TRELLEBORG

Hydrogen Permeation

A PRESENTATION OF THE RESULTS OF PERMEATION TESTING OF POLYMER SEALING MATERIALS FOR THE HYDROGEN MARKET

WHITEPAPER

Trelleborg Sealing Solutions in the energy sector

Trelleborg Sealing Solutions is a leader in solving challenges and driving innovations for the most demanding sealing issues globally within the energy sector. Expertise built from its leading position in sealing solutions over the last 70 years is the foundation for new applications as the energy sector transitions from fossil-based fuels to more sustainable options.

Trelleborg Sealing Solutions is supporting its existing energy customers, new entrants and startups by delivering high-quality, robust and reliable sealing solutions for emerging LNG, hydro, hydrogen, wind, solar and wave power technologies.

Authors

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Manager - Hydrogen Technology

Philipp joined Trelleborg in 2017 as an R&D engineer for customized solutions. He gained experience designing various sealing solutions in elastomers and plastics across multiple market segments.

Since 2021 he has led the development of Trelleborg Sealing Solutions offerings for the hydrogen market. This includes material developments, testing and validation as well as defining the future strategy.

Peter Bashford
Product Leader - Variseal®

Peter has 25 years of experience in Trelleborg proprietary polymer materials technology and developing Variseal® sealing solutions for multiple market segments and a diverse range of applications. His work includes the development of a portfolio of product ranges, specific to application type and performance parameters, as well as customer-specific application solutions. Sealing of gasses and liquid gasses at cryogenic temperatures is a particular area of focus, with the development of sealing solutions dependent on the media and application conditions.

Introduction

The hydrogen market is growing rapidly, driven by its increasing use as a fuel for heavy trucks, trains and ships, as well as its potential as a medium to store surplus energy generated by renewables to balance demand and supply in electricity grids.

Completely new and ever more demanding applications present unique and complex sealing challenges. To support its customers in the development of future hydrogen production, transport and storage, processing and end-use equipment, Trelleborg Sealing Solutions conducted an extensive program to test the permeation rates of elastomer and thermoplastic sealing materials.

This whitepaper details those tests and their results and explores the sealing challenges associated with hydrogen in an ever-changing application landscape.

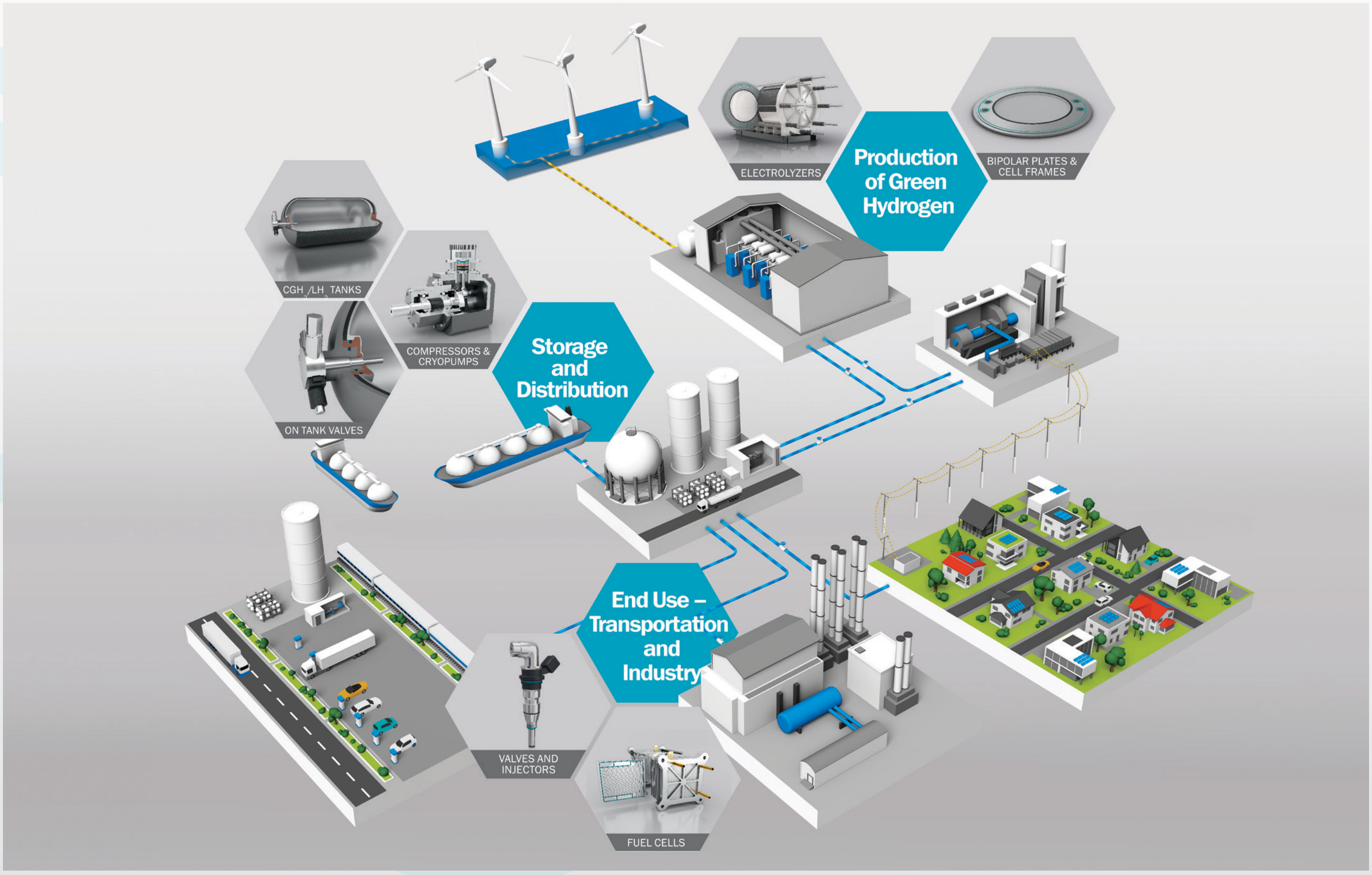

Figure 1: The hydrogen value chain

Hydrogen sealing challenges

Seals used in hydrogen applications have to withstand extreme operating temperatures and rapid gas decompression, and demonstrate wear resistance, low-friction capabilities, dynamic sealing capabilities and high sealing performance. In addition, one crucial sealing challenge specific to hydrogen is related to its characteristic as the smallest of all molecules, allowing it to permeate through sealing materials.

