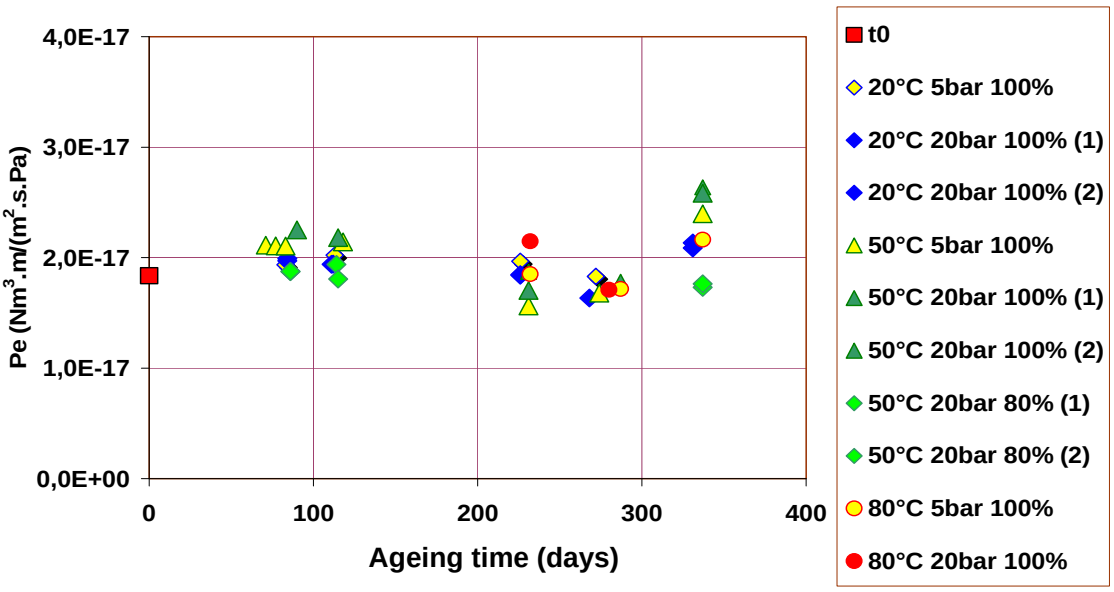

Figure 1: Evolution of the H_2 permeability coefficient in PE100 at 20°C as a function of ageing time.

6 Conclusion

On different experimental devices, the permeability coefficient of H_2 through PE100 and PA11 has been determined in different representative conditions of the pipe life (pressure, temperature, hydrogen content, geometry of the sample). It was shown that PA11 presents a lower permeability to H_2 than PE100, that the evolution with the temperature follows an

Arrhenius law and that no particular effect of the pressure or of the gas composition has to be noticed. Moreover, a good correlation of the measurements between pipe sections and discs samples was obtained which means that no influence of the polymer processing could be noticed.

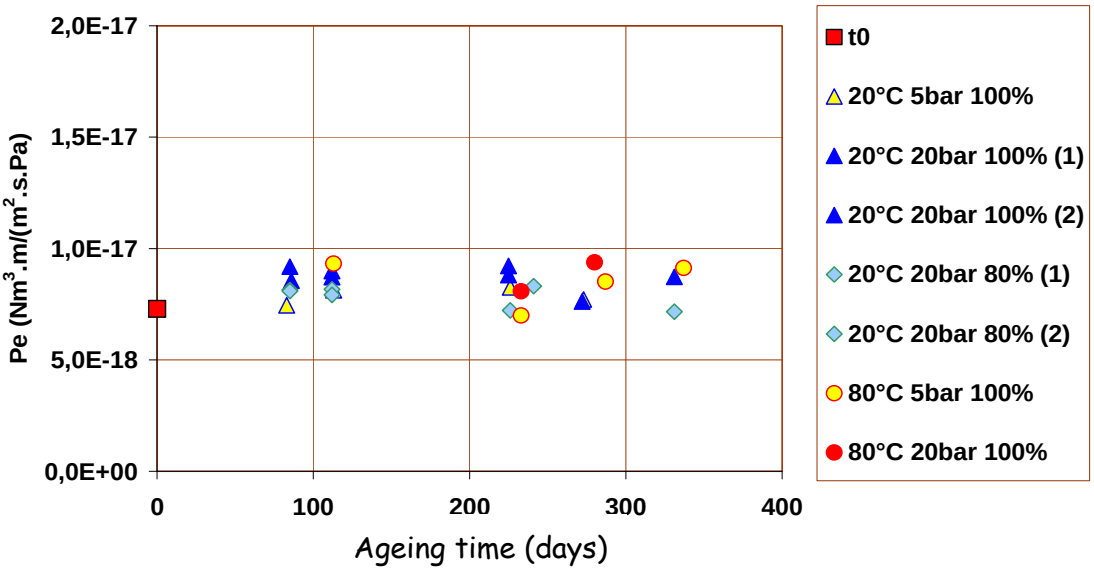

Figure 2: Evolution of the H_2 permeability coefficient in PA11 at 20°C as a function of ageing time.

But the most important point is that the effect of ageing under an hydrogen environment has also been studied. No evolution of the barrier properties of the PE100 or the PA11 system has been observed after more than one year of ageing in various conditions. The same conclusion stands for the aspects of the mechanical behaviour investigated here, i.e. tension, creep and ductile fracture, in both as-received and aged materials.

The study will be completed by an economic assessment of the solutions developed in the framework of the project.

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