Temperature dependent fracture behavior of Rubbers used in the oil and gas industry

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Abstract

Seals and hoses for oilfield applications are often exposed to high temperatures, aggressive fluids and various gases. A specific failure, termed rapid gas decompression failure, can occur during the decompression process of material exposed to high pressure and various gaseous environments. This paper deals with the failure process of the material during these extreme conditions. Especially the crack initiation and the crack growth process were investigated with tear growth experiments and correlated to decompression experiments with an autoclave. Moreover, the experimental material (hydrogenated nitrile butadiene rubber) was tested at different temperatures to catch the temperature influence. Apart from the described experiments also standard material characterizations as well as specific tests to cover polymer and filler interaction were performed [1].

Introduction and Objectives

Elastomer components (seal and hoses) for oilfield applications have to withstand high temperatures, different aggressive fluids and variations of gas. Due to these ambient conditions a specific failure, termed as rapid gas decompression failure, might occur. This failure may cause internal cracking, extensive deformation, swelling, blisters and in some cases catastrophic fragmentation of the vulcanised rubber. Discussions of the failure behaviour have started in the late 50s and still persist [2, 3, 4].

Basically the failure process can be split in two parts: the compression and the decompression phase.
Compression Phase
At the beginning of this phase the seal or component is exposed to high temperatures and high pressure gases. Due to the start of the permeation process, launched by the applied pressure, the material starts to swell until saturation is reached. The observed volume increase at saturation is visible to the naked eye and depends strongly on the testing conditions (temperature, pressure and gas). In this steady state, the material properties as well as the volume change are constant.

Decompression phase
The second phase, the depressurization phase is much more complex and leads to a significant volume increase up to 500% as a result of the rapid pressure drop. For the description of this process, four basic ideas are essential [2]:

- The gas modifies the mechanical and thermal properties of the material.
- With the removal of the pneumatic stress a triaxial tensile stress appears.
- A thermal profile is produced during adiabatic cooling.
- Gas concentration profile is build up within the material.

As a result of the "fast" pressure drop at the beginning the ambient gas is cooling, which leads to a temperature gradient across the material and a thermal shock. Owing to the temperature dependent properties of vulcanised rubber, a mechanical and physical property profile is produced across the material. Beyond the temperature profile also a pressure profile is established, due to the hydrostatic pressure difference between the ambient and the mid-point of the specimen. Moreover, a gas concentration profile across the rubber is produced based on the previous compression phase and the permeation properties of the material. To sum it up, all effects result in stress of the material which causes blistering, bubbling and extended ruptures. More information and a more detailed physical description of the compression and the decompression phase is given by [2, 4].

Failure
During the pressurization process a specific amount of elastic strain is stored in the vulcanised rubber. Based on the pressure difference between the interior and the ambience during the depressurization process this stored strain is released and the elastomer expands. As far as the negative hydrostatic pressure is concerned, cavities are initiated and grow in the material. These cavities start to expand in an unstable manner when a critical pressure difference between the interior and the ambience is reached.

Regarding the crack formation and crack initiation a lot of assumptions were made in the past for unfilled [5, 6, 7] and filled [8, 9, 10] elastomers. Until now, the crack initiation and crack propagation process isn't clear.

Due to the ambient conditions, it is of paramount theoretical and practical importance to characterize the thermo-mechanical behaviour of elastomers over the application relevant temperature range within additional dependences. Therefore, the main objective of this study was to characterize the temperature dependent fracture behaviour of various elastomer grades in terms of crack resistance curves and to establish a correlation of common material characterization methods with the observed material performance during the rapid gas decompression experiment to enhance the material characterization and the knowledge of the material performance.

Experimental

Materials
One experimental material was defined and provided by SKF Economos GmbH (Judenburg, A). This material is based on hydrogenated nitrile butadiene rubber. Due to confidentiality the exact material composition is not given.

Testing Equipment
Crack propagation measurements with tear growth specimens (angle specimen with incision [11]), were performed with a tensile/compression universal testing machine INSTRON 5500 (Instron Deutschland GmbH, Pfungstadt, D). To catch the temperature influence, tests were realized at several temperatures (70°C, 90°C and 110°C) at a constant strain rate of 2.5%/s.

For the realization of the decompression experiments at several temperatures an autoclave testing system manufactured by SITEC (Sieber Engineering AG, Zürich, CH) was used. Moreover, this autoclave was equipped with a camera system (Figure 1a) to record the volume expansion during compression as well as during the decompression phase [1, 12].

