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Investigating the aging behavior of HNBR seal elements in high-pressure high-temperature wellbore environments exposed to H_2S and CO_2

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Abstract

Widely employed as a seal element in the oil and gas industry, understanding the aging behavior of Hydrogenated Nitrile Butadiene Rubber (HNBR) is crucial for both theoretical and practical advancements. This study investigates the degradation mechanisms of peroxide-cured HNBR compounds exposed to H2S and CO2 in a simulated environment at elevated pressure and temperature. Prior to accelerated aging, the mechanical properties and chemical structure of the samples were evaluated . Subsequently, the compounds were subjected to harsh aging conditions in Hc-A (5% vol. H2S and 20% vol. CO2) and Hc-B (20% vol. H2S and 5% vol. CO2) environments at high-pressure/high-temperature (HPHT) conditions of 6.9 MPa and 121°C, respectively. Fourier-transform infrared (FTIR) spectroscopy revealed significant changes in the molecular structure of the aged HNBR samples, resulting in increased swelling, reduced density of -C≡N groups and double bonds, additive migration, and a weakened reinforcing effect of carbon black. Furthermore, the study observed notable changes in the mechanical properties, including

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increased mass, volume, and elongation at break, but decreased hardness, modulus, ultimate tensile strength, and compression set compared to virgin samples. Notably, the results highlight the dominant influence of CO2 in the simultaneous sour gas immersion test on the structure-property relationship of the aged HNBR samples.

Keywords

HNBR, Degradation mechanisms, mechanical properties, H_2S and CO_2 concentration, aging

Introduction

Sealing materials in wellhead and downhole equipment are critically important for well control and integrity, as their failure is a major contributor to well control incidents with operational risks and environmental consequences.[1] Hydrogenated nitrile butadiene rubber (HNBR), fluorocarbon-based fluoroelastomer materials (FKM), and silane-based rubbers are commonly used in these demanding environments due to their excellent physical-mechanical properties and resistance to high pressure, temperature, and aggressive chemicals.[2,3] HNBR, in particular, finds widespread application due to its excellent performance against harsh conditions such as sour gas environments containing H2S and CO2. However, exposure to these extreme conditions, including high temperatures, differential pressure, and aggressive fluids like CH4, CO2, and H2S, weakens the sealing performance of elastomers through various degradation mechanisms.[4,5] Among these agents, CO2 and H2S are the primary contributors to chemical degradation, while CH4 plays a physical role through diffusion and potential swelling.[3] Rubber products further experience volumetric swelling and scission reactions when interacting with various fluids and solvents during well service, particularly at high temperatures, leading to common failures in oil and gas facilities. Several factors influence the interaction between chemicals and elastomers, including crosslink density, permeability, crystallinity, and chemical composition. Lou et al.[4] reported that thermal aging can cause the migration of additives (stearic acid and plasticizer) or the consumption of carbonyl groups. They found that thermal aging in oil leads to the formation of hydroxyl and amide polar groups, altering internal energy distribution and dissolving the non-polar molecular chain due to increased polarity. These changes result in additive breakout from the matrix, void and agglomerate formation, and a decline in rubber properties. The impact of thermal aging on HNBR seals in packer elements was studied, revealing that a crosslinking reaction occurs below 150°C, resulting in increased stiffness and decreased elongation at break. The rubber also displayed brittle behavior at temperatures above 150°C due to chain scission.[6]

