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Testing elastomeric materials in liquified gases

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To ensure safe and reliable products, elastomeric sealing materials in refrigeration systems and heat pumps have to be tested for their compatibility with refrigerants. The test method described in ISO 14903 and ISO 21922 covers aging in liquid refrigerant including a test in "wet" and "dry" condition. As part of a project to investigate the in-situ swelling behaviour of elastomers, the performance of elastomeric materials in liquid refrigerants was studied. The investigation focused on the behaviour of the materials during and after decompression in the autoclave. The data clearly indicate that the test description in the above-mentioned standards does not ensure a comparable test procedure or comparable results.

1 Introduction

Elastomeric materials play an important role as sealing in refrigeration systems and heat pumps. Knowledge of the interaction of these materials with refrigerants is therefore of interest.

The swelling behaviour of elastomers in contact with liquid refrigerants (also mixed with lubricants) is a common indicator of their resistance to the medium and thus an important parameter for the applicability of the polymer seals. Until now, it has only been possible to evaluate changes of the materials which were aged in refrigerants after their removal from the medium, i.e. after the decompression phase. Unfortunately, the data available to date were only of limited significance for the relevant behaviour of the materials during media exposure. Here, a new in-situ measurement method is showing its advantage. The measurement method allows an evaluation of materials under the influence of media (in-situ) and provides a basis for improved test procedures in conventional testing.

2 Compatibility testing of sealings for refrigeration systems and heat pumps

Compatibility tests for sealings used in refrigeration systems and heat pumps are listed in two standards. While ISO 14903 [1] describes the qualification of tightness of components and joints, ISO 21922 [2] covers the requirements, testing and marking of valves.

The general test procedure for elastomers is identical in both standards. The aging resp. exposure is carried out in a pressure vessel (test chamber /autoclave) suitable for safe handling of refrigerants under high pressure. The samples are aged completely submerged in the liquid phase of the refrigerant (which may contain oil). The aging temperature is 50 °C (ISO 14903) or 70 °C (ISO 21922) which is implemented by placing the autoclave in an oven or by direct heating of the autoclave. The minimum duration of exposure is 14 days (two weeks) for rubber seal materials and 42 days (six weeks) for thermoplastic seal materials.

After the aging, the autoclave is cooled down to ambient temperature and the test pieces are taken out from the autoclave. A procedure for removing the refrigerant from the pressure vessel (e.g. depressurization rate) is not described.

For the further testing two material states are specified: “wet” and “dry”. The material is considered to be wet within 30 min of removal from the autoclave. During this time, the hardness, weight and volume of the test pieces are to be determined. For testing in dry state, the samples are subsequently degassed at 50 °C in an oven until a constant mass is reached, and the resulting hardness, weight and volume are determined.

In both standards is noted that “*elastomers tested with CO_2, can accumulate significant amount of CO_2. The CO_2 cannot escape immediately when the test items are exposed to atmospheric pressure (de-gassing). Thus, it can create an immediate volume change larger than 25 %. Provided that no surface damage is made, volume change above 25 % is acceptable for CO_2.”* [1] [2]

3 In-situ testing of elastomeric materials

3.1 Experimental setup

For the in-situ testing, a temperature-controlled autoclave with a sight glass was used, which allows testing at temperatures up to 100 °C and pressures up to 95 bar (Figure 1). To provide the necessary illumination for visual evaluation of the sample, the autoclave was equipped with a pressure-resistant interior light.

The autoclave was heated using a connected thermostat. For measuring the temperature inside the autoclave, a Pt100 resistance thermometer was used. The pressure was monitored with both an analogue manometer and a digital pressure sensor. During the tests, pressure and temperature were recorded with a data acquisition system.

The elastomeric materials were tested as O-rings, which were found to be the most suitable sample geometry for the tests. The rings were placed on an adjustable O-ring holder which allows a defined elongation of the samples (Figure 2). This sample fixture can be rotated when installed in the autoclave so that exact positioning of the O-rings is possible.