The test system consisted of a high pressure autoclave (Figure 1b), a heating unit (Figure 1c) and a data acquisition (Figure 1d) to record the pressure and the temperature during the whole rapid gas decompression process. The volume of the autoclave was approximately 500cm³, calibrated for a maximum pressure of 30MPa and a maximum temperature of 145°C. Pure CO_2 and CH_4 can be used as well as mixtures of these gases to fill the volume of the autoclave testing system. Table 1 summarizes the used testing conditions.

Testing parameter	Used values
specimen geometry	cylindrical Ø8x8mm
temperature	70°C, 90°C, 110°C,
pressure	15MPa
gas	CO_2
decompression rate	10MPa/min
holding time	~21h
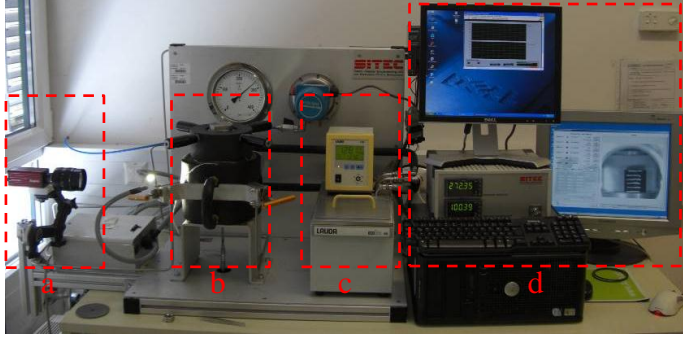
Fig. 1. Test set-up for unconstrained rapid gas decompression tests.

Table 1. Overview of the used testing conditions for the rapid gas decompression experiments

Cylindrical specimens (diameter 8mm, height 8mm) were used to simplify the calculation of the volume expansion during compression and decompression. Figure 2 compares typical images recorded by the camera system at the beginning of pressurization (a), depressurization (b) and at the end of the depressurization phase (c).
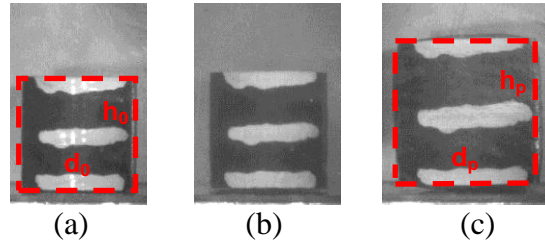

(a)   (b)   (c)

Figure 2: Specimen at the beginning of the (a) pressurization, (b) depressurization and (c) at the end of the depressurization phase.

As depicted in Figure 2 the specimen diameter and the height were measured at several stages during the compression as well as during decompression phase. With these measured values the volume change during the stages was calculated by equation 1.

$$V_i = \frac{d_i^2 \cdot \pi}{4} \cdot h_i \qquad (1)$$

During the depressurization process a large volume increase (depending on the material and the testing conditions) was observed combined with barrelling of the specimen. To counter this, a linear approximation on the height and the diameter was performed. Finally, the percentage volume increase in dependence of the testing time was calculated by differentiation of the start volume.

Data Reduction
Due to the high amount of data and especially for the comparison of the different test set ups the data was reduced on defined values and summarized in the following. Based on the tear growth measurements the crack tip opening displacement (CTOD) was measured and compared with the

force-displacement measurements. The first derivative of the CTOD in dependence of time represents the velocity. This velocity is nearly constant until a critical initial time is reached, t_i. This time represents the time to initiate a crack in the material. Therefore, this time was used to calculate an initial Tearing energy T_i (equation 2) in the load-displacement diagram which is needed to start the crack growth process. Moreover also a second tearing energy, T_{peak} (equation 3) was calculated until the maximum load was reached. This energy represents the required energy to start the rapid crack propagation. Both energies were calculated with the strain energy density, the specimen thickness B and the remaining ligament length (W-a).
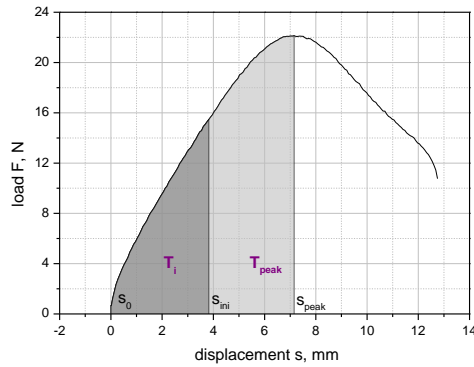
Fig. 3. Load in relation to the displacement for tear growth measurements including representative energies.

