VDMA
Fluid Power Association

22nd ISC

International Sealing Conference

Stuttgart, Germany
October 01 - 02, 2024

Sealing Technology –
Challenges accepted!

UNI STUTTGART

ISBN 978-3-8163-0768-6

Fachverband Fluidtechnik im VDMA e. V. Lyoner Str. 18
50628 Frankfurt am Main
Germany

Phone +49 69 6603-1513
E-Mail maximilian.baxmann@vdma.org
Internet www.vdma.org/fluid

Influence of hydrogen on the material properties of non-metallic materials for sealing applications

Philipp Hirstein, Sandra Kofink, Joel Thompson

Hydrogen entails challenging conditions for all sealing materials. For metals, the effect of hydrogen embrittlement is well known. However, little attention has been paid to elastomers and plastics, which are commonly used as sealing materials. For hydrogen storage and transport, high pressures and extreme temperature situations must be covered. This paper discusses the influence of hydrogen on mechanical properties, volume and weight change as well as compression set. Additionally, the influence of extreme application temperatures on mechanical properties is presented. In general hydrogen has no harmful influence on the compounds presented in this study, which are known as polymers suitable for hydrogen use.

1 Introduction

The hydrogen market is experiencing rapid growth due to various factors such as the need for low-emission mobility, political support and funding [1], as well as technological advancements. It is estimated that the hydrogen market's turnover could reach 840 billion euros by 2050, potentially creating 5.4 million jobs [2]. In addition, the share of hydrogen in global final energy consumption is projected to increase to 19 percent by 2070, which would translate to an annual hydrogen production of 1,084 million tons [3].

However, the use of hydrogen poses certain technical challenges, especially in terms of sealing technology, as different requirements are imposed on seals and materials throughout the entire hydrogen value chain, including production, storage, transportation, and end applications such as fuel cells or combustion [4].

The development of hydrogen seals faces a significant hurdle due to the absence of meaningful global industry standards. The hydrogen industry sometimes utilizes specifications that are intended for high-pressure gases in the oil and gas sector, such as Norsok M-710. However, these standards do not accurately represent the actual conditions of hydrogen applications. A comprehensive analysis of the standards landscape found that only a limited number of specifications are geared towards elastomers and plastics, which are commonly classified as non-metallic materials. The tests that are typically cited include:

- Oxygen ageing (according to ASTM D572)
- Ozone ageing (according to ISO 1431)
- Hydrogen compatibility

However, the fundamental question of how hydrogen impacts the material properties of sealing materials is still not answered. Hydrogen is not an aggressive gas, but it diffuses easily into non-metallic materials such as elastomers and plastics. It is therefore crucial to understand how sealing materials are affected by the absorbed hydrogen molecules. This will help to determine if a component is "hydrogen ready". If components and systems need to be redesigned to make them fit for hydrogen, it can cause significant costs in some cases.

2 Material Properties Relevant for Hydrogen Sealing

For metals the effect of hydrogen embrittlement is well-known and is the subject of many studies. This phenomenon can significantly reduce the ductility and load-bearing capacity, causing cracking and catastrophic brittle failures at stresses below the yield stress [5]. A frequently asked question from designers who are used to working with metal is how much sealing materials will embrittle or change under the influence of high-pressure hydrogen. Especially in the field of hydrogen storage and transport, seals must be able to withstand extreme temperatures and pressures.

When exposed to certain fluids or gases such as hydrogen, elastomers and thermoplastic materials may undergo changes in their physical and chemical properties, consequently affecting their performance and durability. Therefore, it is important to test the compatibility of the sealing material against hydrogen when it is planned to use them in a hydrogen-related application.

First, it is important to know which material properties can be affected by hydrogen. Secondly, there is a need to understand which of these properties are relevant to ensure a good sealing function. This study will investigate how the most relevant parameters change under the influence of hydrogen.

2.1 Mechanical properties

Material behavior is typically characterized by mechanical properties such as tensile strength, stiffness modulus and elongation at break. These universal characteristics need to be investigated for both elastomers and plastics.

