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Research Article

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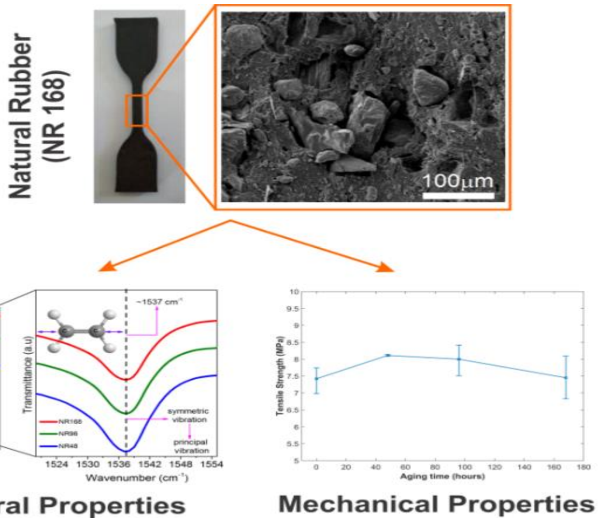
Graphical abstract



Structural Properties

Mechanical Properties

Effect of temperature on the mechanical and structural properties of vulcanized natural rubber: Estimation of long-term polymer degradation

Abstract
Elastomers are widely used materials in industry and engineering applications, such as in coating for conveyor belts, couplings, bellows, hoses, insulators, and seals. Studying the mechanics of the fracture of these materials is important in the design of components subjected to tearing, tension, and wear, among others reasons. The purpose of this work was to study the effect of thermal aging of vulcanized natural rubber (NR) on the macroscopic properties of the material produced by structural changes. The NR was subjected to accelerated thermal aging in an air oven for periods between 0 to 168 h at 100 °C. The thermal aging was evaluated by investigating the mechanical properties and by FTIR and Raman analysis. The results showed that subjecting the material to thermal aging

Keywords
Natural rubber
Thermal agings
Mechanical properties
FT-IR
Raman
Crosslinking

for a longer time decreased the elongation at break, wear resistance, and tear strength and increased the hardness, while tensile strength showed a different behavior following a different trend. These results were attributed mainly to an increase in the crosslink density, which caused increased stiffness and loss of ductility in the material. FTIR and Raman spectroscopy analyses indicated a decrease in the number of double bonds in the polymer, identified in both spectra by a decrease in the intensity of the signal corresponding to C=C with increase in the aging time, the main cause of increased stiffness in the material.

Efecto de la temperatura sobre las propiedades mecánicas y estructurales del caucho natural vulcanizado: estimación de la degradación del polímero a largo plazo

Resumen

Los elastomeros son materiales ampliamente usados en aplicaciones industriales y de ingeniería, tales como Recubrimiento para cintas transportadoras, acoplamientos, fuelles, mangueras, aislantes y sellos. Estudiar la mecánica de la fractura de estos materiales es importante en el diseño de componentes sometidos a desgarros, tensiones y desgaste, entre otras razones. El propósito de este trabajo fue estudiar el efecto del envejecimiento térmico del caucho natural vulcanizado (NR) en las propiedades macroscópicas del material producido por los cambios estructurales. El NR se sometió a envejecimiento térmico acelerado en un horno de aire durante períodos entre 0 y 168 h 100 °C. El envejecimiento térmico se evaluó investigando las propiedades mecánicas y mediante análisis FTIR y Raman. Los resultados mostraron que someter el material al envejecimiento térmico durante más tiempo disminuyó el alargamiento en la rotura, la resistencia al desgaste y la resistencia al desgarro y aumentó la dureza, mientras que la resistencia a la tracción mostró un comportamiento diferente siguiendo una tendencia diferente. Estos resultados se atribuyeron principalmente a un aumento en la densidad de reticulación, que causó una mayor rigidez y pérdida de ductilidad en el material. Los análisis de espectroscopía FTIR y Raman indicaron una disminución en el número de dobles enlaces en el polímero, identificado en ambos espectros por una disminución en la intensidad de la señal correspondiente a C=C con un aumento en el tiempo de envejecimiento, la causa principal de una mayor rigidez en el material.

Palabras clave
Caucho natural
Envejecimientos termales
Propiedades mecánicas
FT-IR
Raman
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Effect of temperature on the mechanical and structural properties of vulcanized natural rubber: Estimation of long-term polymer degradation

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Abstract

Elastomers are widely used materials in industry and engineering applications, such as in coating for conveyor belts, couplings, bellows, hoses, insulators, and seals. Studying the mechanics of the fracture of these materials is important in the design of components subjected to tearing, tension, and wear, among others reasons. The purpose of this work was to study the effect of thermal aging of vulcanized natural rubber (NR) on the macroscopic properties of the material produced by structural changes. The NR was subjected to accelerated thermal aging in an air oven for periods between 0 to 168 h at 100 ° C. The thermal aging was evaluated by investigating the mechanical properties and by FTIR and Raman analysis. The results showed that subjecting the material to thermal aging for a longer time decreased the elongation at break, wear resistance, and tear strength and increased the hardness, while tensile strength showed a different behavior following a different trend. These results were attributed mainly to an increase in the crosslink density, which caused increased stiffness and loss of ductility in the material. FTIR and Raman spectroscopy analyses indicated a decrease in the number of double bonds in the polymer, identified in both spectra by a decrease in the intensity of the signal corresponding to C=C with increase in the aging time, the main cause of increased stiffness in the material.