Fig. 4. Crack tip opening displacement in relation to time and the first derivative of them.

$$T_i = \frac{\int_{s_0}^{s_{ini}} F ds}{B \cdot (W - a_{ini})} \tag{2}$$

$$T_{peak} = \frac{\int_{s_0}^{s_{peak}} F ds}{B \cdot (W - a_{peak})} \tag{3}$$

Similar to the reduction of the data for the tear resistance measurements, also the data for the autoclave tests was reduced to three specific values, the maximum observed volume change ΔV_{comp} (Figure 5) during the compression phase in regions of the saturation, the maximum observed volume change during decompression ΔV_{decomp} and the initial time t_d until the volume increase starts (Figure 6).
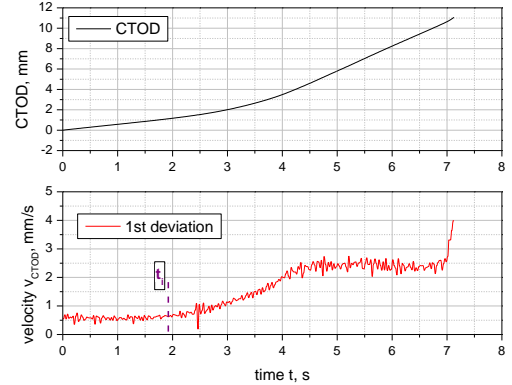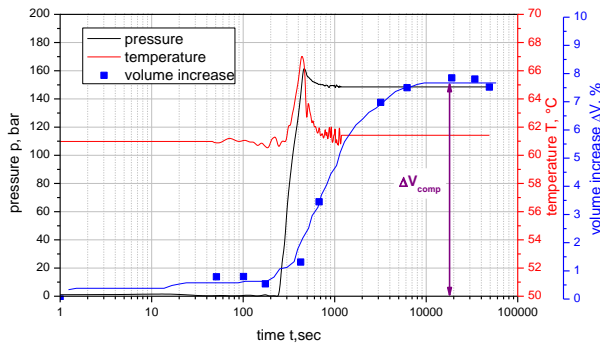

Fig. 5. Pressure, temperature and the volume change ΔV_{comp} for compression phase.
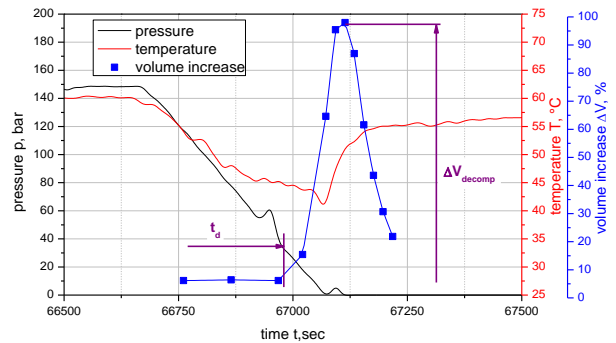

Fig. 6. Pressure, temperature and the volume change ΔV_{decomp} for decompression phase.

These values are used later for the comparison, to catch the impact of the varying temperature and the different testing conditions.

Results and Discussion

Tear growth measurements

Tear growth measurements were carried out at three defined temperatures with a constant strain rate of 2,5%/s. Figure 7 summarizes the different load displacement curves for 3 defined temperatures. As depicted the reproducibility is good with a clear ranking from lower temperatures to higher temperatures. With the lowest temperature the highest load and displacement levels were observed.
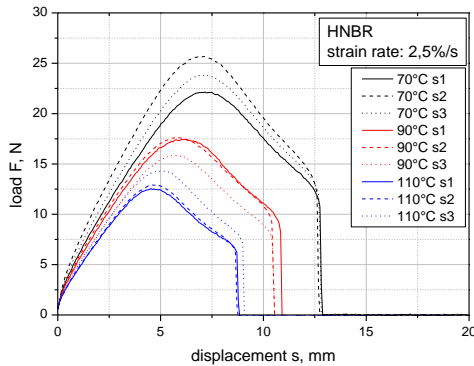
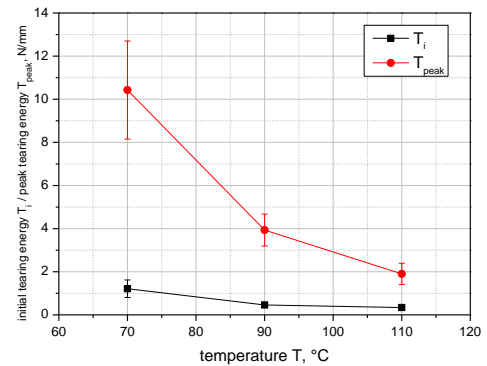Fig. 7. Load in relation to displacement for different testing temperatures.

