Long-term ISO 23936-2 sweet oil ageing of HNBR

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ABSTRACT

A hydrogenated nitrile butadiene rubber (HNBR) compound is subjected to ageing in a simulated oil and gas environment in accordance with ISO 23936-2 standard at two elevated temperatures (130 °C and 150 °C) for a period of up to 9 months. Shore D hardness, thermal expansion, dynamic mechanical analysis (DMA), Fourier transform infrared (FTIR) spectroscopy, compression and compression set (CS) measurements are made before and after the chemical exposure. The hardness, modulus at short times, degree of relaxation and CS increases while the coefficient of thermal expansion in HNBR tends to decrease with ageing time and temperature. Temperature is shown to impose a greater effect on the properties than ageing time in the experiment. The elastic modulus at low frequencies of cyclic deformation (or the equilibrium modulus in stress relaxation) has a more complicated relationship with ageing time at 150 °C. It sharply increases in the first stage of ageing and then decreases later with further exposure which suggests that chain scission dominates in the later stages of hydrocarbon ageing. In contrast with the other materials, the most severely aged HNBR exhibits a much higher glass transition temperature of $\approx +70$ °C manifesting in a very high stiffness at ambient temperature and a low thermal expansion coefficient. This effect is attributed to a dramatic change in the chemical structure of aged HNBR, i.e. complete modification of C≡N groups to amide groups yielding the growth of T_g and the corresponding variation in macroscopic properties. These results are also qualitatively evaluated in the context of potential sealing applications of the material.

1. Introduction

Hydrogenated nitrile butadiene rubber (HNBR) is an important class of elastomers that is very often utilised in the oil and gas production equipment, particularly in elastomer ring seals and packing elements [1]. These sealing elements are typically subjected to a wide range of well bore fluids under high pressure (up to about 100 MPa), various chemicals and high temperature (up to ≈ 160 °C). In underwater oil or gas producing equipment, it is not always possible to retrieve a certain set of components enclosing the seals, therefore these seal materials are often required to retain their properties and facilitate the seal tightness over a long time period, in some cases reaching 30 years. Furthermore, temporary cease of flow or cold cycles in oil and gas systems are often experienced in practice leading to drop of equipment temperature. Therefore, seal materials must possess some degree of ageing resistance and retain their resilience to account for

these changes in flow conditions and temperature during shut-off and resumption of the flow. It is especially crucial for permanently installed elastomeric seals. Thereby, understanding the ageing characteristics and predicting lifetime and performance of HNBR materials exposed to oil and gas media is of paramount importance for the industry.

Ageing of HNBR has received much attention, however most research work so far has been devoted to thermo-oxidative ageing, e.g. [2–15], while thorough scientific publications describing the effect of non-oxidative environment like hydrocarbon media on the materials rarely emerge. Alcock et al. [16,17] reported their results of a hydrocarbon ageing study focusing on typical mechanical properties, apparent cross link density, glass transition and gas diffusivity of an HNBR compound following the ISO 23936-2 ageing test protocol. Particularly, the authors notice a considerable increase in the material stiffness and hardness with ageing time and temperature accompanied by a

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Table 1
Composition of the HNBR compound used in this study.

Component	Content, phr
HNBR	100
Antioxidant	3
Stearic acid	0.5
Zinc oxide	5
Magnesium oxide	10
Plasticizer	20
Peroxide	10
N-330 HAF carbon black	50

reduction in failure strain, gas permeability and the height of $\tan\delta$ peak. These results are attributed to a gradual increase in the cross link density in the ageing process until the point where the segmental mobility is reduced such that the glass transition becomes barely noticeable. Similar ageing media but with hydrogen sulphide gas were used in another ageing study [18] which reveals several degradation mechanisms taking place in HNBR including additional cross-linking (predominantly with sulphur), a noticeable loss of additives and increased filler–filler interaction, all giving rise to the material's stiffness. Despite H_2S presence, the outcome of the latter study is in line with the results obtained after sweet oil or hydrocarbon exposure [16,17]. The increased apparent cross link density was also deemed among the major degradation mechanisms in HNBR aged in crude oil according to [19].

In the discussed articles, the research focus was on deterioration of mechanical properties, e.g. hardness, moduli and strain to failure, in an accelerated hydrocarbon ageing setting. In spite of being beneficial in assessing general material integrity and compatibility with aggressive fluids, these quantities can hardly be related to the seal failure mechanisms such as leakage. Therefore, the problem of HNBR ageing in hydrocarbons needs to be considered from another angle. With respect to seal leakage, changes in viscoelastic characteristics, like time-dependent modulus and compression set in accelerated ageing setting are believed [13,20–23] to be more critical. To the authors knowledge, there exist no publicly available literature on the effect of hydrocarbon ageing on viscoelastic characteristics of HNBR. The present research article aims to fill this knowledge gap using a model HNBR compound rigorously characterised in the previous works [22,24,25]. Contrary to many other studies, the ageing time here was set up to 9 months to reveal any potential long-term effects. The main objective of this work is to evaluate the effect of ageing in HNBR exposed to a simulated oil and gas environment and qualitatively assess the functionality of the aged material in a sealing application.

2. Materials and methods

2.1. Materials and processing

The elastomer studied in the work is formulated using HNBR with 96% saturated butadiene units with 36% acrylonitrile content and 50 phr (parts per hundred rubber) N-330 HAF carbon black. The details of the elastomer composition are given in Table 1.