Therefore, achieving a high level of permeation resistance is critical for hydrogen sealing materials. The need for both sealability and low permeability makes sealing hydrogen applications complex. Finding the balance between these two factors for each specific hydrogen application is key to achieving the best possible sealing performance and longevity.

Permeation of sealing materials

Permeation is the passage, or transport, of gasses and liquids through a second material, such as a solid, by absorption. The driving force of this process is the pressure difference across a solid.

The permeation of gasses and vapor through materials takes place in two stages. First the gas dissolves into the surface of the material, and then the molecules diffuse through the material under the action of a concentration gradient. Permeation is therefore highly dependent on the molecular size of the media being sealed.

Permeation is generally not a concern when sealing high-viscosity fluids like oils or even low-viscosity fluids such as water. However, when dealing with low-molecular gasses like helium or hydrogen, permeation becomes a significant issue. With a diameter 0.276 nm, hydrogen is the smallest molecule in the universe.

Its viscosity is therefore very low, which can lead to high leakage rates. In general, leakage is the sum of three flow paths as illustrated in Figure 2:

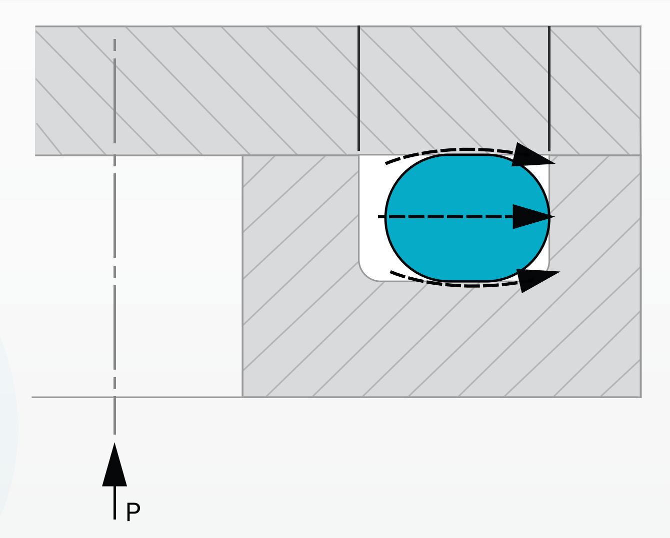

Figure 2: Leakage paths and permeation

Achieving low leakage rates is dependent on two factors; the permeation characteristics of the material and the level of interface leakage.

Material options for hydrogen applications: Permeation

Since many in the hydrogen industry come from the oil and gas sector, the first choice for sealing hydrogen applications has been nitrile butadiene rubber (NBR), fluoroelastomer (FKM), polytetrafluoroethylene (PTFE) and thermoplastic sealing materials. These materials are the traditional choices for sealing high-pressure gasses in oil and gas extraction.

However, as permeation is the most important consideration in certain hydrogen sealing applications, other sealing materials, including a range of elastomer and thermoplastic grades, such as ethylene propylene diene monomer (EPDM), thermoplastic polyurethane (TPU) and metals may offer better options.

To investigate this possibility, Trelleborg conducted a series of permeation tests on its FKM, EPDM and thermoplastic materials.

NBR materials were not tested due to their low compatibility with hydrogen applications, and where NBR could be an option, polyurethane is a much better choice with regards to permeation. Metallic seals are also excluded, as these are considered to be inherently impermeable to light gasses.

This whitepaper presents the results from these permeability tests. It does not endeavor to offer absolute recommendations for sealing materials where permeation is an issue, but to provide information to specify sealing materials that will give the best permeation performance in hydrogen sealing situations.

Testing methods and set up

The permeation tests for elastomers were based on ISO 2871-1:2016 Rubber, vulcanized or thermoplastic – Determination of permeability to gasses – Part 1: Differential-pressure methods, chapter 7: Gas-chromatographic method. For thermoplastics the test method was based, as far as is possible, on ASTM D 1434-82 (Standard Test Method for Determining Gas Permeability Characteristics of Plastic Film and Sheeting).

For both types of materials, circular disk samples had a thickness of 2 mm/0.079 inches and a diameter of 30 mm/1.181 inches, with a circular area under pressure of 16 mm/0.629 inches diameter. These were clamped inside a permeation test vessel and helium gas from a bottle was regulated with a valve to a desired pressure. The area of the test sample exposed to the helium was 201 mm^2/0.312 $inch^2$.

As recommended by ASTM D 1434-82, thermoplastic test samples were conditioned by storing them in desiccant for at least 48 hours prior to testing. The test fixtures had gas-tight fittings on either side, which allowed one face of a sample to be exposed to helium and the opposite side to a vacuum.

The permeation was measured with an Adixen Pfeiffer Vacuum Helium Leak Detector ASM 340, an ultra-high vacuum pump with mass spectrometer, that determines the flow rate of helium.