Research on early packer element failures in CO2 injection wells indicated that the mechanical properties of rubber gradually decline with increasing temperature, pressure, and decompression velocity. It was determined that decompression velocity significantly impacts short-term rubber failure more than temperature and pressure. Higher decompression velocity creates bubbles on the rubber surface, reducing seal performance due to the rubber's inability to quickly expel sudden gas releases, leading to pressure-induced bubble formation and bursts.[5] An investigation into the corrosion behavior of HNBR samples in acidic solutions using mechanical properties and fracture morphology reported a decrease in hardness, elongation at break, and tensile strength, alongside an increase in area cross-section and compression deformation. Tensile fractures displayed primarily brittle behavior.[7] The impact of supercritical CO2 on the corrosion of HNBR sealing rubber was examined, revealing that CO2 corrosion in high-temperature, high-pressure (HTHP) conditions alters both the morphology and mechanical characteristics of HNBR. As exposure time increases, surface bubbles form on the specimen, leading to a reduction in the rubber's tensile strength. A time-dependent Yeoh Model was developed based on uniaxial tension tests to provide a theoretical framework for accurately computing the mechanical properties of HNBR in a supercritical CO2 corrosion environment.[8] The thermal oxidation of HNBR vulcanizates at temperatures ranging from ambient to 150°C was investigated using FTIR and NMR techniques. FTIR spectroscopy revealed the development of ketones, esters, carboxylic acids, and secondary alcohols, confirmed by NMR analysis. Notably, the aging process did not affect the acrylonitrile content, while the residual double bond decreased.[9] Dong et al.[10] studied rubbers under CO2-H2S conditions, revealing mass and volume increases in HNBR, while AFLAS and FKM remained stable. They identified degradation pathways involving crosslinking and chain scission. Cong et al.[11] reported significant reductions in HNBR's mechanical properties after H2S aging, corroborated by other studies.[12,13] Different aging conditions influenced crosslinking and stiffness in HNBR, while reducing CO2 diffusivity and saturation swelling. Improved performance in the explosive decompression test for thermo-oxidatively aged and swollen HNBR samples was noted, possibly due to increased crosslink density and glass transition temperature (Tg).[14] This highlights the interplay between permeation and mechanical properties in rapid gas decompression resistance[15,16]. Significant degradation of HNBR after exposure to sour gas for two weeks at 10 MPa and 155°C was observed. The gas phase consisted of 30% CH4, 2% H2S, and 3% CO2. Findings indicated additional crosslinking and chain scission during aging. SEM/EDX analysis of the HNBR samples revealed elemental changes, with increased oxygen content confirming surface oxidation, while increased sulfur content suggested additional crosslinks, contributing to the observed stiffness increase. Conversely, the decrease in carbon and nitrogen content after aging suggests decomposition of -C≡N groups in the polymer chains.[17] The effects of HTHP exposure to hydrocarbon fluids on HNBR were investigated, revealing a significant increase in tensile stiffness and a decrease in strain to failure, impacting sealing performance. The study suggests that chain scission and crosslinking during aging are the primary degradation mechanisms, leading to reduced chain length, decreased tensile strength and strain to failure, and ultimately, a more cross-linked structure with increased stiffness. Additionally, it was proposed that incomplete curing during manufacturing may contribute to the observed stiffness increase as the aging temperature approaches the curing range.[15] The impact of functional groups on the degradation of HNBR and NBR was studied, finding that C = C double bonds and nitrile groups contribute to chain cleavage and crosslinking, leading to rubber deterioration. Under HPHT thermal aging, double bonds break, creating a cross-linked structure that reduces elasticity and increases brittleness in NBR and HNBR. Nitrile groups can form ladder structures or undergo hydrolysis when heated in acidic conditions. Experiments on NBR and HNBR with varying acrylonitrile (ACN) content showed that nitrile groups are more reactive than double bonds. The combination of both groups in NBR resulted in the highest chemical activity. After H2S exposure, the formation of mono- and disulfide crosslinks in NBR indicated that degradation is mainly due to the presence of both functional groups.[18] The corrosion of HNBR O-rings in a simulated wellbore environment was studied, finding that the compression set increased while hardness, tensile strength, and elongation decreased in both compressed and uncompressed conditions. These changes were attributed to the absorption of corrosive molecules causing volume expansion, bubbles, and cracks; fatigue from differential pressure leading to chain scission and radical formation; and chemical reactions between the solution and rubber chains creating voids and macrocracks. Compressed samples showed smaller changes in mechanical properties due to reduced surface contact and fluid permeation, limiting chemical reactions and oxidation.[19] The effects of temperature and CO2 pressure on Fluorocarbon rubber (FKM) seals were studied, comparing them with HNBR and assessing reinforcements. Both filled and unfilled HNBR and FKM matrices were tested at 60 and 130°C under CO2 pressures of 2, 4, and 6 MPa, as well as vacuum conditions. The study measured CO2 sorption and desorption coefficients and swelling upon decompression for all materials. Results showed that HNBR had lower swelling than FKM when exposed to CO2 and remained undamaged during decompression, indicating its suitability for these service conditions.[20] Prior research has examined the resistance of elastomers to H2S and CO2 separately, but there is a gap in understanding their combined effects under HPHT conditions similar to those near wellbores.

This gap is critical for HNBR, widely used in downhole and wellhead applications. This study designed a test setup to replicate wellbore conditions, investigating the impact of simultaneous exposure to varying concentrations of H2S and CO2 in the gas phase under high pressure and temperature on HNBR vulcanizates. The focus was on evaluating physical and mechanical properties, including hardness, volume/mass, tensile strength, and compression set of HNBR specimens before and after exposure to an aging test solution. Results were supported by pyrolysis-FTIR and ATR-FTIR analysis of both virgin and aged samples.

Experimental

Materials

The compounding materials, including HNBR with 36% acrylonitrile, zinc oxide, peroxide, fusil 200, antioxidant, stearic acid, plasticizer, carbon black, and magnesium oxide were purchased from industrial commercial supply. Arkan Gas Company provided H_2S,

CO_2, and methane gases to create the desired test environments. The Iran Shimi Company also supplied n-octane, n-hexane, n-decane, and toluene solvents for the study.

Rubber compounding and vulcanization

A brief description of the formulation of the peroxide-cured HNBR disks and sheets prepared in this research is shown in Table 1. Based on ASTM D3182, the ingredients were first weighed (Table 1) and then mixed by a two-roll mill with a diameter and length of 25 and 15 cm, respectively, at a temperature range of 40 to 60°C. After the compound was prepared and rested overnight, the HNBR samples were cured in a hot press at 180°C and pressure of 170-180 bar for about 18 minutes, followed by a post-cure at 120°C for three hours in an oven. The optimum cure time was determined based on the curing curve of the MDR rheometer. It should be mentioned that all the samples were prepared according to our previous procedure.[21]

Sample preparation

The samples were obtained from the molded sheet. The cylindrical disks for measuring hardness and compression set of the HNBR with a height of 12.5 mm and a thickness of 29 mm were prepared. Also, the rectangular samples with a size of 20 × 20 mm and a thickness of 2 mm were prepared to measure the mass and volume changes. Some rectangular specimens with a dimension of 20 × 20 × 1 mm were prepared for pyrolysis-FTIR and ATR-FTIR analysis. Acetone was used as an extracting solvent to extract additives. Therefore, the FTIR rectangular specimens were immersed in acetone for 24h in a Soxhlet instrument. Then, these samples were kept at room temperature for a while to extract any residual solvent. At the end, FTIR samples were crushed cryogenically to a size of about 1 mm. A small amount of these purified HNBR samples were put in a small tube in close contact with a flame, and then condensed volatile products were collected. The condensed liquid was placed on KBr plates carefully.[22] This sample preparation procedure was followed after aging for aged samples to compare pyrolysis-FTIR spectra.