The compound (excluding the peroxide) was combined in an internal mixer to yield a single HNBR masterbatch which was then mixed with the peroxide in a two roll mill. Compression moulding and vulcanisation in a press at 170 °C for 20 min followed. Finally, a post-curing operation at 150 °C for 4 h in an oven was carried out. The vulcanised elastomer has Shore A hardness of 85 ± 5. More information about the processing and the material test data are available in our previous publications [22,24,25].
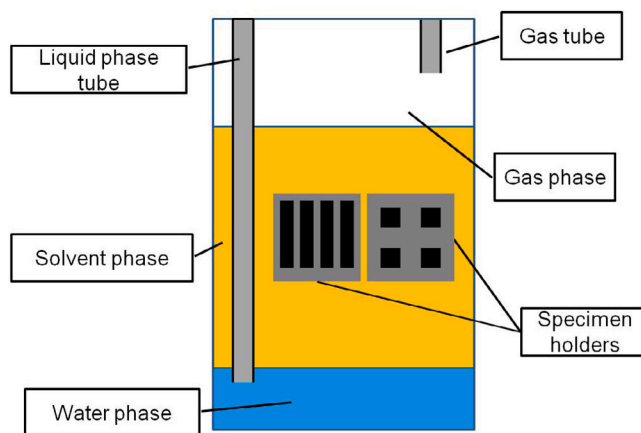

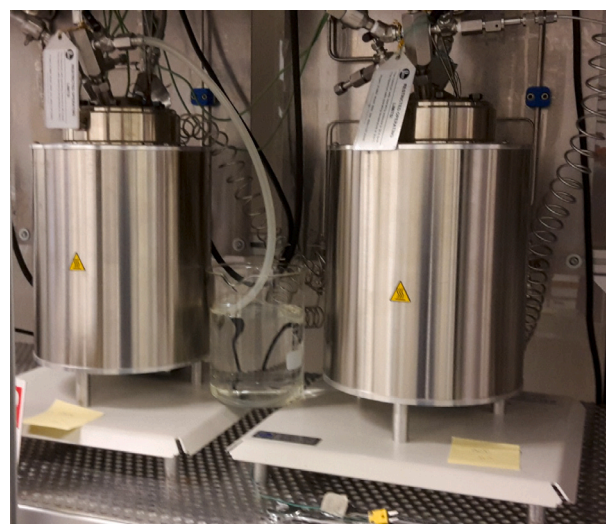**Fig. 1.** Schematic of the specimen fixtures location inside the autoclaves used.

Fig. 2. Photograph of the test set-up with autoclaves at SINTEF.

2.2. Chemical exposure

Ageing of the HNBR compound was carried out in a simulated non-sour oil and gas well medium in accordance with ISO 23936-2 (Norsok M-710) standard using autoclaves rated for 100 bar pressure maintained in the experiment. The ageing fluid composition corresponded to a "sweet" (H_2S-free) environment. The total inner volume in the autoclaves was filled with 60% liquid phase, 10% water and 30% gas phase. The liquid phase consisted of 70% heptane, 20% cyclohexane and 10% toluene (A.1.ii as per ISO 23936-2 Annex A) and the gas phase was mainly CH_4 (95%) with additional 5% CO_2. The specimens were positioned in the liquid phase above the water level using test fixtures as schematically presented in Fig. 1. A photograph of the test set-up is depicted in Fig. 2.

The ageing procedure was in accordance with ISO 23936-2 including the autoclave flushing stage, heating and pressurisation with the gas medium. The maximum chemical exposure time was 9 months (see Table 2). The temperature and pressure were recorded over the entire experiment period. After an ageing period of 3 months, the exposure was halted for one group of specimens to be removed from the autoclaves and another group of specimens to be added for 6 months exposure under the same conditions. During the specimen changeover, the liquid medium was replenished. As in the previous ageing study [16,17], all specimens were dried in air at ambient temperature after release from the autoclaves for evaporation of residual

Table 2
Specimen designation.

Ageing period, weeks	Temperature, °C		
	130	150	23
12	130-3	150-3	–
24	130-6	150-6	–
35	130-9	150-9	S-9

solvents. The rest period prior to any testing was until the rate of mass decay decreased to less than 0.01% per day.

In order to evaluate the effect of exposure to the solvent mix independent of other parameters, another set of HNBR specimens was immersed in the solvent phase and held there for 9 months at room temperature (designation "S-9" in Figs. 7 and 9). After chemical exposure, these specimens were also dried before testing in the same manner as the specimens subjected to elevated temperatures in the autoclaves.

2.3. Testing

After achieving the negligible mass decay rate, the specimens were subjected to several testing methods. Shore D hardness was measured by a Bareiss automated durometer according to ISO 48-4. Following [16,17], the measurements represent the hardness at a 3 s test time. The selection of Shore D hardness method was dictated by a high stiffness of the aged HNBR as will be seen below.

Thermal expansion measurements were conducted using a Netzsch DIL402C dilatometer during heating from −60 to 130 °C at a heating rate of 2 °C per minute. The specimens for dilatometry were $6 \times 6 \times 10$ mm rectangular blocks. For the ease of comparison between differently aged specimens, the linear thermal expansion coefficient (CTE), α, is computed by linear regression using dilatation datasets in a range of temperatures from 10 to 50 °C.

Step-strain compression stress relaxation (CSR) and compression set (CS) measurements were performed using a Netzsch-Gabo Eplexor 150 machine with a 1.5 kN load cell and parallel plate specimen holders, operating in compression mode at 24 ± 1 °C. The compression (CSR) specimens had a cylindrical shape with 10 mm nominal diameter and 6 mm height. No pre-treatment (cycling loading) was applied to remove the Mullins effect. This was to avoid irreversible deformation imposed on the aged specimens during the pre-treatment process. The loading and subsequent relaxation was performed stepwise with a nominal strain step increment of 5%. A silicone grease was always applied in the compression tests to minimise specimens barrelling at large strains. The investigated range of nominal compressive strains ε was 5–20% which is relevant for elastomer seals. After each loading step, the specimens were allowed to relax under constant strain for 10^4 s until the next loading step followed (see an example in Fig. 3). In the end of the test sequence, fast unloading was performed to record the shape recovery (compression set) behaviour of the HNBR specimens for 10^4 s. The compression set was computed in accordance with its usual form:

$$CS(t) = \frac{(h_0 - h_2(t))}{(h_0 - h_1)},$$

where h_0 was the height of the uncompressed specimen, h_1 was the specimen height at compression, $h_2(t)$ was the specimen height during the recovery process and t indicated the elapsed time in the shape recovery part of the experiment.