Additionally, a second vacuum pump was connected to the test vessel to create a coarse vacuum around the sample.

This ensures no external gas can distort measurements. Tests were performed at ambient temperature (+23 °C/+73 °F).

For thermoplastics, helium was supplied to the sample at 0.9 MPa/131 psi and the helium leak detector generated a vacuum of 0.1 MPa/14.5 psi on the opposite face of the sample, creating a delta pressure acting across the sample of 1 MPa/145 psi. Similarly for elastomers, tests were performed at three pressure levels. This allows investigation of the influence of pressure on permeation behavior.

Regulated helium pressure	Delta pressure
0.1 MPa/14.5 psi	0.2 MPa/29 psi
0.3 MPa/44 psi	0.4 MPa/58 psi
0.9 MPa/131 psi	1 MPa/145 psi

Table 1: Pressure levels investigated

The elastomer samples were supported by a 3D-printed structure to prevent deformation under pressure. A wire mesh, as specified in CSA/ANSI CHMC 2:2019 under 5.2.2 (page 20), was used in contact with the sample. The thickness of each sample is measured to calculate the permeation coefficient. According to ISO 2782-1:2016 there are three test pieces measured for each setting.

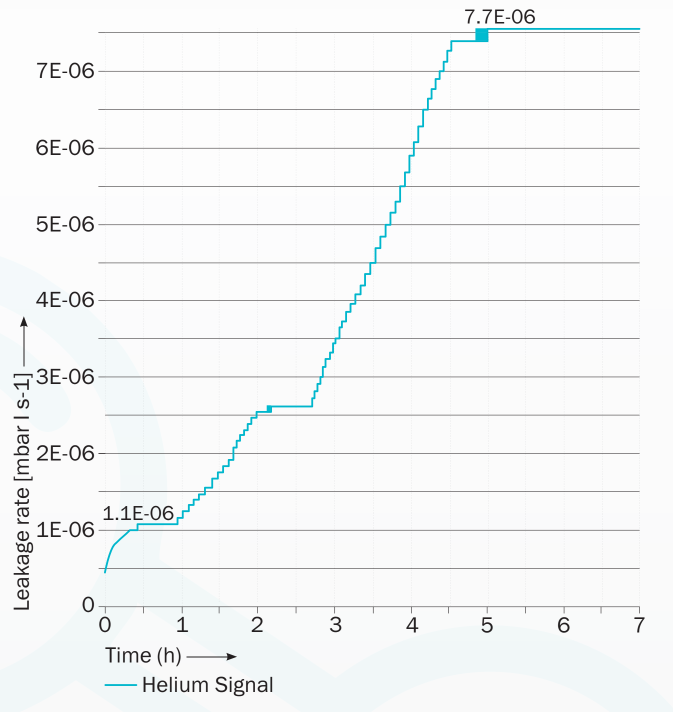

Figure 3: Typical permeation plot

The helium leakage curve generated by the mass spectrometer is a typical permeation curve with steep initial growth and increasing saturation as it reaches the permeation equilibrium. Once a steady permeation was established, pressure was raised to the next level, as illustrated in Figure 3.

