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# Evaluation of lignin as stabilizer in vulcanized natural rubber formulations

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## Abstract

In this study we evaluated the use of eucalyptus lignin as a stabilizer in combination with other stabilizers in a vulcanized elastomeric based on natural rubber. The stabilizers tested were 6PPD (*N*-1,3-dimethyl-butyl-*N'*-phenyl-*p*-phenylenediamine), TMQ (oligomerized 2,2,4-trimethylquinoline), paraffin wax and eucalyptus lignin. At predetermined time intervals, samples were taken from aging conditions and the mechanical properties and additive content were determined. The sample with a combination of wax and lignin in the same formulation showed the greatest resistance to oxidative degradation. In samples with only one stabilizer, the migration test indicated greater diffusion of lignin to the surface. Samples exposed to thermo-oxidative aging showed greater loss in the mechanical properties of tear strength and 6PPD consumption. In the accelerated aging with ozone, all showed a behavior more resistant to aging. We concluded that lignin can be used as a substitute for synthetic stabilizers, without impairing the performance of natural rubber compounds.

**Keywords:** *accelerated aging, lignin, natural rubber, paraffin wax.*

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## 1. Introduction

Natural rubber (NR) is an elastomer obtained from latex extracted from the *Hevea brasiliensis* tree. Natural rubber latex is a colloidal emulsion with 60-70% water and 40-30% rubber, mainly composed of poly(*cis*-1,4-isoprene)<sup>[1]</sup>. After vulcanization, NR presents excellent dynamic-mechanical performance, in relation to its tensile, tear and abrasion resistance properties<sup>[2]</sup>. However, due to its highly unsaturated polymer chain, NR presents low resistance to accelerated aging, mainly due to the action of heat, oxygen, ozone and sunlight<sup>[3]</sup>.

The loss of properties of rubber compounds in service often directly results in mechanical fatigue fracture, initiated by surface cracks<sup>[4]</sup>. The interaction with ozone, heat and oxygen is evidenced when the rubber is stressed or tensioned, resulting in intensification of failures in the direction perpendicular to the applied stress<sup>[5]</sup>. Rubbers with unsaturated bonds near the surface will degrade more easily. Without stress or tension, the double bonds in the volume will not be exposed to external agents. Therefore, the cracks will not grow, remaining only in the surface layer of the material<sup>[6]</sup>. Depending on how the attack is, degradation will occur through molecular scission, which results in smaller chains and a greater number of chain ends, which generates reactive species, which are free radicals<sup>[7]</sup>.

Oxidative aging in elastomers is one of the most important problems in rubber compound technology because the absorption of a small amount of oxygen causes considerable changes in physical and mechanical properties. These changes can be delayed, but not completely avoided, through the use of a stabilizer<sup>[8]</sup>. Stabilizers are chemical compounds that inhibit degradative processes in polymers<sup>[9]</sup>, and generally three factors affect the efficiency of these substances within the NR.

The first is the intrinsic activity of the stabilizer, related to the ability of the stabilizer to delay or interfere with the main chain oxidation process. This may be limited by the molar mass of the stabilizer<sup>[10]</sup>. The second factor is the solubility or compatibility of the stabilizer with the polymer matrix. The polarity difference will result in an insoluble stabilizer in the polymer matrix, which leads to exudation of the material. The third factor is the volatility or loss of the stabilizer, which can affect the performance of the final product<sup>[11]</sup>. Of the three factors, the third is the most important, as it directly affects the persistence of the stabilizer. In this context, several researchers are trying to improve the effect of stabilizers, for which purpose they use combinations of additives with different diffusion coefficients, even knowing

that one of them can be lost by volatilization during the useful life of the elastomeric compound<sup>[12]</sup>.

