J. Eng. Technol. Sci., Vol. 53, No. 3, 2021, 210310

The Effect of Thermal Ageing on the Mechanical Properties of Natural Rubber-based Compounds Used for Rubber Bearings

Manuel Alberto Guzmán Sánchez*, Diego Hernán Giraldo-Vásquez & Ricardo Moreno Sánchez

Faculty of Engineering, University of Antioquia
Calle 67 No. 53 – 108, Medellín, Colombia
*E-mail: malberto.guzman@udea.edu.co

Highlights:

- Changes in the mechanical properties in compression of typical rubber compounds used for rubber bearings due to thermal effects were investigated.
- Uniaxial and transient compressive tests exhibited an increased modulus after thermal ageing due to increases in the crosslink density.
- Despite hardness is one of the most used techniques to characterize rubber compounds, no statistical differences between unaged and thermally aged specimens were observed; therefore, additional tests should be considered to determine the deterioration of mechanical properties of rubber compounds due to the effect of thermal oxidation.

Abstract. Molecular changes due to high temperatures, sunlight, and oxygen, deteriorate the physical properties of rubber compounds, yielding additional crosslinks and molecular chain breakdown. Since oxidative degradation is the most important factor that determines the durability of rubber components, this study evaluated the mechanical behavior of rubber compounds exposed to accelerated thermal ageing. Therefore, three carbon black-reinforced natural rubber-based compounds typically used for rubber bearings were exposed to thermal oxidation and their mechanical properties under typical loading states were assessed through standardized tests. Significant differences were found due to thermal ageing in the compressive modulus, compression set, and creep compliance in compression, exhibiting a stiffening effect caused by additional crosslinks. However, no significant differences were observed in hardness, which is a superficial measurement and a typical test in the rubber industry to characterize rubber compounds. Therefore, the assessment of ageing in rubber bearings should not be limited to a hardness test, which is required in design standards but also addresses compressive, cyclic, and transient tests. The results obtained in this study can be considered in the design process of rubber bearings by limiting the allowable compressive stress and creep deflection due to ageing effects.

Received July 14th, 2020, 1st Revision September 20th, 2020, 2nd Revision November 26th, 2020, 3rd Revision February 28th, 2021, Accepted for publication April 1st, 2021.
 ISSN: 2337-5779,
DOI: 10.5614/j.eng.technol.sci.2021.53.3.10

Keywords: *compression; design; mechanical properties; rubber bearing; thermal ageing; viscoelastic behavior.*

1 Introduction

Rubber bearings are used as vibration isolators of structures like bridges, machinery, industrial equipment, and as seismic protection of buildings due to their vertical stiffness and horizontal flexibility; however, their mechanical properties may vary over time due to ageing. Environmental factors like oxygen exposure, heat, and sunlight, which deteriorate physical properties of rubber bearings such as elasticity and strength, are usually not considered during the design process of rubber bearings. Understanding the degradation of the material properties is considered essential in their lifetime prediction [1-3]. As the service temperature rises, molecular changes take place, resulting in a loss of mechanical properties. Those changes include, initially, the formation of additional crosslinks due to residual sulfur or the so-called post-curing effect (leading to some hardening), scission of crosslinks (causing softening), and molecular chain break down (charring and embrittlement occur) [4-5]. These changes are caused by chemical reactions, which lead to a progressive increase or decrease in hardness and modulus, and a loss of tensile and elastic properties [6]. Nevertheless, in bulky components degradation of rubber normally occurs at the surface level because diffusion of oxygen through oxidized rubber is slower than through new rubber and dependent on the temperature, pressure, exposed surface area, and permeability of the elastomer [4].

Oxidative degradation is the most important factor that determines durability in most engineering applications, including bridge rubber bearings, where the oxygen availability is limited by diffusion [2-3]. Itoh, *et al.* [3,7] have evaluated the evolution of tensile mechanical properties (such as elongation at break and tensile strength) of different types of rubber compounds used for bridge bearings exposed to different ageing tests, including thermal oxidation, ozone, low temperature ozone, ultraviolet radiation, salt water, and acid rain. In other studies, Itoh and collaborators have estimated the variation of material properties in tension of specimens cut from rubber blocks exposed to accelerated thermal oxidation, ozone, and ultraviolet exposure [8], and evaluated the deterioration of high damping rubber through accelerated thermal oxidation to develop life prediction models [2,9]. It was found by the contributions of Itoh and collaborators that changes in rubber properties due to thermal oxidation are significantly higher than other factors [3,7,8]. Abedi Koupai, *et al.* [10] found increased hardness and decreased tensile strength and elongation at break of typical rubber compounds used for seismic isolators exposed to seven days of thermal-oxidative ageing at 70 °C.

The effect of thermal ageing on the properties of rubber compounds for different applications has been reported. The compression set of different rubber compounds exhibiting reduced values due to long-term ageing was studied in [11-12]. The thermal effect on the behavior of natural rubber-based compounds subjected to nonzero-mean cyclic strain (ratcheting) in tension has been evaluated [13]. To estimate the depth of the oxidized layer based on diffusion and chemical reactions theory, Azura, *et al.* [14] studied the effect of thermal-oxidative ageing at different distances from the surface using tensile strips. Kumar, *et al.* [15] identified both chain scission and recombination reactions through Fourier transform infrared (FTIR) spectroscopy during thermo-oxidative ageing of natural rubber. Based on swelling measurements, wide angle X-ray scattering (WAXS), and differential scanning calorimetry (DSC), Grasland, *et al.* [16] found that crosslinking reactions take place during thermo-oxidative ageing due to residual sulfur and that longer exposure times create highly crosslinked domains, owing to sulfur grafted onto the polymer chains. Changes in the crosslink density and thermal ageing resistance of natural rubber vulcanizates are dependent on the reinforcing [17] and curing systems [18-20] used in the formulation of the compound and also on the ageing time and temperature [13]. In other studies, the effect of thermal degradation of rubber compounds was evaluated by measuring changes in the crosslink distribution, establishing that higher levels of polysulfidic crosslinks result in higher mechanical properties [21].