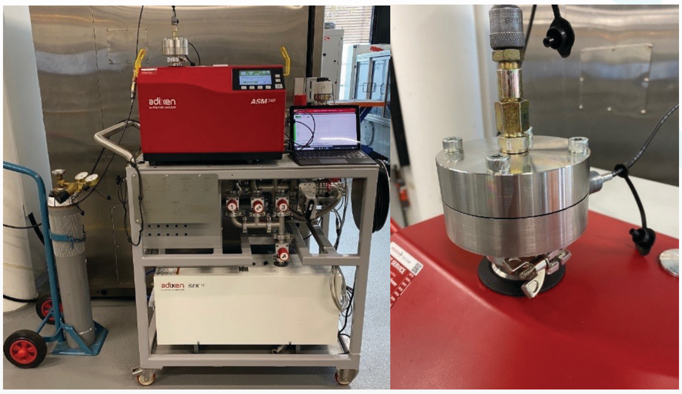

Figure 4: Elastomer test setup

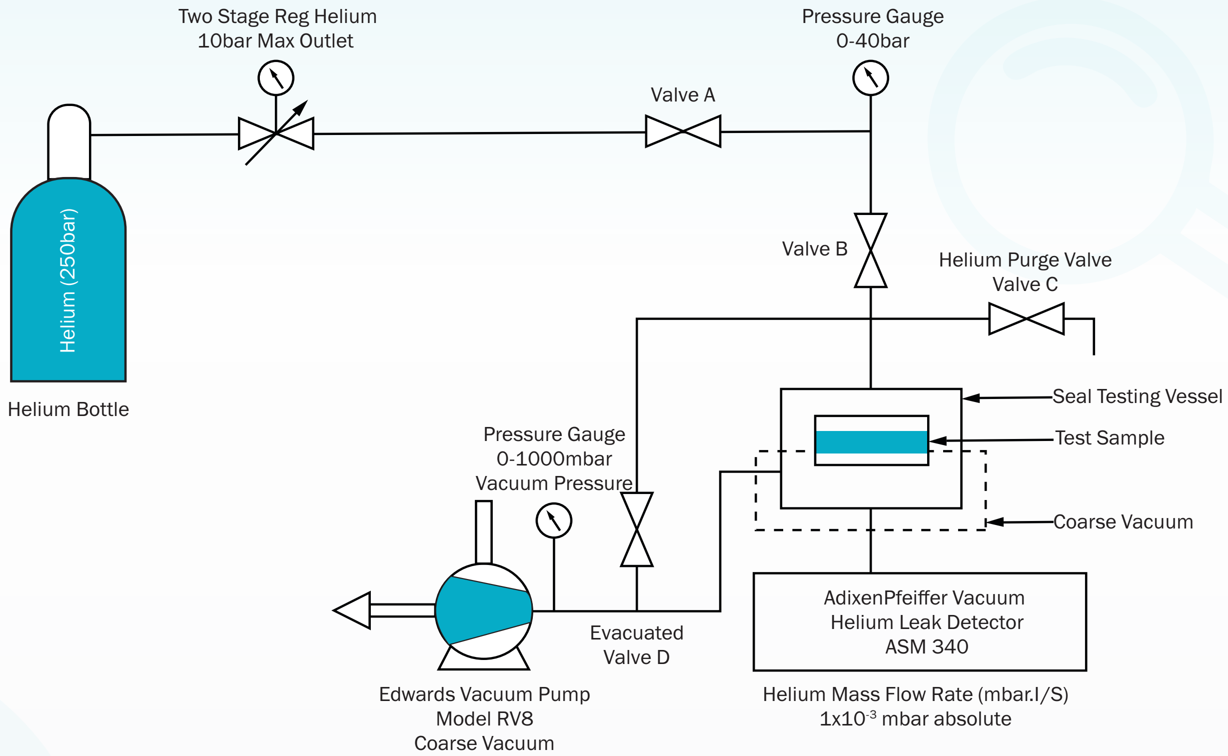

Figure 5: Test setup for permeation testing

Calculations

Permeability has been defined as the ease with which a gas or vapor passes through a solid. The general formula for permeation is:

$$Q=K_pA\,\frac{\Delta P}{L}$$

Where:

Q = rate of mass flow [mbar l s-1]

K_p = permeation rate constant [mbar l cm s-1 cm-2 bar-1]

A = area normal to flow [cm2]

ΔP = pressure drop (partial pressure) along the flow path [bar]

L = length of flow path [cm]

Rearrangement of the general formula gives

$$K_p=\frac{Q\times L}{A\times\Delta P}$$

A comparison of results based on differing pressures and exposure areas was made using the Permeability Rate Constant (K_p).

According to Pfeiffers “Lecksuche Kompendium” (leak-detection rate) the leakage rate for molecular flows can be approximated by using the molecular weight of the gasses. The leakage rate of hydrogen can be obtained by multiplying the leakage of helium by the following factor:

$$Q_{H2}=Q_{He}\times\sqrt{\frac{M_{He}}{M_{H2}}}=Q_{He}\times\sqrt{\frac{4}{2}}=Q_{He}\times1.41$$

However, this conversion does not provide leakage rates at different temperatures or pressure levels. It is only valid to compare different gas types. Other conversion factors can be found in the following Table 2.

This conversion gives only a rough direction as to what leakage to expect; the actual permeation rates in hydrogen should be measured with the gas itself.

Media	Name	Molecular mass [u]	Conversion from gas to helium: Multiply the leakage rate by figures given	Conversion from helium to gas: Multiply the leakage rate by figures given
H_2	Hydrogen	2.02	0.71	1.41
He	Helium	4.00	1.00	1.00
NH_3	Ammonia	17.03	2.06	0.48
N_2	Nitrogen	28.01	2.65	0.38
-	Air	28.96	2.69	0.37
O_2	Oxygen	32.00	2.83	0.35
Ar	Argon	39.95	3.16	0.32
CO_2	Carbon dioxide	44.01	3.32	0.30
CH_4 (R50)	Methane	16.04	2.00	0.20

Table 2: Conversion factors for commonly used gasses in molecular flow

Results and observations

FKM

Material	Shore	Temperature range	Characteristics	Recommended pressure level
VCT14	75	-35 °C to +200 °C/-31 °F to +392 °F	Good low-temperature performance	35 MPa/5,076 psi
V8T73	80	-45 °C to +200 °C/-49 °F to +392 °F	Medium pressure grade, improved low-temperature performance	35 MPa/5,076 psi
V8T3G	80	-45 °C to +200 °C/-49 °F to +392 °F	Medium pressure grade, improved low-temperature performance	35 MPa/5,076 psi
V9T82	90	-45 °C to +200 °C/-49 °F to +392 °F	Robust RGD low-temperature grade	70 MPa/10,153 psi

Table 3: Overview of FKM materials tested

FKM results

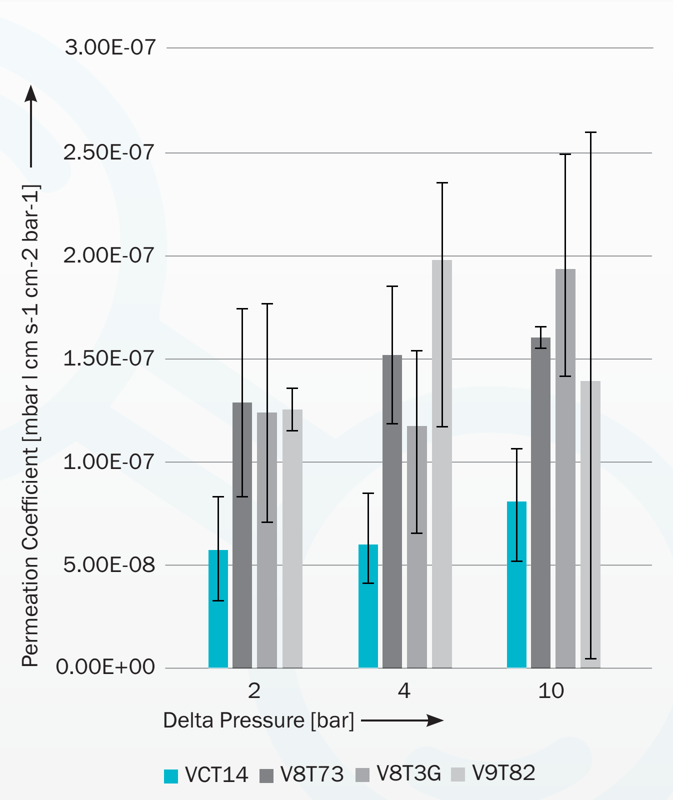

Figure 6: Permeation coefficients for FKMs by pressure

Observations

Surprisingly, 75 Shore A VCT14 has the lowest permeation coefficient across all pressure levels. At low pressures there is also no significant difference between 80 and 90 Shore A materials. With higher pressure, permeation increases for all materials.

