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Evaluation of Stabilizing Additives Content in the Mechanical Properties of Elastomeric Compositions Subject to Environmental and Accelerated Aging

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This research aimed to evaluate the ideal proportion of two stabilizers in elastomeric compositions indicated for tire sidewall. The stabilizers applied in different proportions were *N*-1,3-dimethyl-butyl-*N'*-phenyl-p-phenylenediamine (6PPD) and oligomerized 2,2,4-trimethyl-quinoline (TMQ). Nine compositions were prepared with 0.5, 1.5 and 2.5 phr of 6PPD combined with 0.5, 1.0 and 1.5 phr of TMQ. The compounds were exposed to accelerated aging processes, including thermo-oxidative, photochemical and ozone chamber. Also, the samples were aged in the environment for 440 days. At regular intervals, the samples were evaluated. Gas chromatography was used to quantify the content of 6PPD. Overall, the samples exposed to thermo-oxidative aging showed the greatest loss of mechanical properties (tear and tensile strength) as well as the 6PPD content. From the mechanical strength results, it was possible to conclude that the best combination of stabilizers was 2.5 phr of 6PPD and 1.0 of TMQ.

Keywords: *Elastomers, stabilizers, 6PPD, TMQ, tire sidewall.*

1. Introduction

The tire is composed of components that interact simultaneously and synergistically to ensure its performance during the application and lifecycle. These include the sidewall (the tire side), tread, shoulder, straps and liners[1]; being the belt and sidewall the essential components. During its use, the low bending frequencies of the tire side are related to the balance of the internal pressure that causes tension between the sidewall and the tire belt; and the high frequencies are related to the shear stiffness and longitudinal stiffness[2]. Consequently, it is important to study the aging of the tires' sidewall, because it is in constant dynamic work during use.

Therefore, the tire's performance is assessed by characteristics of the vulcanized compound when exposed to severe conditions of temperature, environment and fatigue. Generally, tests involving tensile strength, compression, and flexural fatigue under accelerated aging conditions provide the information needed about the tire's lifecycle[3].

In natural (NR) and polybutadiene (BR) rubber researches, the most investigated topic focuses on the oxidative effects, which mainly occur when the unsaturation presented in the polymer main chain is attacked by the oxygen[4]. Additionally, another important effect of aging is caused by ozone. Brand and Gent[5] defined that the cracks caused by ozone increase linearly with time and its growth rate are proportional to the ozone concentration. In the Counta et al. research, the results showed that tires are subject to many aging factors, including heat, ozone, UV and dynamic stress.

Regarding aging processes and chemical changes in the polymer structure, the onset of degradation is always related to the break of a covalent chemical bond. Depending on how degradation occurs, disruption of bonds can generate reactive species, which in most cases are free radicals. The addition of stabilizing additive like p-phenylenediamines (6PPD) combined with trimethylquinolines (TMQ) as well as microcrystalline waxes offers satisfactory protection to elastomeric artifacts[7].

During the degradation process, once the chain reaction begins, these radicals quickly combine with oxygen (Figure 1 - Step 1) to form peroxyl radicals (Figure 1 - Step 2). This one, in turn, extracts hydrogen from the rubber macromolecule forming a hydroperoxide as well as regenerating the radical to continue the cycle (Figure 1 - Step 3). In addition, the formed hydroperoxide decomposes into two oxygen radicals (Figure 1 - Step 4), which will increase the propagation of the reaction (Figure 1 - Steps 5 and 6).

The scission of the polymeric chain happens, when the energy applied to the molecule is greater than the binding energy. The reduction of the binding energy in the polymeric chain occurs by the presence of branches, tactics, morphology, mechanical stress, presence of contaminants and conditions of the rubber artifact use. The presence of tertiary carbon atoms, for example, implies the existence of C-H bonds that can be broken more easily than C-H bonds

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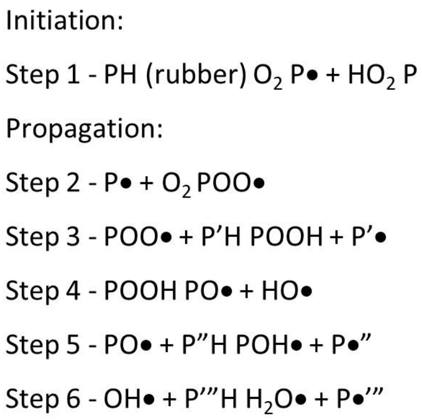

Figure 1. Illustrative scheme of the degradation reaction in an elastomeric matrix[7].

of primary or secondary carbons. Scission can also occur on double-bonded polymeric chains. The presence of the C=C double bond reduces the energy of the adjacent C-H bond[8]. The degradation of vulcanized rubber is associated with both breakdowns of the sulfur bonds as well as the scission of the polymeric main chain (either by chemical reaction or mechanical stress). For both processes, there may be a decrease in the mechanical properties of tensile and tear strength.

