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# The Impact of Thermal Ageing on Sealing Performance of HNBR Packing Elements in Downhole Installations in Oilfield Wellhead Applications

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## Abstract

Hydrogenated nitrile butyl rubber (HNBR) elastomers are highly resistant to chemicals and degradation, and they are good candidates to be adopted in aggressive environmental conditions of high temperature and pressure. As these service parameters are common in oil and gas applications, HNBR is popular in applications such as elastomer packers in wellhead installations. This study investigated the thermal ageing behaviour of HNBR elastomers to better predict the long-term sealing performance of the packers. Elastomer compounds were thermally aged and FTIR-ATR and differential scanning calorimetry techniques were used to indicate dominant chemical reactions during ageing. Furthermore, the mechanical performance of the aged compounds were studied to investigate the effect of dominant ageing reactions on performance. It was indicated that crosslinking reaction was dominant in the ageing process of HNBR compounds up to 150 °C. This resulted in increased stiffness and alleviated elongational strains at the break. However, compounds behaved brittle at ageing

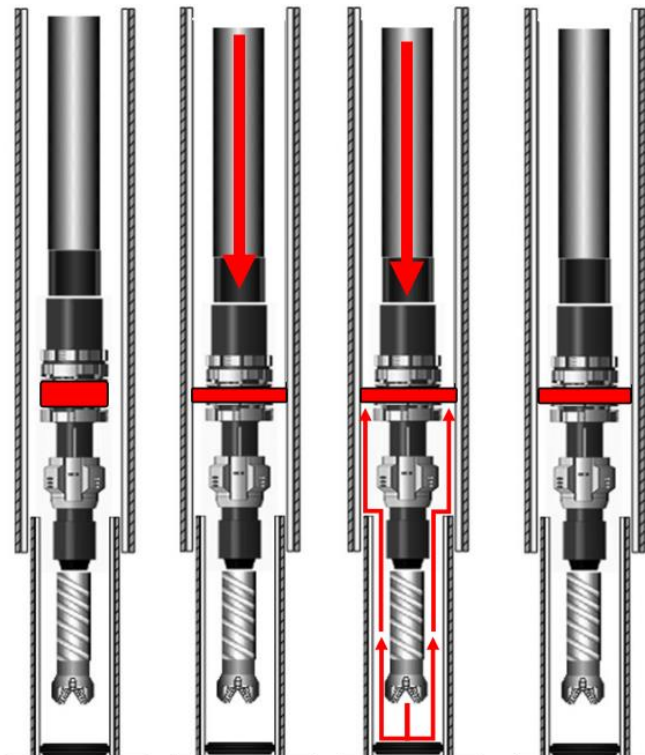
temperatures above 150 °C, and from the thermal analysis, it was concluded that at those temperatures chain scission reactions overtook the ageing mechanism. Finally, an approach for life-long prediction of mechanical characteristics of the specimens showed while long-term ageing promotes elastic failure, ageing temperatures above 150 °C facilitate rupture because of the brittle response of the compounds.

## **1. Introduction**

Elastomer packers made of hydrogenated nitrile butadiene rubber (HNBR) are widely used in wellhead installations in the oil and gas industry. HNBR finds applications in many sectors such as the marine, automotive, and oil and gas industry [1]. A wellhead is a pressure-containing component at the surface of an oil well that provides the interface for drilling, completion, and testing of all subsea operation phases [2]. They perform the function of sealing downhole installations, typically forming barriers inhibiting the transmission of fluid and or gas from one zone to another. Packing elements are mechanically installed and are compressed by hydraulic pressure to expand radially and seal the gap between the mandrel and the well wall (Figure 1).

The packers performance deteriorate inservice due to high pressure and elevated temperatures of the oilfield environment leading to seal failure. Consequently, this leads to well pressure drop, leakage and causes damage to the equipment and directly impacting the efficiency and cost of installations. The packers failure often means the tubing string must be re-run causing high well control risks and an increase in construction costs and operation time. Different areas of the packers performance have been studied in the literature. For instance, Li et al [3] investigated the failure behaviour of the packing elements by modelling packers performance in high temperature and high-pressure environments. Their behaviour was linked to the size of the packers (dimensionless length), as well as gas output rate which both affect heat transfer throughout the length of the packer.

Ekinović and Yalcin [4] studied the material properties of the packers focusing on swellable packers while McLaughlan and Grimes-Ledesma [5] evaluated properties optimisation to exploit the self-healing properties of the swelling elastomers. Elsewhere, Akisanya et al [6] focused performance of packing elements consist of two types of hard and soft elastomers. The modelling work studied the behaviour of each elastomer and modelled resistance of the dual-material packers in extrusion failure. It was reported that while harder elastomers around the edges of the packer prevent extrusion failure, it is important that the two materials used in the packers' designs not to have distinctive properties as that can lead to interface debonding and non-uniform load transfer. In the area of material properties, the effect of creep relaxation parameter have also been investigated on the extrusion behaviour of the packing elements [7-8]. Viscoelastic characteristics of the elastomers were modelled to predict extrusion failure and it was reported that other parameters such as the extrusion gap and the axial load on the packers play an important role on failure initiation and propagation.



(a) (b) (c) (d)

Figure 1- Packing elements in downhole installations: (a) The packer is in place- (b) The packer is mechanically pushed in place, compression occurs, and the packer seals the gap- (c) and (d)- The packer is subjected to hydraulic pressure from downside by downhole gases and fluids.

The packing elements' performance in the oil and gas sector is typically validated by the manufacturer or the end-user according to the ISO14310 standard [9]. Through the standard procedure, packing elements are mechanically installed in the casing under pressure and at elevated temperatures, and their performance is evaluated for a pressure drop to meet the approval status. The failures in the packing elements can be categorised into three main types; cracks and rupture, elastic failure, and extrusion [10]. While following the testing standard pursues the performance of the packers under the required pressure and temperature to replicate the real-life situation, it does not provide due considerations regarding the effect of ageing. This is even though packers are expected to perform sealing for an extensive time under high-temperature conditions. Furthermore, most of the previous studies in the literature performed on packing elements or on test specimens were completed on unaged elastomers [3-6]. However, a clear understanding of the ageing mechanisms is vital to sustaining the functional performance of the packers.

The ageing behaviour of HNBR elastomers has been studied in the literature [11-12]. Chaudhry et al. [13] demonstrated that elastomers with high molecular weight exhibited a higher degree of chain scission (i.e., degradation of polymer main chain) while the dominant reaction in the lower molecular weight HNBR elastomers was crosslinking. The two degradation mechanisms in the ageing of elastomers are crosslinking and chain scission [5,11,12]. While crosslinking reactions increase the stiffness of the elastomers, chain scission reactions cause a decrease because of shortening the chain length and hence a reduction of the structural integrity in the elastomer network. Usually, both reactions occur at the same time. However, the chemical structure of the elastomer and the ageing environment make one of the reactions dominant. Several variables such as temperature, oxygen, ultra-violet (UV) radiation, and time accelerate the ageing process of elastomers [14]. HNBR materials with

higher acrylonitrile rubber (ACN) content generally exhibit higher chemical resistance due to the high electronegativity and activation energy of the nitrile bond. Furthermore, the molecular weight of the elastomer chains can also affect the degradation process. Other factors, such as the chemical structure of elastomer and compound formulation, can also broadly influence the ageing mechanisms [12-14].

It is therefore paramount to understand the governing mechanism of ageing and influential variables to predict the mechanical performance for a specific product application. However, there is a lack of information on how ageing promotes different failure modes in the packing elements in the oil and gas industry. The current research, therefore, investigates the thermal ageing of HNBR compounds for the manufacturing of packers used in oil and gas drilling wellheads. It focuses on the dominant ageing mechanisms using structural changes and the acquired study results are then applied in a lifetime prediction modelling study to predict HNBR packers long-term performance. The impact of accelerated thermal ageing failure modes and the safety margin for service conditions in real-life applications are critically evaluated.