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1. Introduction

Elastomers are widely used materials in industry and engineering applications, such as in coating for conveyor belts, couplings, bellows, hoses, insulators, and seals [1–7]. Studying the mechanics of the fracture of these materials is important in the design of components subjected to tearing, tension, and wear, among others reasons. Similarly, it is vital to know the behavior of these materials when they are subjected to various external agents, in order to be able to optimally select the application intended for each elastomeric element. One of the unfavorable characteristics of elastomers is their known degradation over time due to various factors, such as high temperatures[1,8–10], UV exposure[11,12], and thermo-oxidation[2,13–15]. Accelerated thermal aging is one such type of degradation and refers to the accelerated variation of mechanical properties over time. In a study of accelerated thermal aging [1,9,10], the material is subjected to extreme conditions much more severe than a natural environment for a relatively short period. There are equations that allow to relate the natural aging that an elastomer suffers with the applied accelerated aging[16,17] so that it is possible to evaluate the effect on the material subjected to high temperatures for controlled times. Several investigators have conducted studies on failure mechanisms in elastomers. In relation to the tear strength, Ismail and Poh[18] studied a blend of Standard Malaysian rubber (SMR) with epoxidized natural rubber (ENR) and evaluated the effect of varying the percentage of ENR on the tear strength, observing that it increased until the amount of ENR in the mixture was 50 % (w/w) and when the ENR content exceeded 50 %, the resistance began to decrease. Moreover, on subjecting the material to thermal aging, its strength tended to decrease as the amount of ENR increased.

On the other hand, Hassine et al.[1] attempted to predict the elongation at break for ethylene-propylene-diene monomer (EPDM) subjected to thermal aging in an air oven at temperatures of 130, 150, and 170 °C for various exposure times. In another study, Ha-Anh and Vu-Khanh[2] evaluated the influence of thermal aging of polychloroprene rubber (CR) on Mooney-Rivlin parameters by testing tensile specimens according to the ASTM D412 Type C standard. The study involved aging at temperatures between 100 and 160 °C for periods from 7 to 168 h and it was observed that as the aging time increases, the increase in the values of the parameters adopts an exponential tendency and the higher the temperature, the more drastic is the increase.

Authors such as Molnar et al.[19] evaluated the wear resistance of a natural rubber (NR)/styrene butadiene rubber (SBR)-based conveyor belt. For this, they performed 2- and 3-body abrasion tests according to ISO 4649[20] and ASTM G65[21], respectively. In addition, they measured the tensile and tear strength, which were compared with the wear results. They concluded that there is a linear relationship ($R^2 = 0.96$) between the 3-body abrasion mechanism and the trouser-type tear strength measured according to ISO 34-1[22]. In this context, Shipway and Ngao[23] studied 3-body abrasion on several polymers and evaluated the influence of different parameters such as the slip distance and load on the abrasion rate. To compare experimental results with theory, they used the Ratner-Lancaster wear model[24], which relates wear to ultimate tensile properties (tensile strength and elongation at break). Most studies and tests described above are related to the macroscopic properties of the material, such as tearing, wear, and tension. When these materials are subjected to aging processes, their micro-structures change due to several reasons, such as possible degradation effects of the polymer chains[2,13,14], secondary reactions of the residual monomers of some additives with poor aging properties[8], an increase or decrease in the degree of cross-linking[2], or the compound showing inhibitory properties toward aging[14]. However, monitoring the mechanism of aging of elastomers is complex because the usually applied spectroscopic techniques are sometimes inconclusive.

For example, many authors have focused on FTIR and Raman spectroscopy to study elastomers. Le Gac et al.[25] used FTIR spectroscopy to study the effects of oxidative aging of vulcanized CR, focusing on the consumption of double bonds. Jovanović et al.[9] verified that the interaction between carbon black (CB) and a mixture of NR, polybutadiene rubber (BR), and SBR produces a shift in the absorption band from 1451 to 1455 cm^{-1}, corresponding to the CH_2 deformation vibration in plane. Liu et al.[10] used ATR FT-IR to detect chemical changes on the surface of nitrile butadiene rubber (NBR) by subjecting the material to accelerated thermal aging, whereas Xianru et al. [14] used it to study the mechanism of aging of the same compound. In comparison to FT-IR, the Raman technique is used less frequently to analyze these materials. Zhao et al.[11] used it to detect chemical changes in EPDM by subjecting the material to an artificial environment produced by fluorescent UV; however, clear changes in the intensity for the 1603 cm-1 band, corresponding to the double bond C=C, were not observed in the spectrum, suggesting that UV does not affect the thermal stability of EPDM. Taksapattanakul et al.[26] used Raman spectroscopy to determine the composition ratio of each component of thermoplastic vulcanizates (TPVs) and proved that Raman mapping can be used to calculate the phase size of the cross-linking for the elastomeric part of the TPVs; however, they got different results for different runs of the experiment.