Additionally, industrial standards widely used in America, British and ISO standards contain testing methods to evaluate the properties of the elastomer, including hardness limits, tensile properties, high-temperature resistance, compression set, and determination of the shear modulus, which are quality-control tests and cannot be directly related to performance [22]. A relation between standardized tests and field performance is needed and according to [22] Young's modulus should be estimated, by compressing a cylindrical specimen, and creep and stress relaxation, which affects the service life, are variables not measured and used as often as they should. Mechanical testing of actual rubber bearings exposed to real environmental and loading conditions can be expensive and difficult to implement. Therefore, the assessment of the thermal-oxidative effect on the mechanical behavior of rubber bearings evaluating standardized specimens subjected to real loading conditions is required.

The present study took into account the variation of physical properties of rubber bearings due to molecular changes caused by chemical reactions that occur during the exposure to environmental conditions. This study evaluated the mechanical properties of carbon black-reinforced natural rubber-based compounds typically used in rubber bearings exposed to thermal oxidation by evaluating standardized

specimens through uniaxial compressive, cyclic and transient tests, which are typical loading states observed in rubber bearings.

2 Experimental

2.1 Materials

Three carbon black-reinforced natural rubber-based compounds, hereafter called NR15, NR30, and NR45, that are typically used in elastomeric bearings with 15, 30, and 45 phr (parts per hundred of rubber) of carbon black, respectively, were obtained using an open two-roller mill using the same ingredients, with only the carbon black content varying among them. The curing parameters and rheometric and viscoelastic properties of the compounds have previously been studied in [23]. Table 1 shows the rubber formulation with a semi-efficient vulcanizing system since conventional vulcanizing systems have poor resistance to reversion, resulting in a larger drop in properties compared to efficient vulcanization systems; furthermore, compounds used for rubber bearings normally use a semi-efficient vulcanizing system, which possesses characteristics between both conventional and efficient systems [24]. Twenty phr of Rubbersil RS-200® precipitated silica was added to the rubber compounds as a processing aid in order to increase the fatigue resistance, improve the adhesion of rubber to metals and decrease heat build-up. Precipitated silica and N550 carbon black have been used in compounds for isolation applications [8]. Although silica affects certain properties of carbon black-filled natural rubber compounds, the changes in the behavior of the compounds evaluated in this study are attributed to the changes in the carbon black content. The ingredients of the formulation (Table 1) were acquired from Industrial del Caucho in Medellin, Colombia.

Table 1 Formulation of the compounds (in phr).

Ingredient	phr
Natural rubber, SGR10 (standardized Guatemalan rubber)	100
Antiozonant, 6PPD (N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine)	1.5
Antioxidant, TMQ (2,2,4-Trimethy1-1,2-Dihydroquinoline)	1
Paraffinic oil	15
Silica, RS200®	20
Zinc oxide	5
Stearic acid	1
Wintag95®	10
Sulphur	2
Accelerator, CBS (n-cyclohexyl-2-benzothiazole sulfonamide)	1.5
Accelerator, TMTD (tetramethyl thiuram disulfide)	1
Santogard®, PVI (N-(cyclohexylthio) phthalamide)	1
Carbon black, N550	15, 30, 45

Cylindrical specimens with nominal dimensions of 28.6 ± 0.1 mm in diameter and 12.5 ± 0.5 mm in height were obtained following the recommendations of the ASTM D575 standard [25]. The specimens were vulcanized using a hydraulic press at 160 °C with an approximate pressure of 4.6 MPa. The vulcanization time was 25 minutes based on a t_{100} of 7 minutes, obtained from moving die rheometry (MDR). Furthermore, vulcanized sheets of 150 x 150 mm and 2 mm thick were obtained with a hydraulic press at 160 °C for 7 minutes with an approximate pressure of 0.9 MPa. From the vulcanized sheets, C-type dumbbell specimens were cut for uniaxial tensile tests according to the ASTM D412 standard [26].

2.2 Testing Methods

Thermal ageing of the cylindrical and tensile specimens was carried out in a Binder air circulating oven at 70 °C for 168 hours according to the recommendations of ASTM D573 [27]. Since ozone has a superficial effect, thin tensile specimens were exposed to ozone for 100 hours following the recommendations of ASTM D1149 [28] under a controlled ozone atmosphere of 50 ± 5 pphm and a temperature of 40 ± 2 °C. Although low temperature also affects the mechanical performance of rubber bearings, because crystallization occurs, this study was carried out in locations where temperatures were always above 15 °C and no seasons were expected, so the effect of low temperature could not be considered.