## **2. Experiment**

### **2.1. Materials and samples manufacturing**

A commercial HNBR compound grade used in this study was 96% saturated with 36% ACN content. High saturation elastomer was compounded with pellet form carbon black (90 phr) as filler, and peroxide (5 phr) as the curing agent. The carbon black was used as received from the manufacturer to enhance both mechanical performance and compound thermal stability [17].

The uncured compound was received after mixing from the supplier and test specimens were moulded from the compound and cured according to the manufacturer guidance for 20 minutes at 165 °C. Cured specimens were then post-cured for 4 hours at 150 °C to complete the manufacturing process to ensure any remaining curing agent from the primary curing stage is consumed.

Flat moulds of 2 mm thickness were used for tensile dumbbells, which were stamped after the curing process to meet the ISO ISO37 Standard type I (gauge length of 33 mm) [18]. Furthermore, the compression buttons with a diameter of  $29 \pm 0.5$  mm and a thickness of  $12.5 \pm 0.5$  mm were moulded directly to button shapes moulds (Figure 2).



Figure 2- Unaged Compression buttons and tensile dumbbells before testing- Diameter of 29.5 mm and a thickness of 12.5 mm. Tensile dumbbells size I according to the standard with a thickness of 2 mm.

## 2.2. Test specimens preparation

Thermal ageing was carried out according to the ISO 11346 test standard to allow estimation of the thermal endurance of rubbers from exposure to elevated temperatures for given periods at constant temperatures in a hot air circulating oven [19]. Previous research [20] has shown that HNBR specimens of 10 mm thickness exhibited diffusion-limited oxygen (DLO) effect above 150 °C and after 30 days. To limit DLO in the specimens, the test samples were aged for a maximum of 30 days. Furthermore, due to the low thickness of the test specimens (2mm for tensile dumbbells and 12.5mm for compression buttons), the risk of inhomogeneous ageing was decreased. It was taken that the rate of ageing remained constant throughout the thickness of the samples.

It should be noted that ageing elastomers in the presence of oxygen may lead to inhomogeneous ageing and the DLO effect [21] which occurs when the rate of oxygen consumption in the outer layer of the elastomer is more than that of oxygen diffusion through inner layers. As a result, the outer layer of the elastomer ages more rapidly and prevents degradation of the inner layers resulting in heterogeneous ageing. Inhomogeneous ageing distorts the analytical results and long-term predictions as it does not account for the different ageing regime of the inner parts. Elevated temperature, material, accessibility of oxygen, and size of the elastomer part influence the DLO effect. These considerations of our sample geometrical properties and testing conditions led to the ageing criteria as summarised in Table 1.

Table 1- Test specimen ageing conditions.

Temperature [°C]	Period [days]				
	3	5	9	14	30
<b>75</b>	3-75	5-75	9-75	14-75	30-75
<b>100</b>	3-100	5-100	9-100	14-100	30-100
<b>150</b>	3-150	5-150	9-150	14-150	30-150
<b>175</b>	3-175	5-175	9-175	14-175	30-175

### 2.3. Characterisation

The surface microstructures of the aged and unaged HNBR compounds were characterised with Carl Zeiss scanning electron microscopy (SEM- mode: LS10) and a voltage of 20 kV and a working distance of 8.5 mm with X2000 magnification. Samples were not coated due to the carbon black content in the HNBR compounds and their conductivity. The changes of chemical structures and ageing mechanisms were studied by Fourier transform infrared- attenuated total reflection (FTIR -ATR) using Thermo scientific Nicolet instrument (model: iS20). Various positions of the surface and cross-section of the specimens were analysed. All reported data in this work are related to the surface properties of the specimens unless specified otherwise.

The thermal behaviour of the aged and unaged specimens was studied with Perkin Elmer differential scanning calorimetry (Model: DSC 8000). The technique was used to measure the



compounds' glass transition temperature and to investigate the effect of ageing on thermal characteristics. Five to seven milligrams of the cured rubber was heated from -60°C to 160°C at a heating rate of 10°C/min. The minimum temperature was decided based on the glass transition temperature of HNBR (~-128°C), and the maximum temperature was selected to capture any crystallisation melting peak. Samples were conditioned at an initial temperature for at least 10 minutes to ensure the start temperature of the specimen was the same as in the chamber.

#### **2.4. Mechanical Testing**

To determine the tensile properties, the tensile tests were performed using an Instron 3382 Universal testing machine fitted with a 100 kN load cell equipped with Bluehill 3 software. Specimens were loaded in tension at a constant crosshead speed of 50 mm/min until failure. All tests were performed at ambient temperature, and at least five samples were tested for each condition according to the Standard ISO37 using type I samples [18] and the stress-strain relationship determined from the measured data sets.

The compression tests were tested according to the ISO 7743 test standard for the determination of the compression stress-strain properties of vulcanised or thermoplastic rubber using a standard test piece as per ISO 7743 test method A [22] and using the same equipment as tensile testing. The testing procedure included two stages of conditioning and compression. In the first stage, specimens were loaded up to 25% strain and unloaded for three cycles. The loading-unloading cycles were dictated by the ISO 7743 test standard procedure performed following the conditioning stage, after which specimens were compressed up to approximately 65% (to fulfil radial expansion of 20%) strain at a constant crosshead speed of 10mm/min. All tests were performed at ambient temperature, and at least three specimens were tested for each condition.

The international rubber hardness degrees (IRHD) hardness of the specimens were measured using a Wallace IRHD tester (model: H14). The hardness measurement was performed at the surface of the specimens to provide further details of the stiffness of the aged samples, and data were correlated with the moduli of the aged specimens to trace the homogeneity of ageing through the thickness of the specimens.

### **3. Results and discussions**

#### **3.1. Thermal properties and ageing mechanisms**

The DSC study results show that the glass transition temperature of the specimens aged at higher temperatures was increased compared to the unaged samples as presented in Figure 3. This was attributed to the additional crosslinking in the ageing process reduced the degree of freedom of the molecules. Therefore, elastomer chains needed a higher amount of energy for the transition from a glassy to a rubbery state, which is translated as a higher glass transition temperature (Figure 4) in the aged specimens. The heights of the transition shift were also changed with increasing the exposure temperature. The endothermic step of the glass transition is proportional to the thermal capacity of the structure. While it is not clear how the ageing of a structure can change its thermal capacity, the consistency of the results with literature confirmed that the same underlying mechanisms [23] governed the ageing process.

The peaks observed in the DSC thermograms of the HNBR elastomer were referred to as melting of the crystalline regions of the network. The ageing process in elastomers also lessened this endothermic peak due to increased crosslinking and the restrictions for crystal formation in the structure. Baba et al. [24] also reported that crystallinity was decreased with the ageing of HNBR elastomer and was reflected in the endothermic melting peak of the DSC curve. Barely any transition point from glassy to rubbery, and any melting peak was traced for the specimens aged at 175 °C, which was referred to different ageing mechanisms in these specimens.