The use of additives from renewable sources in rubber compositions has gained attention and is currently becoming an attractive option for reducing environmental impacts<sup>[13]</sup>. Thus, the use of lignin as an elastomer stabilizer can be considered. Lignin can act as a stabilizer because the phenolic groups in its structure are similar to the structure of the hindered phenolic stabilizers used as primary stabilizers in the polymer industry<sup>[13,14]</sup>. The presence of hindered phenols in lignin favors the scavenging of free radicals and offers a protective effect against thermo-oxidative aging<sup>[15]</sup>. Paraffin waxes are predominantly mixtures of paraffin hydrocarbons<sup>[16]</sup>. At the temperatures at which most rubber products cure, petroleum waxes dissolve completely, and as the rubber cools after vulcanization a supersaturated solution of wax will form. In rubber, the waxes migrate to the surface and form a thin, inert film, which acts as a physical barrier<sup>[17]</sup>. Secondary aromatic amines are the most used primary stabilizers for unsaturated polymers like synthetic and natural rubber. These materials are processed by vulcanization in the presence of sulfur compounds and contain carbon black to increase their abrasion resistance<sup>[18]</sup>. In spite of the benefit of additives in rubber compounds, some researchers have shown that there is a tendency of some stabilizers to distribute among tire parts, reaching an equilibrium concentration. The migration of additives is affected by the polymer structure, presence of fillers, molar mass, and temperature<sup>[19]</sup>.

In this study we used 6PPD (*N*-1,3-dimethyl-butyl-*N'*-phenyl-*p*-phenylenediamine) and TMQ (oligomerized 2,2,4-trimethylquinoline), classified as primary stabilizer, both of which are of the secondary aromatic amine type. Regarding the 6PPD stabilizer combined with TMQ for elastomers, few studies have been performed, and mainly to evaluate the behavior synergistically in accelerated aging. Paraffin wax and lignin were also used. Wax forms a physical barrier against aging agents, while TMQ and 6PPD form a chemical barrier, because they react with ozone and oxygen, preventing the premature degradation of the artifact<sup>[20]</sup>. In this context, the objective of this research was to evaluate the use of eucalyptus lignin as a stabilizer for vulcanized natural rubber in combination with other commercial stabilizers that

are routinely used by the industry. The performance of nine formulations was studied before and after their exposure to accelerated aging tests.

## 2. Materials and Methods

### 2.1 Materials

The materials used in this work were: NR (Hevea-Tec Indústria e Comércio Ltda), carbon black N550 (CB-N550, Aditia Byrla), stearic acid (Sabões Fontana), zinc oxide (ZnO, Votorantim Metais), sulfur (Eastamn Chemicals Company), 1,3-diphenylguanidine accelerator (DPG, General Química), 2-mercaptobenzothiazole accelerator (MBT, Lanxess), 6PPD (Lanxess), TMQ (Chemtura), lignin (Suzano Pulp and Paper) and paraffin wax (GeQuímica). All suppliers are from Brazil.

### 2.2 Preparation of specimens

Nine formulations were prepared (Table 1), four with individual stabilizer, four with combined additives and one formulation without additive. The amounts of stabilizers were chosen based on the previously published group results<sup>[8]</sup>. The components were mixed in an internal mixer (Banbury type Copé) using 1.250 kg per batch, a rotor speed of 50 rpm, at 150 °C for 150 s. Sulfur and accelerator incorporation was performed in an open roller mixer (Lab Mill 350, Copé), at 80 °C, with a cylinder friction ratio of 1:1.25, for 2 min. Samples with dimensions of 150 × 150 × 2 mm were prepared by compression molding in a Shultz PHS 15 T hydraulic press, vulcanized at 150 °C, 15 MPa for 15 min. Specimens were cut according to the specific ASTM for the different tests.

### 2.3 Migration test

The samples of 6PPD, TMQ, lignin and wax were vulcanized in 150 × 150 × 1.0 mm thick plates, without the addition of carbon black. Subsequently, each sample plate containing the additive (source disk) was placed between two non-additive rubber plates (receiver disks) and maintained under a pressure of 30 Pa at 25 °C. After 30, 60 and 120 days, the systems were dismantled, and 1 g of

**Table 1.** Composition of the formulations studied.

Components	Compositions (phr)*								
	6PPD	TMQ	Lignin	Wax	6PT	6PTW	6PL	6PLW	WA
CB-N550	60	60	60	60	60	60	60	60	60
Stearic acid	2	2	2	2	2	2	2	2	2
ZnO	3	3	3	3	3	3	3	3	3
Sulfur	2.24	2.24	2.24	2.24	2.24	2.24	2.24	2.24	2.24
DPG	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
MBT	2	2	2	2	2	2	2	2	2
6PPD	2.5	-	-	-	2.5	2.5	2.5	2.5	-
TMQ	-	2.5	-	-	1	1	-	-	-
Lignin	-	-	2.5	-	-	-	1	1	-
Paraffin wax	-	-	-	2.5	-	2	-	2	-