Table 1. Formulation of HNBR evaluated in the present study.

Component	Phr
Zeon 2010	100
N550 Carbon black	70
Plasticizer	20
Peroxide	10
Antioxidant	1
Zinc oxide	10
Stearic acid	2
Fusil 200	10
Magnesium oxide	8

Small pieces of virgin and aged samples (by both solutions of Hc-A and Hc-B) were cut into 1mm-thickness films, and then their surfaces were cleaned with acetone and prepared for ATR-FTIR. For tensile tests, some sheets with a thickness of 2 mm and size of 150 × 150 mm were prepared. The test replication was done 3 to 5 times to examine the repeatability of the obtained data.

Pyrolysis-FTIR and ATR-FTIR tests

The KBr plates were introduced to a Nexus 670 ThermoNicolet (Germany) Fourier transform infrared (FTIR) spectrometer (pyrolysis method) to study different functional groups of the aged and virgin HNBR vulcanizates in transmission mode. A minimum of 16 scans were averaged with a resolution of 4 cm^{-1}. The range of spectra was 600-4000 cm^{-1}. For further investigation and more accurate peak identification, the results were then analyzed by applying an attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy. Therefore, a Bruker Equinox 55 spectrometer (Germany) was used, and Infrared spectra were taken at room temperature. At least 32 scans of each sample (both aged and un-aged) were taken by this analysis with a resolution of 4 cm^{-1} and spectral width between 600-4000 cm^{-1}. All spectra were obtained in ATR on a ZnSe selenide crystal.

Immersion aging tests

Elastomer aging tests were conducted using a specially designed testing setup. The test procedure, aimed to assess the physical and mechanical properties as well as chemical structural changes in elastomers after exposure to harsh sour environments. Essentially, all physical properties and chemical structures were evaluated both before and after exposure. This comparative evaluation allowed the identification of any alterations in mechanical properties or structural integrity caused by the aging process.

The liquid phases for all experiments were the same, such that the vessel was charged, and a specific amount of the premixed hydrocarbon liquid was added (Figure 1(I)) to occupy the 5% (volume) of the test vessel. Then, water equal to 5 vol% of the vessel was

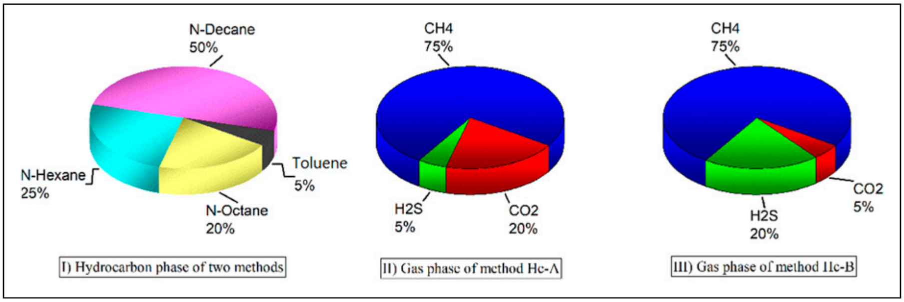

Figure 1. Composition of hydrocarbon and gas phases for each test method (Hc-A and Hc-B).

poured. As mentioned, pyrolysis-FTIR and ATR-FTIR spectroscopy were carried out on virgin samples. The physical properties of virgin specimens were also evaluated before exposure to harsh media. Samples were then put in the vessel using a sample holder. A fixture was designed and the compression set specimens were compressed to simulate practical conditions in the wellbore. None of the samples came in contact with the liquid phase during the test. The vessel then purged with nitrogen at least three times to reduce the air content to less than 5 ppm. In the last step, the vessel was pressurized using a container containing pre-mixed gas phase components of high purity, in accordance with methods Hc-A and Hc-B. The proportion of the total volume of gas-phase for each test method (Hc-A and Hc-B) is shown in Figure 1(II) and (III). The test conditions, consistent for both methods Hc-A and Hc-B, are outlined in Table 2.

The vessel was heated to 121°C for 4 hour. After that, the initial pressurization was carried out in a way that resulted in a pressure of 6.9 ± 0.7 MPa. During the aging test, pressure and temperature were monitored to maintain within the limitation range. After 160°hours of immersion, the depressurization was started while the temperature was 121°C. The rate of reducing the gas pressure in the vessel was steadily and slowly, not more than 140 kPa/minute. After depressurization, nitrogen was purged to remove the remaining H_2S in the vessel. Following the immersion test, the specimens were cleaned using ethyl alcohol. Subsequently, all the test specimens were characterized physically and chemically.