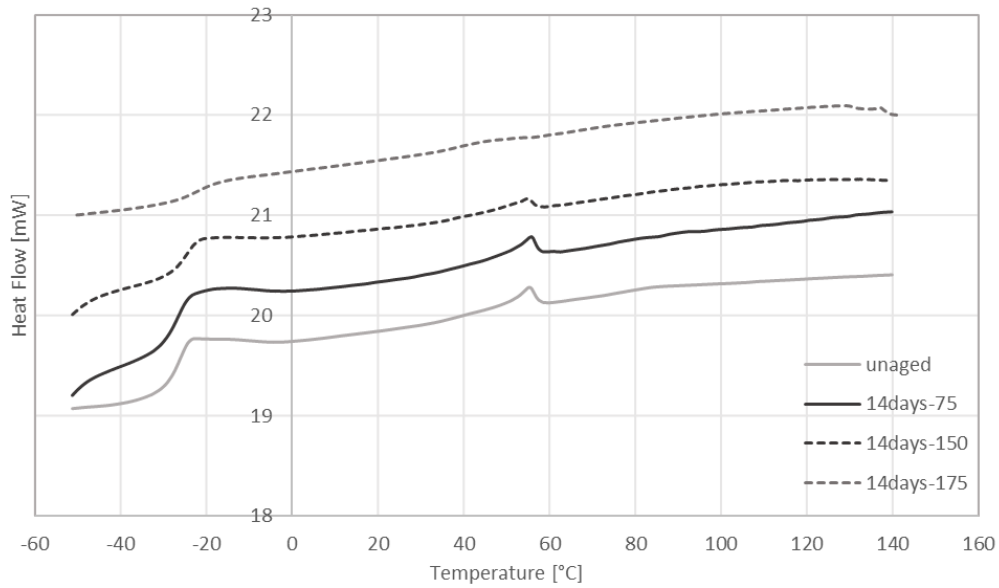


Figure 3- DSC thermograms of the elastomer compounds aged at 150°C.

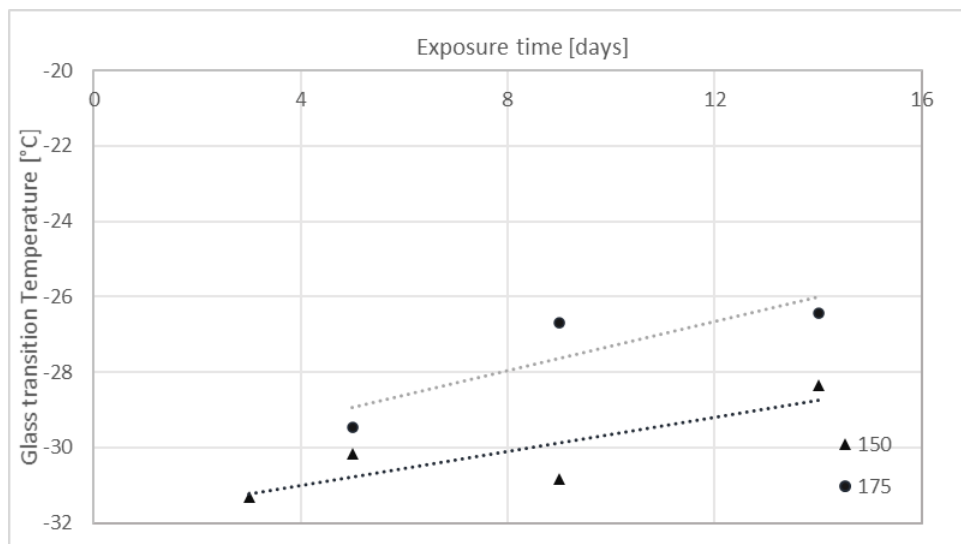


Figure 4- Glass transition temperature of the aged compounds at 150°C.

Although DSC characterisation revealed some information on how ageing can alter the physical properties of the HNBR compounds, it did not provide any further details on the possible chemical reactions through ageing.

The surface microstructure of the specimens before and after ageing were also compared in Figure 5. From the SEM images, the change in the microstructure was evident. While in unaged specimens uniform dispersion of the compound was observed, signs of agglomeration

and localised oxidation was indicated for the specimens aged at different ageing temperatures. This came in support of the reactions and their intensities that were observed in FTIR spectra.

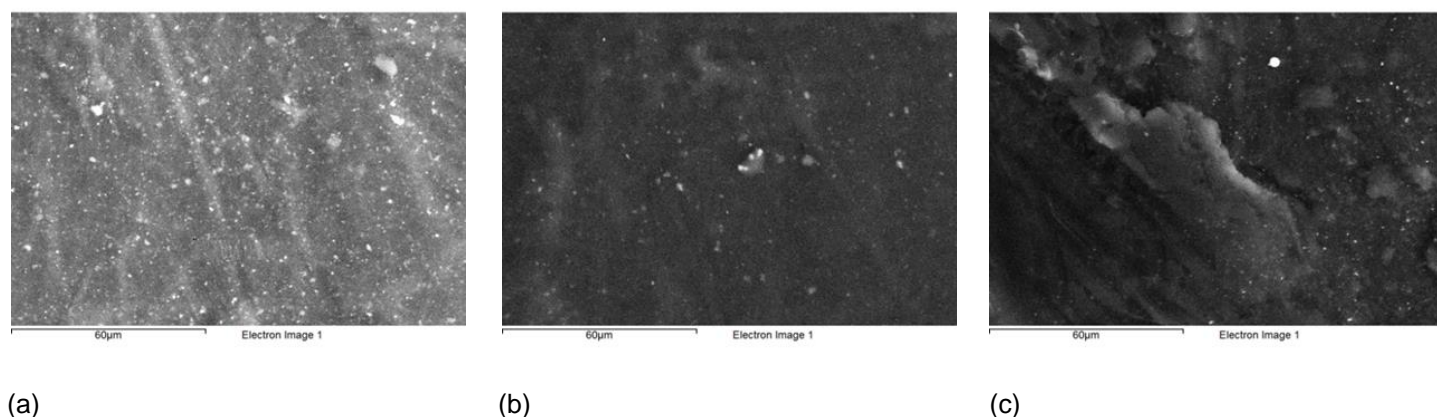


Figure 5- SEM microscopy of the (a) unaged, (b) aged at 100 °C and 30 days, and (c) aged at 150 °C for 30days.

In the hydrogenation reaction, carbon-carbon double bonds in the backbone of the rubber are saturated. The process, which decreases the degree of unsaturated C=C bonds enhances the resistance of the rubber to oxidation and degradation [25-26]. This is because Since the HNBR is a copolymer of acrylonitrile rubber (ACN) and butadiene rubber (BR), and is made by saturation of the double bonds in nitrile butadiene rubber (NBR). After hydrogenation, some degree of the unsaturated double bonds (RDB) may remain in the backbones of the elastomer, which can affect the degradation process of the HNBR [27]. Therefore, the saturation degree of HNBR is an essential characteristic feature and is identified for different grades of HNBR commercially available in the market. Previous work on the structural parameters has also exhibited the critical role of ACN [28] content, as well as the molecular weight of HNBR [13].

The FTIR-ATR spectra of the unaged and aged specimens were presented in Figure 6 **Error! Reference source not found.** and provided more details on possible reactions in thermal ageing. The two peaks between 2800 and 3000  $\text{cm}^{-1}$  were representative of  $-\text{CH}_2-$  vibrations and a small peak at 2200  $\text{cm}^{-1}$  were attributed to CN bond in the HNBR backbone. The CN peaks were diminished in the aged specimens at higher temperatures, which could be due to the nitrile reactions and radicalisation of the side chains through autocatalytic reactions at high

temperatures, as Bender has also explained [29]. Nitrile reactions at high exposure temperatures lead to alcohols, ketones and carboxylic acid formation as well as recombination of the free-formed radicals. These simultaneous reactions in ageing HNBR which are named hydroperoxide reactions result in R=O and -C- O- formation along with abstraction of water and other small molecules [25]. Two peaks at 1735 cm<sup>-1</sup> and 1180 cm<sup>-1</sup> were due to these reactions which were also intensified with ageing temperature up to 175 °C.