\*6PPD: Samples with only 6PPD as a stabilizer; TQM: Samples with only TQM as a stabilizer; lignin: Samples with only lignin as a stabilizer; Wax: Samples with only paraffin wax as a stabilizers; 6PT: Samples with the combination of 6PPD and TQM; 6PTW: Samples with the combination of 6PPD, TQM and paraffin wax; 6PL: Samples with the combination of 6PPD and lignin; 6PLW: Samples with the combination of 6PPD, lignin and paraffin wax; and WA: Samples without additive.

each vulcanized formulation was cut and soaked for 40 h in acetone at room temperature. Stabilizers were quantified by gas chromatography using a Clarus 600 Perkin Elmer gas chromatograph and the conditions can be seen in section Gas chromatography.

## 2.4 Elemental analysis (CHN)

The elemental compositions of the 6PPD, TMQ, lignin and wax samples were determined using a Perkin Elmer 2400 CHN elemental analyzer (Waltham, MA, USA). The relative quantities of carbon, hydrogen and nitrogen were measured directly with the analyzer. The oxygen contribution was estimated as the difference between the summed carbon, hydrogen and nitrogen concentrations and 100%.

## 2.5 Oxidation induction time test

The oxidation induction time (OIT) of samples WA, 6PT, 6PTW, 6PL and 6PLW was determined on a Differential Scanning Calorimeter, DSC Q2000 TA Instruments, according to ASTM D 3895-98<sup>[21]</sup>. The samples were first equilibrated at 30 °C, then heated at 20 °C/min to 60 °C. Subsequently, they were kept at 60 °C for another 3 min with a nitrogen flow of 50 mL/min and then heated to 200 °C. After reaching 200 °C, the nitrogen gas atmosphere was exchanged for oxygen for 120 min. The first exothermic event after the introduction of oxygen was considered the oxidation induction time.

## 2.6 Crosslinking density

Crosslinking density was determined using the analyzer RPA 2000 (Alpha Technologies). The elastic modulus ( $G'$ ) measurements were performed on uncured and cured compounds at 100 °C, with 0.25° deformation and frequencies of 5 Hz and 0.5 Hz, respectively. From the  $G'$  values of the samples before and after vulcanization and using Equation 1, the physical and chemical crosslink densities were determined:

$$X_{total} = X_{chem} + X_{phys} \quad (1)$$

where  $X_{CHEMICAL}$  is the chemical crosslinking density and  $X_{PHYS}$  is the physical crosslinking density. The  $X_{PHYS}$  is related to the crosslinking chains in the non-vulcanized sample and can be approximated to  $G'$  values at a high oscillation frequency and the  $X_{TOTAL}$  is related to the crosslinking chains in the vulcanized sample and can be approximated to  $G'$  values at a low oscillation frequency (Equations 2 and 3, respectively):

$$X_{phys} = \frac{G'_{before\ cure}(5Hz)}{2RT} \quad (2)$$

$$X_{total} = \frac{G'_{after\ cure}(0.5Hz)}{2RT} \quad (3)$$

where  $G'_{BEFORE\ CURE}$  is the elastic modulus measured at 5 Hz frequency for uncured rubber;  $G'_{AFTER\ CURE}$  is the elastic modulus measured at 0.5 Hz frequency for cured rubber;  $R$  is a universal gas constant (8.31 J K<sup>-1</sup>mol) and  $T$  is the work temperature in Kelvin. Therefore, the  $X_{CHEM}$  was calculated using Equation 4.

$$X_{chem} = X_{total} - X_{phys} \quad (4)$$

## 2.7 Mechanical test

The tear strength (ASTM D 624-98<sup>[22]</sup>) and tensile strength (ASTM D 412-06<sup>[23]</sup>) were conducted using type C specimens, a load cell of 5 kN and the displacement rate of 500 mm min<sup>-1</sup>, in a Tensiometer Universal Testing Machine T2000 (Alpha Technologies). From the stress vs. elongation curve, the elongation at break and modulus at 100% were calculated. All tests were performed in quintuplicate.