Another important parameter which is relevant for a reliable sealing function is the change in weight and volume. Due to the small size of hydrogen molecules, diffusion into the polymer matrix is inevitable and will cause swell. In real applications, this can become critical if the sealing groove is overfilled, leading to damage of the sealing material or the surrounding hardware. However, shrinkage can be more concerning as it can easily cause leakage in sealing applications. Since hydrogen diffuses easily into the polymer matrix, it will also escape after pressure releases. Therefore, it is vital to differentiate between reversible swell, which is important for the design of a sealing system, and permanent volume change, which indicates changes in the polymer.

If weight loss is present, it means part of the polymer was extracted and is now floating in the hydrogen gas, indicating that material properties are most likely changed. Additionally, this could result in damaging sensitive downstream systems like fuel cells.

Furthermore, for elastomer sealing the change of hardness and compression set are crucial to understand if hydrogen affects the sealing properties of a compound. For plastics this is not relevant, because the plastic seals are typically activated by pressure, metal springs or elastomer energizers. Compression set describes the loss of elasticity, meaning the permanent deformation that remains after a seal has been compressed over a longer period of time. When selecting a sealing material, it is important to ensure that compression set is still in an acceptable range considering the influence of the surrounding media.

2.2 Temperature-related material properties

Especially for elastomers, the temperature limits are very important to consider when selecting a compound. At very low temperatures the elastomer will not only shrink, but also lose its elasticity, resulting in leakage. The lower temperature limit is determined by the glass transition temperature T_G and by the T_{R10} value. The latter describes the temperature at which an elastomer has 10 percent of its elasticity, which is the minimum requirement for a good sealing function. In combination with high pressures, these limits will increase, commonly known as T_G-shift. For most elastomers the T_G-shift lies in the range of two to three Kelvin per 10 MPa pressure increase. Since this phenomenon is independent of the media and not specific for hydrogen only, it will not be considered in this study.

The upper temperature limit of plastics and elastomers is largely determined by the base material. At higher temperatures, mechanical properties decrease, and degradation is accelerated. Materials for sealing applications should be selected below their upper temperature limit. Therefore in this study the change of temperature limits is not considered, but rather the influence of extreme application temperatures on the mechanical properties of sealing materials.

3 Materials and Methods

In this study we investigate four ethylene propylene diene monomer rubbers (EPDM), one fluoroelastomer (FKM) and one thermoplastic polyurethane (TPU) as elastomer sealing materials. For the plastics side one ultra-high molecular weight polyethylene (UHMW PE) and six high-performance plastics with a PTFE-matrix as listed in Table 1 are tested. The compounds are selected according to common industrial practice and hydrogen market experience.

3.1 Compatibility testing

A very established method for testing media compatibility is ISO 1817. This standard specifies a procedure for determining the resistance of vulcanized and thermoplastic rubbers to the effects of liquids or vapors in accordance with specified conditions. The method involves immersing test specimens of elastomers in a test liquid or exposing them to a test vapor for a specified duration and temperature, and then measuring the changes in their mass, volume, hardness, tensile strength and elongation at break.

Table 1: Materials used in this study

Material Family	Compound Name	Hardness	Temperature Range
EPDM	E7T30	70 Shore A	-45 °C to +150 °C
	E8T31	80 Shore A	-45 °C to +150 °C
	E8T24	80 Shore A	-50 °C to +150 °C
	EBT25	86 Shore A	-50 °C to +150 °C
FKM	V9T82	90 Shore A	-45 °C to +200 °C
TPU	ZLT	93 Shore A	-60 °C to +110 °C
Turcon® PTFE	T01	22 Ball Ind.H.	-200 °C to +260 °C
	T05	24 Ball Ind.H.	-200 °C to +260 °C
	MF2	22 Ball Ind.H.	-200 °C to +260 °C
	MF6	32 Ball Ind.H.	-200 °C to +260 °C
	MF8	55 Shore D	-200 °C to +260 °C
UHMW PE	Z80	29 Ball Ind.H.	-200 °C to +80 °C

The test method was enhanced to mirror hydrogen specific challenges to the materials. The samples were immersed for 168 hours at nominal working pressure (NWP, typically 70 MPa) and then pressure was released to ambient conditions within less than one second [6]. This approach is based on the toughest requirements for RGD-testing, namely ISO 17268 and SAE J2600.