The time-dependent swelling behaviour of the samples was recorded with a high-resolution camera system. Depending on the fluid density and the changing refractive index, the camera was focused manually. The recorded single pictures were analysed with image processing software. For each sample, the cross-section width of the O-ring cords as well as the distance between the cords were measured, (Figure 2). To eliminate errors due to different refractive indices of the test fluids, the sample holder was used as a calibration scale.

Figure 1: Autoclave system with camera

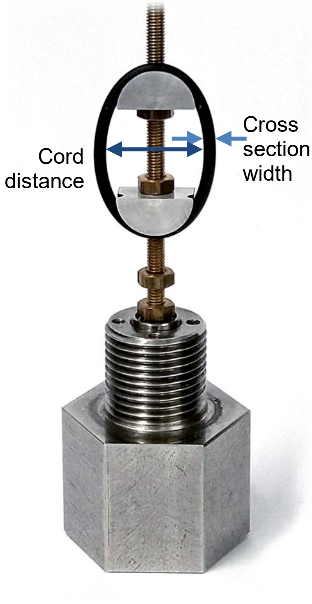


Figure 2: Sample holder

3.2 Samples and test conditions

The tests were performed with 20 x 2 mm O-rings placed on the specimen holder with a preload corresponding to an elongation of the rings of 5 %. The preload was kept the same for all tests in order to guarantee secure positioning of the samples and prevent them from slipping off the holder.

For the investigations, EPDM and HNBR were chosen. All elastomers tested are generally compatible for use with R744 (CO_2) and R1234yf. For clarity, only the investigations of the HNBR with R744 are presented here.

The tests in the liquid refrigerant were carried out at room temperature. The pressure given in the table (Table 1) is the equilibrium pressure of the refrigerant above the liquid phase.

Table 1: Test conditions for in-situ-tests with liquid refrigerants

	R744	R1234yf
Temperature [°C]	25	25
Pressure [bar]	64	7
Fluid density [g/cm³]	0.711	0.109

3.3 Results

In all tests, a short-term reduction in the sample volume occurred during the autoclave filling. This effect is related to the temperature reduction during the filling process.

The pressure reduction from 65 to 1 bar at the end of the test was realized by evaporation of the liquid refrigerant over a period of approximately 15 min. This also resulted in a temperature reduction, which is compensated to a certain extent by a corresponding counter-heating of the autoclave (external temperature control).

In contact with the liquid refrigerant, the samples showed an increase in volume. Depending on the material, a stationary state of swelling was reached after 15 min to 3 h when stored in liquid R744. After this exposure time, the volume of the sample did not increase any further (Figure 3).

During and after removing refrigerant from the autoclave, the samples showed a significant volume increase. Especially in a period of several minutes after reaching the ambient pressure, the liquid refrigerant dissolved in the material evaporates and causes the material to swell (Figure 3 and Figure 4).

The time required for the O-ring to regain a volume corresponding to that of the steady state during storage in liquid R744 was between 20 min and 2 h, depending on the material. After 1.5 to 4 hours, the samples have returned to their initial volume.