Other works in the literature have also reported [30] trace reactions of the nitrile group in hot air ageing in the IR spectra although Bender [29] did not report such observations. No visible peak was captured at 1640 cm<sup>-1</sup> that could be linked to C=C double bonds. Therefore, it was concluded that there was insignificant RDB in the system in either case (aged and unaged) to be traced by FTIR. The RDB are one of the main sites on the HNBR elastomer where oxidation initiates during ageing through the formation of free radical sites and reaction with other substances in the system or the adjacent HNBR molecules. The HNBR grade used in this work was 96% saturated and specimens were post-cured in the oven. Therefore, it was expected that the RDB in the cured specimens to be negligible which was the case in the FTIR spectra. As specimens were aged at higher temperatures, the intensity of CH<sub>2</sub> peaks decreased initially at 75°C due to the loss of small molecules additives such as lubricants [31] and increased at higher ageing temperatures.

This phenomenon has been also reported elsewhere [32] in the literature and it was associated with the crosslinking reactions that led to the formation of further C-H bonds in the compound. Remarkably, barely any peak was detectable for specimens aged at 175°C. The peaks for C-H vibrations and C=O were also less pronounced compared to other spectra. As explained in the DSC and FTIR results it was concluded that the ageing mechanisms at this temperature were dominated by chain scission rather than crosslinking. Ivan et al. [30] demonstrated that chain scission reactions in the ageing mechanisms of HNBR compounds with the presence of the nitrile group in HNBR favours the  $\alpha$ - $\beta$  scissions. Although chain scission reactions are not favoured in HNBR as in other elastomers such as ethylene

propylene diene monomer (EPDM) rubber, they still occur at high energy levels and at high temperatures, where the activation energy is fulfilled [29].

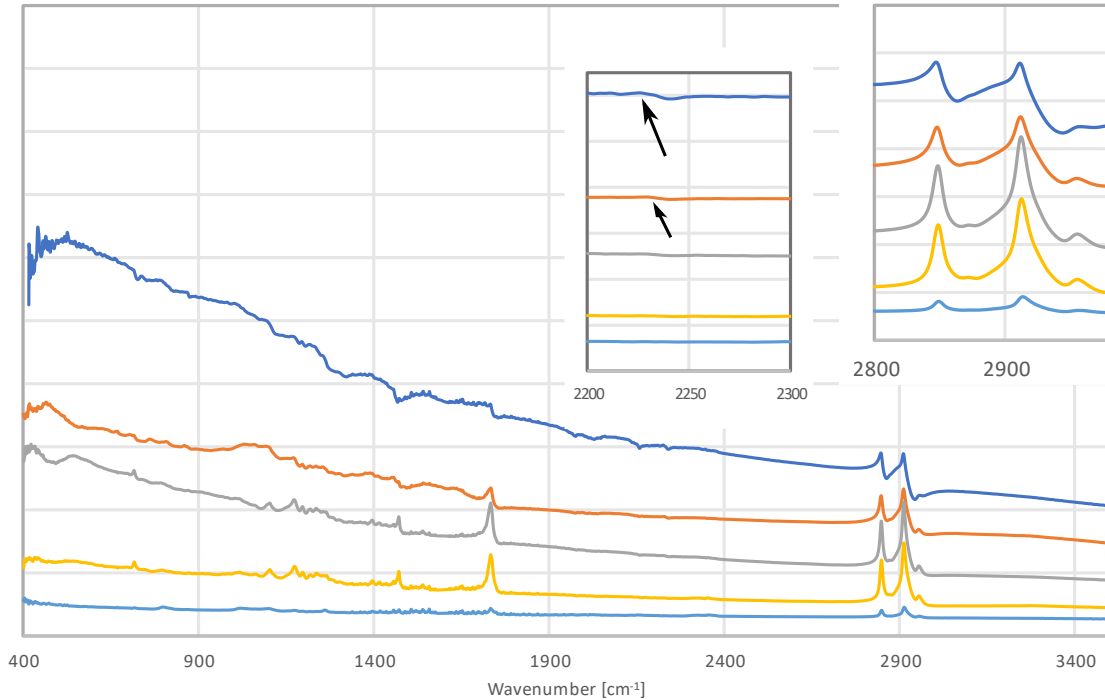


Figure 6-FTIR-ATR spectra of aged and unaged specimens at different temperatures for 30 days.

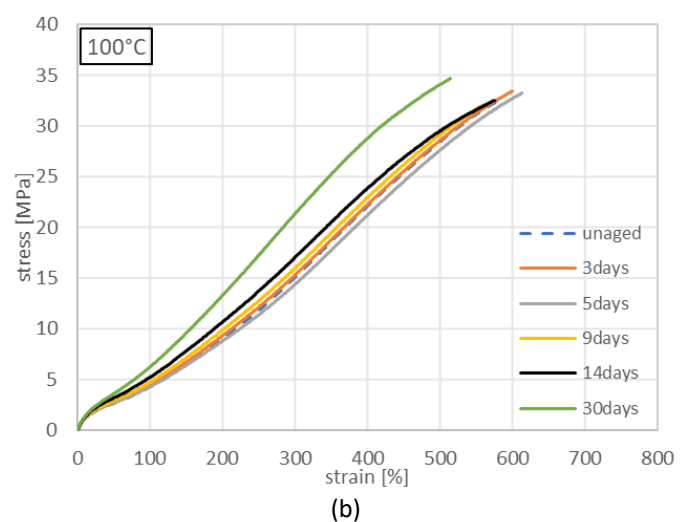
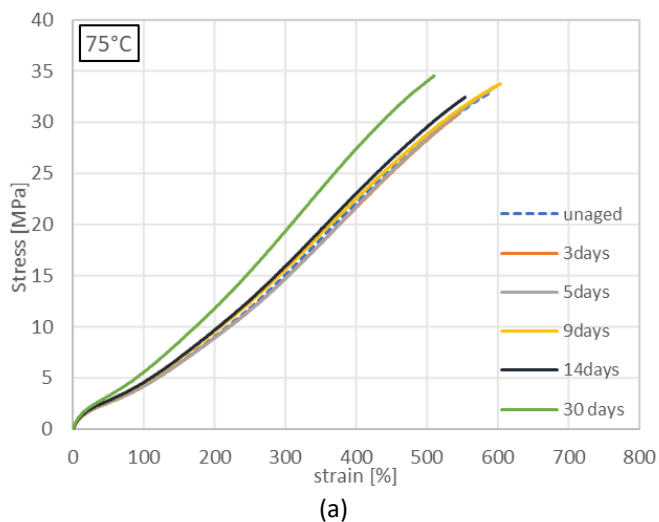
### 3.2. The effect of thermal ageing on tensile properties

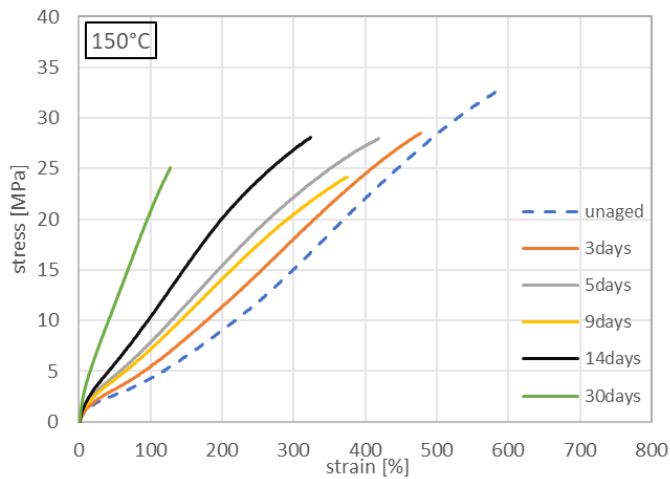
The representative stress-strain curves of the aged elastomer compounds are shown in Figure 7. At 75°C, no specific change was exhibited in the aged materials except for 30 days of exposure, where the moduli of the specimens were increased. Increased stiffness of the specimens was associated with a slight decrease in the elongation break, while the strength had minimal change from the unaged state of the material. At the exposure temperature of 100°C, the same behaviour for the tensile behaviour of the specimens was reported, which was referred to the same ageing mechanisms in the compounds at both temperatures.