The mechanical properties of the compounds were evaluated before and after the ageing process as follows. Three uniaxial, fully-reversed, compressive cycles were performed on the cylindrical specimens at a deformation rate of 12 ± 3 mm/min according to ASTM D575 (test method A – compression test at specified deflection) [25] equivalent to 0.01 ± 0.0025 min^{-1}, i.e. test conditions that are not based on service conditions since rubber bearings are subjected to dynamic loading. Sandpaper between the contact surfaces was used to avoid slippage [25]. Furthermore, creep tests in compression were carried out on the cylindrical specimens by applying a constant stress of 0.95 MPa for 3 hours. Shore A hardness was measured according to ASTM D2240 [29] using a CEAST calibrated durometer. Compression set tests were performed to cylindrical specimens by applying a constant compressive strain of 25% for 22 hours in a Binder air circulating oven at 70 °C, following the recommendations of ASTM D395 [30]. Tensile tests were carried out to both the thermally aged and the ozone exposed specimens at a deformation rate of 500 mm/min following the recommendations of ASTM D412 [26]. All compressive, creep, and tensile tests were carried out using a Shimadzu AGS series unidirectional testing machine with a 50 kN load cell and a resolution of 0.01 N.

3 Results and Discussion

3.1 Compressive Tests

The third cycle of the compressive tests of the specimens is presented in Figure 1, since the first two cycles were for conditioning the specimens and where Mullin's effect [31] was observed as expected. Among the unaged compounds, a stiffening effect was observed due to the carbon black content; thus, the amount of silica of the compounds was generally used in combination with carbon black as reinforcement filler; however, no coupling agent was used since the optimum silica loading in the absence of a coupling agent is close to 20 phr [32]. Furthermore, an accentuated non-linear behavior was observed in all compounds beyond a deformation around 20%. This non-linear behavior and time-dependence of the stress-strain response results in a complex behavior of rubber compounds used for laminated rubber bearings [33]. Moreover, thermally aged specimens of all compounds exhibited an increased compressive behavior compared to the unaged specimens (Figure 1).

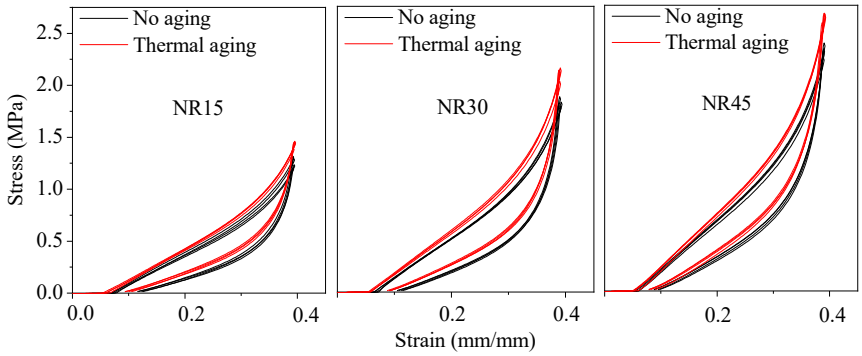

Figure 1 Third compressive cycle of the cylindrical specimens. Four specimens of each compound were tested.

Additionally, the compressive modulus of the specimens is highly related to the instantaneous compressive load of real rubber bearings due to the weight of the structure. Therefore, the compressive modulus of the compounds before and after thermal ageing, calculated as the initial slope of the third loading cycle from the uniaxial compressive tests, is shown in Figure 2. It can be seen from the unaged compounds that as the carbon black content increased, the compressive modulus increased as a result of the reinforcement. And for each compound, an increased compressive modulus resulted after thermal ageing owing to increases in the crosslink density. Enlarged mechanical properties due to increases in the crosslink density have been reported [21]. Those increases are dependent on the

type of reinforcement filler; furthermore, the use of coupling agents in carbon black and silica-filled compounds results in higher crosslink density due to thermal ageing. The corresponding activation energies increase continuously using carbon black as reinforcement filler, while silica-filled compounds exhibit a quasi-steady state [17]. Nevertheless, thermal ageing resistance is also dependent on the curing system, consumption of antidegradants, and even the particle size of the ingredients [18,34]. More accentuated differences in the compressive modulus were observed for the NR45 compound, which had the highest carbon black content. As an effect of thermal ageing, the mean values of the compressive modulus increased from 2.84 ± 0.11 to 3.01 ± 0.09 MPa, from 3.78 ± 0.08 to 4.06 ± 0.09 MPa, and from 4.73 ± 0.09 to 5.14 ± 0.06 MPa for the NR15, NR30, and NR45 compounds respectively. The p-values from the analysis of variance (ANOVA) are presented at the bottom of Figure 2 for each compound to determine the differences between the mean values of the compressive modulus before and after thermal ageing. Since the p-values were less than 0.05 there were statistically significant differences at a 95% confidence level.

Restraining slippage of the loaded surfaces of the specimen as recommended by ASTM D575 causes bulging, a phenomenon usually observed in laminated rubber bearings due to the restriction of slippage of the inner rubber layers [35-37]. Moreover, additional stiffness is developed due to the kinematic constraint; therefore, a higher load is required to produce the same strain level compared to unbonded or lubricated surfaces. Furthermore, part of the dissipation of the input energy can be expended in frictional sliding of the contact surfaces instead of the inherent damping capacity of the compounds [38]. The current standards regulate only uniaxial compression tests due to the lack of availability of procedures for biaxial compression [39]; therefore, uniaxial compressive tests were carried out in this study, following the recommendations of ASTM D575. Furthermore, during homogeneous uniaxial compression, the principal stretch in the loading direction becomes compression and tension in the other two directions and, considering isotropy and incompressibility, the principal stretches will depend only on the compressive stretch [40].