Test samples of each material were loaded into a pressure vessel to be filled with gaseous hydrogen. Once pressurized, the vessel was placed into a temperature chamber. A typical pressure vessel is shown in Figure 1. After 168 hrs, the final pressure was recorded before depressurizing to verify that the gas did not leak during the test.

Figure 1: Compatibility test pressure chamber

The change in mass and volume was measured after one hour for the first interval and a second time after 24 hours. In contrast, tensile testing was only carried out after 24 hours as the change of mechanical properties was to be detected without the influence of remaining swelling due to hydrogen.

3.2 Compression set testing

For elastomeric sealing materials, the compression set is one of the most important values. It is a method to evaluate the ability of the material to recover to its original shape after being compressed for a period of time. Usually, the value is measured after ageing in air at a temperature dependent on the actual application temperature. The surrounding media can improve or impair the compression set of a material depending on the interaction between material and media. Tests were carried out in a hydrogen atmosphere to determine the influence of this gas on the compression set of elastomers. All tests were performed according to ISO 815-1A in which the material is compressed between two metal plates. Compression rate depends in this case on the hardness of the material as described in the standard.

Sample materials were 13 x 6 mm buttons clamped between two stainless steel plates. The fixture and compressed samples were loaded into a pressure chamber to be filled with hydrogen. A vacuum was pulled on the chamber to remove ambient air prior to pressurizing with gaseous hydrogen to 0.01 MPa. The filled gas chambers were then placed into a temperature-controlled chamber at the specified conditions for 72 hrs. Post-test material properties were measured upon test completion.

4 Results

Given the distinct nature of elastomers and plastics which results also in different test results to be investigated, the results presented in this chapter are separated by material type. Results of mechanical properties are obtained from S2 dog bone samples. Results for volume and weight change are measured on O-Ring samples, typically one hour after pressure release.

4.1 Elastomers

4.1.1 Room temperature tests

When immersed at room temperature, the samples show small changes of volume and weight (see Figure 2). Weight change is close to zero and therefore negligible. Volume increases for all elastomers, whereas the TPU material, ZLT and the FKM material, V9T82, show very small swell of much less than one percent. The EPDM materials with 80 Shore A show higher swell of around 1.5 percent. Compared to compatibility tests in other fluids, this is however still very low.

Looking at the changes of tensile strength and elongation at break, it can be stated that hydrogen does not cause embrittlement of the elastomers. The change of IRHD hardness shown in Figure 3 further confirms this. Four out of the six materials displayed show changes of less than five percent, which is negligible in the elastomer world. The TPU material, ZLT, had an 11 percent change in tensile strength and elongation values when compared to pre-test results. The absorbed hydrogen seems to cause a slight softening of the material.

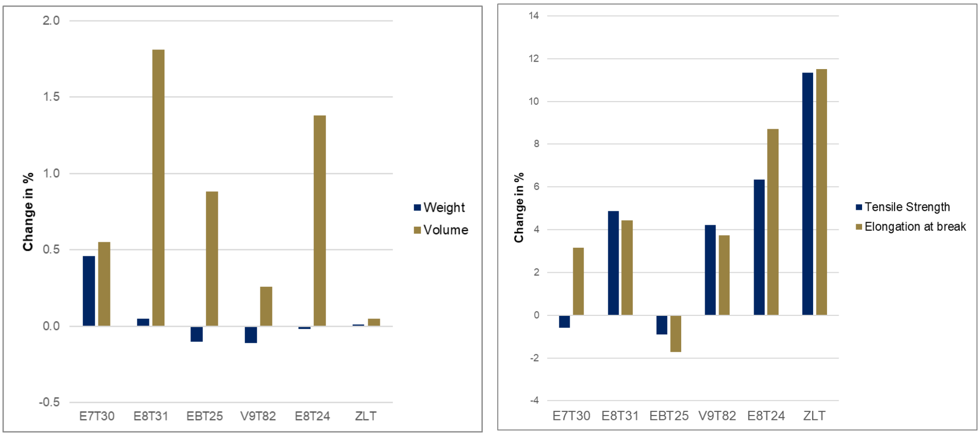

Figure 2: Change of volume, weight, tensile strength and elongation at break of different compounds after immersion in H2 for 168 h at +23 °C and 70 MPa