The same Netzsch-Gabo Eplexor 150 machine but equipped with a 150 N load cell was used for linear dynamic mechanical analysis (DMA) of HNBR in tension mode. The oscillating loading was carried out with a pretension strain of 0.05% and a strain amplitude of 0.02%. The frequency scan was made over a wide range of temperatures from −70 to +120 °C with a temperature increment of 5 °C and 2.5 °C in the region from −30 to +30 °C at 10 frequencies. DMA master curves were constructed using the same numerical procedure as in [22,23]
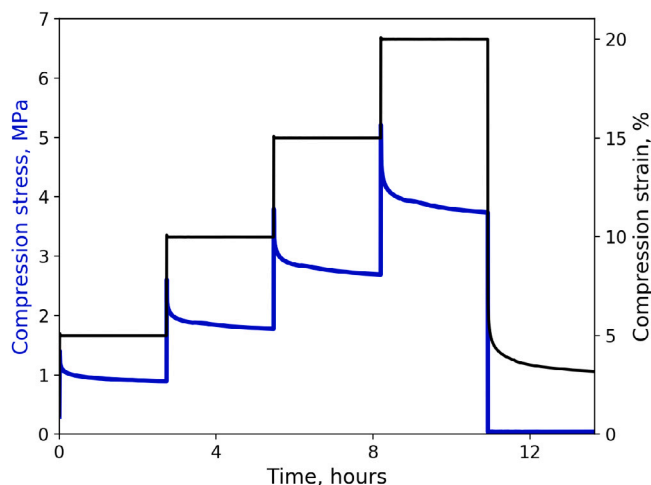

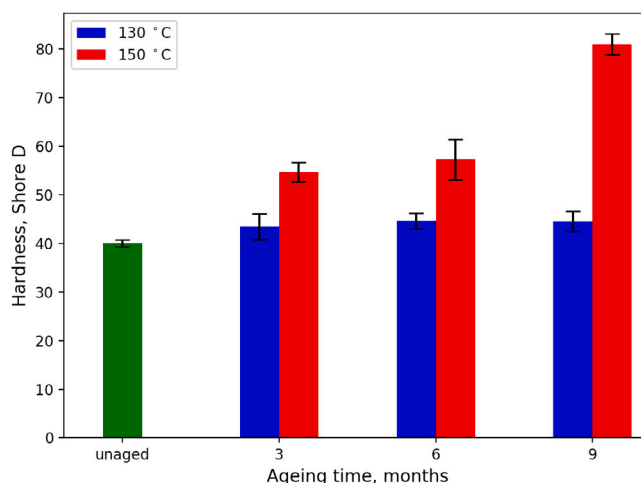**Fig. 3.** An example of the step-strain compression experiment sequence.

Fig. 4. Shore D hardness of HNBR subjected to the indicated ageing parameters. The column height represents average of 3 measurements with the error bars indicating the standard deviation.

Fourier transform infrared (FTIR) spectra were recorded in the Attenuated Total Reflectance (ATR-FTIR) mode using GladiATR FTIR spectrometer equipped with a germanium crystal. Spectra were obtained at 4 cm^{-1} resolution, with 50 scans over a wavenumber range from 900 to 4000 cm^{-1}.

3. Results

3.1. Hardness

The results of hardness measurements are summarised in Fig. 4. The hardness clearly tends to increase with ageing time which is more pronounced at the highest ageing temperature in the experiment. This observation is consistent with the outcome of other hydrocarbon ageing studies of HNBR [16–18]. An almost twofold increase in Shore D hardness is observed after 9 months chemical exposure at this temperature if compared with the results for unaged HNBR. At 130 °C, a minor increase in hardness also takes place, however the hardness level stabilises after 3 months of ageing and does not increase much further with exposure time.
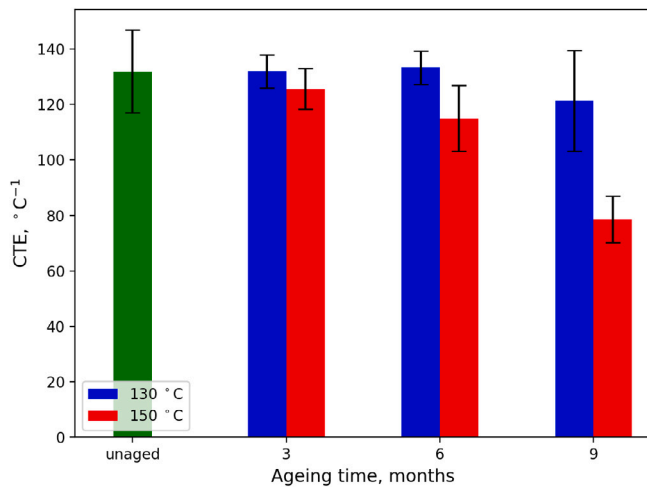
Fig. 5. The computed CTE of HNBR subjected to the indicated ageing parameters. The column height represents average of 3 samples with the error bars indicating the standard deviation.
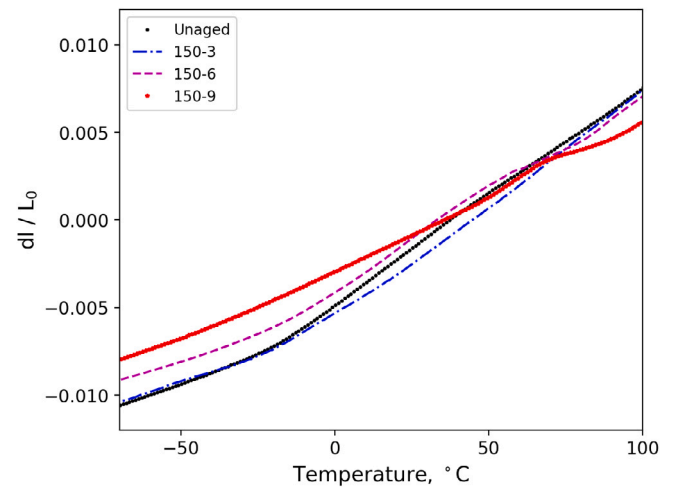