Energy dissipation (Figure 3) was calculated from the area enclosed by the hysteretic loop in the third compressive load. It was observed that while the content of carbon black as reinforcing filler increased among the unaged compounds, the energy dissipation increased due to the mobility and slippage of the rubber molecules and the break and reformation of the filler transient network, a process that is also related to the viscoelasticity and damping behavior of natural rubber-based compounds [41]. However, from the p-values > 0.05 (shown at the bottom of Figure 3), no significant differences between the energy dissipation before and after thermal ageing were observed within each compound, with a confidence level of 95%; nevertheless, Gu & Itoh [7] proved, from tensile tests

and longer ageing times, that the effect of hardening reduces the ability to deform and absorb energy. However, in this study, energy dissipation was calculated from cyclic compressive tests, which are typical loading states that rubber bearings are subjected to.

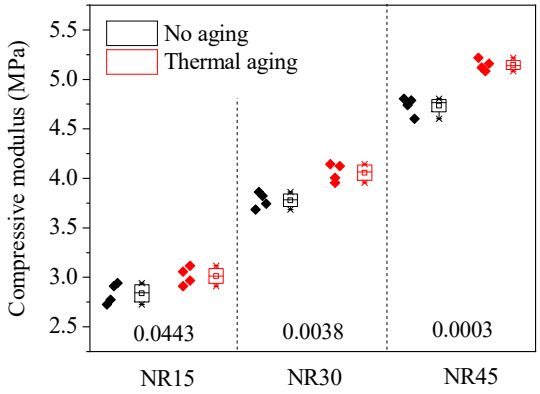

Figure 2 Box plot of the compressive modulus of the NR15, NR30, and NR45 compounds before and after thermal ageing. The dots on the left correspond to individual data. P-values from the ANOVA are presented for each compound.

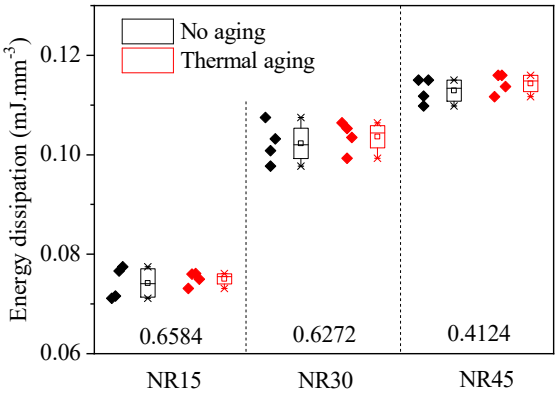

Figure 3 Box plot of the energy dissipation of the NR15, NR30, and NR45 compounds before and after thermal ageing. The dots on the left correspond to individual data. P-values from the ANOVA are presented for each compound.

3.2 Creep Tests

Creep is a typical long-term loading state that rubber bearings are subjected to due to the weight of the structure. In this work it is proposed as the most important

factor to be added to traditional design processes, especially creep after ageing. Moreover, the assessment of long-term properties are essential to evaluate the performance of rubber bearings as isolators due to dynamic loads. Figure 4 shows the strain curves of long-term compression at a defined stress level (0.95 MPa) from the creep tests of the standardized specimens. The viscoelastic behavior of the compounds was evaluated with the creep compliance (a stress-strain relation analogous to Hooke's law for a material that is time-independent) defined as $D(t) = \varepsilon(t)/\sigma_0$, where the strain as function of time $\varepsilon(t)$ changes exponentially under a constant stress (σ_0 = 0.95 MPa), as shown in Figure 4. It was observed that the thermally aged specimens of each compound (red curves) showed reduced strain (and therefore reduced creep compliance) to maintain the same stress level. Deformation mechanisms of creep are associated with the long-chain molecular structure since a continuous loading state induces strain accumulation as the molecules rotate and unwind to accommodate the load; therefore, less strain is needed to maintain the same stress level [42]. When molecular changes take place during thermal ageing due to increases in the crosslink density, the ability to rotate and unwind are reduced; therefore, increased long-term mechanical properties in compression arise [21]. Similar to the compressive modulus results, a stiffening effect due to thermal ageing is observed, as the strain to reach the same stress level to reach the same stress level is lower for each compound.

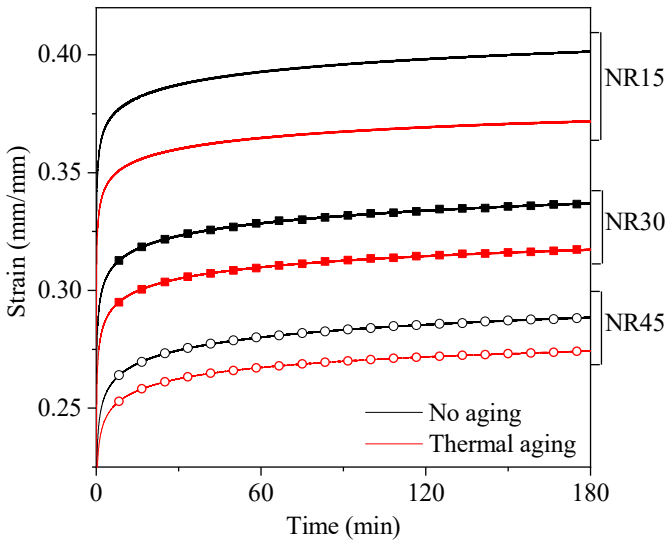

Figure 4 Creep results of the unaged and thermally aged compounds. The shown curves correspond to a representative specimen from triplicate tests for each compound.