With increasing the ageing temperature above 100°C, elastomers' moduli were increased further, and specimens failed at lower elongational strains, which also led to decreased

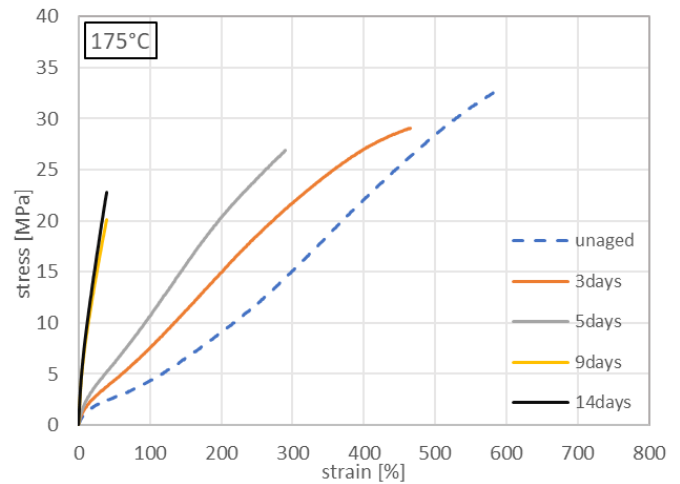
ultimate stress. While increasing the stiffness was continued at a higher ageing temperature of 175°C, the overall response of the HNBR compound was changed from ductile to brittle at this temperature. This was attributed to a change in the ageing mechanism of HNBR compounds at high temperatures, as mentioned earlier in thermal analysis.

Figure 8- summarised the stiffness of the compound at 100% strains. It is common to report elastomers' stiffness at strains of 100% or 200%, while for other materials, the modulus is usually reported as the slope of the stress-strain curve in the elastic region. The stiffness of an elastomer network is defined by restrictions of the polymer chains to move in response to an external force. In compounds, these resistances are caused by additives (e.g. fillers), crosslink density, and the effect of physical entanglements. As explained earlier in the characterisation section, the two dominating mechanisms in thermal ageing of the elastomers are chain scission and additional crosslinking. Chain scission reactions decrease the stiffness by shortening the chain length, reducing entanglements, and freeing the chains' movements. However, crosslinking reactions enhance the stiffness by creating further restrictions in chains' movements. Furthermore, the effect of entanglements is not much reflected in the elastic modulus because, at low strains, chains can slide with respect to each other and the mechanism of stretching is dominated by slippage rather than the resistance of the entanglements. Therefore, reporting the 100% stiffness provided a better perspective of the dominating mechanism in ageing, as it captures the overall effect of both mechanisms.





(c)



(d)

Figure 7- Tensile stress-strain curve of the rubbers aged at different temperatures and periods. (a) aged at 75°C, (b) aged at 100°C, (c) aged at 150°C, and (d) aged at 175°C. (Color Figure).

Ageing mechanisms of HNBR elastomers have been discussed widely in the literature [24-26] and crosslinking reactions were affiliated to the dominant ageing mechanisms for HNBR compounds in agreement with our work as noted in the characterisation study (see section 3.1). Crosslinking reactions increased the molecular weight of the network, as well as the density of crosslinks. Increasing the crosslinks in the network created a stiffer network with more constraints to move. Nitrile bonds reactions are characterised as either imide or ketimine reaction [12-27].

Additional crosslink formation decreased chain length between the crosslinks, and the elastomer network became stiffer. However, at 175 °C specimens failed long before they reached 100% strain and behaved very brittle. Comparing the behaviour of the compounds at 175 °C with other aged specimens and results from the thermal analysis, showed that the dominating mechanism at this temperature was different from what has explained so far and chain scission reactions were dominant. It could be noted that as the network approached the saturation level for crosslinking, degradation of the chain took the pace in ageing and resulted in a brittle elastomer network that failed at low strains.



The ultimate strengths of the aged rubbers were shown in Figure 9.a ultimate strengths of the aged compounds showed only a slight decrease with time and temperature except for the specimens aged at 175 °C, where a sharp decrease was reported for the ultimate stresses. As explained earlier, the abrupt reduction in the ultimate strength was referred to as the change in the ageing mechanisms where chain scission reactions resulted in breaking the backbone and weakening the structure. Figure 10- presented the change of the strength with temperature. As seen, increasing temperature slightly improved the strength of the elastomer compounds initially before they decreased. Increasing the strength was referred to as the additional crosslink formation. While as the exposure temperature and time was increased, the consequence of the stiffer network with less flexibility and lower failure strain resulted in a slight decrease in the ultimate strength of the compounds. Therefore, it worth noting that the strength of the compounds should be interpreted in the context of the full stress-strain curves rather than being justified as an independent trend. Therefore, the overall response of the aged elastomers in Figure 7 better showed the response over ageing.

Results of the elongations at the break in Figure 9.b were explained by the same trend discussed for the strength. Elongations at break of the aged elastomers exhibited a slight increase at 100 °C, following a sharp decrease with temperature and time. While the reason for the slight increase at 100 °C was not clear, the following decrease at higher temperatures was referred to the additional crosslink formations that led to a decrease in the elongational break of the elastomer compounds. Additional crosslinks made restrictions in the network to rotate and move and created stress concentration points and resulted in failure of the specimens at lower strains. Specimens failed at strains less than 10% and at very low strengths at 175 °C. It was assumed that at this temperature, chain scission reactions could overtake crosslinks' formation and resulted in short chains with minimum strength and lack of structural integrity.

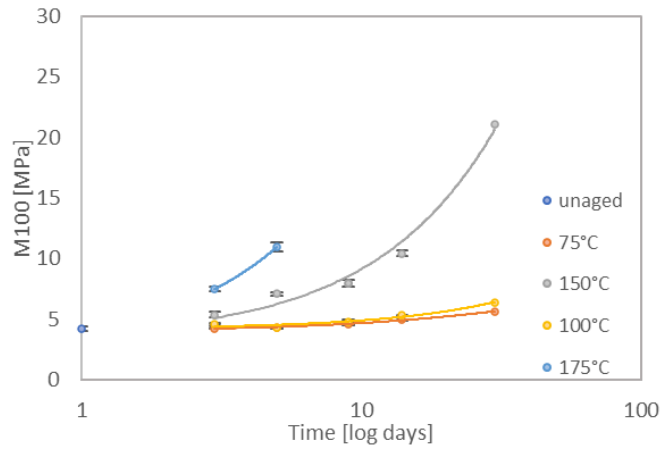
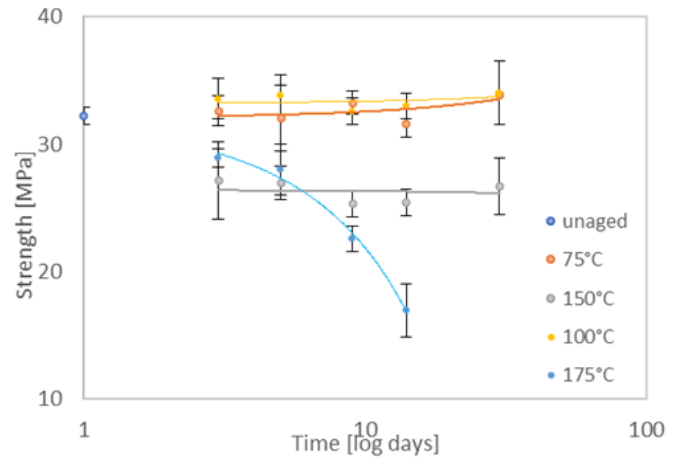
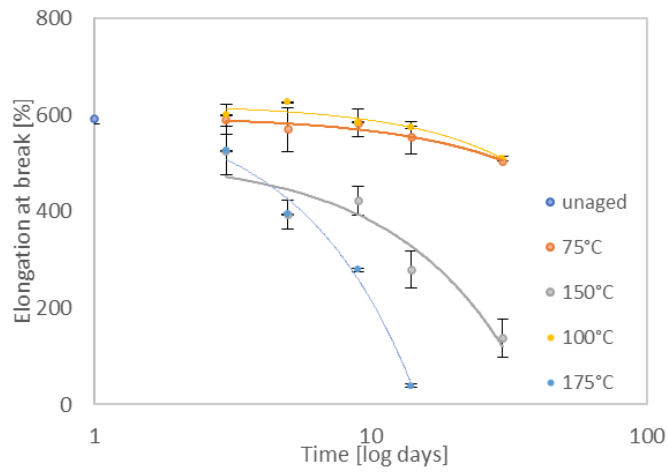