The ozone attack resistance testing on cured rubber compounds occupies a prominent place in polymer degradation. The compounds' loss of properties during service often results directly in mechanical fatigue fracture initiated by superficial cracking caused by the ozone attack[9]. The interaction with ozone is observed when rubber is tensioned in use, which results in the fail intensification perpendicularly to the applied stress[10]. Only rubbers with unsaturated chains will be degraded by ozone. In the absence of stretching or tensioning, the inner layers of double bonds will not be exposed to ozone. Therefore, the cracks will not grow, remaining only on the superficial layer of the material[11,12]. Usually, the reaction with ozone is electrophilic and starts in places, where the electron density is high[13].

The term 'stabilizer' is used to describe a wide range of chemical compounds that inhibit degradative processes in polymers. Therefore, there are antioxidants, photostabilizers, metal deactivators and antiacids[14]. The secondary aromatic amines are the most commonly used as primary stabilizers in C=C double-bonded polymers, such as synthetic rubbers and NR. These materials are vulcanized in the presence of sulfur compounds and contain carbon black to increase their abrasion resistance. In this context, Dweik and Scott[14] proposed a mechanism, where the stabilizer is regenerated in an autocatalytic cycle that involves the intermediate formation of nitroxyl radicals and participation of sulfur compounds.

The compounds used as secondary stabilizers are the trivalent phosphorus compounds such as phosphites or phosphonites; the organic sulfur compounds such as sulfides and metal salts of dialkyldithiocarbamates and dithiophosphates. However, the use of secondary stabilizers in some applications tends to decrease due to their toxicity[8].

In this research, *N*-1,3-dimethyl-butyl-*N'*-phenyl-p-phenylenediamine (6PPD) and oligomerized 2,2,4-trimethylquinoline (TMQ) were used and they are classified as primary stabilizing additives. Additionally, both are of the secondary aromatic amine type. The TQM is an amine (quinoline type) considered to be of high molar mass, low volatility and low cost.

As the stabilizer with a function of antioxidant, it tends to interrupt the sequence of degradation reaction by capturing the free radicals formed and/or by ensuring that the peroxides produced break down into less reactive fragments[15,16]. In turn, the p-phenylenediamines in the 6PPD are stabilizers that have the function of breaking the chain (via donation of a hydrogen atom) forming an aminyl radical[17].

According to Narathichat[18], 6PPD has a lower thermal stability than the TMQ. However, TMQ has lower oxidative protection than 6PPD for NR at elevated temperatures. This behavior can be attributed to its lower mobility within the rubber compound due to its high molar mass. Additionally, the energy required to remove the active H atom in TMQ is greater than in 6PPD[18].

In view of all these aspects, this research aims to evaluate the ideal proportion of 6PPD and TMA stabilizers in tire sidewall elastomeric compounds that require long term performance.

2. Materials and Methods

2.1 Materials

The materials and additives used in the research were provided by Borrachas Vipal S.A (Brazil). The following neat materials were used: zinc oxide (ZnO) (Votarantim Metais), stearic acid (Sabões Fontana), natural rubber (NR) of the SMR type 5L (Lee Rubber), polybutadiene rubber (BR) (ND 40 - Lanxess), carbon black (NF 330) (Columbian Chemicals of Brazil), stabilizer 6PPD 96% (Lanxess), stabilizer TMQ (Chemtura), sulfur (Intercuf Indústria e Comércio Ltda), CBS accelerator (*N*-cyclohexyl-2-benzothiazole sulfenamide) (Lanxess) and TRAE aromatic rubber oil.

2.2 Compounding

From a standard sidewall tire compound, various compositions have been developed according to Table 1.

First, the mixing process occurred in a Banbury internal mixer, Copé brand, with an amount of 1,250 g per batch, rotor speed of 50 rpm with discharge at a temperature of 150 °C for 30 min. In the partially homogenized mixture, the acceleration components (sulfur and accelerator additives) were incorporated into an open mixer under the following conditions: temperature of approximately 80 °C and cylinder friction ratio of 1:1.25 for 2 min.