3.3 Compression Set

Compression set is expressed in terms of a percentage of the original deflection after a long-term compression. Values of 0% mean a fully recovered height, while 100% means no recovery [12]. The compression set results of the unaged and thermally aged specimens of the different compounds are shown in Figure 5. Among the unaged specimens it was observed that as the carbon black content increased, the ability of the compounds to retain their elastic properties was increased due to the stiffening effect of the carbon black as reinforcement (Figure 2). Moreover, compression set was reduced for all compounds after the specimens were exposed to thermal ageing, with a greater reduction for the NR15 compound, which had the lowest carbon black content. As an ageing effect, compression set was reduced from 50.94 ± 1.50 to 30.51 ± 2.42%, from 35.90 ± 2.80 to 21.16 ± 0.16%, and from 26.31 ± 0.85 to 16.78 ± 1.64% for the NR15, NR30, and NR45 compounds respectively. P-values less than 0.05 were obtained from the ANOVA show statistical differences between the compression set of the unaged and thermally aged specimens of each compound, at a confidence level of 95%. These results show an enhancement of the compounds to retain their elastic properties in compression after thermal ageing, possibly due to the consumption of residual sulfur, which is the main mechanism responsible for the increase in elastic active chain density [16].

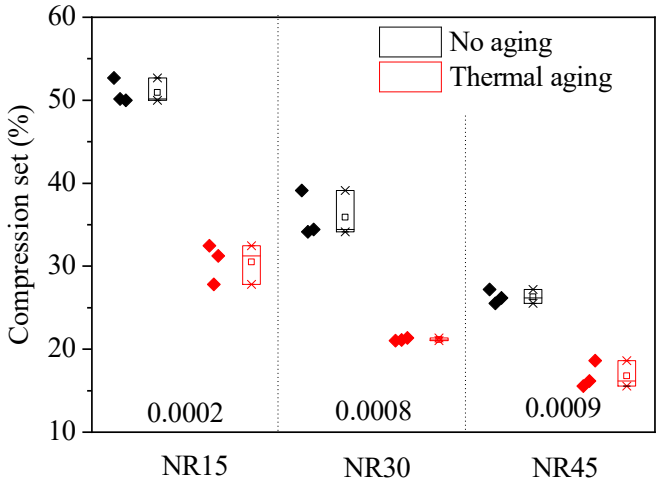

Figure 5 Box plot of the compression set of the NR15, NR30, and NR45 compounds before and after thermal ageing. The dots on the left correspond to individual data. P-values from the ANOVA are presented for each compound.

3.4 Hardness

Figure 6 shows the Shore A hardness results. As expected, it was observed among the unaged specimens that the reinforcing effect of the carbon black resulted in compounds with increased hardness as the carbon black content increased. Nevertheless, the hardness of the thermally aged specimens showed no statistically significant differences compared to the unaged specimens except for the NR45 compound, which had the highest carbon black content. Figure 6 also shows the corresponding p-value of each compound, at a confidence level of 95%. Increases in the hardness have been reported [8,12], both due to molecular crosslinking between chains and due to decomposition of chains; however, when degradation accrues, hardness exhibits a reducing trend [11].

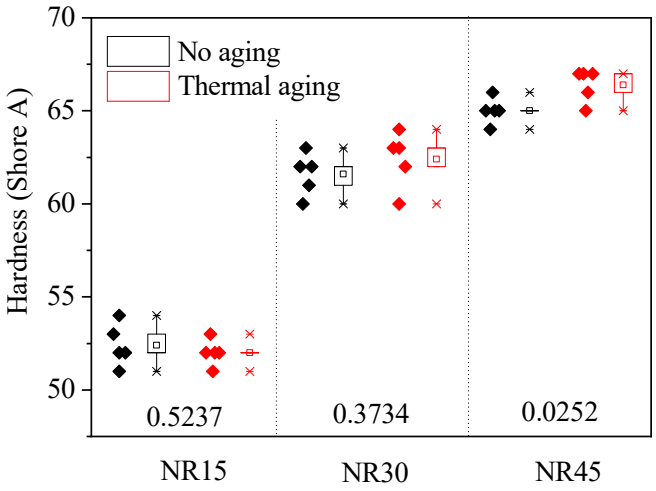

Figure 6 Box plot of the Shore A hardness of the NR15, NR30, and NR45 compounds before and after thermal ageing. The dots on the left correspond to individual data. P-values from the ANOVA are presented for each compound.

3.5 Tensile Tests

The results from the tensile tests are shown in Figures 7 and 8, where the M100 and M300 modules, tensile strength, and elongation at break are plotted. No statistical differences at 95% confidence level are visible in the M100 and M300 modules for the NR15 compound between unaged and thermally aged specimens (Figure 7); however, as the carbon black content increases, significant differences are observed. Due to the ageing effect, for the NR30 compound, the mean value of M100 increased from 2.02 ± 0.18 to 2.78 ± 0.11 MPa, M300 increases from 6.32 ± 0.53 to 8.33 ± 0.32 MPa. For the NR45 compound, M100 increases from

2.77 ± 0.11 to 3.81 ± 0.11 MPa, M300 increases from 9.06 ± 0.38 to 12.27 ± 0.26 MPa.