Fig. 6. Representative dilatometric data. Note, the linear CTE in Fig. 5 is computed by linear regression using dilatation datasets in a range of temperatures from 10 to 50 °C.

3.2. Thermal expansion

The long-term ageing at the highest temperature has also a noticeable effect on the thermal expansion of the studied HNBR which is seen from Fig. 5 and also Fig. 6. The CTE of HNBR is appreciably reduced with ageing time when HNBR is exposed to the Norsok environment at 150 °C, while it does not considerably change when the material is aged at 130 °C. The highest decrease in CTE from $\approx 130 \times 10^{-6}$ C^{-1} to $\approx 70 \times 10^{-6}$ C^{-1} occurs in the most severely aged HNBR which is similar to the CTE of the HNBR ($\approx 60 \times 10^{-6}$ C^{-1}) in the glassy state computed by linear regression of the dilatation data between −60 and −30 °C.

Representative dilatometric curves of virgin HNBR and HNBR aged at 150 °C are depicted in Fig. 6. A great difference in thermal expansion behaviour between HNBR exposed to 9 months ageing and other HNBR samples is evident. While in the most cases the glass transition takes place in the vicinity of −20 °C as would be expected for this HNBR, the most aged HNBR demonstrates a thermal transition at temperatures greater than 60 °C. The shift in the transition temperature is also supported by the DMA measurements as will be apparent below. The second transition is also noticeable in the specimen aged over 6 months. The presence of both of these transitions (ca. −20 °C and 60 °C) in the HNBR sample aged for 6 months at 150 °C (150-6 in Fig. 6) might be attributed to inhomogeneous ageing across the HNBR cross section leading to regions with different chemical structures. The evolution of these thermal transitions could be further investigated by measuring the properties of HNBR materials aged at additional time points between 6 and 9 months, although that is outside the scope of the study reported in this paper.

3.3. Compression behaviour

The difference in the compression stress relaxation behaviour between the unaged HNBR and the material aged at the specified conditions is illustrated in Fig. 7. Aged HNBR possesses a higher degree of viscoelastic contribution to the modulus which is manifested in larger stress relaxation if compared that of the virgin HNBR. As demonstrated in Fig. 7, this effect becomes more pronounced as the severity of ageing (primarily due to the elevated ageing temperature) increases. The CSR behaviour of HNBR exposed to the solvent mix at ambient temperature does not significantly differ from that of the virgin material.

As with the rate of relaxation and hardness, the stiffness of HNBR (at short times) slowly increases with the ageing duration and more rapidly with the ageing temperature. This effect can be observed in Fig. 8. The
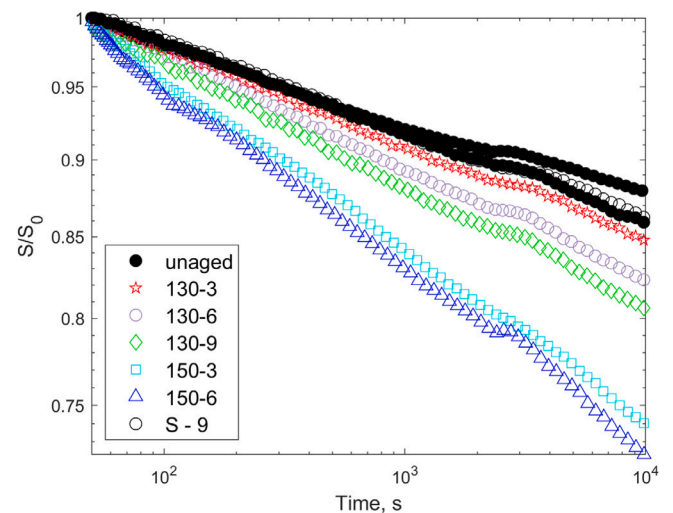

Fig. 7. Compression stress relaxation data for the studied HNBR subjected to the indicated ageing parameters. The first 50 s of time are omitted in the relaxation data in order to minimise the effect of the loading step. The values of compression stress taken at 20% nominal strain are normalised by the instantaneous value of stress. The stress relaxation curve for the most aged HNBR (150-9) was not recorded due to its high stiffness as will become evident later in the text.

increase in HNBR stiffness is rather small at 130 °C ageing temperature (i.e. from ≈ 3.2 MPa to 4 MPa if Neo-hookean material model parameter C_{10} is taken as a measure of the material stiffness), whereas at 150 °C a much greater rise in the stiffness is noticeable. More specifically, the magnitude of Neo-hookean material parameter exhibits a more than twofold growth after 3 months of chemical exposure at 150 °C ($C_{10} = 7.4$ MPa). A longer exposure up to 9 months in the same medium at this temperature leads to an even greater increase in stiffness such that the loading capacity of the testing machine becomes insufficient to carry out the full loading sequence as programmed.