2.3 Specimen preparation

The specimens were prepared by compression molding in a Shultz PHS 15T hydraulic press operating at 150 ºC, pressure of 15 Bar and optimum vulcanization time of 15 min (determined by oscillatory disc rheometry (MDR). After the 150 X 150 X 2 mm plates were produced, specimens were cut with specific imprints for the tensile strength and tear strength mechanical tests.

Table 1. Compositions studied in this research.

Compounds (phr)	Compositions									
	0	1	2	3	4	5	6	7	8	9
NR	50	50	50	50	50	50	50	50	50	50
BR	50	50	50	50	50	50	50	50	50	50
NF 330	50	50	50	50	50	50	50	50	50	50
Oil	10	10	10	10	10	10	10	10	10	10
Stearic acid	2	2	2	2	2	2	2	2	2	2
ZnO	3	3	3	3	3	3	3	3	3	3
Sulfur	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75
CBS	1	1	1	1	1	1	1	1	1	1
TMQ	-	0.5	0.5	0.5	1	1	1	1.5	1.5	1.5
6PPD	-	0.5	1.5	2.5	0.5	1.5	2.5	0.5	1.5	2.5

2.4 Mechanical tests

The tear strength test was performed according to ASTM D 624–12 specimen Type C[19]. The tests were conducted on a Tensometer 2000 (T2000) universal testing machine, Alpha Technologies, using a load cell and speed of 5 kN and 500 mm min^{-1}, respectively.

In turn, the tensile strength test was performed according to ASTM D 412-06 specimen Type C[20]. A 5 kN load cell and speed of 500 mm min^{-1} were used in a Tensometer 2000 (T2000) Alpha Technologies universal testing machine.

2.5 Gas chromatography (GC)

From the aged and non-aged specimens, 1.0 g of the material was ground and immersed in acetone for 16 h at room temperature for the 6PPD extraction. Subsequently, the acetone solution was injected into the Clarus 600 Perkin Elmer gas chromatograph, according to ASTM D 3156-96[21]. The conditions of the analysis were: initial temperature of 20 °C, heating rate of 20 °C min^{-1}, final temperature of 300 °C during 29 min, flame ionization detector and detector temperature of 330 °C, glass column (100% polysiloxane) with a length of 30 m, diameter of 25 mm and a 0.30 µm film thickness. The injection volume was 1.0 µL and the flow 1.0 mL min^{-1}. The carrier gas used was helium.

Fragments of 1.0 g of the 1.5 phr TMQ and 2.5 phr 6PPD samples were aged for 72 h in an oven at 70 °C within a sealed vial. The gas formed in the vial was extracted with a 10 mL syringe and diluted with 1.5 mL of acetone. Subsequently, acetone was analyzed by gas chromatography with a flame ionization detector. The detector temperature was 330 °C.

2.6 Thermo-oxidative aging

The samples were submitted to accelerated thermo-oxidative aging (thermolysis) conducted in an oven (Marconi, model MA 035), with forced air circulation and absence of light for 24, 48 and 72 h at 70 °C, according to ASTM D 572-04[22]. After aging, the samples were tested by tensile and tear strength and 6PPD content. From the results, the property retention for each aging time was determined according to Equation 1:

$$\%retention = \left(\frac{P_{final}}{P_{initial}}\right) 100 \qquad (1)$$

where,

P_{final} is the value of the properties measured after aging; and $P_{initial}$ is the properties measured before aging test.

2.7 Photochemical aging

The photochemical accelerated aging (photolysis) was conducted in a UV chamber according to ASTM G 154-06[23] operating at 50 °C for 120, 240 and 480 h into two cycles of 4 h: 50% of the time subjected to condensation and 50% subjected to UVB radiation. The retention of the tensile and tear strength properties, as well as the 6PPD content, was calculated according to Equation 1.

2.8 Ozone chamber aging

Ozone chamber accelerated aging test was conducted at 40 °C and 50 pphm of ozone concentration during 90, 180 and 360 h, based on the ASTM D 1149-2007[24]. Property retention calculations were performed according to Equation 1.

2.9 Environmental aging

The environmental aging test was performed at the *Borrachas Vipal* Rubber company for a period of 440 days, from November of 2011 until February 2013, based on ISO 877-2[25]. Table 2 shows the weather condition such as average rainfall, minimum and maximum temperature, and relative humidity which were obtained from the *Embrapa Uva e Vinho*, Meteorological Station, Brazil (coordinates 29°09'52.4"S 51°32'02.8"W)[26].