The aim of the present study is to understand the reasons behind natural rubber showing changes in mechanical properties when subjected to accelerated thermal aging, in order to facilitate optimal selection of the material and its application in the industry considering environmental consequences and how the application might affect the mechanical properties. Thus, the mechanical properties of NR subjected to degradation by accelerated thermal aging will be evaluated and the samples will be analyzed by FT-IR and Raman spectroscopy to determine structural changes in the material, thereby correlating the microstructure of the material and its macroscopic properties while the material degrades. Therefore, it will be possible to know, compare, and analyze the effect of temperature and exposure time on the mechanical and structural properties of this material.

2. Experimental section

2.1 Materials and methods

The material used for this investigation was vulcanized natural rubber (NR), obtained from Schüssler S.A. (Concepción, Chile) as sheets with dimensions of 500 × 500 mm^2 and thicknesses of 6-8 mm.

Tear and tensile tests were performed according to the ASTM D624[27] and ASTM D412[28] standards, respectively, and specimens were obtained from the sheets of 3 ± 0.4 mm thickness using cutting dies (Figure 1) with the help of a hydraulic press. In the case of abrasive wear tests, rectangular 25 × 76 mm^2 specimens with a thickness of 6-8 mm were used according to ASTM G65 [21].

2.2. Accelerated thermal aging

The material was subjected to thermal aging by placing the samples in a Thermo Scientific Thermolyne model F6010 air oven at high temperatures for established periods of time, according to ASTM D573[16]. The temperature and aging times were 100 °C and 0, 48, 96, and 168 h[2,8], producing four families of samples: NR0 (unaged), NR48, NR96, and NR168, respectively. The set temperatures and times correspond to an accelerated aging configuration such that the degradation of the polymer is equivalent to deterioration achieved in up to 5 years at ambient temperature. This calculation performed using equation 1 relates the accelerated aging times (h) to real aging times (months), utilizing the ambient temperature (TRT), accelerated aging temperature (TAA), accelerated aging time (AAT), normal aging time (RT), and a conservative aging factor Q10 = 2, whose value is set according to the rate conventionally accepted for first-order chemical reactions, according to ASTM F1980 [17].

$$RT = \frac{1}{720} AAT \cdot Q_{10}^{[(T_{AA}-T_{RT})/10]} \qquad (1)$$

Setting TAA = 100 °C, TRT = 19 °C, and AAT = (48, 96, 168 h), a relationship between the actual (normal) and accelerated aging times was obtained, as presented in Table 1.

2.3. Hardness and density measurements.

The hardness of the material was determined according to ASTM D2240[29], using an Amsler Härteprufer Shore A durometer whose full penetration reached 2.5 mm. The density of the material was calculated according to ASTM D792 [30], which describes the method to determine the specific density of a material, and then its density was calculated using equation 2, based on the principle of thrust of a body into water. To avoid subsequent corrections, the standard recommends weighing at a temperature of 23 °C.

$$\rho = 0.9975.\frac{apparent\ mass\ in\ air}{apparent\ mass\ in\ water}\left(\frac{g}{cm^3}\right) \qquad (2)$$

2.4. Mechanical tests

Mechanical tests of tear and tensile strength and 3-body abrasive wear were carried out on the material under investigation. Tear and tensile tests were performed on a KARG Industrietechnik model smarTens005 tensile machine, with a load cell of 5 kN capacity and 500 mm/min rate of jaw separation.

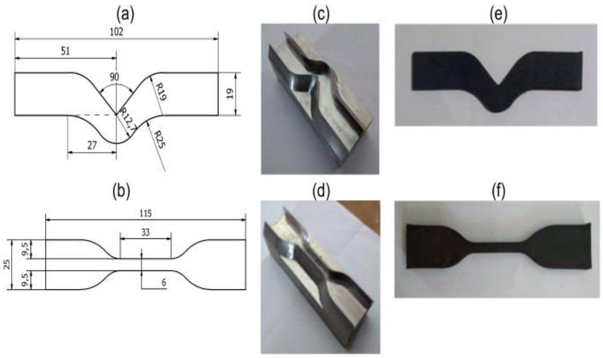

Figure 1. Materials to develop the investigation: Dimensions of the specimens for tear (a) and tensile (b) test. Die cutting for tear (c) and tensile (d) specimens. Specimens for tear (e) and tensile (f) test.

The environmental conditions of the tests were 50 % relative humidity and an ambient temperature of 23 °C.