As with the other characteristics, prolonged ageing also gives rise to the compression set in HNBR. Compression set is a very useful indicator of sealing performance in dynamic applications and where a partial release of seal compression is expected [20,21], e.g. due to pressure induced expansion in tubular vessels. Therefore, the time dependence of compression set in HNBR depicted in Fig. 9 is evaluated here. Considering times longer than 100 s, the increase in compression
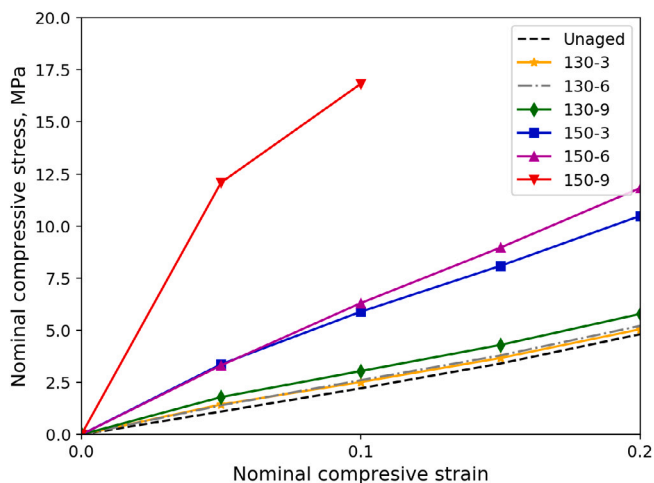
Fig. 8. Instantaneous compression stress strain curves of virgin and aged HNBR built based on the step-strain relaxation data.
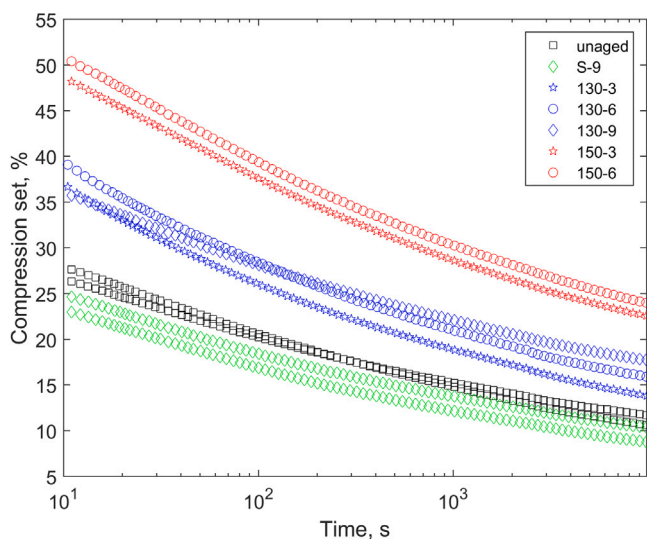

Fig. 9. Compression set as a function of time at the indicated ageing conditions. The compression set in the most severely aged HNBR (150-9) was not measured due to the high stiffness of the material.

Fig. 10. Dynamic storage modulus, E', measured at 1 Hz as a function of temperature at the indicated ageing conditions, for unaged HNBR and after exposure to the indicated ageing parameters.

Fig. 11. Tanδ as a function of temperature at the indicated ageing conditions reported at 1 Hz frequency. The measurement for 150-9 was repeated using another specimen to confirm the remarkable shift in the Tanδ peak.

set in HNBR aged at 130 °C is not greater than 7%, while ageing at 150 °C results in slower shape recovery manifested in compression set values of 15–20% higher than those observed in the virgin material. It is interesting to note that the exposure of HNBR to the solvent phase alone at ambient temperature has negligible effect on the compression set. The HNBR exposed to solvent could even exhibit a small reduction in CS predominantly due to release of some additives into the solution prior to drying.

3.4. Dynamic mechanical analysis

The outcome of dynamic mechanical analysis is shown in Figs. 10, 12, Table 3 and Fig. 11. Fig. 10 shows the effect of ageing parameters on the dynamic storage modulus of selected specimens, as a function of measurement temperature. The unaged specimen shows a transition from high to low stiffness with a midpoint at ca. −20 °C, which is consistent with T_g of HNBR. Specimens 130-9 and 150-6 show slight increases in stiffness above the T_g, in agreement with increases in hardness shown in Fig. 4 and instantaneous compression stress strain curves in Fig. 8. However, specimen 150-9 is remarkable
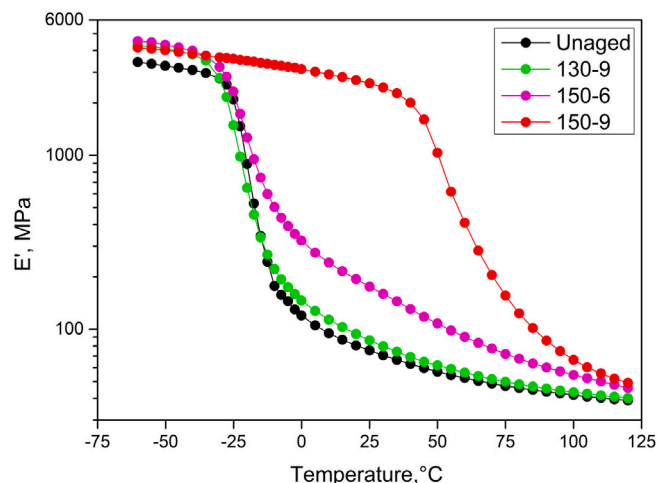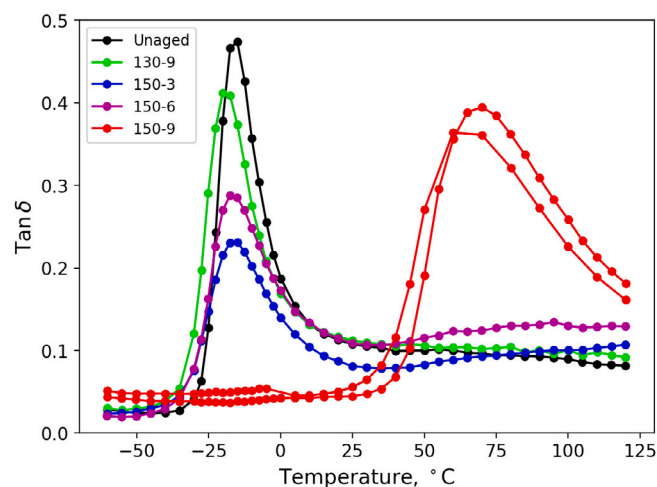
in that the transition from high to low stiffness occurs at a much higher temperature with a midpoint ca. 75 °C.