The increase however is not linear and cannot be linked to the material hardness. In the case of 90 Shore FKM V9T82, unstable permeation behavior is observed.

However, the standard deviation indicates that more test data is necessary to accurately determine the material's behavior. Further testing is required to explore the relationship between hardness and permeability.

EPDM

Material	Shore	Temperature range	Characteristics	Recommended pressure level
E5T30	50	-45 °C to +150 °C/ -49 °F to +302 °F	Low-pressure grade	10 MPa/1,450 psi
E7T30	70	-45 °C to +150 °C/ -49 °F to +302 °F	Good compression set and low level of extractables	35 MPa/5,076 psi
E7T41	70	-45 °C to +150 °C/ -49 °F to +302 °F	Low compression set	35 MPa/5,076 psi
E8T31	80	-45 °C to +150 °C/ -49 °F to +302 °F	Higher pressure capability	35 MPa/5,076 psi
EBT25	87	-50 °C to +150 °C/ -58 °F to +302 °F	Robust in high pressures and against RGD	70 MPa/10,153 psi

Table 4: Overview of EPDM materials tested

EPDM results

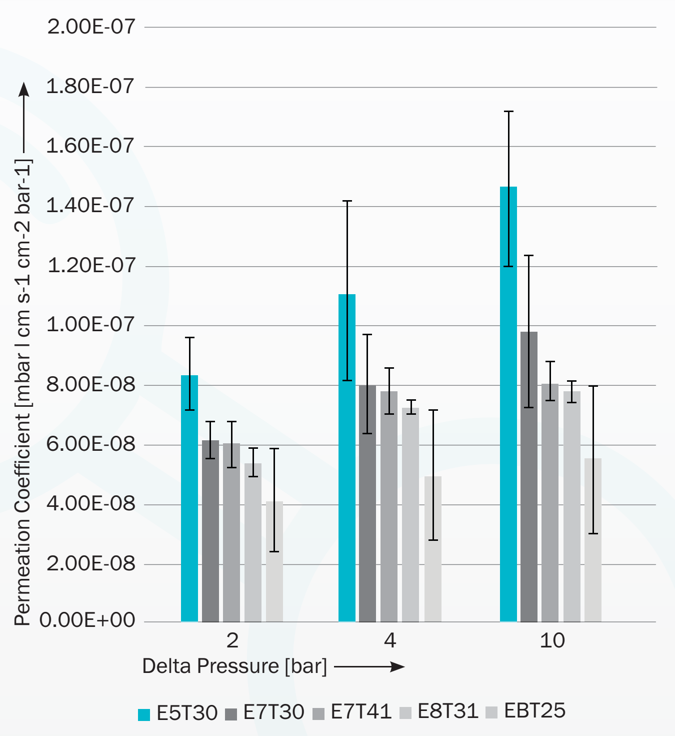

Figure 7: Permeation coefficients by pressure for EPDMs

Observations

For EPDM materials, a clear relationship between material hardness and permeation coefficient is observed. As hardness increases, the permeation coefficient decreases. This occurs because a higher hardness typically involves a greater amount of fillers, which reduce the number of free permeation paths between the polymer chains.

The results also show the permeation coefficient rises with increasing pressure; in particular for E5T30 with a hardness of 50 Shore A.

Permeation characteristics become more pressure dependent in sealing materials with a lower hardness. Therefore, when comparing permeation of elastomer compounds, the hardness should always be considered. Further investigation is needed to determine whether the influence of hardness diminishes at higher pressures above 10 bar.

Thermoplastics

Materials tested

Trelleborg has undertaken several studies on the permeability of a wide range of thermoplastic materials in low molecular gasses.

- September 2021: Helium supplied at 0.9 MPa/131 psi, vacuum at -0.1 MPa/-14.5 psi = 1 MPa/145 psi pressure differential
- September 2023: Helium supplied at 0.9 MPa/131 psi, vacuum at -0.1 MPa/-14.5 psi = 1 MPa/145 psi pressure differential

Within this whitepaper these results are combined.

The types of thermoplastic materials tested were:

- Torlon® Polyamideimide (PAI)
- Polychlorotrifluoroethylene (PCTFE)
- Zurcon® Polyetheretherketone (PEEK)
- Turcon® Polytetrafluoroethylene (PTFE)
- Zurcon® Thermoplastic polyurethane (TPU)
- Zurcon® Ultra-high-molecular-weight polyethylene (UHMWPE)
- Fluorinated ethylene propylene (FEP)