The tensile properties of the elastomeric materials were assessed according to ASTM D412 (Method A), both before and after immersion testing, using a tensile test apparatus (SANTAM, STM-20). A minimum of five dumbbell-shaped specimens for each set of test conditions were punched out from the sheets. Five hardness measurments were conducted to evaluate the initial hardness value and after chemical exposure (ASTM D2240, Type A rubber hardness measurement Durometer (Shore A)). The compression set property was determined before and after aging test using a minimum of two standard test specimens and a fixture, following the testing protocol outlined in ASTM D395 (Method B – Type 1 specimen) standard. The conditions of the compression set test are summarized in Table 3.

Table 2. The test conditions for Hc-A and Hc-B methods.

Parameters	Values	
Pressure (MPa)	6.9±0.7	
Temperature (°C)	121 ± 3°C	
Time (hr)	160 ± 2 hours	
Liquid phase 10%	De-ionized water 5% Hydrocarbon Phase 5%	
Gas phase 90%	Hc-A	Hc-B
CO2 percentage	20 vol%	5 vol%
H2S percentage	5 vol%	20 vol%

Table 3. Test conditions for compression set measurement.

	Virgin sample	During immersion aging
Deflection	25%	Similar
Temperature (°C)	121	Similar
Time (hr)	24	160
Environment	Air	Component of method Hc-A and Hc-B

Three test specimens was chosen to determine elastomers' mass and volume variation before and after immersion, according to the test procedure emphasized in NACE TM 0187. The change in mass of the test specimens was calculated by applying equation (1) as follows:

$$\Delta M(\%) = \frac{M_2 - M_1}{M_1} \times 100 \tag{1}$$

The change in volume of the test specimens was calculated by applying equation (2):

$$\Delta V(\%) = \frac{(M_2 - M_4) - (M_1 - M_3)}{(M_1 - M_3)} \times 100 \tag{2}$$

In the mentioned equations, M1, M3, M2, and M4 represent the specimen's weight in the air, weight in distilled water, weight after exposure to the test media and taking out to ambient conditions, and the weight after exposure to the test media in distilled water, respectively. The average value of mass and volume change was calculated and reported.

The samples were removed from the vessel following 160 hours of exposure. Subsequently, detailed visual inspections were conducted, and photographs of the aged specimens were captured and documented. Furthermore, as described previously, suitable samples were readied for pyrolysis-FTIR and ATR-FTIR spectroscopy to analyze structural alterations in the aged specimens.

Results and discussion

Mass and volume changes of HNBR vulcanizates after aging tests

The influence of sour gas aging according to methods Hc-A and Hc-B on the volume and weight of the specimens was evaluated. Figure 2 illustrates the average percentage of weight and volume change after exposure. Based on the results, the sample mass increase was similar at approximately 6.7% for both methods. During aging, absorption of solvent molecules might occur through the HNBR surface into the bulk and diffuse into free spaces between the rubber chains. At this high temperature, diffusion will be continued to establish an equilibrium solubility of H_2S, CO_2 (and the inert balance gas) within the bulk. Permeation of medium molecules and chemical interaction or physical entrapment is the result that causes mass gaining, which remains even after removing samples from a vessel.

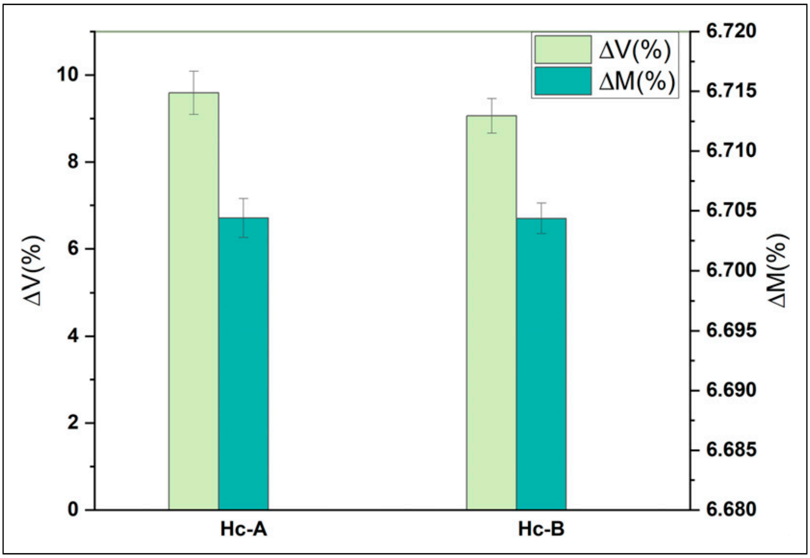

Figure 2. The percentage of increase in mass and volume of the aged HNBR samples.