The specimens were arranged on the exposed metallic structure at 3 meters from the ground located in an open area without being exceeded by other objects. The specimens were collected and evaluated after periods of 20, 40, 80, 120, 160, 320 and 440 days of exposure. The specimens were gently cleaned using a towel and left in air for 24 h at room temperature before proceeding to the required test. The retention of properties was calculated according to Equation 1.

2.10 Dynamic-mechanical thermal analysis (DMTA)

A vulcanized compound was subjected to the DMTA test at a frequency of 10 Hz, strain 0.06% in the temperature ranging from -125 °C to 0 °C and heating rate of 2 °C min^{-1}. The test was performed using a TA Instruments DMA Q800 testing machine operating in a single cantilever for 1.89 X 6.07 X 13.72 mm specimen.

Table 2. Weather parameters throughout the environmental test (November of 2011 until February 2013).

Year	Solar radiation	Relative humidity	Winter temperature	Summer temperature	Precipitation	Sunstroke	Average Wind speed
	(kJ/m^2)	(%)	(min to max ºC)	(min to max ºC)	(mm)	(W/m^2)	(m/s)
2011-2012	826.0	73	7.3 to 22.8	15.5 to 29.3	116.7	215.6	2.5
2013	839.7	75	7.3 a 19.6	14.6 to 28.2	163.8	204.7	2.2

3. Results and Discussion

3.1 Definition of 6PPD and TMQ content in the compositions

The results of the 6PPD retention are based on the compositions showed in Table 1. Since 6PPD is consumed during the vulcanization process, Figure 2 shows the difference of 6PPD before versus right after the vulcanized composition. The amount of 6PPD retained after the vulcanization process are: compositions 1, 4 and 7 (~81.5%); compositions 2, 5 and 8 (~71.2%); compositions 3, 6 and 9 (~71.4%). This value was used to determine the retention content in this study.

The first part of this study was the definition of the 6PPD and TMQ ratio in the rubber compound. Hence, it was evaluated nine compositions (Table 1) to define the stabilizers' ratio in the rubber compounding aging resistance. Following, specimens for tear and tensile strength were prepared and submitted to aging tests and further evaluation by tensile properties.

As a result of the tensile tests, the retention of the tear strength indicated that in environmental aging the properties maintenance is independent of the protective content used. However, for the aging in the ozone chamber, the properties were maintained with 1.5 phr of 6PPD and 0.5 phr of TMQ (composition 2).

Additionally, for the photochemical aging in a UV chamber, the properties maintenance occurred with 1.5 phr of 6PPD and 1.5 phr of TMQ (composition 8), while for the thermo-oxidative aging in the oven, this occurred with 2.5 phr of 6PPD and 1.0 phr of TMQ (composition 6). In turn, for the environmental aging, stress at break was maintained regardless of the protective content. For the aging in the ozone chamber, property maintenance occurred with 0.5 phr of 6PPD and 0.5 phr of TMQ (composition 1).

Regarding the results of the photochemical aging in the UV chamber, it was observed that the properties maintenance occurred with 2.5 phr of 6PPD and 0.5 phr TMQ (composition 3), and for thermo-oxidative aging in an oven, properties maintenance occurred with 2.5 phr of 6PPD and 1.0 phr of TMQ (composition 6).

On the other hand, for the retention of the elongation at break, we observed that in environmental and ozone chamber aging the properties maintenance was independent of the protective ratio content. For photochemical aging, the properties were maintained with the lowest protective content, while for the thermo-oxidative aging in the oven, the property maintenance occurred with 2.5 phr of 6PPD and 1.0 phr of TMQ (composition 6).

For environmental aging in ozone chamber and photochemical in UV chamber, the best retention occurred with 0.5 phr of TMQ and 2.5 phr of 6PPD (composition 3), while for thermo-oxidative aging in an oven the best retention occurred at 1.5 phr of TMQ and 0.5 phr of 6PPD (composition 7).

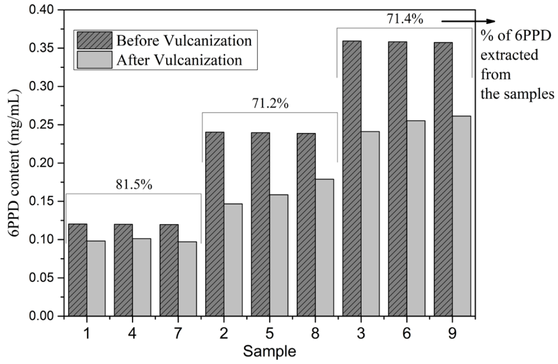

Figure 2. 6PPD content measured after vulcanization process.

