Whitepaper

Envalior
Imagine the Future

FUEL LOCK LINER MATERIAL STANDS UP TO *HYDROGEN PERMEATION*

Hydrogen storage is an essential element for the hydrogen driving powertrain of automotive vehicles.

Hydrogen storage is an essential element for the hydrogen driving powertrain of automotive vehicles. Hydrogen as an energy carrier is characterized by its relative high energy density per mass and its relative low energy density per volume. Its relative high energy density per mass is illustrated by the fact that in practice for a passenger car typically 5 kg of hydrogen provides a driving range of 500 km. This contrasts with gasoline for which typically 30 kg is required. The volume of 5 kg hydrogen at 1 bar at room temperature however is 60 m^3. To accommodate for this low energy density per volume, different storage scenarios for hydrogen are feasible. Physical storage via adsorption or absorption in solid media might be considered, but also storage of pure hydrogen under cryogenic conditions or storage under high pressure.

For automotive storage applications, the industry embraces the last scenario. Hydrogen is stored in high–pressure hydrogen tanks with typical operating pressures of 700 or 350 bars. Two crucial performance features of these high–pressure tanks are low weight and safety. Low weight is realized by moving away from metal tank solutions and designing the tank based on polymer–based materials. Safety is realized by a careful selection and development of polymer materials and proper design of the high–pressure tank.

Continued on pg. 2

Currently so-called type IV tanks are being commercialized for this specific application. A type IV tank typically consists of two parts; a full thermoplastic liner and a polymer based composite shell. The composite might be based on continuous glass- or carbon fibers embedded in an epoxy matrix. This combination of liner and composite material provides a light-weight tank. There are several ingredients contributing to the safety performance. The composite shell provides sufficient mechanical strength to withstand the high hydrogen operating pressures and sudden impact incidents. The liner contributes to safety by providing sufficient hydrogen gas barrier- and blister performance.

This paper is about the hydrogen tank liner material with the focus on the safety performance as provided by gas barrier and blister functionality.

Over the last years within Envalior (former DSM Engineering Materials and LANXESS HPM), the so-called Fuel Lock product family has been developed based on world-class barrier material expertise and solid product development. One part of this product family is especially developed as a liner material for hydrogen tank applications and provides state-of-the-art functionality.

HYDROGEN GAS BARRIER– *SMALL SCALE STUDY*

One important functionality of the liner of the hydrogen tank is to provide a sufficient hydrogen gas barrier.

A non-sufficient gas barrier of the tank might lead to hydrogen gas escaping the tank wall and accumulating outside the tank, and in combination with its low ignition barrier and flammability, leading to a potentially dangerous situation. A hydrogen permeation norm is in place and is defined as the maximum hydrogen gas volume as measured under standard conditions (room temperature and 1 bar) that is released from a tank per liter of internal tank volume per hour: $P_{H2} = 6cm^3/(l\ hr)$.

Fuel Lock grades have been developed to comply with this norm for realistic tank volumes of several tens of liters or more. Liner materials that are applied commercially are HDPE and polyamide-based materials. Within the polyamide family, PA11 and PA6 are being used. An aim of this paper is to provide scientific and technological sound arguments showing PA6 is the preferred choice among these materials.

In Figure 1, the intrinsic hydrogen permeation at room temperature of several commercial polymer materials is presented based on open literature values and own permeation measurements (Envalior-PA6). The hydrogen permeation of Envalior-PA6 material in this graph is presented as the reference material to which all other materials are normalized. The takeaway from this graph is that Envalior-PA6 material is superior to PA11 and HDPE, but also superior to other polymer materials such as PET, PEEK and PP.