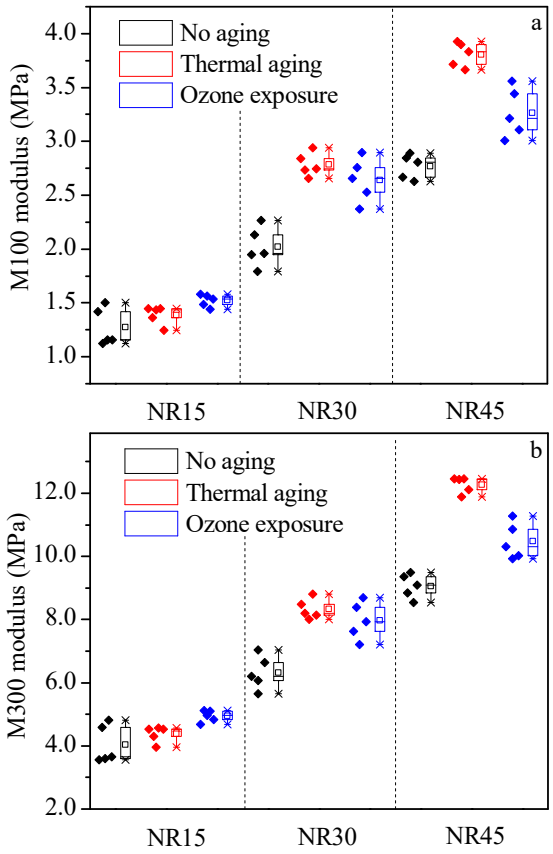

Figure 7 Box plot of (a) M100 module and (b) M300 module of the NR15, NR30, and NR45 compounds before and after thermal ageing and ozone exposure. The dots on the left correspond to individual data.

Although tensile strength did not show significant differences after thermal ageing in this study, a significantly reduced elongation at break (Figure 8) was exhibited by the NR30 and NR45 compounds, as reported in [8], because rubber becomes harder and more brittle [7]. Furthermore, changes in tensile mechanical properties due to carbon black loading have also been reported previously [43,44]. Elongation at break (Figure 8) decreased from 432.34 ± 17.65 to 379.80 ± 18.47% and from 486.14 ± 0.12 to 384.60 ± 10.48% for the NR30 and NR45 compounds respectively. The effect of ozone exposure in the

aforementioned tensile properties also showed significant differences for the NR30 and NR45 compounds but to a lesser extent compared to the thermally aged specimens.

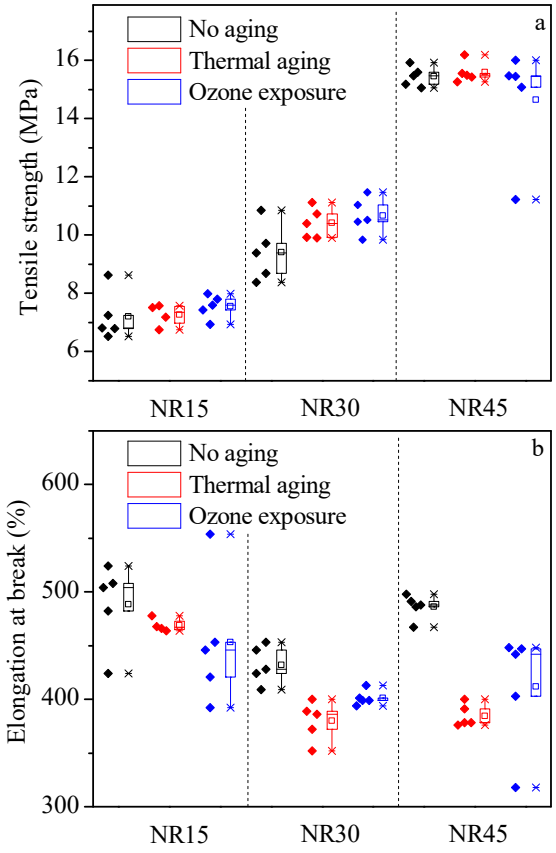

Figure 8 Box plot of (a) tensile strength and (b) elongation at break of the NR15, NR30, and NR45 compounds before and after thermal ageing and ozone exposure. The dots on the left correspond to individual data.

4 Conclusions

The effect of thermal ageing on the mechanical properties of natural rubber-based compounds typically used in rubber bearings was studied. Three different compounds were used with only the carbon black content varying among them for this type of application. From the uniaxial compressive tests, it was observed that the thermally aged cylindrical specimens showed an increased modulus due

to increases in crosslink density. The compressive modulus of the thermally aged specimens increased by 6.20, 7.36, and 8.68% as the carbon black content of the compounds was varied between 15, 30, and 45 phr respectively. However, energy dissipation showed no significant differences between the unaged and thermally aged specimens. The creep results showed a stiffening effect due to thermal ageing, exhibiting decreased creep compliance, i.e. decreased strains to maintain a constant stress level. Hardness, which is superficial and one of the most used techniques to characterize rubber compounds, showed no significant differences compared to the thermally aged specimens, proving that this simple test is not sufficient to determine the deterioration of mechanical properties of rubber compounds due to the effect of thermal oxidation. Furthermore, the ability of the compounds to retain their elastic properties was also affected by the thermal oxidation expressed in the reduction of the compression set by 40.11, 41.06, and 36.21% for the NR15, NR30, and NR45 respectively. Finally, the tensile tests showed increased values after thermal ageing and ozone exposure of the M100 and M300 modules, especially for the compounds with a higher carbon black content (NR30 and NR45 compounds) and reduction of the elongation at break.