In both of these aging methods, the percent of ΔV is greater than the percent of ΔM, and the density of un-swollen samples is more than swollen pieces. This might be because gas molecules are lighter than elastomers. As Zeng et al.[23] suggested, the chains with various lengths attracted the external area of carbon black (CB), and therefore, pores between the rubber chains alter (formation and vanishing) by micro-Brownian movement. The dissolution of H_2S and CO_2 in water caused the production of corrosive agents such as HS^- and HCO_3^-. These ions then form S^{2-}, CO_3^{2-} and H^+. The H^+ ions then combined to form H_2. The presence of H_2S, CO_2, and H_2 and trapping them in the pores between the chains leads to swelling. This may result in 3D expansion and volume increase. The presence of elevated levels of CO2 facilitates the formation of a greater quantity of carbonic acid, thereby resulting in a higher concentration of H+ ions. In contrast, H2S exhibits a different behavior when dissolved in water. H2S dissociates to a lesser extent compared to CO2, leading to the production of fewer H+ ions. The dissociation constant of H2S is substantially lower than that of carbonic acid, indicating that it generates a reduced quantity of H+ ions in solution. Consequently, the concentration of H+ ions in the H2S and water solution is significantly lower than that in the CO2 and water solution. This reduced concentration of H+ ions results in a diminished degree of swelling of the elastomer. In addition, CH_4 does not chemically react with the elastomer. However, it could diffuse into the elastomer and lead to physical changes. This also might lead to loss of mechanical properties. However, there was a disparity in volume increase among specimens, with those aged using method Hc-A exhibiting a greater increase compared to those aged using method Hc-B. In other words, the specimens aged by method Hc-A with a higher proportion of CO_2 compared to H_2S had a 9.6% volume increase, while method Hc-B with a higher proportion of H_2S caused a 9.0 % volume increase.

Influence of the aging tests on the hardness of the specimens

The changes in HNBR hardness after aging with two different methods were investigated. As depicted in Figure 3, aging with both solutions led to a decrease in hardness properties compared to the virgin samples. The ACN content of HNBR plays an essential role in the specimen properties because its polarity causes strong, attractive forces that consequently lead to a decrease in flexibility and an increase in hardness. However, during the aging experiments, breaking the acrylonitrile -C≡N bond and weakening the reinforcement of carbon black can influence the mechanical properties such as decreasing hardness.[23] To clarify, heterolysis and homolysis are the two reactions causing HNBR degradation because H_2S transforms to H^+ and HS^- ions or $H^\cdot$ and $HS^\cdot$ radicals. H^+ is the cause of hydrolysis of C≡N groups, whereas HS^- interacts with C = O and produces C = S and C—C = S groups. In the case of homolysis, $HS^\cdot$ is the agent reacting with the polymer chain resulting in the formation of macromolecule radicals. These radicals then interact with other mercapto radicals, and a reaction cycle starts, which end up breaking down triple bonds in C≡N groups to double and single bonds. As a result, the C-S-C bonds increase. This mechanism is the reason for elastomer degradation.[3,23] More importantly, CO_2 molecules in HPHT conditions can be dissolved in water and produce H^+, which may react with uncoupled electrons of carbon black and result in the decrease of chemical attraction of CB and reducing the carbon black strengthening effect and thus reduction of

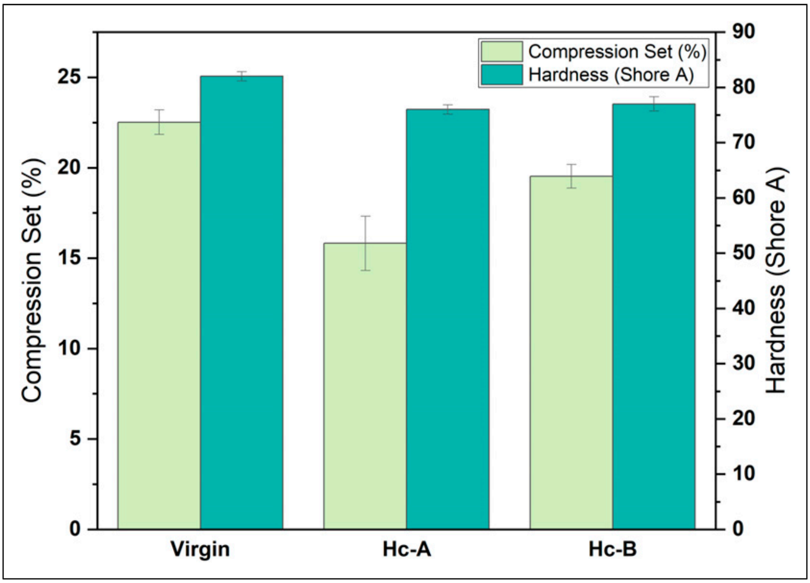

Figure 3. The hardness and Percent of compression set for virgin and aged HNBR samples.

mechanical properties of the HNBR. In fact, because of stable double bonds in CO_2, it is less likely to interact with elastomers chemically. However, some researches suggested that the dissolution of CO_2 results in a weak acidic solution in which H^+ may attack the C≡N groups of HNBR and cause the production of amide groups (R-CO-NH2).[24,25] Although the decrease in hardness was roughly the same in both methods, it should be mentioned that the specimens aged by method Hc-A had slightly lower hardness than those aged by method Hc-B. This might be due to the more significant volumetric swelling that consequently causes more degradation. Similar results have been reported by Salehi et al.,[26] showing that the hardness of rubber samples is inversely dependent on volumetric swelling.

Effect of different test compositions on compression set of HNBR specimens

As shown in Figure 3, the effect of the two aging environments on the compression set property of the aged specimens compared with virgin HNBR. It is needed to consider that the compression test for virgin specimens was carried out in air, while for aged specimens, it was done after removing from the solutions Hc-A and Hc-B. Based on the findings, the percentage of compression set of virgin specimens was higher than the aged specimens. The presence of gaseous fluids in high-pressure and high-temperature conditions caused them to diffuse into the rubber. After depressurization, these trapped fluids diffuse out and lead to swelling, which can help the elastomer restore its initial condition. Therefore, for virgin samples that were not aged in a pressurized condition, the percentage of compression set is higher. In the case in which HNBR aged by method Hc-A, the material exhibited less percentage of compression set compared to the HNBR aged using method Hc-B. This is because of higher swelling and volume increase in method Hc-A, which helped the material compensate for the compressive stress and restore its initial condition. Another explanation for that might be associated with the results of the hardness tests, which indicate that the samples aged by method Hc-A had a lower hardness. The samples with lower hardness exhibit more flexibility, resulting in lower compression set results.