A typical variation of the loss ratio (tanδ) for the studied HNBR specimens with temperature is presented in Fig. 11. The peak height of the specimens is greatest before ageing and decreases with increasing ageing temperature. The position of the tanδ peak does not change significantly for the specimens except for the most aged HNBR specimens (150-9). For specimen 150-9, a large displacement of the tanδ peak is observed (corresponding to the dramatic decrease in stiffness seen in Fig. 10) indicating a change in the glass transition range towards elevated temperatures. In this case, the loss ratio peak is translated by more than 70 °C. Contrary to the dilatometric data, the secondary transition is not yet clearly apparent in 150-6, however there might be a rather broad peak with a low height at 60–90 °C. It should be noted that the main tanδ peak of 150-6 is higher than that of 150-3. The difference might be attributed to a loss of additives in 150-3 and reduction in free volume, see the discussion section below.

Fig. 12 demonstrates constructed master curves of the storage modulus of HNBR exposed to the ageing environment. Table 3 summarises values of the Williams–Landel–Ferry (WLF) [26] equation coefficients for the horizontal shifting factors used to build the master curves (this
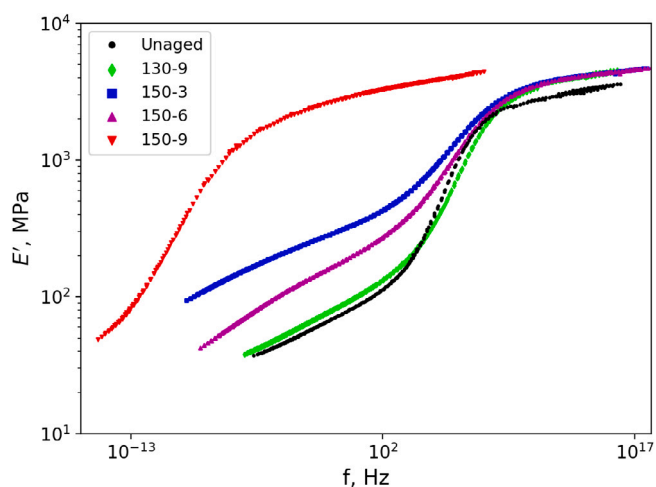
Fig. 12. Storage modulus (E') master curves at the specified ageing conditions (T_{ref} = 20 °C).

Fig. 13. ATR-FTIR spectra of the HNBR at the indicated ageing parameters. A baseline correction was applied to the FTIR data.

Table 3
WLF equation coefficients obtained by fitting of the horizontal shifting parameter data.

Ageing time, months	Ageing at 130 °C		Ageing at 150 °C	
	C1	C2	C1	C2
0	10.078	99.627	10.078	99.627
3	12.042	119.519	29.637	208.294
6	12.772	119.001	24.280	175.995
9	13.200	122.109	26.813	77.182

will be discussed later in the text). An increase in modulus in all aged HNBR elastomers is evident at low (rubbery state) and high (glassy state) frequencies. The relative increase in rubbery state modulus due to ageing tends to be higher than that in the glassy state. It is interesting to note that the modulus at low frequencies in 150-3 is greater than its counterpart in 150-6 (≈ 2 times difference). A possible explanation for this effect could be a quick loss of additives [11] and increasing cross-link density [17] in the first stage of ageing leading to a temporary increase in modulus which is followed by chain scission at later stages of the ageing process. The most drastic effect of the chemical exposure entails in a significant shift of the storage modulus curve for the most severely aged HNBR with respect to the curves for other aged and virgin HNBR. Based on these results, HNBR would be predicted to exhibit modulus values of a rubber-like material only at frequencies lower than $\approx 10^{-10}$ Hz at the reference temperature.

3.5. FTIR

ATR-FTIR was performed with a purpose to identify alternations in the chemical structure of HNBR and associate it with the most prominent changes in macroscopic properties undergone during the sweet oil medium exposure at 150 °C. The materials subjected to ageing at 130 °C were not studied by FTIR. The recorded FTIR spectra are given in Fig. 13. The FTIR peak allocation to specific functional groups present in HNBR are summarised in Table 4. The most striking feature appears to be the absence of the peak at 2234 cm^{-1} in the spectra for the most severely aged HNBR while the peak is present in the other spectra. The peak at 2234 cm^{-1} is attributed to C≡N stretching vibration [27,28] and is a characteristic peak for nitrile rubber. Formation of a wide peak or a group of peaks within 3200–3400 cm^{-1} takes place in the aged elastomer and can be linked to emergence of –OH and/or NH2 groups in the material. The appearance and growth of a double peak at 1699 cm^{-1}, and 1658 cm^{-1} as well as peaks at 1600 cm^{-1} and 1413 cm^{-1} suggests that the chemical exposure results
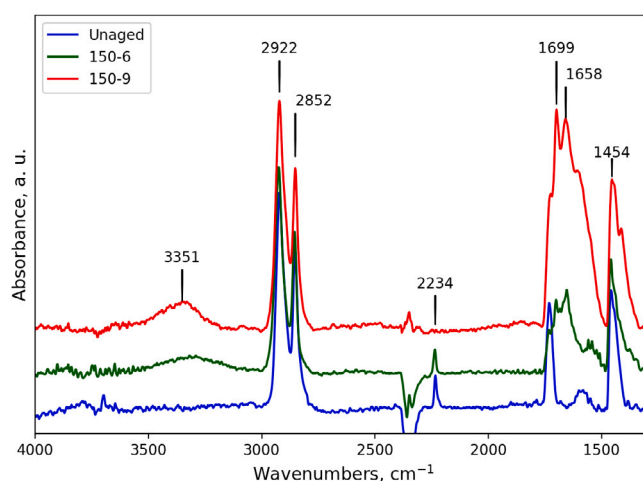
in formation of amide groups [12,29]. Other functional groups also mentioned in the literature [28], i.e. imides and NC in isonitrile, are not evident as they would have given peaks at ≈ 2100 cm^{-1} [29] and 2134–2183 cm^{-1} [27], respectively.