Figure 8- Stiffness of the HV elastomer specimens after thermo-oxidative ageing.



(a) (b) Figure 9- (a) Ultimate strength. (b) Elongation at break of the HV elastomer specimens after thermo-oxidative ageing.

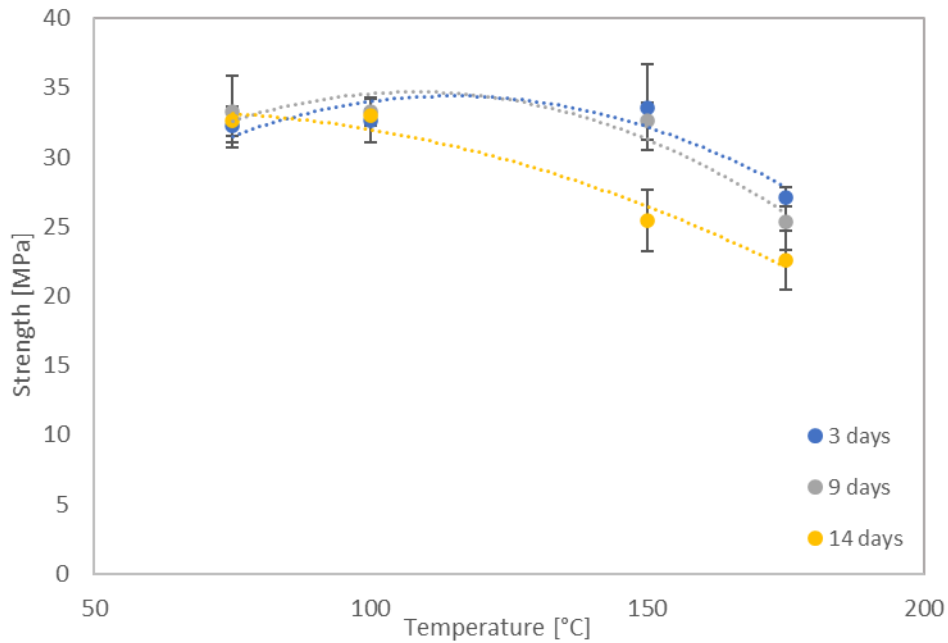


Figure 10- Strength of the aged HNBR elastomer compounds with time and temperature.

Understanding the tensile behaviour of the filled elastomer compounds shed some light on the limitations of the materials based on their application. Packing elements used in the oil and gas industry are used in aggressive environmental conditions for a longer period than what was studied in the current work. Therefore, the life-long behaviour prediction of the material provided further details on the mechanical characteristics of the parts. However, other influencing factors such as the DLO effect can distort data and invalidate predictions. There is an approach that was followed in the current work to address this issue. As explained earlier, the criteria for ageing specimens were decided so, that the DLO effect is minimised during ageing. Furthermore, hardness measurements from the surface of the aged specimens were also used to validate the negligible DLO effect in specimens.

### 3.3. The influence of thermal ageing on hardness property

The hardness of the same elastomer compounds was presented in Figure 11. Tensile properties of the aged specimens studied earlier, reflected the properties of the bulk of material as the load was applied to the cross-section of the test specimens. However, hardness data

revealed data on the surface stiffness of the specimens. As could be seen, at 175 °C the hardness of the aged specimens was increased with a steeper slope compared to the trend observed for other samples. This can be referred to as the accelerated rate of ageing of the specimens as the temperature was increased, and is in line with earlier discussions on the tensile behaviour of the aged compounds at this temperature.

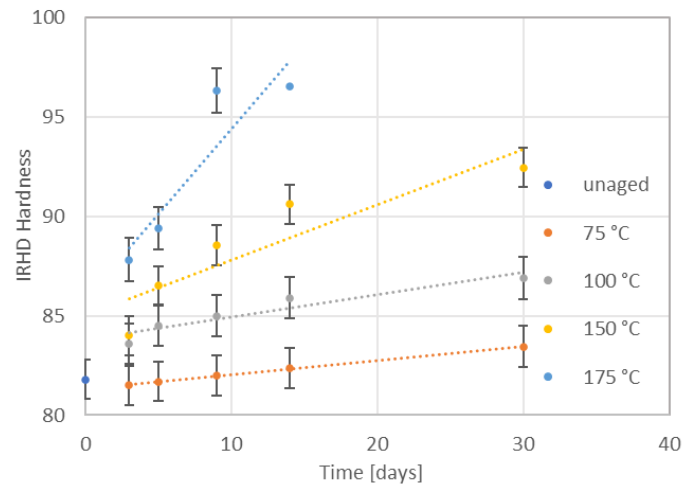


Figure 11- Hardness of the HNBR compounds aged at different temperatures and exposure times.

The relationship between hardness and the tensile moduli of the elastomers were plotted in Figure 12. This technique is used to report the hardness of the compound as the representative value of its modulus and is valid when specimens are homogeneously aged and the DLO effect was negligible [31]. As studied here, hardness values and moduli of the aged specimens relatively fit together, and this was used in this study to confirm that DLO effect was limited in the aged specimens due to the selected exposure time, temperature, and low thickness of the specimens.

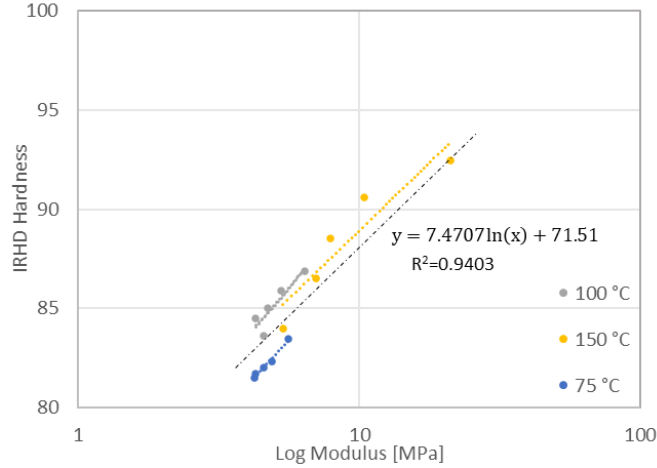


Figure 12- Surface hardness of the aged specimens versus their tensile moduli. Results on the data at 175°C were not included as no modulus for the specimens aged at 175 °C and longer exposure time of 5 days was recorded.