Tear tests were performed according to ASTM D624 27. The specimens used correspond to ASTM D624 Method C or "angle type" (Figure 1a), which allow measuring the rupture or tear initiation strength in the material; 6 specimens were used for each NR family. The results obtained from this test were translated to tear strength vs displacement curves and the maximum value of the strength was averaged for each family of specimens, to obtain final values with error bars. The tear strength TS (N/mm) was calculated as the maximum force (Fmax) applied divided by the thickness of the specimen, as indicated in equation 3.

$$T_S = \frac{F_{max}}{t} \qquad (3)$$

Tensile tests were performed according to ASTM D412 [28]. The specimens were subjected to ASTM D412 Method C (Figure. 1b); 5 specimens were tested per family. The tensile strength and elongation at break were investigated. The tensile strength σ_u was calculated by dividing the maximum force (F_{max}) by the initial area A_0 of the cross-section of the narrow zone, as indicated in equation 4.

$$\sigma_u = \frac{F_{max}}{A_0} \qquad (4)$$

Elongation at break λ_u (equation 5) corresponds to the ratio between the maximum length (l_{max}) and initial length (l_0 = 30 mm) of the specimen. To determine the elongation, two points were marked in the narrow zone of the specimen and a video recording of the test was obtained. Then, using the software Image-J, the initial and final lengths of the specimen were measured. Finally, the results were averaged and presented with their respective error bars.

$$\lambda_u = \frac{l_{max}}{l_0} \qquad (5)$$

Abrasive wear tests were performed according to ASTM G65[21] with the conditions presented in Table 2. In this test, the specimens were subjected to a 3-body abrasion (rubber wheel, dry sand, and specimen). The results obtained from this test correspond to the abrasion rate (Equation 6), which is calculated as the volume loss of the specimen divided by the lineal distance, equal to the perimeter of the wheel ($\pi\varphi$) multiplied by the number of revolutions (n). To determine the volume loss, the sample needs to be weighed before and after the test, in addition to knowing the density of the material.

Table 1. Relation between real aging and accelerated aging of polymers according ASTM F1980.

AAT (days)	AAT (hours)	RT (months)	RT (years)
2	48	18	1.5
4	96	36	3
7	168	64	5.3

Table 2. Parameters for 3-body abrasion test.

Parameter	Value
Load	130 N
Wheel speed	198.35 RPM
Wheel diameter (φ)	218 ± 4 mm
Sand flow	320 g/min
Number of turns (n)	500
Specimen dimensions	76 mm x 25 mm x 6-8 mm
Lineal distance (L)	342 m

$$W = \frac{\Delta V}{L} \qquad (6)$$

2.5. Spectroscopic analysis.

2.5.1 Fourier transform infrared spectroscopy (FTIR)

The FT-IR spectra of the samples were acquired through a Perkin-Elmer 1720x infrared spectrometer using KBr tablets. Each spectrum was obtained by consecutive scans made on random points of the sample with a 1 cm^{-1} resolution within the interval range 4000-500 cm^{-1}.

2.5.2 Raman

Vibrational analysis was acquired through Raman spectroscopy using a high-resolution confocal LabRamHR Evolution Horiba Jobin Yvon microscope, using a source of 633 nm edge laser red line excitation with a power of 13.3 mW, an acquisition time of 60 s, and a 3.2 % filter. The laser spot was focused on the sample using an Optic

Objective Olympus 100x VIS and NUV camera (B/S UV 50/50 + Lens F125 D25).

3. Results and discussion

The study of accelerated thermal aging in vulcanized rubber is important for the selection, design, and manufacture of elastomeric elements, since the operating conditions will subject the material to unfavorable environments such as high temperatures, which might cause the rubber to not achieve the optimal required function, thereby requiring repeated maintenance. Therefore, mechanical tests of different natures were carried out to evaluate how the time-temperature factors affect the performance of the rubber. Later, the effect of temperature on the material was studied using spectroscopy, in order to relate chemical-structural changes to changes in a macroscopic level, corresponding to the mechanics of the material.

3.1. Mechanical properties

The results of hardness tests shown in Figure 2 show that the material hardness increases as the thermal aging increases, starting at 68 Shore A and reaching 78 Shore A after 168 h, increasing by 15 %. This is comparable to results obtained by other researchers: Jovanović et al.[9] obtained a hardness of 37 Shore A before aging for a NR/BR/SBR blend and 41 Shore A after 168 h aging at 100 °C an increase of 11 %, and argued that one of the consequences of aging is structural changes in the material, i.e., crosslinks and terminated macromolecular chains. Similarly, Gujel et al.[31] obtained a 10 % increase in the hardness of a mixture of EPDM, due to an increase in the molecular stiffness after aging at 70 °C for 7 days.