## 2.8 Aging test

Different aging tests were performed. After each test, the samples were tested for tensile strength; the tear strength and content of 6PPD, TMQ, lignin and wax were analyzed by gas chromatography (see section Gas chromatography). All tests were performed in quintuplicate. From the results, the percentage of property retention for each aging time was determined using Equation 5.

$$\%retention = \frac{P_{final}}{P_{initial}} \times 100 \quad (5)$$

where  $P_{FINAL}$  is the property value after aging and  $P_{INITIAL}$  is the property value before aging.

## 2.9 Thermo-oxidative aging

The samples were submitted to accelerated thermo-oxidative aging in an oven (Marconi, model MA 035) at 100 °C with forced air circulation and absence of light. The exposure time was 24, 48 and 72 h according to ASTM D 572-04<sup>[24]</sup>.

## 2.10 Photochemical aging

The samples were subjected to photochemical accelerated aging in a UV chamber model HD 704, according to ASTM G 154-06<sup>[25]</sup> operating at 50 °C for 240 and 480 h, in two cycles of 4 h each: 50% of the time subjected to condensation and 50% subjected to UVB radiation.

## 2.11 Ozone chamber aging

An ozone chamber accelerated aging test (model SIM, 6300) was conducted at 40 °C, 50 ppm ozone concentration for 6, 12 and 24 h, according to ASTM D 1149<sup>[26]</sup>.

## 2.12 Gas chromatography

From the aged and non-aged samples submitted to tension and tear tests, 1 g of material was minced, dipped and left for 16 h at room temperature in acetone for extraction of 6PPD, TMQ, lignin and wax. Subsequently, the extracted solution was injected into the Clarus 600 Perkin Elmer gas chromatograph according to ASTM D 3156-96<sup>[27]</sup>. The initial temperature was 20 °C, with a heating rate of 20 °C min<sup>-1</sup>, end temperature of 300 °C, run time of 29 min, flame ionization detector and detector temperature of 330 °C, column of 100% polysiloxane of 30 m length, 25 mm diameter and a film thickness of 0.30 µm. The carrier gas used was helium, the injection volume was 1 µL and the flow was 1 mL min<sup>-1</sup>.

### 3. Results and Discussion

#### 3.1 Migration test

Knowing the diffusion capacity of additives in tire formulations can be very useful in predicting the useful life of rubber compounds. Intermolecular interactions between stabilizers and vulcanized elastomeric matrices affect the migration behavior of the material, because the stronger these interactions are, the slower the migration of the stabilizers<sup>[28]</sup>. The ability of the stabilizers to migrate was quantified in the 6PPD, TMQ, lignin and wax formulations (Figure 1). The lignin sample showed the highest migration (4.5%) compared to TMQ (0.5%), 6PPD (3.5%) and wax (4.0%). This behavior occurred because lignin has few interactions with the polymer matrix, since it has a significant number of polar phenolic groups in its structure (confirmed by CHN analysis; 58.2% carbon, 5.58% hydrogen and 36% oxygen). Wax showed the second highest migration percentage in relation to other additives, due to the presence of linear chains of low molar mass hydrocarbons, which facilitate its migration to the surface of the vulcanized material<sup>[29]</sup>.

TQM and 6PPD stabilizers are primary additives and both are secondary aromatic amine types. However, TQM is an amine (quinoline type) considered to have a high mass in relation to 6PPD. This fact explains the lower migration of samples with TQM. Furthermore, TQM interacts strongly with the elastomeric matrix because it has C-C and C-H bonds (confirmed by CHN analysis; 82.9% carbon, 8.96% hydrogen and 7.85% nitrogen). According to Khinnavar and Aminabhavi<sup>[30]</sup>, the diffusion profiles of solid accelerators in a natural rubber matrix indicated that the diffusion rate decreases with increasing molar mass of the diffusing species. The highest diffusion of lignin to the surface is a positive effect, because thermal and photochemical degradation reactions initiate at the surface of the vulcanizate and propagate to the bulk.