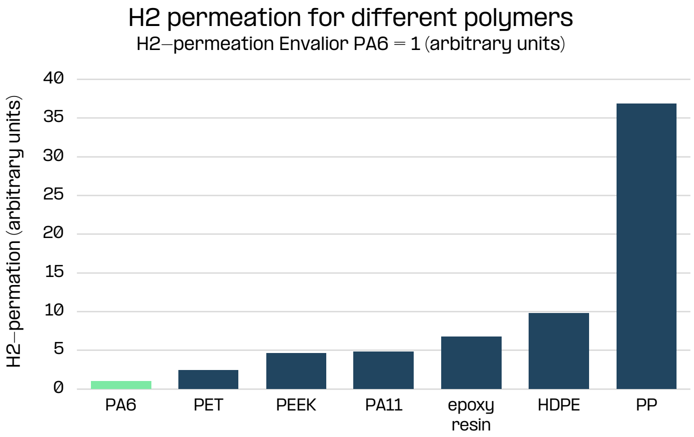

Figure 1
Intrinsic hydrogen permeation values of several polymer materials at room temperature (based on open literature; PET: Permeability and other film properties, Plastics Design Library, ISBN-1-884207-14-6; other materials: Sandia report SAND2013-8904, R.R.Bart et al, Polymers for hydrogen infrastructure and vehicle fuel systems).

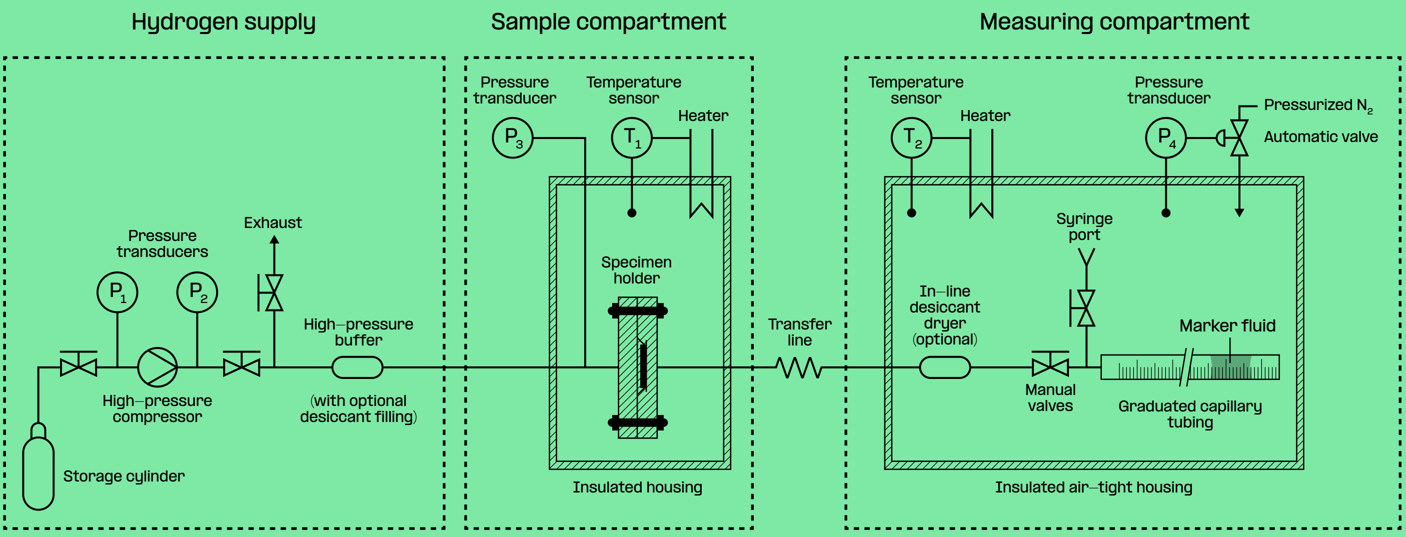

Figure 2
Schematic graph of experimental hydrogen permeation set–up
(image: courtesy of Testnet GmbH).

Let us now focus on a more detailed study of the hydrogen permeation of Envalior–PA6 material. Permeation experiments were conducted at Testnet (Munich, Germany). A schematic representation of the measurement scheme is depicted in Figure 2. For this test, dry as molded plaque samples are used with a thickness of 2mm. In view of the purity of the applied hydrogen for this tank application, the expected water content of the hydrogen gas is expected to be very low. Refilling over time will lead to a situation where the liner is and remains relatively dry.