The tear tests were performed according to ASTM D624 Method C[27], which allow determination of the resistance of the material to crack initiation, as indicated in the experimental section, and the results of these analyzes are shown in Figure 3. The graph shows that the tear strength decreases as the aging time increases, from 32.04 N/m to 22.82 N/m, so that it decreases by 29 % in a period of 168 h. Between 0 and 48 h, the resistance decreased slightly (8 %) compared to aging at 168 h, indicating that the microstructure of the elastomer possibly begins to be affected by the aging process. Other researchers have evaluated the tear strength in elastomers subjected to aging processes using temperatures and times similar to those of the present study. For example, in a study comparing SMR and ENR; H. Ismail and B.T. Poh found that, after 48 h at 100 °C, SMR resistance decreased by 30 %, while that of ENR decreased by 70 %: the difference is associated with the poor aging property of ENR and the breakdown of crosslinks[8]. In the case of hydrogenated nitrile butadiene rubber (HNBR), the resistance decreased by 60 % on aging it for 90 days at 90 °C, implying that scission of the molecular chains during thermal aging decreased the material strength [32].

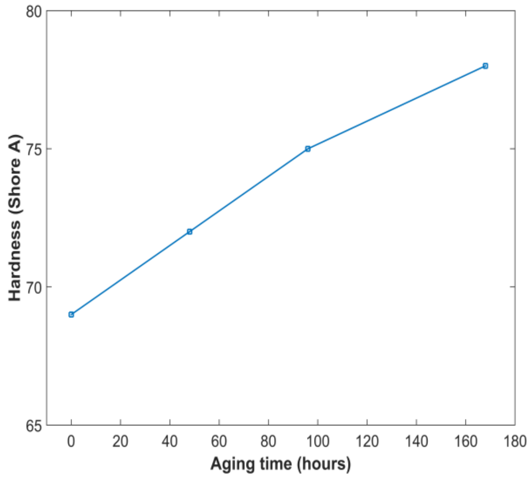

Figure 2. Evolution of the hardness of NR in function of aging time.

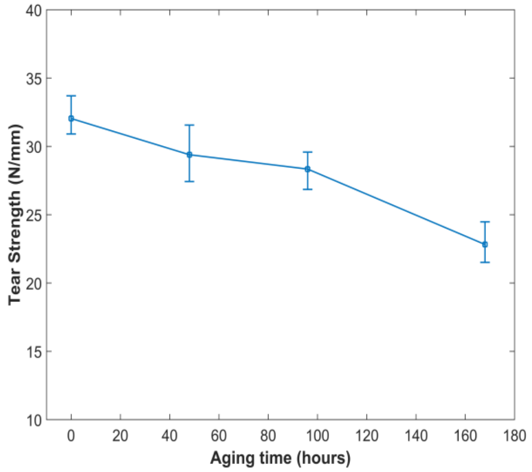

Figure 3. Evolution of Tear Strength of NR in function of aging time.

Wear was measured according to ASTM G65 [21], which proposes a 3-body abrasive wear mechanism, as indicated in the methodology. Figure 4 shows the wear tests for the aged samples, and it was evident that the abrasion rate increased from 5.32 mm^3/m to 7.90 mm^3/m in the interval of 0 to 168 h, corresponding to a 48 % increase, indicating that the aged material is more prone to lose volume during a wear process. However, unlike the case of the tear tests, Figure 4 shows that the material loses wear resistance much faster from 0 to 48 h; in this interval, the abrasion rate increased by 32 % while in the range of 48 to 168 h, it was 12 %.

It was observed that as the material increases its resistance to tearing, the abrasion rate decreases (Figure 5), which is in agreement with the findings of Molnar et al.[19], which correlated these mechanical properties, finding a linear relationship ($R^2 = 0.96$) between them.

When comparing the hardness and tear strength (Figure 6), an inverse relationship was found between them, i.e., at higher hardness, the tear strength was lower, as observed by Tangudom et al.[7] in his studies with NR.

The results of tensile strength tests according to ASTM D412 Type C[28] are presented in Figure 7. This graph does not show a clear trend as seen in tear and wear analyses; at 0 h, the strength obtained was 7.42 MPa and after 168 h, it was 7.45 MPa. These values did not show any significant difference; in addition, the range of error in the measurements was wide: the reason why it was concluded that aging does not considerably affect the tensile resistance of the elastomer. However, in the range of 0 to 48 h, a 10 % increase in resistance was observed, as the strength reached 8.11 MPa.

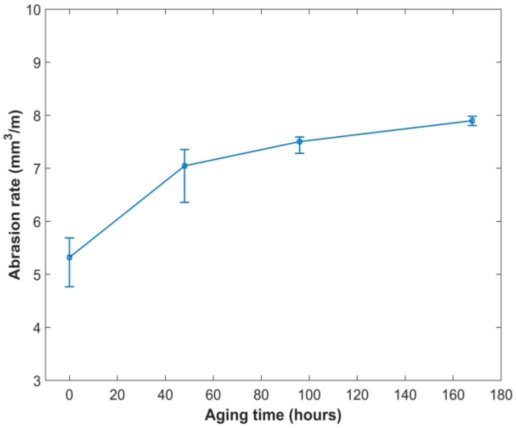

Figure 4. Evolution of Abrasion rate of NR in function of aging time.