Material	Shore	Temperature range	Characteristics
Turcon® T01	PTFE	-253 °C to +260 °C/-423 °F to +505 °F	Static gas and cryogenic applications
Turcon® T05	PTFE	-200 °C to +260 °C/-328 °F to +505 °F	Low-duty dynamic and gas applications
Turcon® T10	PTFE	-60 °C to +300 °C/-76 °F to +572 °F	High pressure and low lubrication
Turcon® T40	PTFE	-60 °C to +300 °C/-76 °F to +572 °F	Excellent wear and low friction
Turcon® T78	PTFE	-200 °C to +300 °C/-328 °F to +572 °F	Low pressure rotary
Turcon® M03	PTFE	-253 °C to +260 °C/-423 °F to +505 °F	Cryogenic, low-pressure gas
Turcon® MF2	PTFE	-253 °C to +260 °C/-423 °F to +505 °F	Good gas tightness, cryogenic application
Turcon® MH6	PTFE	-200 °C to +260 °C/-328 °F to +505 °F	Dynamic and cryogenic application
Turcon® MH8	PTFE	-200 °C to +260 °C/-328 °F to +505 °F	Dynamic and cryogenic application
Zurcon® Z22	PU	-45 °C to +110 °C/-49 °F to +230 °F	Low temperature with high robustness
Zurcon® ZLT	PU	-55 °C to +110 °C/-67 °F to 230 °F	Lower temperature with high robustness
Zurcon® Z43	PEEK	-200 °C to +260 °C/-328 °F to +505 °F	Back-up rings and corner reinforcement rings
Zurcon® Z431	PEEK	-200 °C to +260 °C/-328 °F to +505 °F	Back-up rings and corner reinforcement rings
Zurcon® Z53	PU	-45 °C to +110 °C/-49 °F to +230 °F	Cast PU general purpose
Zurcon® Z54	PU	-45 °C to +110 °C/-49 °F to +230 °F	Cast PU higher hardness
Zurcon® Z80	UHMWPE	-200 °C to +90 °C/-328 °F to +194 °F	Water-based dynamic applications
Zurcon® Z83	UHMWPE	-200 °C to +130 °C/-328 °F to +266 °F	High-cleanliness applications
Zurcon® DH3	PCTFE	-270 °C to +140 °C/-454 °F to +284 °F	Cryogenic H2 applications
Torlon® Q4A	PAI	-40 °C to +260 °C/-40 °F to +505 °F	Excellent compressive and impact strength
Torlon® Q4B	PAI	-40 °C to +260 °C/-40 °F to +505 °F	Excellent compressive and impact strength
Torlon® Q4C	PAI	-40 °C to +260 °C/-40 °F to +505 °F	High strength with good dimensional stability
Zurcon® ZH2	PEEK	-253 °C to +260 °C/-423 °F to +505 °F	Cryogenic application
Zurcon® ZH1	PEEK	-200 °C to +260 °C/-328 °F to +505 °F	Cryogenic application
FEP	FEP	-200 °C to +200 °C/-328 °F to +392 °F	Tough, flexible fluoropolymer

Table 5: Materials tested over all studies

Thermoplastic results

In the table below the data is sorted in order of tightness, and where there are multiple results, it takes into account the lowest tightness for the order.

Material	Helium Permeability Rate Constant k_p [mbar l cm s-1 cm-2 bar-1]	
	Sept 2021	Sep 2023
Turcon® T01		1.66E-08
Turcon® T05		1.69E-08
Turcon® T10		7.73E-08
Turcon® MH6		9.38E-08
Turcon® T78		9.62E-08
Turcon® M03		1.16E-07
Turcon® T31		1.22E-07
Turcon® MH8		1.42E-07
Turcon® T40		1.52E-07
Turcon® MF2	1.99E-07	