The plaque sample is positioned in a metal specimen holder that is placed in a thermostatic housing (see mid part of Figure 2). The left part of the graph shows the high–pressure hydrogen infrastructure and regulates the hydrogen pressure to which one planar surface of the sample is exposed to. The right part of the graph shows the part to which the other planar sample surface is exposed to. The permeating hydrogen gas through the polymer sample is collected and is analyzed by a volumetric gas measurement device. For relative long measurement times a constant steady–state permeation is measured. For relative short measurement times, a non–steady state situation is expected during which the permeation increases as a function of time since it takes a while before diffusing hydrogen reaches the other side of the sample. From this measurement, the steady–state hydrogen permeation and hydrogen diffusion coefficient can be extracted directly, and indirectly the hydrogen solubility value can be calculated. The hydrogen permeation value P is expressed in the following application related units and represents a material related property allowing comparison of different materials with each other: (cm^3 mm)/(m^2 day atm).

This permeation value represents a volumetric mass flux through the sample (cm^3) per unit area (m^2) per time (day). The gas volume is expressed under standard conditions of 1 atm and room temperature. This flux is normalized with respect to sample thickness (calculated back to 1mm) and hydrogen gas pressure difference (calculated back to 1 atm). In general, the mass flux scales linearly with gas pressure difference and reciprocal with sample thickness. The permeation value is often expressed in scientific units: mol/(m s MPa) with flux expressed in mol/(m^2 s) and permeation normalized for sample thickness in (mol m)/(m^2 s) or (mol)/(m s). For hydrogen gas, a permeation value of 10^{-9} mol/(m s MPa) corresponds with 193.5 (cm^3 mm)/(m^2 day atm).

The diffusion coefficient D is expressed in m^2/s while the hydrogen solubility is stated in mol/(m^3 MPa). Please note that the permeation flux is the results of the diffusion process and solubility behavior: $P=D^*S$.

In Figure 3, the experimental results for hydrogen permeation normalized for sample thickness (1mm) is given for Envalior–PA6 as measured at different applied hydrogen pressures at room temperature. There is some spread in the experimental outcome, but from the experimental results it is indeed conformed that hydrogen permeation scales linearly with pressure. This hints towards Henry's behavior for the hydrogen solubility, i.e. a linear pressure dependency. The hydrogen permeation is represented by the slope of the line and equals 0.084×10^{-9} mol/(m s MPa) or 16.25 (cm^3 mm)/(m^2 day atm).

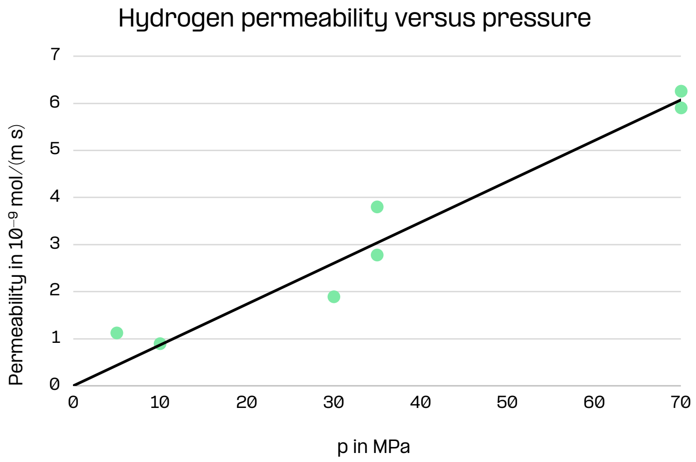

Figure 3
Hydrogen permeability vs hydrogen pressure for Envalior–PA6 at room temperature.

This hydrogen permeation value for Envalior–PA6 is compared with other polymer materials, see Table 1 first and second columns. Permeation values for other materials are taken from a Sandia study (Sandia report SAND2013–8904, R.R.Bart et al, Polymers for hydrogen infrastructure and vehicle fuel systems). It is clear from this table that Envalior–PA6 outperforms HDPE by a factor 10 and PA11 by a factor 5.