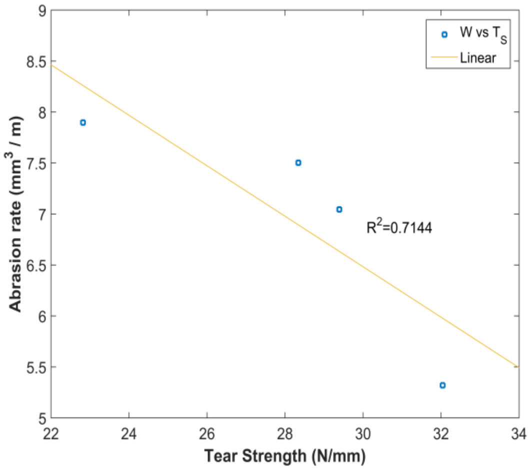

Figure 5. Correlation between Abrasion rate vs Tear strength

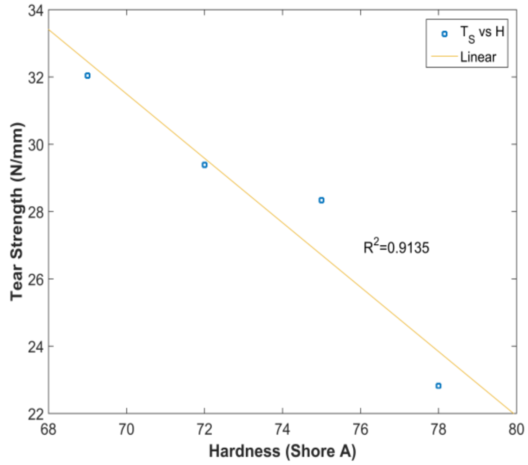

Figure 6. Tear strength vs Hardness of NR

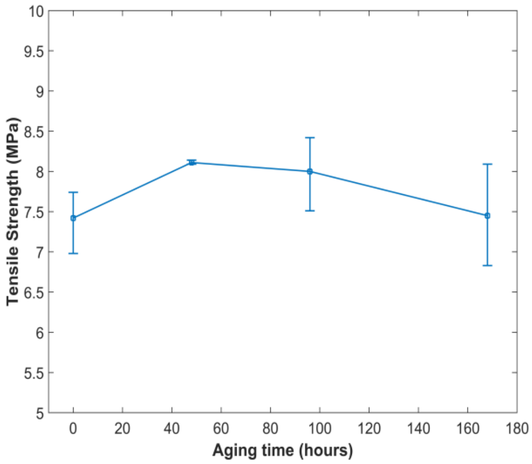

Figure 7. Evolution of Tensile Strength of NR in function of aging time

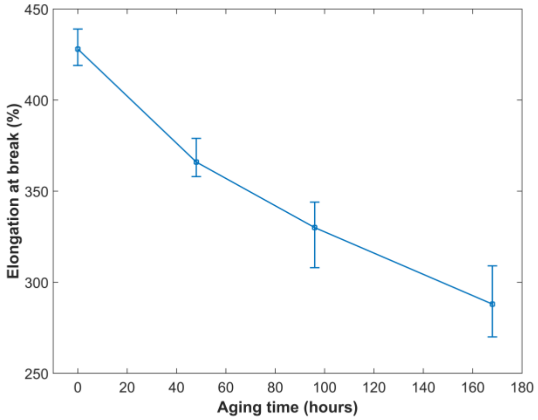

Figure 8. Evolution of Elongation at break of NR in function of aging time

This behavior is possibly due to residual monomers in the elastomer matrix, which, with increasing temperature, can initiate crosslinking processes with the sulfur used in the vulcanization process, causing an increase in strength and loss of elasticity[2, 9,10,14,15,31–33]. Then, from 48 to 168 h, a tendency of decrease was obtained, which can be explained by the fact that the thermal aging process mainly comprises two phases: crosslinking and chain scission[9,25]. In phase I, the resistance increases with increase in the crosslinks density due to a greater number of connections between the chains, causing increase in the tensile strength, whereas in phase II, when the crosslink density reaches a certain critical value, the effective mobility of the chains is limited, which disturbs the normal orientation of the network chains, causing stress concentrators, reducing the number of effective network chains, and thus causing a decrease in the tensile strength[10,31].

Elongation at break results are presented in Figure 8; it was observed that the effect is clearly degradative and that the ductility of the material decreased as the aging time increased. For NR0, the elongation at break was close to 430 % and after 168 h of aging, it reached 288 %, losing 33 % of the ductility. This suggested that prolonged application of heat on the elastomer causes less ductility and they gradually lose their hyperelastic properties. Several aging studies have evaluated the elongation at break in elastomers: EPDM aging investigations show that, for an extreme case, where the material is subjected to a temperature of 170 °C for 3000 h, the elongation at break goes from approx. 900 % to 100 %, decreasing by 89 %[1]. For CR after 168 h at 120 °C, the elongation at break decreased from 370 % to 210 %, with a 43 % ductility loss, as reported by Ha-anh and Vu-khanh[2.] In other studies, with NBR-based layered double hydroxide composites using sodium p-styrenesulfo-nate hydrate (NBR/LDH-SSS) aged at 90 °C for 96 h, a 15 % decrease in elasticity was obtained, from 1502 % to 1272 %[14], whereas with hydroxy-terminated polybutadiene (HTPB) subjected to thermo-oxidation for 266 days at 80 °C, a 68 % decrease in ductility was observed due to the formation of additional crosslinks, responsible for the loss of elasticity[15.]