#### 3.2 Oxidation induction time

The oxygen molecule is a highly reactive chemical species, as it has two unshared electrons, which favors a spontaneous and very rapid reaction with any free radical present in the medium, forming a peroxy radical. Through the DSC technique, it was possible to observe the beginning of oxidation reactions, evidenced by the heat release characteristic of oxidative degradation<sup>[12]</sup>. In this work, the OIT was the time registered at the onset of the exothermic oxidation reaction. Usually, the more resistant the sample is to oxidative degradation, the higher the OIT value<sup>[31]</sup>. The OIT obtained were: 7 min, 18 min, 80 min, 63 min and 130 min, for WA, 6PT, 6PL, 6PTW and 6PLW, respectively. Note, that the vulcanized natural rubber was immediately oxidized in the absence of stabilizers, with a short OIT of 7 min. The 6PLW sample has the longest OIT (130 min), when compared to the other samples. The efficient antioxidant performance of the 6PLW sample can be attributed to the combination of wax and lignin in the same formulation, where the phenolic hydroxyl groups of lignin act as stabilizers of the reactions caused by oxygen and its free radicals<sup>[32]</sup>. These results corroborate the data presented in Figure 1 of the surface migration of stabilizer. The lignin and wax are more likely to migrate to the surface, making the 6PL and 6PLW samples more protected.

#### 3.3 Crosslinking density

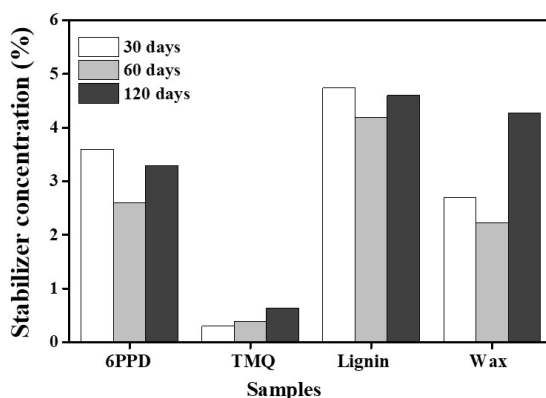
Generally, there is an important relationship between the resulting properties of rubber composites and the crosslinking density of the rubber chains<sup>[13]</sup>. Figure 2 shows the crosslinking density results of the formulations, determined by the RPA method.

It should be noted that the sample without a stabilizing agent showed the highest crosslinking density ( $16.4 \times 10^{-3} \text{ mol cm}^{-3}$ ), and the rest of the samples with stabilizers (6PT, 6PTW, 6PL and 6PLW) showed similar values. The crosslinking density is reduced with the presence of stabilizers, as they capture free radicals and cause a lower crosslinking density, interfering with the vulcanization of the compounds. There are some authors who report the use of stabilizers in the devulcanization process<sup>[33]</sup>. Jiang et al.<sup>[34]</sup> observed that the crosslinking density of epoxidized natural rubber formulations was continuously reduced with increasing lignin content.

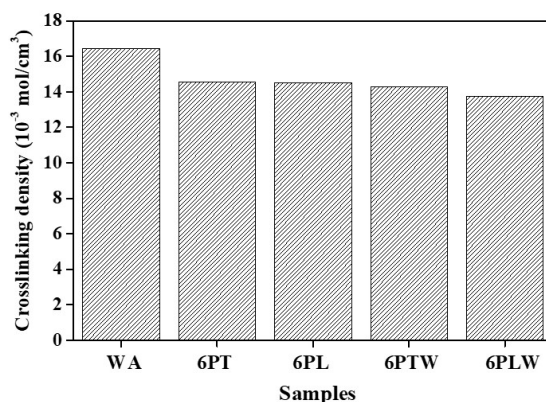
#### 3.4 Aging tests

##### 3.4.1 Thermo-oxidative aging

According to Ahagon et al.<sup>[35]</sup>, thermo-oxidative aging is the result of different mechanisms, whose consequences