Material	Hydrogen permeation in 10^{-9} mol/m s MPa	Hydrogen diffusion coeff. in 10–10 m^2/s	Hydrogen solubility in mol/m^3 MPa
HDPE	0.82	1.9	4.3
LDPE	3.1	0.47	65
PA11	0.40	0.65	6.2
PEEK compr. molded	0.39	0.24	16
PP	3.1	–	–
Envalior–PA6	0.084	0.29	2.9
FLX40–HP	0.132	0.34	3.9
FLE–LP	0.122	–	–

Table 1
Hydrogen permeation characteristics for Envalior–PA6, FLX40–HP and FLE–LP compared with other materials as measured at room temperature (other materials based on Sandia study (Sandia report SAND2013–8904, R.R.Bart et al, Polymers for hydrogen infrastructure and vehicle fuel systems).

The effect of temperature for the hydrogen permeability of Envalior–PA6 was studied and is represented in Figure 4. An Arrhenius analysis using the expression $P = P_0 \exp(-E_{act}/RT)$ learns that the activation energy equals 29 kJ/mole which seems very reasonable.

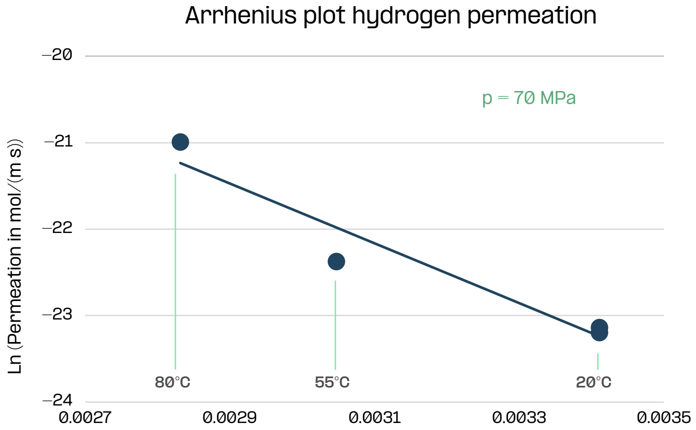

Figure 4
Temperature dependency of hydrogen permeability for Envalior–PA6.

An example of the result of an experimental non–steady state permeation study is shown in Figure 5. The normalized hydrogen permeation is represented versus time. It takes a while before the diffusing hydrogen has reached the other side of the sample and for this case, after approximately 105 seconds, a steady state situation is reached. A Fickian analysis was performed (see white line in figure) and for Envalior–PA6 this leads to a value for the hydrogen diffusion coefficient of 0.29×10^{-10} m²/s. Since, S=P/D the value for the solubility of hydrogen in PA6 is 2.90 mol/(m³ MPa). In table 1 these values for Envalior–PA6 are put in context and are compared with values for other materials like HDPE and PA11. The lower hydrogen permeation value for PA6 compared to PA11 and HDPE stems from the fact that hydrogen diffusion coefficient as well as hydrogen solubility are lower for PA6 compared with PA11 and HDPE. In a detailed molecular modelling activity (E.Voyiatzis, A.Stroeks; J.Phys.Chem.B, 2022, 126, 6102) the solubility of hydrogen in PA6 and HDPE was studied. The modelling predictions of that study resulted in a hydrogen solubility in HDPE being a factor 1.6 higher compared to PA6 which agrees well with the experimental solubility results as given in table 1. The cause for this solubility difference, as revealed by the modelling study, is the fact that the interaction between the hydrogen permeant and the polymer is somewhat more attractive for HDPE compared to PA6. It is anticipated that, because the chemical structure of PA11 is in between PA6 and PE, the interaction between permeant and PA11 will also be somewhat more attractive compared to PA6 resulting in a somewhat higher solubility in PA11 compared to PA6. This is indeed confirmed by experiment. The modelling study also led to the conclusion that the solubility of hydrogen in the crystalline phases of HDPE and PA6 is practically zero in view of the extreme high insertion energy penalties involved. This explains the fact that the experimental solubility in HDPE is lower compared to PA11 in view of the large difference in crystallinity level between the two polymers (70% vs. 25%).