Evaluating the impact of two different aging methods on UTS and elongation at break

The ultimate tensile strength and the elongation at break of the aged and virgin HNBR were measured, and the results are shown in Figure 4. Notably, the ultimate tensile strength of the aged specimens was lower than that of the virgin HNBR. The ultimate tensile strength of the specimens was almost the same for both conditions of the Hc-A and Hc-B methods. This may be attributed to the fact that the total amount of CO2 and H2S was the same in both methods. In contrast, the elongation percentage at the break of HNBR increased after exposure to both Hc-A and Hc-B solutions. To explain the reasons, according to heterolysis and hemolysis reactions and reduction of the strengthening effect of carbon black, which was described before, reducing the density of -C≡N groups in HNBR caused a decline in mechanical properties. Some research shows that the reactivity of HNBR samples has been observed with no more crosslink formation.[22,25] Other than

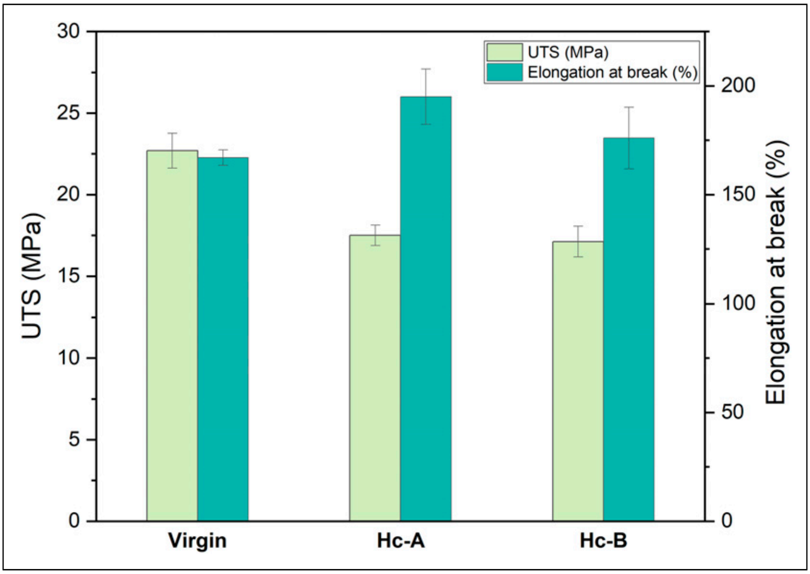

Figure 4. Elongation at break and ultimate tensile strength of virgin and aged samples of HNBR.

that, as mentioned before, H_2S can react to disrupt existing crosslinks and/or rubber chains and reduce stiffness, which will increase strain to break. In addition, acrylonitrile creates attraction between HNBR molecules, thus increasing in volume and breaking -C≡N groups, resulting in a ladder structure and more strain and, therefore, higher elongation at break. More importantly, after depressurizing and the start of de-swelling, fluids trapped between the rubber chains decrease, and movement of chains becomes easier. As a result, rubber molecules' flexibility increases, resulting in more elongation at break. As is shown in Figure 5, the ultimate tensile strength of specimens was almost the same for both conditions of Hc-A and Hc-B methods. This may be attributed to the fact that the total amount of CO_2 and H_2S was the same in two methods. However, a more significant volume increase of specimens aged by method Hc-A leads to a higher percentage of elongation at break than those aged by method Hc-B.

The modulus of virgin and aged HNBR at 25%, 50%, and 100% elongation was measured and presented in Figure 5. Aged specimens had lower modulus than virgin specimens. The mechanical analysis of HNBR showed that exposure to a sour environment results in a loss of modulus, likely because of losses of side groups. In addition, modulus usually increases with an increase in hardness. Therefore, virgin samples have the most excellent modulus value, and 25%, 50%, and 100% modulus are higher for HNBR aged by method Hc-B due to the greater hardness values. Also, based on the report by Salehi et al.,[27] CO_2 is a more damaging gas than H_2S; thus, aging with a higher proportion of CO_2 might significantly decrease the modulus compared to the test method containing more H_2S, especially at higher elongation. At lower elongation, the severity and volumetric increase in the presence of a more proportion of CO_2 was not noticeable compared with higher