As shown by the results obtained from the tests carried out in this study to standardized specimens, which are typical loading states that rubber bearings are subjected to, namely cyclic and long-term compression, are affected by thermal ageing, which should be taken into account in the design process of rubber bearings. The compressive modulus can elucidate the expected deformation of real rubber bearings due to the instantaneous compressive load because of the weight of the structure. Deterioration of long-term properties must be assessed by creep tests to evaluate their performance after ageing. Therefore, limiting the allowable compressive stress and creep deflection between 94% and 91% of the total capacity of the bearing should be considered as the rubber compounds increase the carbon black content from 15% to 45%. Nevertheless, longer exposure times and low temperatures (crystallization of the compounds should be considered despite it being a reversible phenomenon that can be countered with heat build-up due to cyclic loading) and heat build-up effects should be evaluated to study an appropriate relationship between accelerated ageing tests (suggested by the standards and specifications of rubber bearings design) and their effect on the mechanical properties of rubber compounds.

Acknowledgement

This work was supported by the Mechanical Design Group and the Polymeric Materials Group at the University of Antioquia, which contributed with materials and facilities to the execution of the tests.

References

[1] Chou, H. & Huang, J., *Effects of Cyclic Compression and Thermal Aging on Dynamic Properties of Neoprene Rubber Bearings*, Journal of Applied Polymer Science, **107**, pp. 1635-1641, Oct. 2007.

[2] Itoh, Y., Gu, H., Satoh, K. & Yamamoto, Y., *Long-term Deterioration of High Damping Rubber Bridge Bearing*, Doboku Gakkai Ronbunshuu A. **62**, pp. 595-607, 2006.

[3] Itoh, Y., Gu, H., Satoh, K. & Kutsuna, Y., *Experimental Investigation on Ageing Behaviors of Rubbers Used for Bridge Bearings*, Structural Engineering/Earthquake Engineering, **23**, pp. 17-31, 2006.

[4] Stevenson, A. & Campion, R., *Durability, in Engineering with Rubber – How to Design Rubber Components* 3rd ed., Carl Hanser Verlag GmbH & Co., 2012.

[5] Pimolsiriphol, V., Saeoui, P. & Sirisinha, C., *Relationship Among Thermal Ageing Degradation, Dynamic Properties, Cure Systems, and Antioxidants in Natural Rubber Vulcanizates*, Polymer-Plastics Technology and Engineering, **46**, pp. 113-121, Feb. 2007.

[6] Yura, J., Kumar, A., Yakut, A., Topkaya, C., Becker, E. & Collingwood, J., *NCHRP Report 449 – Elastomeric Bridge Bearings: Recommended Test Methods*, Washington D.C., 2001.

[7] Gu, H. & Itoh, Y., *Ageing Behaviour of Natural Rubber and High Damping Rubber Materials Used in Bridge Rubber Bearings*, Advances in Structural Engineering, **13**, pp. 1105-1113, Nov. 2010.

[8] Itoh, Y., Asce, M. & Gu, H., *Prediction of Aging Characteristics in Natural Rubber Bearings Used in Bridges*, Journal of Bridge Engineering, **14**, pp. 122-128, Mar. 2009.

[9] Gu, H., Itoh, Y. & Satoh, K., *Effect of Rubber Bearing Ageing On Seismic Response of Base-isolated Steel Bridges*, Fourth International Conference on Advances in Steel Structures, **2**, pp. 1627-1632, Sep. 2007.

[10] Abedi Koupai, S., Bakhshi, A. & Valadoust Tabrizi, V., *Experimental Investigation on Effects of Elastomer Components on Dynamic and Mechanical Properties in Seismic Isolator Compounds*, Constrution and Building Materials, **135**, pp. 267-278, Mar. 2017.

[11] Wu, J., Dong, J., Wang, Y. & Gond, B., *Thermal Oxidation Ageing Effects on Silicone Rubber Sealing Performance*, Polymer Degradation and Stability, **135**, pp. 43-53, Nov. 2016.

[12] Kömmling, A., Jaunich, M. & Wolff, D., *Revealing Effects of Chain Scission During Ageing Of EPDM Rubber Using Relaxation and Recovery Experiment*, Polymer Testing, **56**, pp. 261-268, Dec. 2016.

[13] Zhang, Z., Sun, J., Lai, Y., Wang, Y., Liu, X., Shi, S. & Chen, X., *Effects of Thermal Aging on Uniaxial Ratcheting Behavior of Vulcanised Natural Rubber*, Polymer Testing, **70**, pp. 102-110, Sep. 2018.

[14] Azura, A., Muhr, A. & Thomas, A., *Diffusion and Reactions of Oxygen During Ageing for Conventionally Cured Natural Rubber Vulcanisate*, Polymer-Plastics Technology and Engineering, **45**, pp. 893-896, Feb. 2007.

[15] Kumar, A., Commereuc, S. & Verney, V., *Ageing of Elastomers: A Molecular Approach based on Rheological Characterization*, Polymer Degradation and Stability, **85**, pp. 751-757, Aug. 2004.

[16] Grasland, F., Chazeau, L., Chenal, J. & Schach, R., *About Thermo-oxidative Ageing at Moderate Temperature of Conventionally Vulcanized Natural Rubber*, Polymer Degradation and Stability, **161**, pp. 74-84, Mar. 2019.

[17] Choi, S. & Kim, J., *Influence of Reinforcing Systems on Thermal Aging Behaviors of NR Composites*, Elastomers and Composites, **46**, pp. 237-244, 2011.