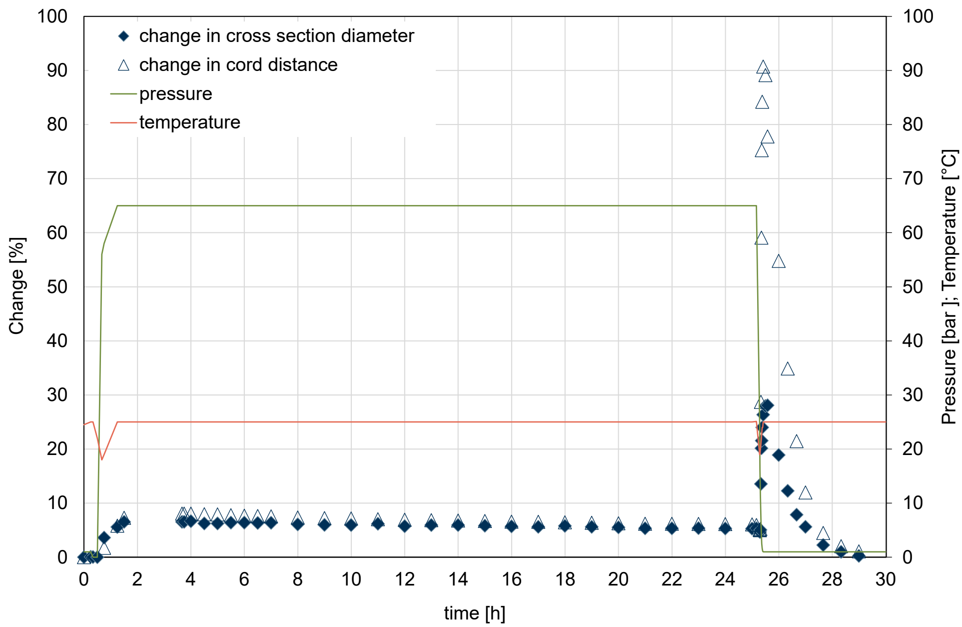
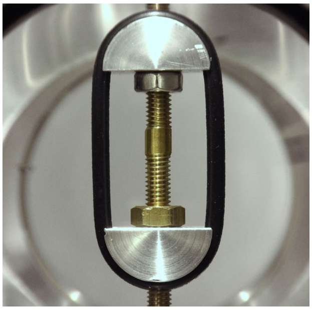
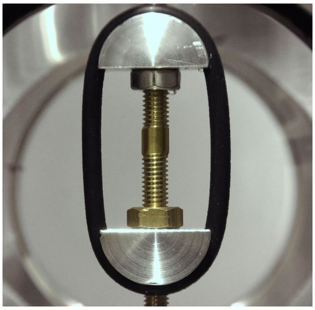


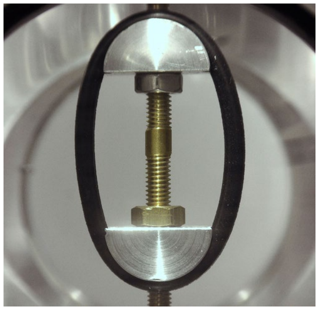
Figure 3: Changes of HNBR O-ring during and after storage in liquid R744



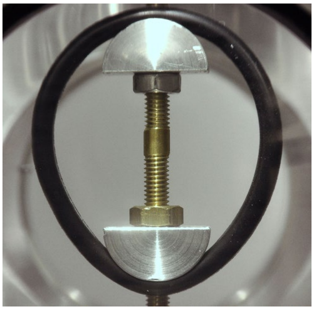
HNBR in air (prior to the test)



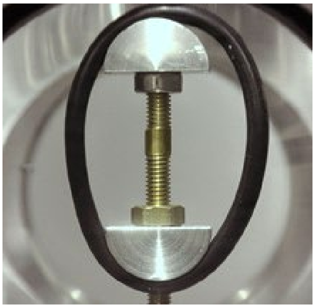
HNBR in R744 (l) at 65 bar after 4 h



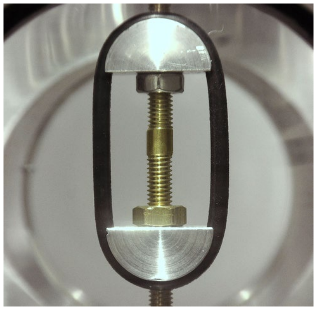
HNBR in R744 (g) at 7 bar; approx. 10 min after starting pressure release



HNBR in R744 (g) at 1 bar; approx. 15 min after starting pressure release



HNBR in R744 (g) at 1 bar; approx. 45 min after starting pressure release



HNBR in R744 (g) at 1 bar; after 28 h

Figure 4: HNBR O-ring during storage in liquid R744 and after pressure release

4 Conventional tests and comparison with in-situ tests

To evaluate and compare the results of the in-situ tests, conventional autoclave tests were performed. The samples were aged in autoclaves under the same test conditions than in the in-situ test (Table 1). In contrast to the in-situ tests, some of the samples were also tested for mechanical properties after aging.