Jovanović et al. [9] studied a mixture of NR/BR/SBR subjected to thermal aging for 168 h at 100 °C; they observed a 50 % decrease, going from 200 % to 100 %, whereas Liu et al. [10] obtained a noticeable decrease in the maximum NBR elongation, from 430 % to 130 %, corresponding to a loss of 70 %, attributed to the continuous increase in crosslinking during aging at 65 °C for 90 days. In another study with NBR, a decrease of 43 % was obtained for the elongation at break after 300 h at 100 °C, which was related to the thermal oxidation of the polymer matrix, especially the evolution of carbonyl products[33.] Thus, it can be suggested that the mechanical property of elongation at break always decreases as aging time increases and high temperatures cause major deterioration of the material. According to values reported here, when the crosslink density is high, the molecular weight of the elastomeric chains increases and mobility of the chain segments is restricted. This increases the stiffness of the elastomer and reduces its elongation at break[31].

3.2 FT-IR and Raman Spectroscopy

Some of the cited authors have reported that crosslinking density, molecular weight, and chain motility play a major role in determining the mechanical properties of the elastomer; thus, these attributes must change as the aging time increases.

Therefore, a vibrational spectroscopic study was carried out using FT-IR and Raman spectroscopy to explain the trends found in the macroscopic properties. Figure 9 shows the results of the FTIR analysis and Figure 10 shows those of Raman spectroscopy for different aging times. The FTIR spectra obtained are shown in Figure 9a.

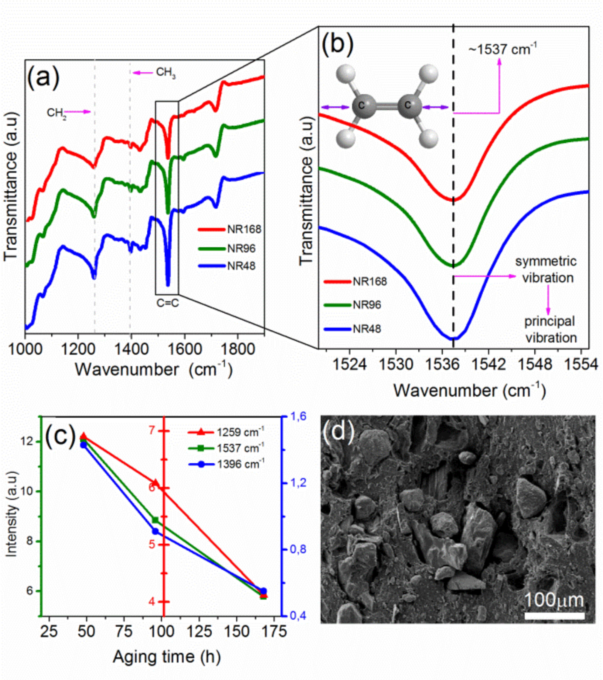

Figure 9. FT-IR results: FT-IR spectra comparison for NR in 1000-1900 cm^{-1} range (a), detail of peak at 1537 cm^{-1} (b) and Intensity changes in representative wavenumbers (c) and SEM image for NR168.

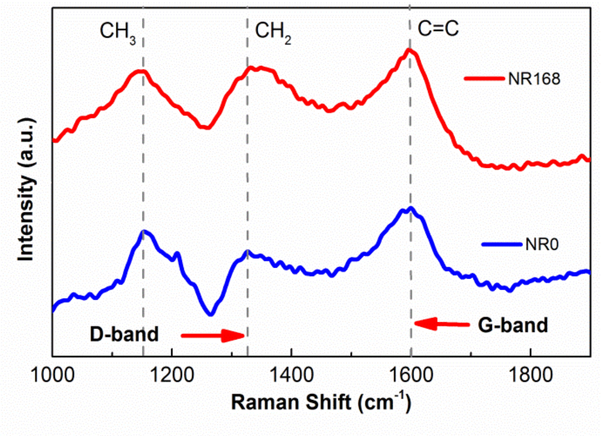

Figure 10. NR0 and NR168 Raman spectra comparison for 1000-1900 cm-1 range.

Peaks were observed at 1259 cm^{-1}, 1396 cm^{-1}, and 1537 cm^{-1}, corresponding to the twisting vibrations of the groups (CH_2)[34], asymmetric deformation of (CH_3)[35], and stretching deformation of (C=C)[13], respectively, which was verified with the groups referenced for elastomeric materials, presented in Table 3. If we observe carefully, the signal corresponding to the double bond (C=C) decreased in transmittance intensity from NR48 to NR168, as illustrated in the detail of Figure 9b. The tendency shown in Figure 9c demonstrates that the intensity of the peaks decreases with aging time, as shown in Table 4. These microstructural changes in the material may be due to the increase in the degree of crosslinking of the polymer chains, which leads to reduction in the free conformational volume of the material, causing an increase in the stiffness of the elastomer, which is in total agreement with the observations related to the mechanical properties, especially the elongation at break and increase in the abrasion rate and decrease in tear and tensile strength, which could be explained from a microscopic point of view by FT-IR.