4. Discussion

In general, the results demonstrate that long-term ageing of HNBR in a sweet oil environment at 130 °C does not induce significant deterioration of the material properties, nor does it affect the functionality in sealing applications expressed in terms of the compression set. The material still retains decent shape recovery characteristics and most likely performs well in a seal at room or elevated temperatures. Its behaviour at lower temperatures, i.e. below room temperature (or much shorter times than used in the present experiments) is inferior to the one of the virgin elastomer, therefore the sealing capability might be somewhat compromised. However, no concrete estimates or predictions of sealing behaviour can be given due to the absence of low-temperature compression set experimental data. The sealing capability depends also on how fast the release of compression would be undertaken in this case. It should also be noted that HNBR exposed to the ageing environment for 9 months exhibits a notable hardness increase which is rather close to the hardness acceptance limit stipulated by ISO 23936-2 (± 5 units). This might indicate that the hardness criterion established by the standard might not be an adequate metric of the state of an elastomer material subjected to the hydrocarbon ageing. This assertion is in line with previously made conclusions [32,33] on little relevancy of the standard criteria in defining sealing failure in hydrocarbon ageing experiments.

A more interesting case is HNBR ageing at 150 °C where a marked change in material properties is observed. Here, the HNBR mechanical properties and hardness go beyond ISO 23936-2 acceptable change limits already after 3 months exposure which could be a clear failure in accordance with the standard. The longest chemical exposure of 9 months results in a dramatic increase in T_g of the material and associated changes in macroscopic properties, from hardness to viscoelastic characteristics. The elevation of T_g is caused by a dramatic change in the chemical structure of HNBR. It is believed that transformation of C≡N groups to amide groups observed in the FTIR spectra is a primary factor for the notable change in T_g. The conclusion corroborates the results from Lou et al. who presented the results of a hydraulic oil ageing study [12] in which disappearance of the C≡N peak and formation of amide groups was also observed although the glass transition was not evaluated there. The possible reaction in HNBR during the ageing

Table 4
FTIR peak allocation in unaged HNBR.

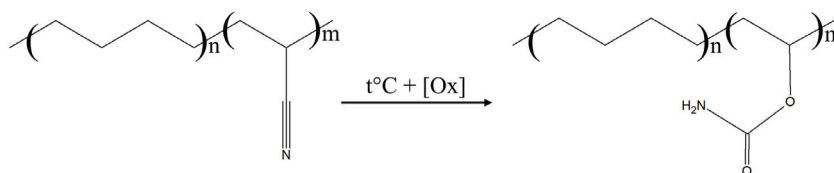| Wavenumber, cm^{-1}	Peak assignment	Reference
1454	–C–H bending vibration in CH2 group	[12,19,30]
1580	C–O–C stretching vibration originated from additives	[12,31]
1732	–C=O stretching vibration	[12,19,30,31]
2234	–CN stretching vibration	[27,28]
2852	–C–H stretching vibration in CH2 group	[12,19,30]
2922	–C–H stretching vibration in CH2 group	[12,19,30]

Fig. 14. Schematic of the oxidation reaction leading to changes in the chemical structure of HNBR.

period is schematically illustrated in Fig. 14. Even though air was flushed away before commencing the exposure in autoclaves, oxidation could have occurred due to reduction of carbon dioxide under the high temperature and pressure with an influence of water. Since oxygen was not directly present in the ageing medium, it could have taken longer time for HNBR to reach the same state as in [12]. The rubber aged over 3 months exhibits no notable signs of the change in T_g, whereas the same material already demonstrates another transition in the dilatometric curve after 6 months of the chemical exposure. In the end of the chemical modification process after 9 months ageing, the material resembles more a polyamide in structure and properties than an HNBR elastomer.

In addition to the chemical structure modification, the changes in properties can be attributed to the cross-link density alternating with ageing time and a gradual decrease in the free volume. The cross-links inhibit the motions of the polymer backbone chains and, thus, lead to increase in the apparent stiffness and compression set at short times. This change in free volume can be estimated using WLF [26] equation parameters. As proposed in [26], the temperature dependence of time–temperature superposition factor a in the glass transition region and at higher temperatures is expressed as

$$a(T) = -\frac{C_1(T - T_{\text{ref}})}{(C_2 + T - T_{\text{ref}})},$$

where T is temperature, T_{ref} is the reference temperature, C_1 and C_2 are the equation parameters. C_1 parameter is related to the free volume in a polymer material as [26]