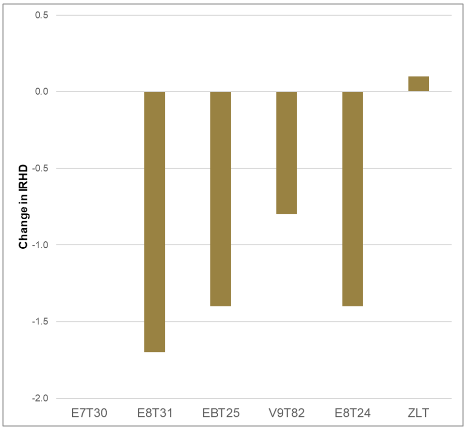

Figure 3: Change of IRHD hardness of different compounds after immersion in H2 for 168 h at +23 °C and 70 MPa

Mechanical properties are normally measured on dog bone specimens, whereas in real applications the seal is molded into a shape e.g. an O-Ring. Comparing the volume change of these two specimen types produces interesting results, see Figure 4. All materials show a much greater volume change when tested as an S2 sample; E8T31 swells three times more, EBT25 eight times more and ZLT even 10 times more. The reason for this phenomenon lies in the manufacturing method of the samples. When produced as an O-Ring, the material experiences a greater amount of shear stress in the molding tool and the polymer network is more dense than in a test sheet. Therefore, the hydrogen molecules are able to more easily enter a specimen cut from a test sheet. Thus, if a material passes a certification test based on results from a dog bone sample, the final seal will likely swell less in a real application. This phenomenon should be considered in design and certification processes.

The volume change considered here is measured one hour after taking the material out of the hydrogen atmosphere. If you compare the swell 24 hours later, it becomes obvious that the volume change is not permanent. This indicates that the hydrogen gas likely did not have any adverse effects on the polymer. The volume increase of V9T82 shown in Figure 4 is small and still within the measurement error.

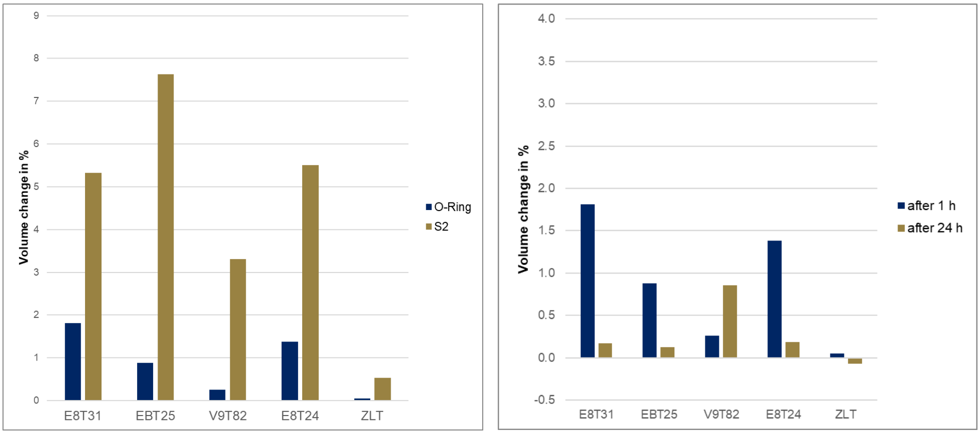

Figure 4: Volume change depending on specimens (left, 1 hour) and time of measuring (right) after immersion in H2 for 168 h at +23 °C and 70 MPa

4.1.2 Influence of the temperature

Hydrogen seals need to cover a large temperature window from typically -40 °C to +85 °C. Results for volume change at room temperature and at the temperature limits are shown in Figure 5. E8T31 shows higher swell at elevated temperature but stays overall in a small percentage range.