The increase of the hydrogen diffusion coefficient in the series PA6 – PA11 – HDPE can be related to the glass transition temperatures decreasing for this series leading to an increase in the (sub)segmental mobility. This effect apparently dominates over the fact that the crystalline phase acts as blockades for the permeant to migrate; HDPE has the highest diffusion coefficient despite its higher crystallinity compared to PA6 and PA11.

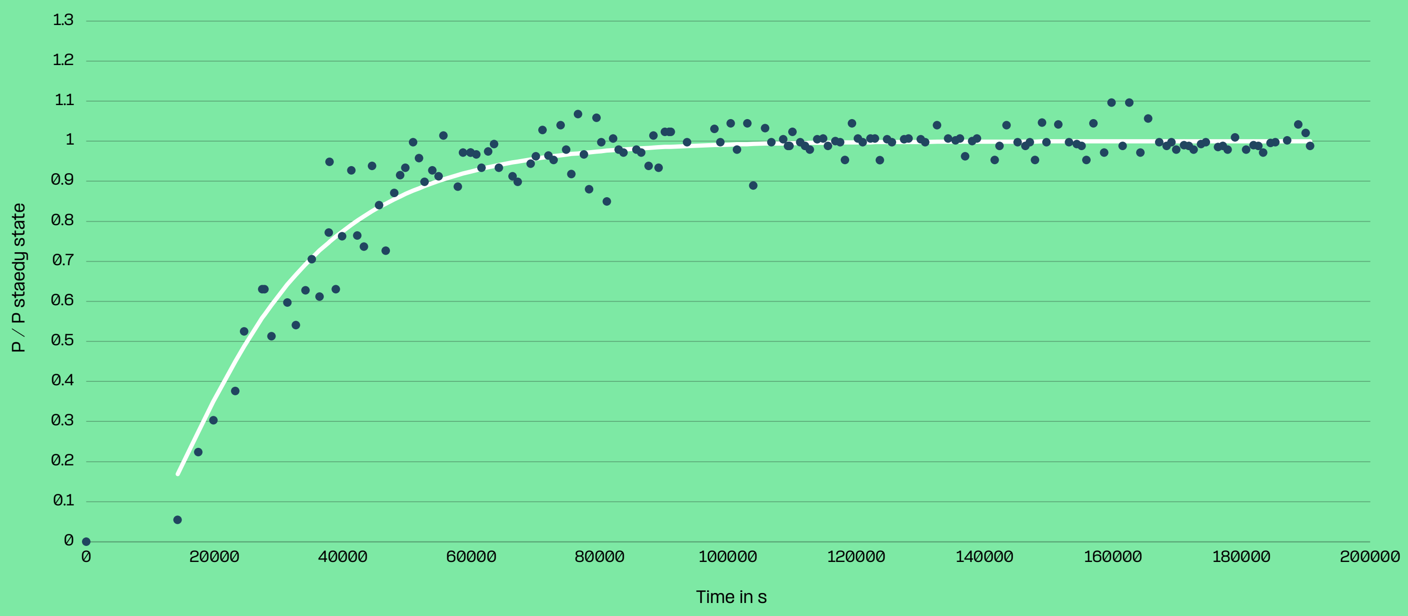

Figure 5
Example of an experimental non–steady state hydrogen permeation result at room temperature and hydrogen pressure =700 bar as measured on 2mm thick plaque.

> *Hydrogen diffuses rather fast in HDPE compared to PA6 and PA11 despite its higher level of crystallinity. Fast diffusion leads to lower barrier performance.*

Material	Hydrogen permeation in 10^{-9} mol/(m s MPa)	Hydrogen permeation in (cm^3 mm)/(m^2day atm)
PA6	0.084	16.25
FLE–LP	0.122	23.60
FLX40–HP	0.132	25.50

Table 2
Hydrogen permeation characteristics for Envalior–PA6 and two IM–PA6 grades as expressed in scientific– and application oriented units at room temperature.