**Figure 1.** Migration of additives 6PPD, TMQ, lignin and wax to the surface of vulcanized rubber samples.



**Figure 2.** Crosslinking density of formulations WA, 6PT, 6PL, 6PTW and 6PLW.



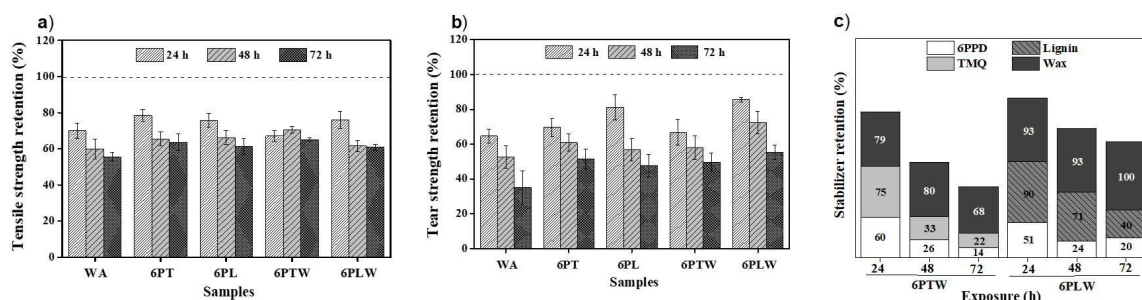
on the material properties can be contradictory, and depend strongly on the aging temperature. In this work, the tensile strength, tear strength and stabilizer content were determined for samples WA, 6PT, 6PL, 6PTW and 6PLW aged in the oven for 24, 48 and 72 h. In Figure 3a, we observe that for all three times, the WA sample showed the greatest reduction in the tensile strength retention property. This is due to the absence of stabilizer, which causes a higher crosslinking density, and consequently reduces the mobility of polymer chains, leading to rigid artifacts<sup>[36]</sup>. The rest of the samples, considering the standard deviation, showed similar retention. The stabilizer initially protect the vulcanized compound, but the level of stabilization decreases with age. Our results are in agreement with Oliani et al.<sup>[37]</sup>, who explain that the tensile strength can increase or decrease with aging time and with temperature, indicating changes in the crosslinking density during the aging process.

In Figure 3b, we present the tear strength retention results. After 72 h of exposure, there is a significant decrease in tear strength for all samples, which occurred gradually over time. Samples 6PT, 6PTW, 6PL and 6PLW showed better retention of properties when compared to the sample without protection. The loss of mechanical properties is mainly due to the increase in stiffness of the elastomeric compound, caused by the increase in the crosslinking density as a result of aging<sup>[38]</sup>. In thermo-oxidative aging, there are more changes in crosslinking density than in chain division, so the behavior was similar among all samples with stabilizer<sup>[39]</sup>. The 6PLW sample had the highest tear strength retention, indicating a positive synergistic effect between lignin and wax, which resulted in better protection against the aging effect.

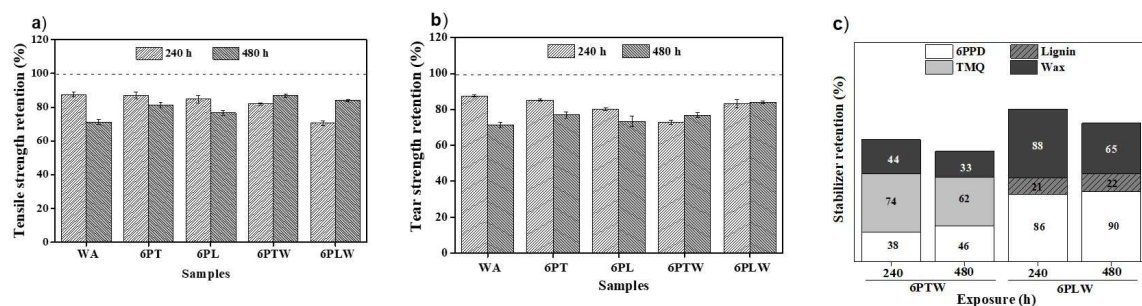
Using gas chromatography, we quantified the content of stabilizers extracted in samples 6PTW (6PPD, TMQ and wax) and 6PLW (6PPD, lignin and wax) (Figure 3c). After 72 h of oven aging in the 6PTW sample, the concentrations of 6PPD, TQM and wax were reduced to 86%, 78% and 32%, respectively, while in the 6PLW sample, the reduction was 80% of 6PPD, 60% of lignin, and there was no wax reduction. In this sample, the presence of lignin apparently prevented wax volatilization. When vulcanized rubbers are heated to a high temperature, the diffusion of stabilizers to the surface occurs and, consequently, their loss by volatilization. Lignin reacts with free radicals due to the presence of phenolic groups in its structure, which allows it to be thermally stable, and its lower loss in relation to TMQ indicates a greater stabilization effect, as observed in the OIT results.