Fig. 8. Initial tearing energy T_i / peak tearing T_{peak} energy in relation to the temperature.

The different calculated energies were summarized by Figure 8. Based on this, the energy for crack initiation as well as the energy needed to start rapid crack propagation clearly decreases with increasing temperature. This suggestion is also supported by the observed CTOD values with different testing temperatures (Figure 9 and Figure 10).
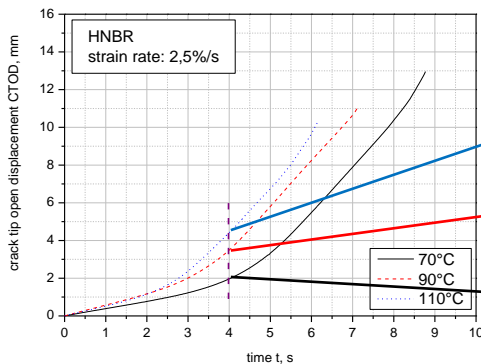

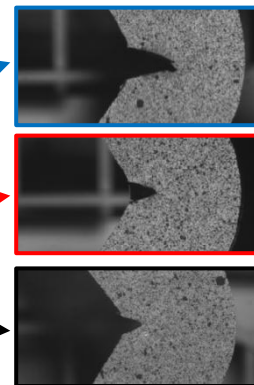Fig. 9. CTOD in relation to the time for different temperatures.

Fig. 10. Comparison of CTOD at different temperatures and a defined time (t=4s).

With the observed CTOD values the velocity v_{CTOD} was calculated to sum up the material performance at different testing temperatures (Figure 11). For all 3 temperatures the velocity in the first 1,5s is constant due to the constant strain rate during the test. Depending on the material resistance against crack initiation the initiation time t_i varies with different temperatures. When reaching t_i the second process, the crack propagation, starts. This process starts with acceleration to

a temperature independent plateau of the velocity at 2,5mm/s and leads finally to a separation of the used angle specimens.
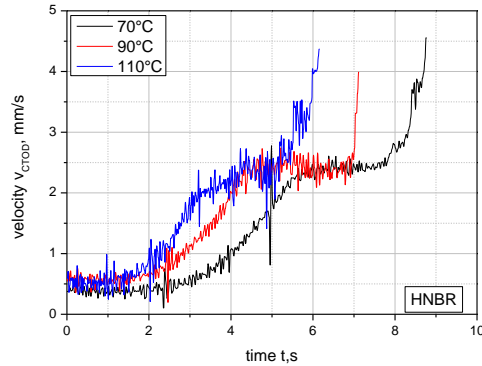

Fig. 11. CTOD velocity in relation to time and
different temperatures.

However, a clear influence of the temperature on the material performance during tear growth measurements was observed. The energies clearly decrease (T_i and T_{peak}) which go well with the observed velocity for the CTOD (compare Figure 8 and Figure 11). Especially the acceleration after the initiation time and the acceleration after the constant crack growth strongly depend on the temperature.

Autoclave measurements
As described above, the autoclave measurements were carried out at 15MPa and a CO_2 atmosphere with a constant decompression rate and a varying temperature. During the compression phase a nearly constant volume increase (between 6,5% and 8,5%) was observed with increasing temperature (Figure 12).
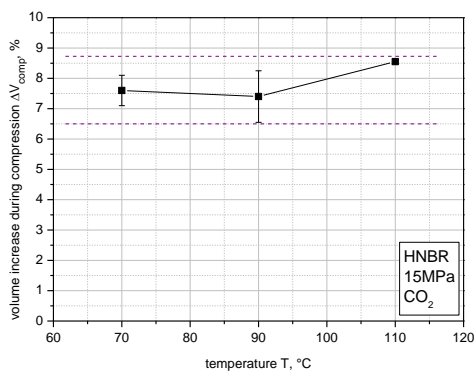

Fig. 12. Volume increase during compression in
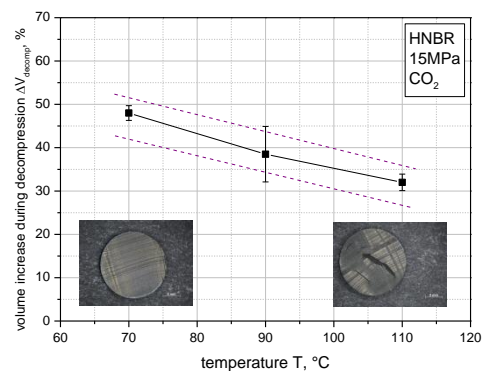relation to the temperature.