The mass and volume resp. cross section diameter as well as the hardness and tensile properties were determined in defined time intervals after removing samples from autoclave. The measurements were carried out every minute for the first 10 min, then the intervals were increased. Complete depressurisation (reaching 1 bar) in the autoclave was defined as the starting point for the time measurements.

The results clearly show that the major changes in dimensions were found within the first 15 min. The time dependent behaviour of the mechanical properties was similar.

The comparison of the in-situ tests and the conventional autoclave tests show a good correlation regarding changes in cross section diameter of the O-rings (Figure 5).

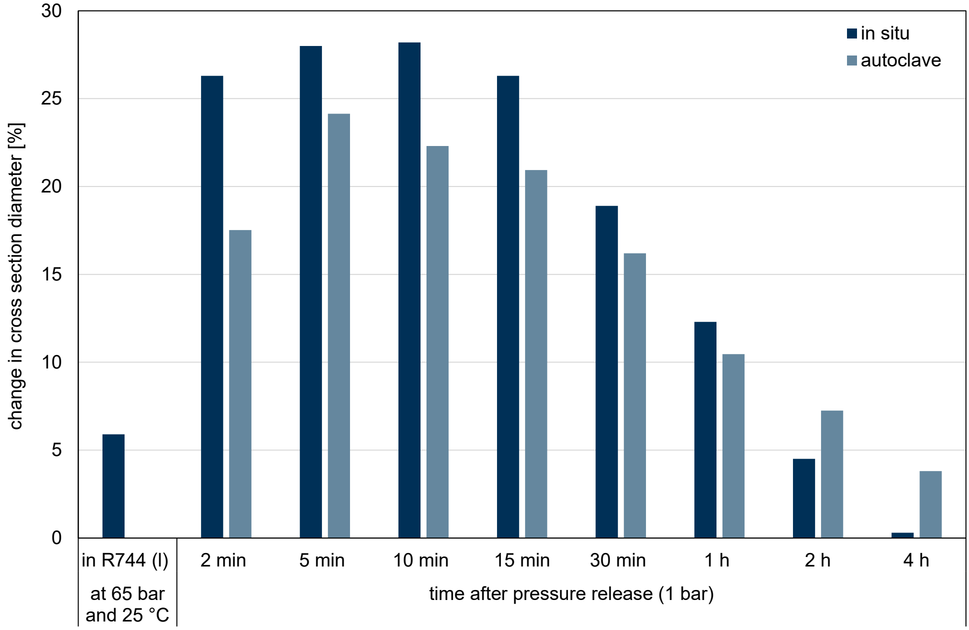


Figure 5: Changes in cross section diameter of HNBR O-rings during and after storage in liquid R744

5 Consequences for compatibility testing in liquid refrigerants

As shown in the previous sections elastomeric materials show a volume increase after removing from a liquid refrigerant. These changes occur with a time delay after the samples are taken from the autoclave and are associated with the outgassing of refrigerant dissolved in the elastomer. The volume change during storage in liquid refrigerant was found to be significantly lower.

The procedure for compatibility testing described in ISO 14903 or ISO 21922 defines a testing in “wet” state within 30 min after removal from the autoclave. Assuming that the autoclave is opened immediately after pressure release, this is exactly the period in which dissolved refrigerant outgasses and the volume change is greatest (Figure 6). For the tested HNBR it was found, that at the end of the 30 min period after pressure release the change in cross section diameter was still significantly higher than during storage in liquid R744.