Figure 6 shows the change of tensile strength and elongation under the influence of temperature. Typically, elongation tends to increase at +85 °C and decrease at -40 °C. However, V9T82, E7T30, E8T24 and EBT25 show almost no change in elongation at break at elevated temperature compared to prior hydrogen immersion. A reason could lie in the higher mobility of the polymer chains which allows entrapped hydrogen molecules to escape faster. The tensile tests were done at room temperature 24 hours after pressure relief. For tensile strength there is similarly no clear trend visible. Only E8T31 shows a slight increase in tensile strength over temperature. For ZLT, the previously described slight softening is reduced at higher temperatures. After exposure to -40 °C hydrogen, the polymer shows a small embrittlement. However, it should be investigated if this effect persists after a longer period. Due to the very dense structure of this polymer, some hydrogen molecules could still be trapped in the matrix after 24 hours.

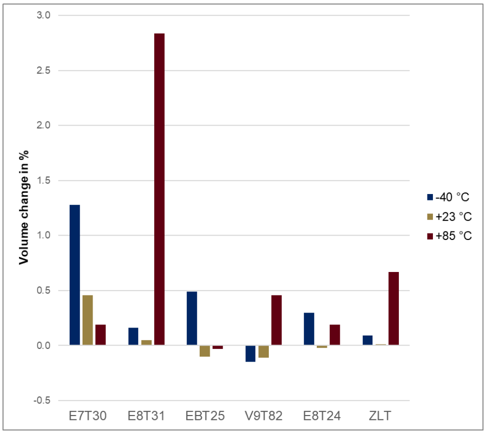

Figure 5: Volume change after immersion in H2 for 168 h at different temperatures and 70 MPa

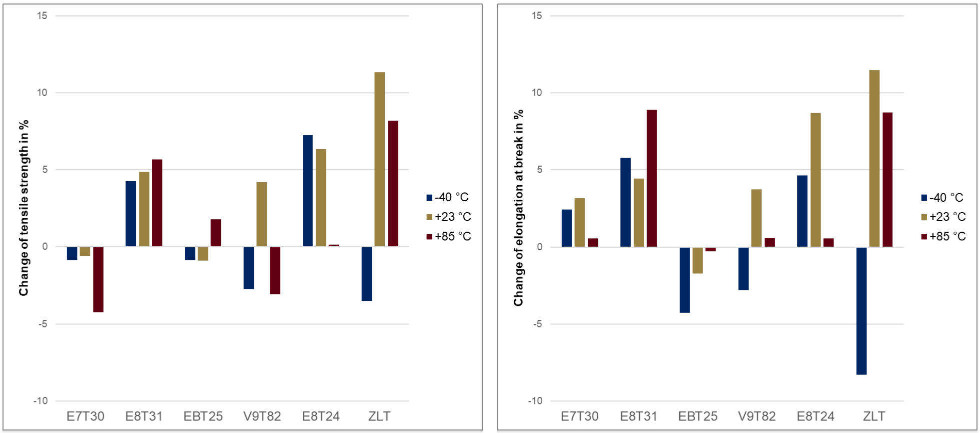

Figure 6: Change of tensile strength and elongation at break after immersion in H2 for 168 h at different temperatures and 70 MPa

In essence, the results show that there is no critical influence on the mechanical properties of the tested elastomers. Compared to immersion tests in some fluids, the changes observed here are relatively very small.

4.1.3 Compression set

When elastomer seals lose their elasticity over lifetime, leakage can occur easily. It is therefore vital to understand if the compression set changes under the influence of hydrogen. The results of five elastomers are shown in Figure 7. Except for E8T24, hydrogen has no or even a positive impact which comes most likely from the absence of oxygen. Ageing elastomers in air allows oxygen to attack the polymer chains, which is why a hydrogen atmosphere helps to reduce this effect. Small differences like in the case of V9T82 can also originate from the higher swell due to hydrogen, which could compensate the actual compression set. The reason for E8T24 showing higher compression set in hydrogen needs to be studied further.