### 3.4.2 Photo-oxidative aging

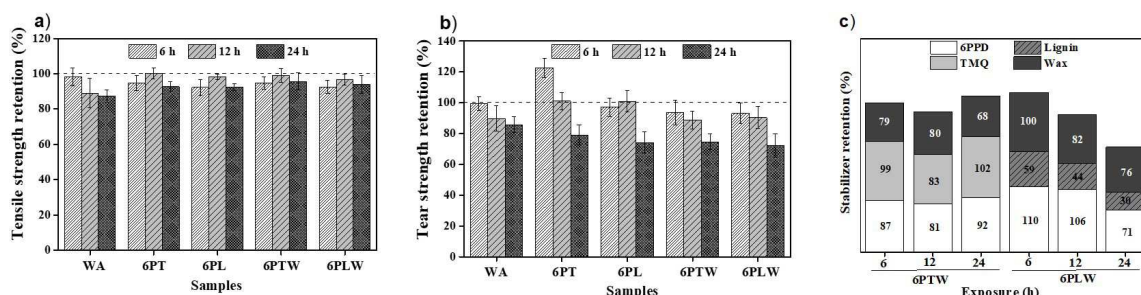
The photo-oxidative aging test in the UV chamber occurred at 240 and 480 h. The results of tensile strength retention are shown in Figure 4a. The other samples, 6PT, 6PL, 6PTW and 6PLW, showed *ca.* 80% property retention. Compared with the results of aging in the oven, the stabilizer provided greater protection in the UV environment. When UV radiation is intense, the changes caused by photo-oxidation occur close to the surface. This is because the oxygen diffusion process occurs at the surface, before it propagates into the interior of the elastomer<sup>[37]</sup>. It is important to remember that oxygen diffusion is more pronounced when the samples are subjected to mechanical stress, a fact that did not occur in this study<sup>[36]</sup>. Regarding the retention of tear strength (Figure 4b), the WA sample showed the lowest retention



**Figure 3.** Retention of properties of (a) tensile strength, (b) tear strength relative to the properties before aging (the dotted line corresponds to 100%) and (c) additive content in oven-aged formulations for 24, 48 and 72 h.



**Figure 4.** Retention of the properties of (a) tensile strength, (b) tear strength relative to the properties before aging (the dotted line corresponds to 100%) and (c) additive content in formulations aged by photo-oxidation in UV chamber for 240 and 480 h.



**Figure 5.** Retention of the properties of (a) tensile strength, (b) tear strength relative to the properties before aging (the dotted line corresponds to 100%) and (c) additive content in formulations aged ozone for 6, 12 and 24 h.

after 480 h (70%). We noticed that samples 6PTW and 6PLW showed an increase in tensile strength and retention of tear strength from 240 to 480 h of irradiation, probably due to surface crosslinking induced by UV light. According to Figure 1, wax and lignin migrate to the surface, which favors protection from photo-oxidation, letting free radicals recombine and form crosslinks.

Figure 4c shows the percentage retention for each additive after aging. In the 6PTW sample, there was a significant loss of wax and 6PPD after 480 h, 67 and 54%, respectively, and the TMQ concentration was reduced by 38%. For the 6PLW sample, the reduction of wax and 6PPD was lower, 35 and 10%, respectively; however, the lignin concentration was reduced by 78%. The migration of the wax to the surface forms a physical barrier, which favored protection against UV aging in combination with other stabilizers<sup>[17]</sup>. The persistence of the wax in the 6PLW sample indicates that the lignin prevented its migration and subsequent loss by volatilization. Furthermore, the higher concentration of 6PPD in this sample after 480 h of irradiation favored the protective effect of lignin<sup>[40]</sup>.

### 3.4.3 Ozone aging

Ozone resistance testing on cured rubber compounds is widely performed in polymer degradation research. In Figure 4a and 4b, we observed that aging accelerated by ozone was less aggressive when compared to the two previous aging studies (Figure 3 and 4). Considering the standard deviation, the tensile strength property after 24 h in the ozone chamber did not show significant variations, all samples having values greater than 90%. In the tensile strength test, during elongation, the molecular and sulfur chains linked to the elastomer, not broken by aging, slide over each other, becoming more oriented and making it difficult to break<sup>[41]</sup>.