Fig. 13. Volume increase during decompression
in relation to the temperature.

The volume increase during decompression in relation to the testing temperature is depicted in figure 13. A clearly decreasing maximum volume change during the decompression is recorded. An interesting material performance (crack process) in relation to the volume change was measured. With lower temperatures a higher volume change and no cracks were observed. In contrast at a temperature of 110°C a 33% lower volume increase was measured with at least 4 cracks across the specimen diameter. This means, that in this case the volume change is not the driving force for the material performance but the testing temperature.

Therefore the volume kinetics as well as the velocity of the volume change were considered. Figure 14 shows the volume change observed in relation to the temperature. The decompression phase starts at t=0s with a constant decompression rate of 10MPa/min. At the beginning of the decompression phase the pressure decreases and a pressure difference establishes across the specimen diameter. After reaching a critical pressure difference (after t_d=70s) the volume starts to increase. As discussed in literature this critical pressure difference is independent of the testing temperature and only a function of the tested material [2]. Only the next step, the volume increase seems to strongly depend on the temperature with a clear trend of a slower and smaller volume increase with increasing temperature.
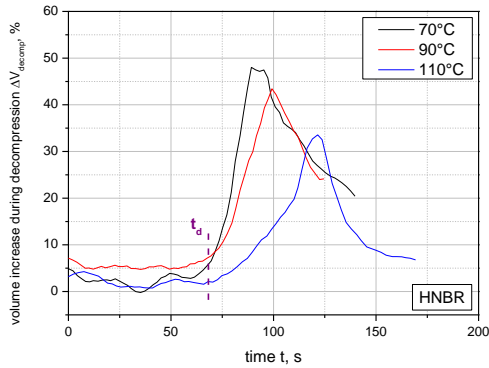

Fig. 14. Comparison of the temperature dependent volume increase in relation to the time.
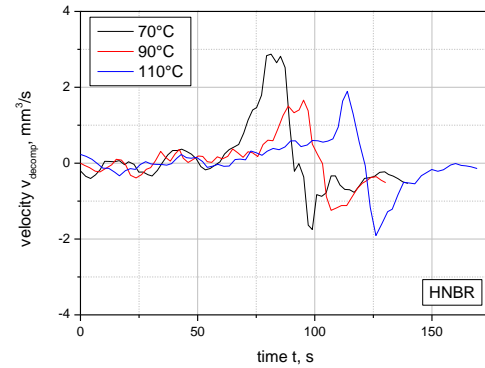
Fig. 15. Comparison of the velocity of the volume change for different temperatures in relation to the time.

Additionally, the velocity of the observed volume change during the decompression phase was also calculated (Figure 15). A clear ranking for the velocity was observed for the tested temperatures, with an earlier velocity increase with decreasing temperature.

Conclusion
Based on the experimental investigations above, some conclusions may be drawn:
- The maximum load as well as the maximum displacement clearly decreases with increasing temperature for the tear growth measurements.
- Initial tearing energy T_i as well as peak load tearing energy T_{peak} decreases with higher temperature.
- During the compression phase the volume change reveals a nearly independent material behaviour with rising temperature.
- When starting the depressurization process no tendency was observed until the initial time t_d, to establish the critical pressure difference Δp, runs out. This initial time seems to be independent of the testing temperature and according to the literature only a function of the tested material [2].
- Smaller and slower volume change with increasing temperature was found.

To conclude, earlier crack propagation in the material is recorded for increasing temperature concerning the tear growth measurements. Also the acceleration of the CTOD starts earlier and needs less energy for the crack initiation. This fits well to the observed material performance during the decompression experiment. With decreasing pressure the pressure inside the material increases leading to a three dimensional stress state [2]. Therefore, for 70°C the crack needs more energy to initiate in comparison to 110°C. The material at 110°C cannot withstand the pressure increase and

the crack initiates and accelerates earlier leading to a smaller and slower volume increase but not to a better material performance. This assumption will be reinforced by future tests of different materials and different specimen geometries. Moreover, also other testing conditions (e.g. different pressures, different gases) as well as the permeation performance of the material will be the aim of future experiments.

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