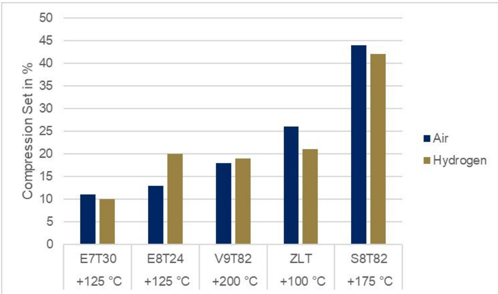

Figure 7: Compression set after immersion in H_2 and air for 72 h according to ISO 815-1A

4.2 Thermoplastic polymers

In the initial testing phase for thermoplastic polymers, the goal was to investigate the effect of hydrogen on the volume and mechanical properties of the seal material. In Figure 8, the PTFE-based compounds show a small noticeable swell independently of the filler content. This is due to the sintered structure of PTFE materials. When it comes to mechanical properties, only MF2 and T05 show an increase in strength and elongation, whereas the other PTFE compounds show a small embrittlement of less than five percent, which is normally not a reason for concern.

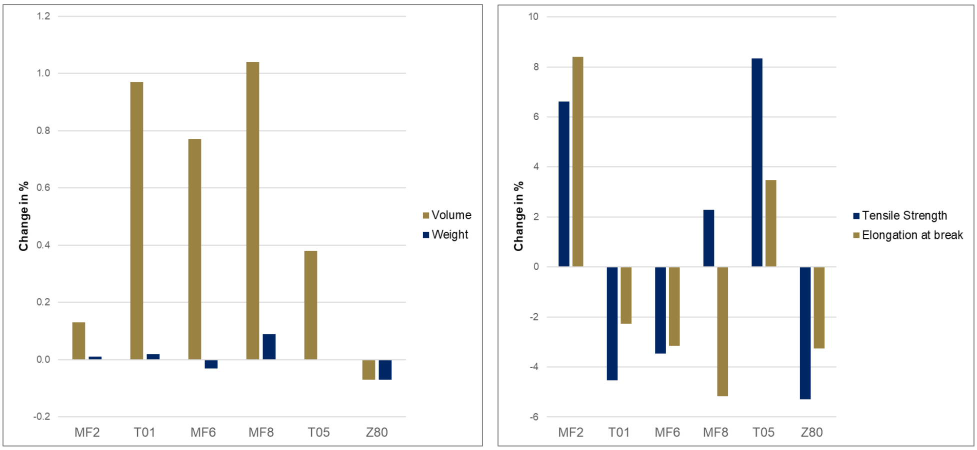

Figure 8: Change of volume, weight, tensile strength, and elongation at break of different compounds after immersion in H_2 for 168 h at +23 °C and 70 MPa

Z80 is a UHMW polyethylene with a solid thermoplastic matrix, which is why there is almost no weight or volume change, since the amount of hydrogen molecules absorbed must be very small. The mechanical properties also show a slight embrittlement below five percent.

Thermoplastic sealing materials are preferably used when the application temperature exceeds the limits of elastomers. With high temperatures, volume increases a bit more, but still below two percent as shown in Figure 9. The increase is slightly smaller in unfilled PTFE, which is T01, due to less diffusion paths for hydrogen along the fillers.

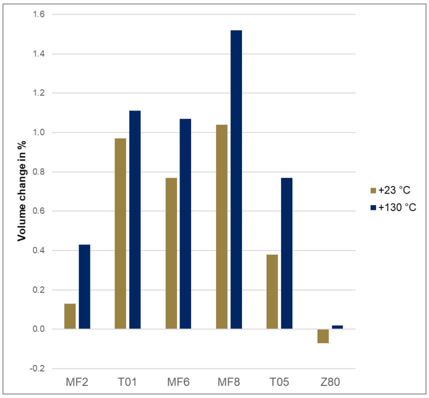

Figure 9: Volume change of thermoplastic compounds after immersion in H_2 for 168 h at +23 °C and 70 MPa

Figure 10 compares the mechanical properties at room temperature and +130 °C. Z80 is not shown, because its upper temperature limit is +80 °C. Overall higher temperatures tend to make the materials slightly more brittle. This can be observed in MF2, MF6, MF8 and T05 with low percentages. The amount of change however is