Commercial Fuel Lock materials are based on impact modified PA6 material (IM–PA6) to meet stringent mechanical requirements imposed on tank materials, primarily low temperature impact performance. The impact modifier typically is a functionalized highly amorphous ethylene copolymer. Blending with the PA6 matrix material will trigger reactive compatibilization via graft formation over the rubber/po lyamide interface. This leads to dispersed submicron rubber particles in a continuous matrix of PA6 which is optimal for mechanical impact performance. Two Fuel Lock materials have been studied: FLE–LP which is a grade developed for injection molding purposes and FLX40–HP which is a blow molding grade. The hydrogen permeation of these two commercial grades is studied at room temperature and 700 bar hydrogen pressure and is compared with PA6, see table below.

An increase of approximately 50% for the hydrogen permeation is observed moving from PA6 to the IM–PA6 grades. An increase is expected since the rubber material, due to the highly amorphous character, low Tg value and a–polar character, will exhibit higher permeation values compared to PA6.

Temperature dependencies of the hydrogen permeation of these commercial grades have been studied and compared with PA6, see next figure. The IM–PA6 grades show much larger temperature dependencies resulting in an activation energy for these grades of 46 kJ/mol versus 29 kJ/mole for PA6. This indicates that permeation in the rubbery phase is much more temperature dependent compared to the permeation in the polyamide matrix.

For one IM–PA6 grade (FLX40–HP), the non–steady state permeation performance was analyzed at room temperature and based on this the diffusion coefficient and solubility for hydrogen were estimated, see next table. A comparison is made with PA6.

As anticipated, the addition of apolar, highly amorphous and low Tg rubber material to PA6 leads to an increase in the diffusion coefficient as well as the solubility of hydrogen.

From Table 1, it is clear that the commercial impact modified PA6 versions (FLX40–HP and FLE–LP) still show superior hydrogen barrier performance over other polymer materials such as PA11 and HDPE.

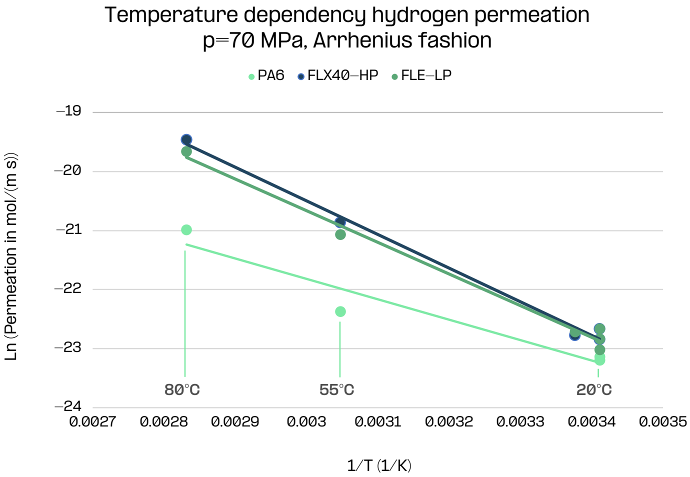

Figure 6
Temperature dependency of hydrogen permeability for IM–PA6 grades compared to PA6.

Material	Hydrogen permeation in 10^{-9} mol/(m s MPa)	Hydrogen diffusion coeff. in 10^{-10} m^2/s	Hydrogen solubility in mol/(m^3 MPa)
IM–PA6	0.34	3.9	4.3
PA6	0.29	2.9	65

Table 3
Hydrogen diffusion coefficient and solubility for IM–PA6 compared with PA6 at room temperature.

HYDROGEN GAS BARRIER– *TRANSLATION TO TANK APPLICATION*

The previous paragraph deals with the experimental study of hydrogen permeation on small scale plaque samples and the rationalization of the results in terms of the materials applied. This section deals with the translation of these results towards the high–pressure hydrogen tank application.