According to Mathew and De<sup>[39]</sup>, when the elastomers are tensioned, the attack by the ozone is more effective, resulting in deep cracks in the direction perpendicular to the applied tension. In our study, during aging the samples were not stressed, therefore, a small surface area exposed to ozone attack resulted in small changes in mechanical properties. In the retention of tear strength (Figure 5b), there was a gradual decrease in the properties with time, but this also occurred in the sample without stabilizers (WA). During the test, samples 6PT, 6PTW and 6PLW showed similar retention properties, and for sample 6PL

there was no decrease in property in the first 12 h, which could be explained by the migration of lignin to the surface of the sample, as shown in Figure 1. TMQ and 6PPD form a chemical barrier, as they react with ozone and oxygen, preventing premature degradation of the formulations and providing good protection<sup>[29]</sup>. On the other hand, TMQ and lignin combined with 6PPD show good stabilizing properties when the samples are not stressed.

In the research by Cataldo<sup>[29]</sup>, carried out in an ozone chamber, 80 pphm, dynamically, it was observed that the tensile properties at rupture of the samples with TMQ-6PPD-paraffin wax were superior to the sample that contained only 6PPD-paraffin wax, and this was superior to the sample with TMQ-paraffin wax. Cataldo concluded that when TMQ is used in combination with another stabilizer such as 6PPD, better resistance to ozone aging is achieved. TMQ is a stabilizer that stops the propagation of the degradation cycle by donating the hydrogen atom.

In the 6PTW sample, 6PPD and TMQ were not consumed by ozone aging, while the wax concentration decreased by 32% after 24 h. According to Varghese et al.<sup>[42]</sup>, paraffin wax gives effective protection against ozone aging in combination with other stabilizers, as it migrates to the surface of the vulcanized sample and forms a physical barrier. Aging with ozone for 24 h caused a reduction of all stabilizer concentrations in the 6PLW sample: 29% 6PPD, 70% lignin and 24% wax. As shown in Figure 1, the surface migration of lignin and wax was higher than TMQ and 6PPD, which may favor good protection against ozone reaction with the unsaturated groups of natural rubber. In this study, the content of stabilizers was probably more influenced by the scission of the elastomeric chain than the possible changes in the crosslinking density.

## 4. Conclusions

Nine formulations were prepared combining natural and commercial stabilizing agents. For the first time, we evaluated the synergistic behavior of lignin with other stabilizers in the accelerated aging of natural rubber compounds. In the three aging processes tested, significant differences were observed in the tear strength property, when compared to the tensile strength. The longest oxidation induction time determined by DSC was evidenced by the sample with a combination of wax and lignin in the same formulation. In thermo-oxidative aging, due to the higher temperature

(100 °C) there was a greater decrease in the mechanical properties and consumption of stabilizer. However, even with a significant loss of properties, formulations with different stabilizers showed similar results. In photo-oxidative aging, the samples with the least reduction of properties were those that used the combination of three stabilizing agents (6PTC and 6PLC). In the accelerated aging with ozone, the samples showed greater retention of properties, so they were more resistant to aging. According to the results, we conclude that lignin has the potential to be used as a stabilizer, replacing the synthetic stabilizers currently used, because its use in vulcanized NR formulations did not impair the performance of elastomeric artifacts. This result is financially and environmentally beneficial, as there are companies that generate lignin as a by-product, as well as companies that consume bio-based raw materials.

## 5. Author's Contribution

- **Conceptualization** – Marco Aurelio De Paoli; Janaina da Silva Crespo.
- **Data curation** – NA.
- **Formal analysis** – Gelsa Adriana Carpenedo.
- **Funding acquisition** – NA.
- **Investigation** – Gelsa Adriana Carpenedo.
- **Methodology** – Gelsa Adriana Carpenedo; Marco Aurelio De Paoli; Janaina da Silva Crespo.
- **Project administration** – Marco Aurelio De Paoli; Janaina da Silva Crespo.
- **Resources** – NA.
- **Software** – NA.
- **Supervision** – Marco Aurelio De Paoli; Janaina da Silva Crespo.
- **Validation** – Gelsa Adriana Carpenedo.
- **Visualization** – NA.
- **Writing – original draft** – Gelsa Adriana Carpenedo.
- **Writing – review & editing** – Gelsa Adriana Carpenedo; Nayrim Brizuela Guerra; Marcelo Giovanela; Marco Aurelio De Paoli; Janaina da Silva Crespo.

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