Table 6: Helium permeability results using constant K_p for Turcon® materials

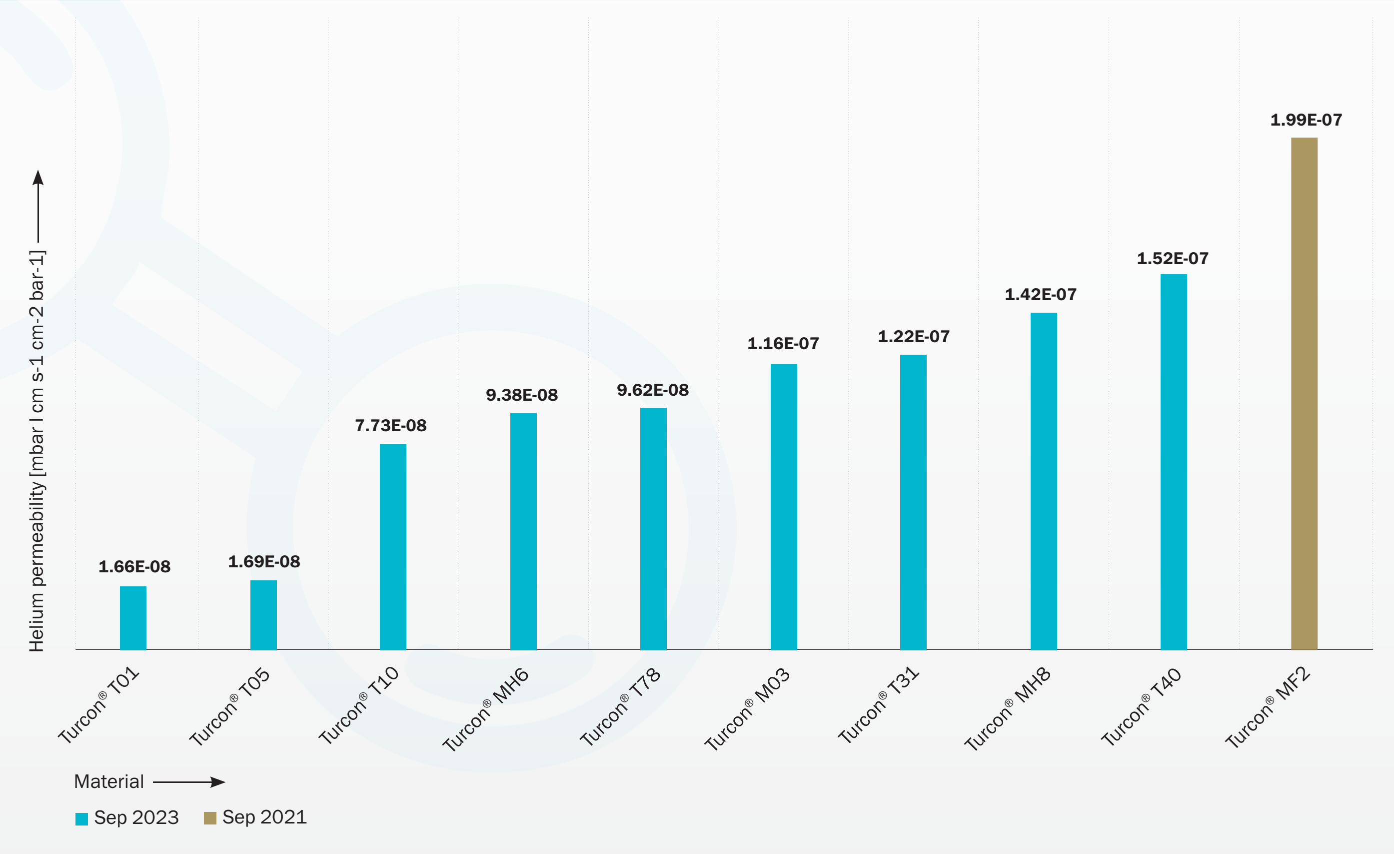

Figure 8: Helium permeability results using constant K_p for Turcon® materials

Material	Helium Permeability Rate Constant k_p [mbar l cm s-1 cm-2 bar-1]	
	Sept 2021	Sep 2023
Zurcon® Z53		2.72E-09
Zurcon® Z431	9.15E-09	4.01E-09
Zurcon® Z54		6.74E-09
Torlon® Q4B	6.87E-09	
Torlon® Q4A	7.56E-09	
Zurcon® ZH1	8.33E-09	
Zurcon® Z83		8.93E-09
Zurcon® Z43		1.29E-08
Zurcon® ZH2	1.49E-08	
Zurcon® DH3	2.09E-08	
Zurcon® Z80	2.29E-08	
Zurcon® Z22 (TPU)	3.78E-08	
Zurcon® ZLT (TPU)	4.38E-08	
Torlon® Q4C	5.52E-08	
FEP		1.19E-07

Table 7: Helium permeability results using constant K_p for Zurcon® materials

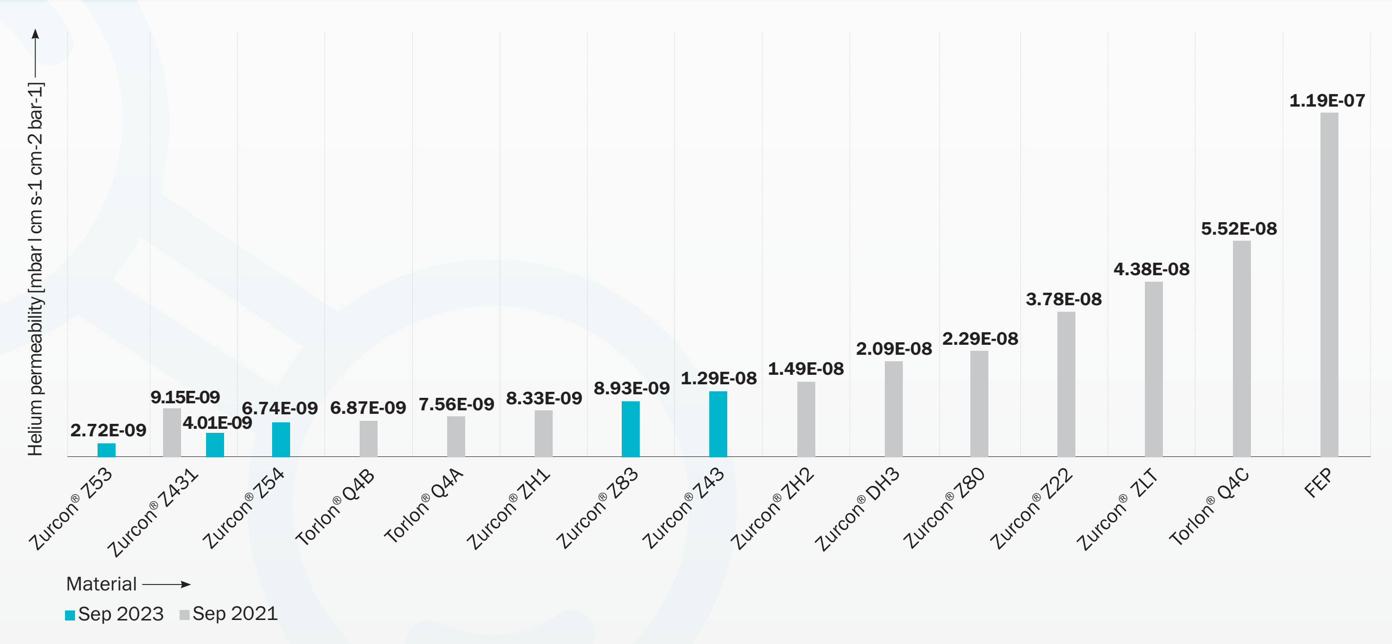

Figure 9: Helium permeability results for Zurcon® materials

Observations

Permeation coefficients range from 2.73E-09 to 1.99E-07 [mbar l cm s-1 cm-2 bar-1]. The test results indicate that thermoplastic materials exhibit lower permeability to light gasses than elastomer materials. This should be considered alongside other sealing criteria to select the most suitable material. The results suggest a pattern where materials with higher crystallinity and density demonstrate lower levels of permeability.