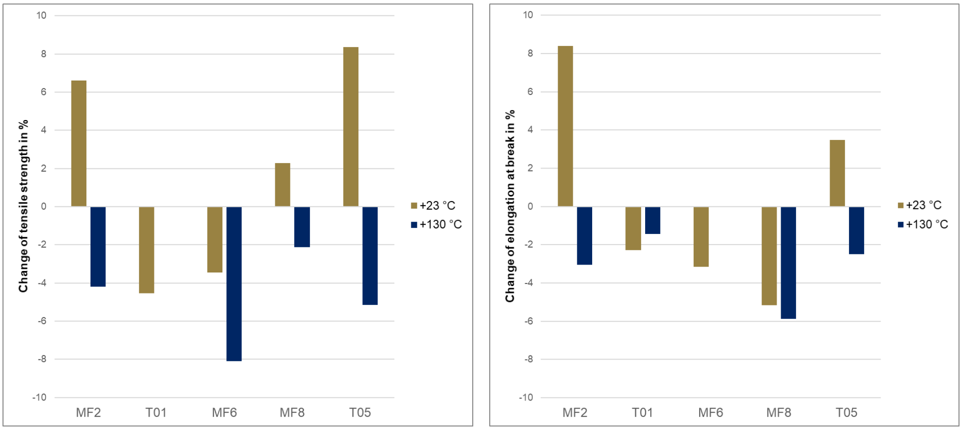

Figure 10: Change of tensile strength and elongation at break after immersion in H2 for 168 h at different temperatures and 70 MPa

still not at a worrying level. More research is needed to differentiate temperature aging effects from the influence of hydrogen at elevated temperatures.

5 Summary and Conclusion

In this study, the influence of hydrogen on non-metallic sealing materials, namely elastomer and plastics, is investigated. Focus lies on the change of mechanical properties, as well as volume, weight and hardness after hydrogen exposure at high pressure. Compression set under hydrogen atmosphere is also studied for elastomers, because it is highly relevant for the sealing performance.

The results show no embrittlement of the elastomers tested. Only in the case of one TPU material could a slight softening be observed. Also, extreme application temperatures of -40 °C and +85 °C show no critical influence on the mechanical properties of tested elastomers. The volume change is below two percent and is largely temporary. However, the results of volume change are highly dependent on the shape and production method of the samples. O-Ring samples show less change after hydrogen immersion. This phenomenon should be considered in design and certification processes. Compression set under hydrogen atmosphere shows no significant deterioration except for one compound, which needs to be studied further.

The swell of plastic materials under hydrogen atmosphere in this study is around one percent and does not depend on the filler level. The change of mechanical properties depends on the specific compound. Some improve and some decrease, but not more than five percent, which is usually not a concern. The influence of hydrogen at high temperature tends to show a slight embrittlement of the polymers investigated. More research is needed to differentiate temperature aging effects from the influence of hydrogen at elevated temperatures.

It is concluded that hydrogen has no significant influence on the compounds investigated in this study, which are known to be polymers suitable for hydrogen use. The findings should therefore not be generalized for all compounds of their material families. Specific testing may be needed to ensure a safe use in hydrogen applications.

6 References

[1] Bundesministerium für Wirtschaft und Energie: *Die Nationale Wasserstoffstrategie*, June 2020

[2] European Commission: *A Hydrogen Strategy for a Climate-Neutral Europe*, Brussels, June 2020

[3] IEA: *The Future of Hydrogen. Seizing Today's Opportunities*, 2019

[4] Trelleborg Sealing Solutions: https://www.trelleborg.com/de-de/seals/your-industry/hydrogen-sealing, visited on April 30, 2024.

[5] Barrera, O., Bombac, D., Chen, Y. et al.: *Understanding and mitigating hydrogen embrittlement of steels: a review of experimental, modelling and design progress from atomistic to continuum*. J Mater Sci 53, 6251–6290, 2018.

[6] DIN EN ISO 17268:2017-03: *Gasförmiger Wasserstoff - Anschlussvorrichtungen für die Betankung von Landfahrzeugen*, S.18

7 Authors

Trelleborg Sealing Solutions Germany

Schockenriedstr. 1, 70565 Stuttgart, Germany

Philipp Hirstein, M. Sc., Philipp.Hirstein@trelleborg.com

Sandra Kofink, M. Sc., Sandra.Kofink@trelleborg.com

Trelleborg Sealing Solutions Americas

2509 Bremer Rd, Fort Wayne, IN 46803, United States

Joel Thompson, M. Sc., Joel.Thompson@trelleborg.com

https://doi.org/10.61319/4IQN23QS