To verify and compare other studies that was reported in this work, a complementary study using Raman spectroscopy was performed, where 3 peaks were found at the frequencies 1150 cm^{-1}, 1330 cm^{-1}, and 1600 cm^{-1}, corresponding to the molecular vibrations of the wagging motion of (CH_3) and (CH_2)[35] and stretching deformation of (C=C)[11], respectively. As expected, the principal modes corresponding to the G and D bands, characteristic of carbon-rich materials, were manifested. Figure 10 and Table 5 provide information on the peaks obtained by Raman spectroscopy; it was observed that the intensity of these peaks decreased with longer aging times, attaining a maximum for NR0 and a minimum value for NR168.

In a study of thermo-oxidative aging using NR, the intensity of the absorbance for the peak corresponding to C=C increased as the aging time increased, which translated to transmittance corresponding to a decrease in the intensity and the results of the elongation at break showed a change from 437 % to 422 % after 120 h at 80 °C[13], showing a decrease in ductility and an increase in the stiffness of the material. In another study analyzing the aging of a NBR blend, after 96 h at 90 °C, a decrease in the transmittance intensity (from 4.97 to 3.94 a.u.) was obtained for the peak corresponding to C=C, corresponding to a decrease in the double bond content[14].

Some mechanisms of aging (such as that using fluorescent UV) do not alter the molecular structure of the material, as shown by Zhao et al. [11] in their studies with EPDM, where they exposed a sample to UV radiation for 90 days, and analyzed it by Raman spectroscopy, noting that there were no significant changes in the peak intensity for C=C, implying that the double bond was not consumed

Table 3. Wavenumber and Raman shift attributed to polyisoprene bonds.

Bond	Wavenumber (cm^{-1})	Vibration type	Spectra.	Reference
CH_3	1150	Wagging	FT-IR	[34]
CH_3	1154	Wagging	Raman	[35]
CH_2	1252	Twisting	FT-IR	[35]
CH_2	1254	Twisting	FT-IR	[34]
CH_2	1330	Wagging	FT-IR	[34]
CH_2	1330	Wagging	Raman	[35]
CH_2	1368	Wagging	FT-IR	[9]
CH_3	1415	Assym. deform.	FT-IR	[35]
CH_2	1433	Deform. Vibration	FT-IR	[10]
CH_2	1451	Plane deform.	FT-IR	[9]
C=C	1538	Stretching	FT-IR	[13]
C=C	1597	Stretching	FT-IR	[14]
C=C	1603	Stretching	Raman	[11]

Table 4. Summary of FT-IR spectroscopy results

Peak (cm^{-1})	Bond	Intensity (a.u)		
		NR48	NR96	NR168
1537	C=C	12.1	8.82	5.78
1396	CH_3	1.43	0.91	0.55
1259	CH_2	6.9	6.08	4.12

Table 5. Summary of Raman spectroscopy results

Peak (cm^{-1})	Bond	Intensity (a.u)	
		NR0	NR168
1597	C=C	1574	1084
1150	CH_2	1110	912
1330	CH_3	1323	945

consumed during the process and thus indicates that the aging mechanism does not affect the thermal stability of the material, but other mechanisms such as temperature do, as we found in this work, where we verified a clear relation between the degradation of the mechanical strength of the polymer and a decrease in the amount of C=C bonds, as indicated by measurements by FT-IR spectroscopy and corroborated by the Raman technique.

4. Conclusions

Mechanical tests of tensile, tear, wear, and hardness were performed on aged vulcanized natural rubber at 0, 48, 96, and 168 h and their structural changes were studied by FT-IR and Raman spectroscopy. In the obtained results, the degradative effect of thermal aging on the mechanical properties of tear strength, elongation at break, and resistance to wear was evident. This behavior is directly related to an increase in crosslinking of the elastomeric chains owing to the increase in temperature. On the contrary, the hardness tends to increase, for the same reason. The tensile strength has a different behavior: it first presents an increase and then a decrease. The increase is due to an increase in the density of crosses, but after this density reaches a certain critical value, a phenomenon involving internal stress concentrators occurs, due to the significant extent of crosslinking, and thus the mobility of the chains becomes limited and the resistance decreases.

The main results of the analyses by means of spectroscopy indicates that the material loses more double bonds as the aging time applied is increased, which leads to an increase in the rigidity of the material, as verified when determining the mechanical properties. These studies provide valuable information that allows us to know the state of an elastomeric element exposed to high temperatures for extended periods, making it easier to take preventive actions to replace the component in order to avoid failures in some production processes in the industry.

Conflict of interest

No conflict of interest.

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