Materials with lower permeability tend to have higher hardness levels, necessitating a greater load to achieve interface tightness than elastomeric materials. Other factors affecting thermoplastic permeability include the size and type of fillers used in a compound; for example powder-filled materials are generally less permeable than fiber-filled, and compounds containing smaller particles tend to demonstrate lower permeability.

Balancing seal permeability with other sealing characteristics

Permeation is only one aspect of hydrogen sealing and each specific application requires seals with different characteristics to address different challenges.

The results show that generally harder elastomers and thermoplastics demonstrate superior resistance to permeation. However, these materials can present sealing performance challenges; harder elastomers may not fill gaps effectively, while thermoplastics lack elasticity.

A careful balance must be found for each application between permeability and the additional sealing characteristics required for effective functionality.

Static sealing

In some static applications, for instance gaskets, the hardness or the lack of elasticity of a material is not a critical issue.

O-Rings need to fill a groove and harder materials may not do this effectively. The material used must balance this requirement with the necessary level of permeability. Likewise, harder thermoplastic materials require higher interface loads compared to lower-hardness versions and elastomers to achieve tightness.

Wear life and dynamic resistance

In dynamic applications, hard non-permeable seals can cause significant wear and shorten the life of rods and pistons. When selecting harder thermoplastic materials for dynamic applications, the hardware surface must be considered to avoid surface wear. The permeability of coatings and platings is essential to consider alongside hardness.

In a self-contained system featuring a central piston and hydrogen either side, the transmission of hydrogen across the seal is less critical than ensuring the piston moves without excessive wear. For static applications, a permeation-resistant sealing material should demonstrate maximum leak tightness where necessary.

Interface leakage

Materials with lower levels of permeability typically exhibit higher density and hardness. This increased hardness can impact a seal's interface tightness and should be factored into material selection. Improved hardware surface finish and increased interface loading of the seals can alleviate this issue; thermoplastic seals can provide equivalent tightness performance to elastomer seals in specific sealing applications.

There is therefore a dilemma between material permeability and achieving an interface fit that ensures effective sealing that must be considered for each specific application to determine the optimum solution.

Temperature

The temperature range of the application must be considered when selecting the most suitable material. Lower temperatures influence the hardness of the materials and with that the interface tightness. Furthermore, at low temperatures, it's essential to consider pressure levels, as high pressures can affect the low-temperature performance of sealing materials.

Chemical compatibility and RGD

It is critical to assess the chemical compatibility of the selected material with the media to prevent degradation of seal performance or contamination of the media. Furthermore, the ability to withstand rapid gas decompression (RGD) must be considered, particularly when selecting elastomer-based seals, as abrupt changes in application pressure can result in material damage from gas release.

Surface finish

It is more difficult to achieve a robust interface seal with a hard material. However, smoother surface finishes contribute to more effective interface sealing; in dynamic applications thermoplastics offer better wear performance.

Surface finish must align with the specific parameters and requirements of each application. When leak-tightness is a priority, a smooth surface finish is essential. This is particularly critical for effectively sealing hydrogen at low temperatures.

Seal configurations

In many applications, seals do not function alone, for instance in fluid power systems. Sealing experts can develop configurations where each seal fulfils its intended function and, if necessary, is positioned to minimize contact with hydrogen in the case of permeable materials.

Conclusions

This study compares the permeation properties of several elastomers and thermoplastics that are frequently used in hydrogen sealing applications.

Among the elastic sealing materials tested, TPUs demonstrate the lowest permeation due to their thermoplastic nature. The EPDM compounds show less permeability than FKM materials which are best suited to high-temperature environments or blue hydrogen applications where mineral oil or hydrocarbons may also be present. In applications where the material is exposed to oil, such as in compressors and valves, EPDM is less effective than FKM. Therefore, EPDMs are often favored for pure hydrogen applications.

Different grades within the same material family exhibit varying performance levels in hydrogen applications. As the hydrogen market evolves and sealing requirements become more defined, new materials are being specifically engineered to seal hydrogen. Two examples are Trelleborg's EPDM material H2Pro™ EBT25 and thermoplastic polyurethane (TPU) Zurcon® H2Pro™ ZLT.

The permeation results of thermoplastics can guide engineers when selecting the most suitable compound for hydrogen applications. The tests indicate that sintered materials such as PTFE compounds tend to show a higher permeation level. To improve wear and friction as well as mechanical properties, PTFE materials are usually enhanced with fillers.

Therefore among the PTFE grades, unfilled PTFE demonstrates the lowest permeation due to fewer diffusion paths for hydrogen through the fillers.

Achieving optimum sealing and seal longevity in hydrogen environments requires an application-specific analysis of each material that considers factors beyond permeability, including its ability to prevent leakage, friction characteristics, chemical compatibility, temperature resistance and interface fit.

Sealing configuration designs can also allow for the combination of materials, for example a lower-density material to optimize interface sealing alongside a denser polymer to minimize sectional permeability.

The involvement of sealing experts like Trelleborg from the concept stage is critical to understanding the relative importance of material characteristics for specific applications and thereby optimizing overall seal performance.

Trelleborg is a world leader in engineered polymer solutions that protect essential applications in demanding environments. Its innovative solutions accelerate performance for customers in a sustainable way.

Trelleborg Sealing Solutions is a leading developer, manufacturer and supplier of precision seals, bearings and custom-molded polymer components. It focuses on meeting the most demanding needs of aerospace, automotive and general industrial customers with innovative solutions.

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