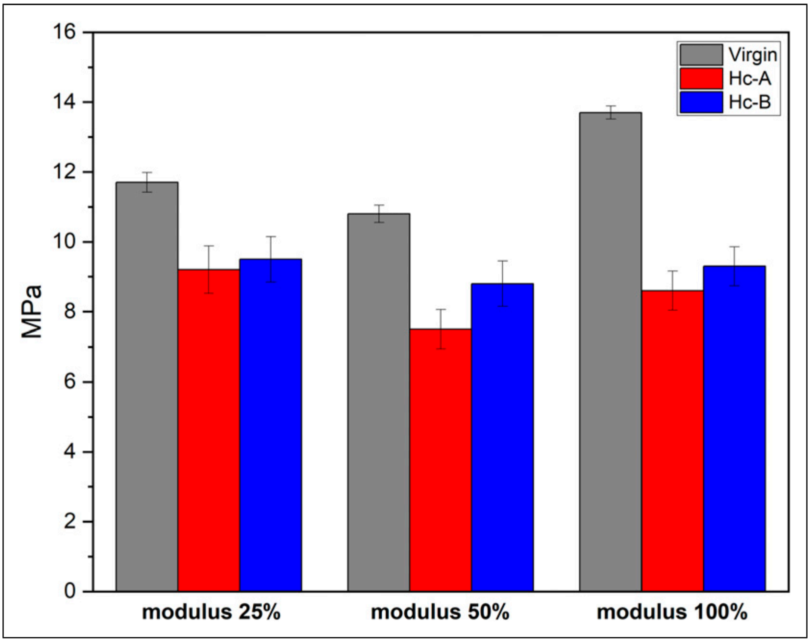

Figure 5. Modulus at 25, 50, and 100% elongation for virgin and aged samples.

elongation of the specimens. However, at higher elongation, the difference between the modulus of aged specimens by method Hc-A and method Hc-B became more considerable.

Macrography of the HNBR specimens

Figure 6 shows the specimens after the aging tests. The visual observation confirms no cracks and blisters on the aged specimens after both aging tests, except for some cracks on the compression set specimens after exposure to the method Hc-B environment. As prescribed, the formation of these cracks might be associated with the dissolution of CO_2 and H_2S and the production of H_2. The presence of CO_2, H_2S, H_2, and CH_4 in the gaseous phase of the high pressurized test vessel, cause them to diffuse into the elastomer and deformation and cracks. In fact, after depressurization, those solvent molecules that are physically trapped diffuse out and can cause cracking. Other than that, the solubility of H_2S gas is almost three times greater than CO_2 gas. However, the dissolution of H_2S makes an acidic solution three times weaker than carbonic acid.[21] A weaker acidic solution means more H+ concentration, leading to more H_2 production and, thus, more hydrogen concentration on the CB surface. In other words, H_2S is a contributing factor that accelerates the motion of H+ from the solution and its absorption on the surface of carbon black, which can cause cracking or bubbling. These results were also reported by Zeng et al..[23] It should be mentioned that the specimens aged by the method Hc-B had greater harness value and this might be the other reason for the formation of cracks. As

Figure 6. Macrography of tensile and compression set specimens of aged HNBR rubbers by a) Hc-A and b) Hc-B method.

mentioned before, compression fixture at HPHT conditions is relatively similar to explosive decompression tests. Hence, upon removing cylindrical compression set samples from the fixtures, gas molecules that were trapped during the aging period begin to diffuse out of the specimens rapidly, leading to the formation of cracks on the surface of the samples. However, the relation between explosive decompression and the aging method applying fixture needs further investigation in future research.

Pyrolysis-FTIR and ATR-FTIR spectroscopy

To investigate the existence of functional groups as well as chemical structural changes in HNBR samples, FTIR spectroscopy was carried out using two methods: pyrolysis-FTIR and ATR-FTIR. The pyrolysis-FTIR spectra of virgin and aged HNBR are shown in Figure 7. The peak at about 2238 cm^{-1} in the spectra is attributed to -CN stretching vibration. The peaks at around 1716 and 1184 cm^{-1} are related to C = O stretching vibration and C–O–C stretching vibration, respectively, indicating some additives as curing agents, plasticizer and stearic acid. The peak at 968 cm^{-1} belongs to the C-H out-

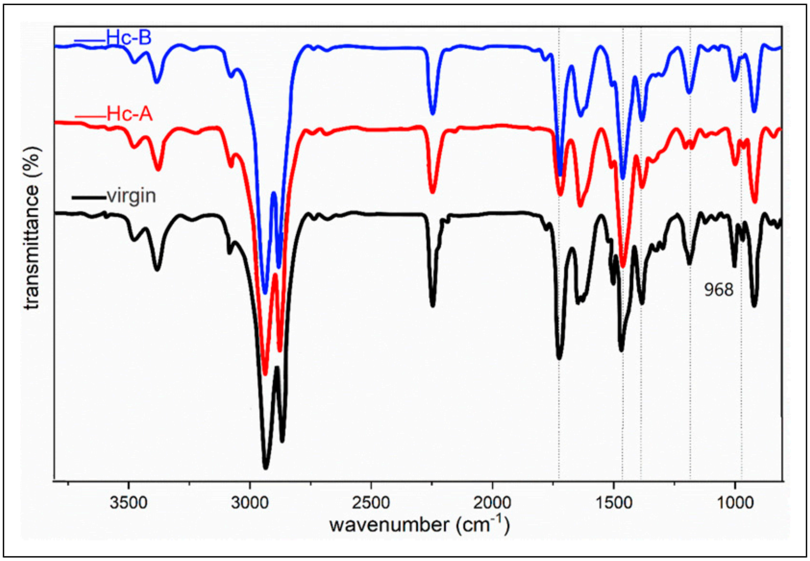

Figure 7. FTIR spectra of virgin and aged HNBR samples by Hc-A and Hc-B test methods.