### 3.4. Master curve and prediction of the life-long behaviour

The approach used in the current work was according to the Standard ISO 11346 [19] and using Williams–Landel–Ferry (WLF) equation. WLF is an empirical equation associated with time-temperature superposition [19]. Based on the WLF theory, for exposure temperatures higher than the glass transition temperature of the polymer ( $T > T_g$ ), time and temperature can be substituted i.e.

$$\log a_T = \frac{-a(T-T_0)}{b+(T-T_0)} \quad (1)$$

where  $T_0$  is the reference temperature,  $a$  and  $b$  are the materials constant, and  $a_T$  is the shift factor. This technique is applied to predict the property in the material with viscoelastic nature in a broader time scale. While elongation at break is a property used to trace degradation of elastomers, stiffness is also used for predicting long-term behaviour of the parts as it reflects the viscoelastic nature of the elastomer after the yield point and at a controlled strain rate [23].

The concept of this approach lies in the higher molecular mobility of polymers at elevated temperatures, which is assumed to be reached at a longer time and lower temperature [36].

In this method, the property of interest was plotted as a function of time for each exposure

temperature. Once the reference temperature was selected ( $T_0$ ), other plots were shifted along the x-axis (time) with reference to  $T_0$  until the curves overlap and the “master-curve” was built. Master-curve of the aged compound was conducted here, as shown in Figure 13. The WLF technique is limited in terms of extrapolation, and care must be taken in translating the results for application. Results of the modulus for the aged specimens at 175 °C were exempted as the underlying ageing mechanism was not the same as for other temperatures. Therefore, it was assumed that at 175 °C degradations of the material is so severe that it is not considered as the service temperature of the HNBR compound. As shown in the master curve, specimens exhibited a change in the slope of the stiffness change with time.

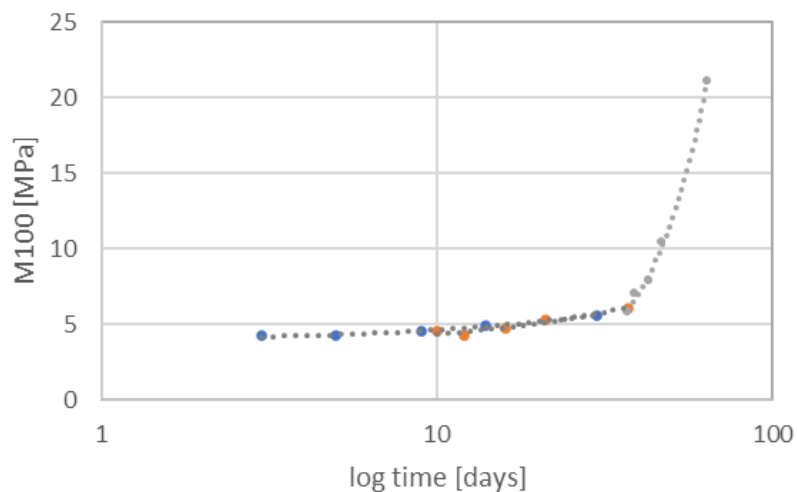


Figure 13- The master curve of stiffness of the elastomer compound at 75°C.

Packing elements are used as a sealant in wellbore installation to prevent downhole fluid from leaking. To pursue this aim, they have remained under compression so that they can seal the gap between the well's wall and the mandrel by expanding radially. To understand the behaviour of the sealants under pressure, the compressive response of the elastomer specimens was studied. As the trends of the aged specimens in compression after ageing were similar to what discussed earlier for tensile behaviour, only the representative stress-strain curves of the aged specimens at 150 °C have been presented here. As shown in Figure 14,

ageing also resulted in increasing compressive stress. In other words, higher compressive stresses were needed to compress specimens.

Assuming that elastomers are incompressible materials ( $\nu \cong 0.5$ ), the overall volume of the parts did not change under compression. In most cases, packing elements are expanded radially up to 20% to seal the annular gap between mandrel and well wall. The stress required for the specimens to expand radially by 20% has been presented in Figure 13, for two exposure temperatures. As seen, the same trend discussed for the tensile stiffness of the aged elastomer is also valid here. An average size packing element is under the pressure of 5000 to 7000 psi (~ 35 to 45 MPa). Comparing the stress-strain curves in Figure 14, this value is far beyond the need for 20% radial expansion for the unaged and short ageing period. However, as the age of the part, two scenarios are probable. Once the required stress to hold packing elements under the required expansion level increases that of the applied stress, parts can face elastic leak as they do not satisfy the sealant requirement any further due to insufficient stress level [11].

The second scenario explains the degradation of the material as seen at the exposure temperature of 175 °C. At this temperature which is a similar case for a long time and lower exposure temperature (WLF theory), degradation and chain scission becomes the dominant mechanisms and overtake crosslink formation. At this temperature, compressing the packing elements results in crack formation and leads to locational cracks' formation and tear, and the packer fails. For the latter case, tested specimens in compression at 175 °C (Figure 16) showed cracks all over the sample and along the length, while for specimens aged at lower temperatures, no visible damage and cracks were seen on the surface of the specimens after compression test. Therefore, the ageing process deteriorates the possibility of elastic failure and tear in the packing elements, and the upper bound of exposure time and maximum service temperature should be considered for environmental service conditions.

Master curve and long-term prediction of the mechanical performance of the elastomer parts are used to predict the approximate end of life of the parts. As explained earlier, size of the

packing elements differ from the test specimens of the study, which make them prone to inhomogenous ageing due to larger size and non-uniform heat transfer through the thickness and it is expected that packers face more aged outer surface than the inner layer. This alters the behaviour of the packers compared to homogenous ageing. Therefore, it is important to consider the master curve developed here as a lower limit for the mechanical performance of the packing elements.

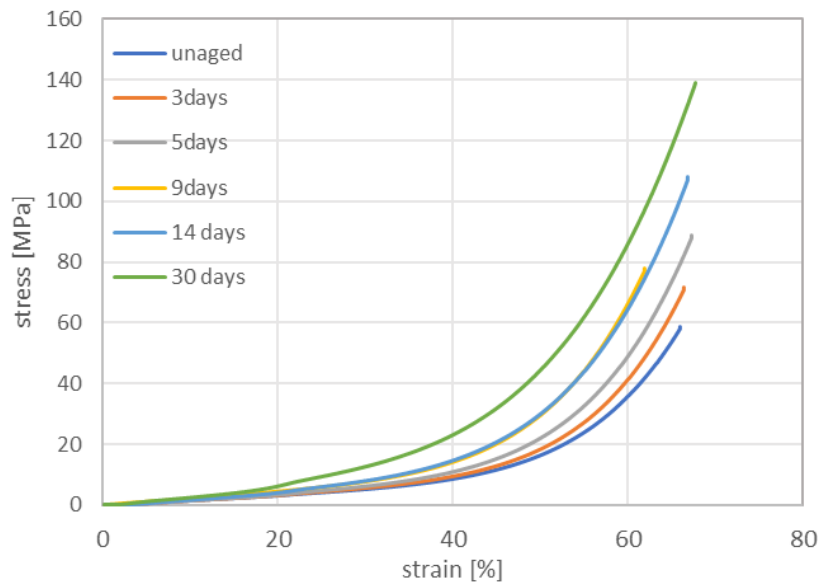


Figure 14- Compression stress-strain curves of the specimens at exposure temperature of 150°C.