As stated before, the hydrogen permeation requirement for a high–pressure hydrogen tank is specified by a maximum tolerable hydrogen gas volume as measured under standard conditions (room temperature and 1 bar) that is released from a tank per liter of internal tank volume per hour:
$P_{H2} = 6 cm^3/(l\ hr)$

This relates to the total amount of hydrogen gas escaping from the tank to the outside world. For a type IV tank, the liner serves as the barrier layer for the tank and the composite shell serves as layer for obtaining sufficient mechanical strength. So, for practical reasons the permeation is related to performance of the liner and the contribution form the composite shell is ignored in the permeation analysis. The permeation of the liner will be to a large extent governed by the permeation of hydrogen through the polymer liner material. One can imagine that a relative small contribution stems from the connects of the polymer material to inserts related to the filling and release opening. This contribution is very much application specific and is ignored in the further permeation analysis.

Since the permeation P scales with the area (A) of the liner, and the permeation requirement is expressed per internal tank volume (V), the surface to volume ratio A/V will affect the permeation value to a large extent. The surface to volume ratio depends on:

- The specific tank geometry
- The internal volume of the tank with this specific tank geometry

As a representative example for a specific tank geometry serves the following geometry essentially consisting of two half spheres and a cylinder with the length of the cylinder twice the radius of the half spheres:

> *For a type IV tank, the liner serves as the barrier layer for the tank and the composite shell serves as layer for obtaining sufficient mechanical strength.*

For this geometry, the following mathematical relationships apply:

$$P \approx A = 2 \times A_{half-sphere} + A_{cylinder} = 4\pi R^2 + 4\pi R^2 = 8\pi R^{2*}$$

$$V \approx 2 \times V_{half-sphere} + V_{cylinder} = 4/3\pi R^3 + 2\pi R^3 = 10/3\ \pi R^{3*}$$

$$P/V \approx 1/R = 1/V^{1/3*}$$

*with the ≈ sign means: –scales with–

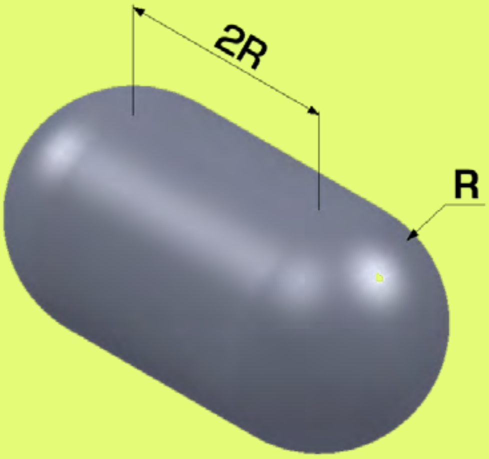

Figure 7
Tank geometry consisting of two half–spheres and a cylinder.

For a liner made from material FLE–LP with a hydrogen permeation of 23.60 (cm³ mm)/(m² day atm) at room temperature, one can calculate P/V as a function of the internal tank volume V for an internal tank hydrogen pressure of 700 atm. The result is given in the next graph together with the permeation norm of 6cm³/(l hr). The calculations were performed for two liner thicknesses: 2 and 3mm.

For a liner wall thickness of 2mm, the permeation is calculated to be lower compared to the permeation norm for tank volumes of 27 liters and more. For a wall thickness of 3mm, permeation for tank volumes of 8 liters and up will fall below the norm. Typical tank volumes for passenger cars are in the order of 50 – 100 liters indicating that for realistic tank wall thicknesses FLE–LP has permeation values well below the norm threshold and the liner thickness can be used to attain a tunable permeation safety factor if desired.