In reality, the so-called wet state corresponds to a decompression state.

Both the rate of pressure release and the time interval between reaching ambient pressure and opening the autoclave are not defined in the standards. This means that the 30 min time window for the measurement can start immediately after depressurization, but also several hours after the ambient pressure has been reached. Furthermore, rapid gas decompression cannot be excluded. Hence, the results of the measurements extremely depend on the particular timing of the tests in the laboratory.

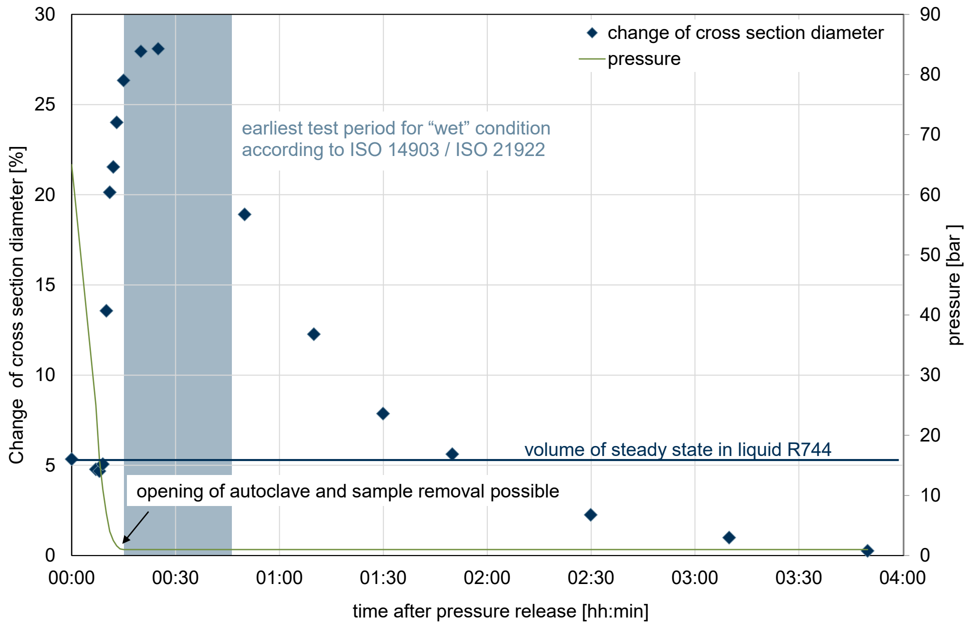


Figure 6: Changes of HNBR O-ring after storage in liquid R744 (detail from Figure 4)

6 Summary and Conclusion

In-situ investigations of elastomeric materials in liquid refrigerants have shown that the volume increase during exposure in liquid R744 is smaller than the swelling after pressure release. The outgassing of the dissolved refrigerant begins as soon as the pressure is reduced and continues even after the ambient pressure has already been reached. Volume changes determined after taking samples from the autoclave will be strongly influenced by this process.

The so-called wet state, as described in ISO 14903 or ISO 21922, is neither a defined condition nor does it represent the state in the liquid refrigerant. As these standards for testing the compatibility of elastomeric materials with refrigerants do not specify an exact test procedure, it is necessary that at least the time between complete depressurization and the measurement is kept the same for all tests and is documented in the test report.

7 Acknowledgements

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8 Nomenclature

R744	carbon dioxide (refrigerant number ac. to ANSI/ASHRAE 34-2022)
R1234yf	2,3,3,3-tetrafluoro-1-propene (refrigerant number ac. to ANSI/ASHRAE 34-2022)
(l)	liquid state
(g)	gaseous state

9 References

[1] ISO 14903:2017: Refrigerating systems and heat pumps - Qualification of tightness of components and joints

[2] ISO 21922:2021: Refrigerating systems and heat pumps - Valves - Requirements, testing and marking

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