$$f = \frac{1}{(2.303 \times C_1)},$$

where f is the fractional free volume. The calculated variation of fractional free volume in HNBR with ageing time for both ageing temperatures is given in Fig. 15. The free volume in HNBR aged to 130 °C tends to decrease with ageing time and temperature in an almost linear manner due to increasing cross-link density and/or potential loss of the additives. This observation is in accordance with the findings in the previous study [17]. The changes in free volume at 130 °C are not that significant as those observed at 150 °C. Here, the free volume first reduces to ≈0,015 after 3 months of the chemical exposure and then increase somewhat after 3 more months of ageing. This effect correlates with the sharp increase in low-frequency modulus after 3 months of exposure to the solvent mix followed by a reduction in the modulus after 6 months of exposure seen in the HNBR master curves in Fig. 12. The most plausible explanation can be that the growing cross-link network and loss of additives dominate in the first stage of ageing at 150 °C, while chain scission takes over the dominating role later in the ageing process. The effect was not observed earlier in [17] as the exposure duration in that study was only 3 months.
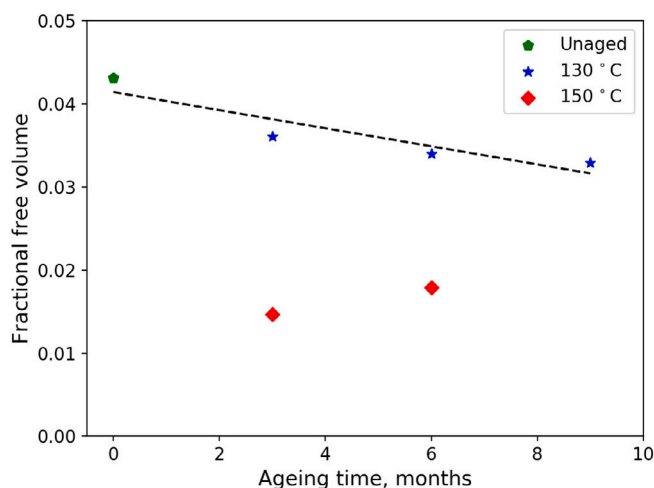

Fig. 15. Fractional free volume as function of ageing time at the indicated ageing temperatures. The WLF equation parameters used for calculations are given in Table 3. The dashed line represents linear fitting of the data.

No analysis on the free volume is made for the most aged HNBR because it represents a polymer with a very different structure after exposure to the solvent mix and cannot function well in virtually any sealing application.

The increased cross-link density and inferior properties would not necessarily mean an immediate failure of a seal made of this material. As long as the structural framework around the pre-compressed seal is immovable and there are no considerable thermal fluctuations ($\Delta T < \approx 50$ °C) in the seal system, the seal tightness would most certainly be maintained [13]. In case of a gaseous medium, the seal leakage through the aged material would be actually even smaller because of the reduced permeability of the material as demonstrated in [8,14,17]. When there is an artificial displacement of the sealing surfaces in the direction opposite to the seal squeeze, i.e. the seal undergoes a partial release of compression, a leakage path might form depending on the rate and magnitude of displacement as well as the seal temperature. Thus, if the seal material is aged at 150 °C the probability of seal failure would be very high as it exhibits a notably inhibited recovery characteristics, especially at short times as shown in Fig. 9.

The aged elastomer seal tightness problem might be complicated by at least three other effects: plasticisation by the sealed fluid, elastomer adhesion to its mating sealing surface both promoting potential seal tightness to a certain degree and a permanent deformation of the seal due to increased cross-linking and chain scission leading to higher

chances for leakage in an event of compression release. The effect of adhesion is very similar to the elastomer adhesion at low temperatures below its glass transition temperature [34]. In fact, for the most aged HNBR with the elastic modulus of 3 GPa, the strength of adhesion in a clean contact might reach an order of 1–10 MPa without taking into account the viscoelastic enhancement factor which directly affects the work of adhesion. Observations from specimens in test fixtures after exposure to the solvent mix (not reported here) indicate that HNBR might stick to the mating surfaces with a high adhesion strength (a pull-off force needed for detachment was estimated in the order of $\approx$ 1–10 kg for the small specimens and contaminated surfaces of the fixtures used here). Since the pull-off force and the adhesion strength further increases with the work of adhesion w as $w^{2/3}$ [34–36], the final magnitude of adhesion strength in a clean contact with an aged HNBR article might be several times higher.

5. Conclusions

In this study, an hydrogenated nitrile butadiene rubber (HNBR) elastomer is exposed to an ISO 23936-2 multi-phase sweet oil medium at 130 °C and 150 °C over 3, 6 and 9 months followed by a rigorous characterisation programme including Dynamic Mechanical Analysis (DMA), Fourier transform infrared (FTIR) spectroscopy and quasi-static compression tests. The hardness, modulus at short times and compression set have tendency to increase with ageing duration and even more with ageing temperature. Coefficient of thermal expansion (CTE) in HNBR tends to decrease with ageing duration and temperature. Modulus at low frequencies increases with ageing time at 130 °C, however at 150 °C, it has a more complex relationship. The modulus grows in the first stage of ageing and then, after 6 months of chemical exposure, it decreases, most likely due to chain scission. The most dramatic change was observed in HNBR after 9 months at 150 °C manifesting in a high hardness of $\approx$80 Shore D, a high modulus at room temperature and a low CTE. This is accompanied by a considerable change in the glass transition temperature from $\approx$-16 °C to $\approx$+70 °C when measured by DMA. The observed shift in the glass transition is attributed to a change in the chemical structure of the material. FTIR results confirm complete dissolution of C≡N groups in the aged material and their substitution by amide groups rendering the changes in macroscopic properties. The most severely aged material analysed in this work probably has more common with polyamides than the original HNBR. Because of this non-trivial variation in the chemical structure and properties of HNBR during the ISO 23936-2 sweet oil ageing process, building a predicative theory for a limit state, e.g. on a basis of an Arrhenius-like equation, will most likely fail for such high temperatures.

The obtained results show that not all HNBR products may be expected to be functional at or even over 150 °C for a long service period, unless this can be validated by reliable long-term ageing data demonstrating not only the adequate material integrity in the service environment, but also sufficient functionality in sealing applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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