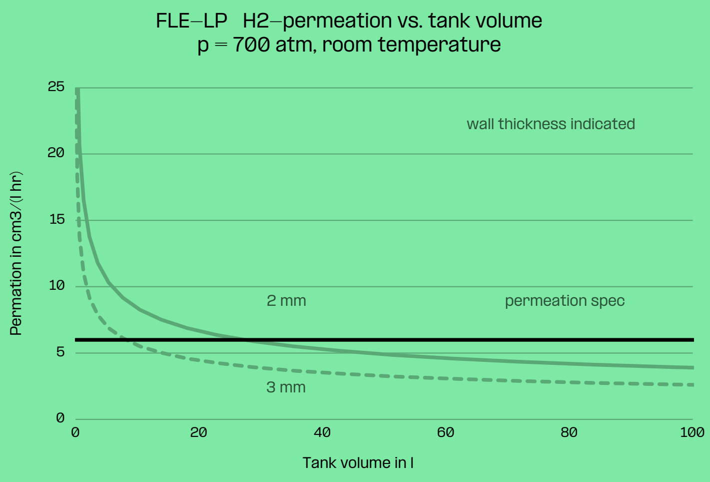

Figure 8
Hydrogen permeation per internal tank volume vs. tank volume for a specific tank geometry as indicated.

In Figure 9, a comparison is made of the liner permeation per internal tank volume for the materials HDPE, PA11 and FLE–LP based on hydrogen permeation values as given in Table 1. The conclusion is that meeting the permeation requirement for HDPE and PA11 is more challenging compared to FLE–LP.

Based on these permeation predictions, PA11 based liners comply with the norm for relatively large tank volumes (appr. 250 l tank volumes for 3mm thick liner). For HDPE is seems that an increased thickness of the liner is required (> 3mm) to be able to comply with the permeation norm.

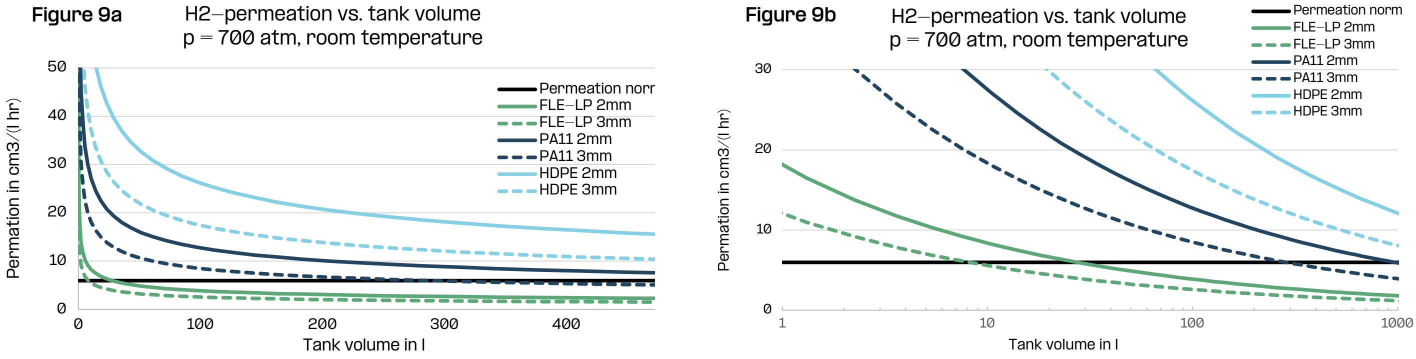
Figure 9a

Figure 9b

Figure 9a/b
HDPE, PA11 and FLE–LP hydrogen permeation per internal tank volume vs. tank volume (with tank volume in fig 9a on a linear scale and in fig 9b on a logarithmic scale) for a specific tank geometry as indicated.

In conclusion, the detailed technical study reveals that the hydrogen barrier performance of PA6 and Envalior's commercial Fuel Lock grades (impact modified PA6 versions) is superior to materials like PA11 and HDPE. This high–pressure hydrogen tank application study, focusing on tank design and current hydrogen permeation specifications, clearly shows that Fuel Lock materials are the materials of choice for liners.

AUTHORS

Alexander Stroeks, principal scientist / Bert Keestra, system expert

To learn more, contact us via Envalior.com.

Envalior is a leading global Engineering Materials company employing around 4,000 people worldwide. With a long track record of customer–focused innovation, Envalior focuses its deep material and application expertise on sustainable and high–performance solutions. The company supplies many of the world's key markets including Automotive, New Mobility, Electronics & Electrical, and Consumer goods.
For more information visit www.envalior.com.

Envalior
Imagine the Future