[18] Choi, S., Jose, J., Lyu, M., Huh, Y., Cho, B. & Nah, C., *Influence of Filler and Cure Systems on Thermal Aging Resistance of Natural Rubber Vulcanizates under Strained Condition*, Journal of Applied Polymer Science, **118**, pp. 2658-2667, Sep. 2010.

[19] Yahya, Y., Azura, A. & Ahmad, Z., *Effect of Curing Systems on Thermal Degradation Behaviour of Natural Rubber (SMR CV 60)*, Journal of Physical Science, **22**, pp. 1-14, 2011.

[20] Choi, S., Kim, J., Lee, S. & Joo, Y., *Influence of the Cure Systems on Long Time Thermal Aging Behaviors of NR Composites*, Macromolecular Research, **16**, pp. 561-566, Aug. 2008.

[21] South, J., Case, S. & Reifsnider, K., *Effects of Thermal Aging on the Mechanical Properties of Natural Rubber*, Rubber Chemistry and Technology, **76**, pp. 785-802, Sep. 2003.

[22] Sommer, J. & Yeoh, O., *Tests and Specifications*, in Engineering With Rubber – How to Design Rubber Components, 3rd ed., Hanser Publications, 2012.

[23] Guzmán, M., Giraldo, D. & Moreno, R., *Rheometric, Transient, and Cyclic Tests to Assess the Viscoelastic Behavior of Natural Rubber-Based Compounds Used for Rubber Bearings*, Materials Today Communications, **22**, 100815, Mar. 2020.

[24] Othman, A., *Property Profile of a Laminated Rubber Bearing*, Polymer Testing, **20**, pp. 159-166, Oct. 2001.

[25] ASTM, *D575-91: Standard Test Methods for Rubber Properties in Compression*, pp. 1-4, 2012.

[26] ASTM, *D412-06: Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers-Tension*, pp. 1-14, 2013.

[27] ASTM, *D573-04: Standard Test Method for Rubber-deterioration in an Air Oven*, pp. 1-6, 2015.
[28] ASTM, *D1149-07: Standard Test Method for Rubber Deterioration-Cracking in an Ozone Controlled Environment*, pp. 1-11, 2007.
[29] ASTM, *D2240-05: Standard Test Method for Rubber Property-durometer Hardness*, pp. 1-13, 2010.
[30] ASTM, *D395-14: Standard Test Methods for Rubber Property-Compression Set*, pp. 1-6, 2014.
[31] Mullins, L., *Softening of Rubber by Deformation*, Rubber Chemistry and Technology, **42**, pp. 339-362, 1969.
[32] Chandra, C., Bipinbal, P. & Sunil, K., *Viscoelastic Behaviour of Silica Filled Natural Rubber Composites-Correlation of Shear with Elongational Testing*, Polymer Testing, **60**, pp. 187-197, Jul. 2017.
[33] Violaine, T., Quang Tam, N. & Christophe, F., *Experimental Study on High Damping Rubber under Combined Action of Compression and Shear*, Journal of Engineering Materials and Technology, **137**, 11007, Jan. 2015.
[34] Lee, Y., Cho, M., Do Nam, J. & Lee, Y., *Effect of ZnO Particle Sizes on Thermal Aging Behavior of Natural Rubber Vulcanizates*, Polymer Degradation and Stability, **148**, pp. 50-55, Feb. 2018.
[35] Pinarbasi, S. & Akyuz, Y., *Investigation of Compressive Stiffness of Elastomeric Bearings*, 6th International Congress on Advances in Civil Engineering, pp. 6-8, 2004.
[36] Koh, C. & Lim, H., *Analytical Solution for Compression Stiffness of Bonded Rectangular Layers*, International Journal of Solids and Structures, **38**, pp. 445-455, Jan. 2001.
[37] Sridharan, K. & Sivaramakrishnan, R., *Compression and Deformation of Cylindrical Rubber Blocks*, Journal Metrology Society of India, **29**, pp. 107-114, 2014.
[38] Gent, A., Discenzo, F. & Suh, J., *Compression of Rubber Disks between Frictional Surfaces*, Rubber Chemestry and Technology, **82**, pp. 1-17, 2009.
[39] Quaglini, V., Dubini, P. & Vazzana, G., *Experimental Assessment of High Damping Rubber under Combined Compression and Shear*, Journal of Engineering Materials and Technology., **138**, pp. 1-9, Jan. 2016.
[40] Amin, A., Wiraguna, S., Bhuiyan, A. & Okui, Y., *Hyperelasticity Model for Finite Element Analysis of Natural and High Damping Rubbers in Compression and Shear*, Journal of Engineering Mechanics, **132**, pp. 54-64, 2006.
[41] Sajjayanukul, T., Saeoui, P. & Sirisinha, C., *Experimental Analysis of Viscoelastic Properties in Carbon Black-filled Natural Rubber Compounds*, Journal of Applied Polymer Science, **97**, pp. 2197-2203, Jun. 2005.

[42] Brinson, H. & Brinson, C., *Polymer Engineering Science and Viscoelasticity - An Introduction*, 2nd ed., Springer, 2015.
[43] Puspitasari, S. & Cifriadi, A., *Design of Elastomeric Bridge Bearing Pad Compound Formula Based on Hydrogenated Natural Rubber*, Journal of Engineering and Technological Science, **51**(5), pp. 649-661, 2019.
[44] Li, Y., Liu, X., Hu, X. & Luo, W., *Changes in Tensile and Tearing Fracture Properties of Carbon-black Filled Rubber Vulcanizates by Thermal Aging*, Polymers for Advanced Technologies, **26**, pp. 1331-1335, Sep. 2015.