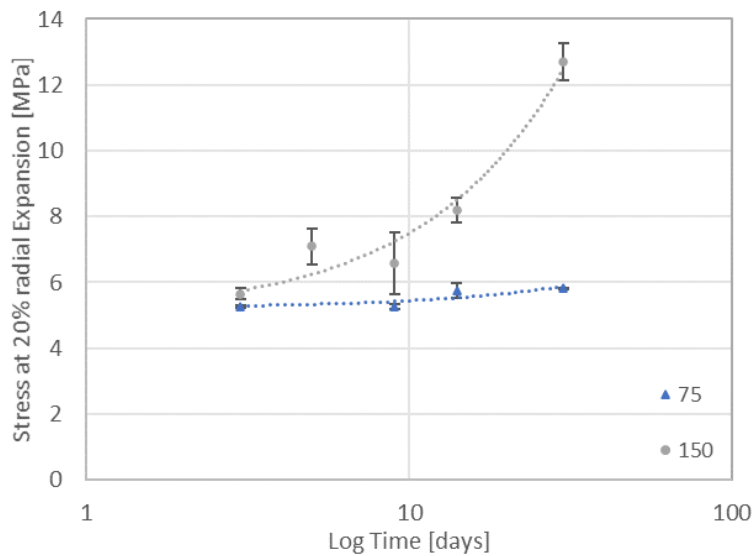


Figure 15- Compressive stress for 20% radial expansion on aged specimens.



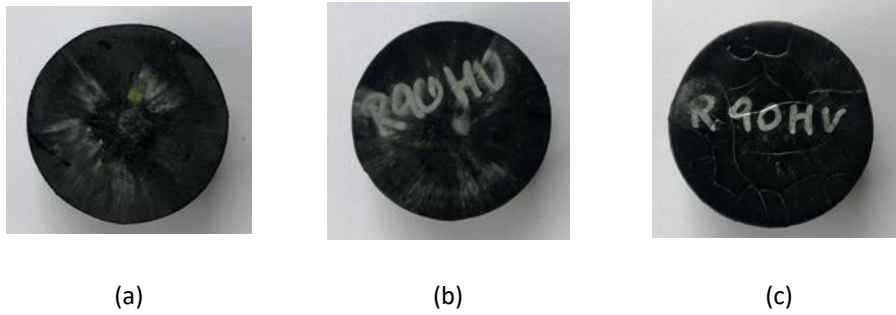


Figure 16- Tested compression buttons after ageing (a) 100 °C, (b) 150°C for 30 days, and (c)175 °C for 14 days.

### **3.5. Loading and sealing effects on HNBR for wellhead application**

As mentioned above, the packing elements are compressed by hydraulic pressure to expand radially and seal the gap between the mandrel and the well wall (Figure 1). This can lead the packing elements to be seated in tension, compression or medium state (e.g. shear) with the potential to withstand pressure difference from top to bottom [37], and failure of the seals could result in pressure drop, leakage, and causes damage to the equipment and installation. Hu et al. [31] found out that the stresses concentrated at the shoulder and inner vertex of the sealing ring can have a direct impact on the damage or failure (e.g., cracks and rupture, elastic failure, and extrusion) of the sealing ring under effective operational conditions. There are examples in the literature where sealing structure design (i.e., force, shape, dimension) has been investigated [30]. Figure 17 shows the loading effect schematic diagram after the packer in place and seals the gap between the mandrel wall and the casing wall.

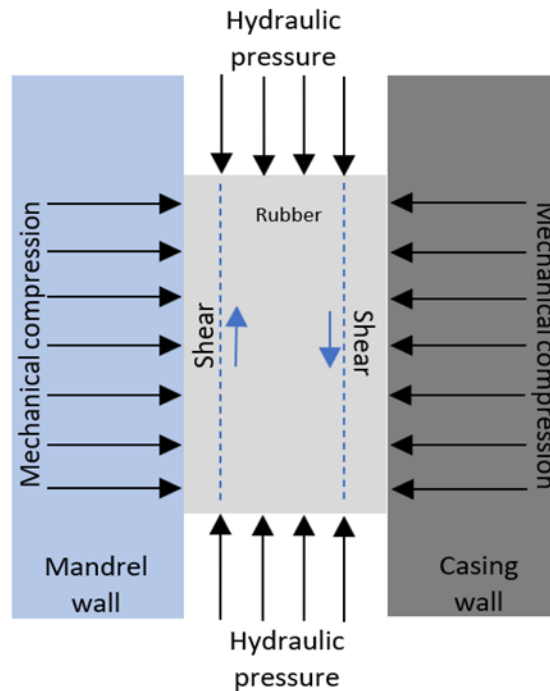


Figure 17- Loading effect diagram after packer in place and seals the gap.

During the loading cycle of the packer in a relatively confined space, the stress state is multi-axial (i.e., hoop or tension, radial compression, axial pressure, shear). Some context of loading behaviour (or deformation leading to sealing) of rubber-like structures can be deduced the follows. To start with, the loading for sealing purpose leads to compression and expansion in rubber, whereas the shear effect is caused by the sealing pressure difference between the top and bottom of the rubber. Since rubber is a non-linear elastic material, the chemistry of rubber manufacturing has a greater influence on the properties of the rubber material (e.g. allowable shear stress, friction coefficient). This aligns with Liu et al. [38] who reported that when the allowable shear strength is constant, the height of the rubber (cylindrical shape) decreases gradually with the increase of friction coefficient. Under the same friction coefficient, the higher the allowable shear stress of the rubber material, the smaller the height of the rubber.

During an earlier stage of mechanical compression between two walls, the radial deformation is assumed to be symmetrical along with the height of the rubber and does not exceed the elastic limit of the rubber. This radial deformation mainly depends on the material used in the

rubber and the working conditions. In the later stage of mechanical compression between two walls, the deformation of rubber depends on the stiffness of the outer sleeve and the wellbore of the packer. In our investigation, the elastic failure was probable to cause leakage once the applied compressive stress did not fulfil the required amount of force for the packing elements to expand and seal the gap.

To summarise, the combination of loading displacement, friction coefficient, and temperature increase could increase the contact pressure between packer rubber and casing wall, and the average contact pressure can be greater than the sealing specific pressure. It is important to note that in our investigation, at higher temperatures, elastomers exhibited brittle mechanical response due to an underlying chain degradation mechanism, which resulted in cracks in the specimens, which could lead to ruptures in the packing elements. Therefore, to reduce the failure of packers, an improved sealing rubber packers or further sealing structure design analysis can be necessary, which can be a reference for optimising the sealing performance and pressure capacity of packers.

#### **4. Conclusions**

The mechanical behaviour of HNBR elastomer packers was studied in thermal ageing. Two mechanisms were defined to occur in the thermal ageing of the specimens: chain scission and crosslinking reactions. HNBR elastomers exhibited enhanced stiffness with ageing, which was referred to the additional crosslinking (tensile and compression results). However, at exposure temperatures higher than 150 °C, elastomers' behaviour was changed drastically, and they responded as a brittle material, failed at low strength and elongational strains. This finding, along with the thermal characterisation analysis (DSC and FTIR), confirmed that at 175 °C, the dominant chemical reactions changed and probably chain scission ruled out the ageing process rather than crosslinking.

It was found that ageing could trigger two types of failure in packing elements; elastic failure and rupture. Elastic failure was caused once the applied compressive stress did not fulfil the

required amount of force for the packing elements to expand and seal the gap. This occurred as the aged specimens exhibited a stiffening effect in which they required a higher amount of compressive stress to expand radially. The second failure mode, rupture, occurred once the service temperatures exceeded 150 °C. At higher temperatures, elastomers exhibited brittle mechanical response due to an underlying chain degradation mechanism. This phenomenon resulted in cracks in the specimens, which could lead to ruptures in the packing elements. Life-long behaviour prediction of the elastomers was adopted with the time-temperature superposition. It was shown that specimens aged at lower exposure temperature showed that the same increased rate in stiffening with time lead to the same failures modes.

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