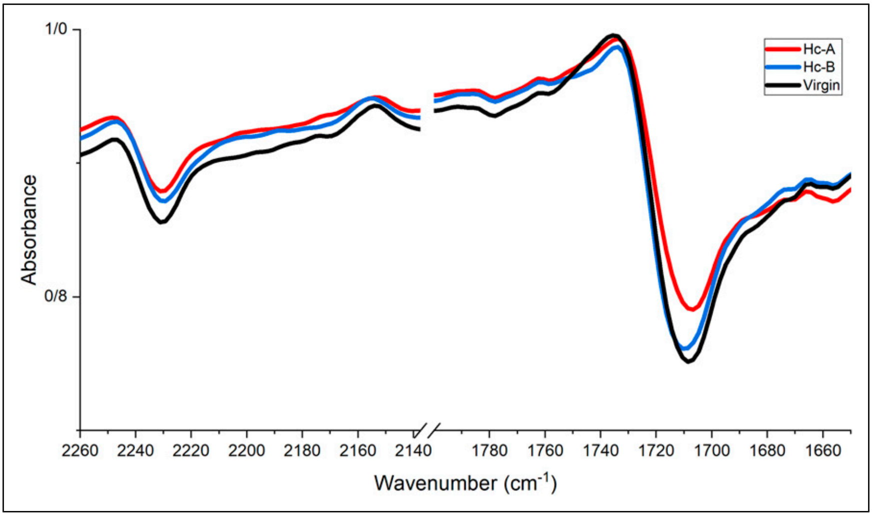

Figure 8. ATR-FTIR spectra of virgin and aged HNBR samples.

of-place bending vibration of trans-1,4 in -CH = CH-, that relate to the residual butadiene bond.[18] According to the FTIR spectra in Figure 7, it was observed that the peak at 968 cm^{-1} has vanished in the spectra of aged samples by both solutions Hc-A and Hc-B which demonstrated the deterioration of residual double bonds as a result of H_2S chemical attack.[27,28]

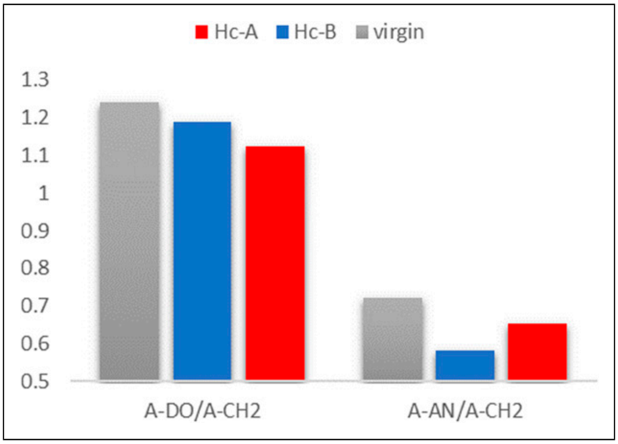

Figure 9. The relative changes in the area under the curve for double bonds(-C = C-) and nitrile bonds(-CN) in HNBR exposed to Hc-A and Hc-B.

The ATR-FTIR spectra of virgin and aged HNBR are illustrated in Figure 8. There was a peak at about 2233 cm-1, which is attributed to -CN groups, reducing the intensity reveals the reaction and deterioration of nitrile groups. According to the spectra, the aged sample had a lower intensity than the virgin specimen. Other than that, the decrease of the peak of aged samples at 1710 cm-1 confirms the migration of additives (stearic acid and plasticizer) or consumption of carbonyl groups.[4]

The relative changes of double bonds and nitrile groups in HNBR exposed to Hc-A and Hc-B, derived from the ATR-FTIR test, are presented in Figure 9. In particular, 1461 cm^{-1} serve as references because these bands did not change after corrosion..[18] The degradation of nitrile groups is significantly higher in H2S (Hc-B) environments compared to CO2 (Hc-A) environments. Nitrile groups have higher reactivity than double bonds, and their absorption is higher than that of the latter.[18]

Conclusions

In the present study, the simultaneous aging effects of CO_2 and H_2S gaseous fluids caused a change in the molecular structure of HNBR samples by chemical reaction and physical entrapment, which led to swelling, reducing the density of -C≡N groups, double bonds, and lowering the strengthening effect of CB. The ATR- FTIR spectra peaked at around 1710 cm^{-1}, indicating the presence of some additives as curing agents and stearic acid. The reduction of the intensity of this peak could be due to the additive migration or consumption of carbonyl groups. In addition, according to the pyrolysis-FTIR spectra, the peak at around 968 cm^{-1}, which is related to C-H out-of-place bending vibration of trans-1,4 in -CH = CH- vanished after aging by both solutions. The peak was also detected by the ATR-FTIR method. According to ATR-FTIR Spectra, after aging by solutions Hc-A and Hc-B, the peak intensity at about 2233 cm^{-1} declined, possibly because of a decrease in the density of -CN groups during the aging process. Samples aged by method Hc-B showed lower intensity, meaning lower density of -CN groups.

Based on the mechanical test study, the results showed an increase in mass, volume, and elongation at the break of the aged HNBR compared with the virgin ones. However, the aged specimens' hardness, modulus, ultimate tensile strength, and compression set were lower than the virgin HNBR. Comparing the two aging solutions (Hc-A and Hc-B) reveals that with the increase in the percentage of CO_2 from 5% vol. to 20% vol., the volume and elongation at the break of the samples increased by 6% and 11%, respectively. In contrast, tensile strength and compression set decreased by 2% and 23%, respectively.

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