From the analyzes performed with the various concentrations of 6PPD and TMQ, the best performance occurred with 2.5 phr of 6PPD and 1.0 phr of TMQ (composition 6) in the thermo-oxidative aging in an oven, which was considered the most aggressive in terms of property loss of tear strength, tensile strength and the consumption of 6PPD content. In this scenario, the formulation 6 was chosen to the second part of this study, where further evaluations were performed. Thus, new specimens were prepared and subjected to aging tests.

Figures 3 to 11 show the results indicating the best stabilizing additive content in thermo-oxidative aging after 72h. Figure 3 shows tear strength in thermo-oxidative aging in an oven using 0.5 phr of TMQ in combination with different 6PPD contents. As can be seen, the best result obtained was using 1.5 phr of 6PPD, reaching 68% of the retention for this property.

In turn, Figure 4 shows the stress at break for thermo-oxidative aging in an oven using 0.5 phr of TMQ in combination with different contents of 6PPD. Here, the best property retention was found with 1.5 phr of 6PPD, reaching 68%.

In the retention of thermo-oxidative aging in the oven using 0.5 phr of TMQ, in combination with different 6PPD contents (Figure 5), we observed that the best retention of properties was found at 1.5 phr, which reached approximately 22%.

Figure 6 shows the retention of tear strength in oven thermo-oxidative aging using 1.0 phr of TMQ in combination with different 6PPD contents. We observed that the superior retention of properties was found with 2.5 phr of 6PPD, which reached approximately 80%.

In Figure 7, we show the retention of tear strength for oven thermo-oxidative aging using 1.0 phr of TMQ in combination with different 6PPD contents. We observed

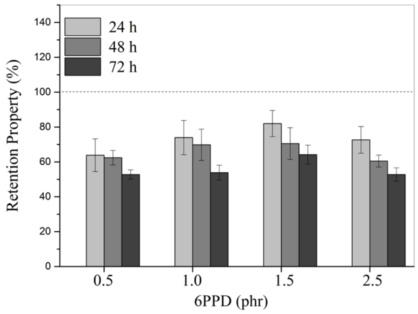

Figure 3. Retention of tear strength in oven thermo-oxidative aging comprising 0.5 phr of TMQ in combination with different 6PPD contents.

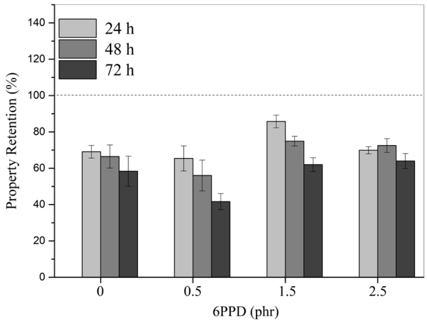

Figure 4. Retention of tensile strength at thermal-oxidative aging in oven comprising 0.5 phr of TMQ in combination with different 6PPD contents.

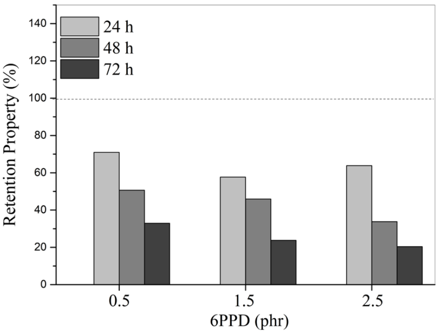

Figure 5. Retention of 6PPD in oven thermo-oxidative aging comprising 0.5 phr of TMQ in combination with different 6PPD contents.

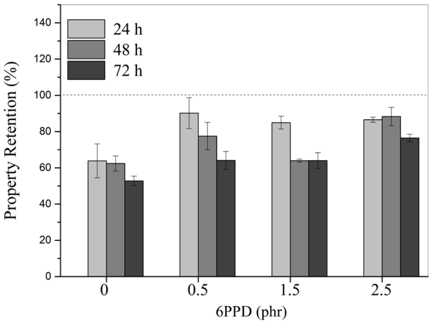

Figure 6. Retention of tear resistance in oven thermo-oxidative aging comprising 1.0 phr of TMQ in combination with different 6PPD contents.

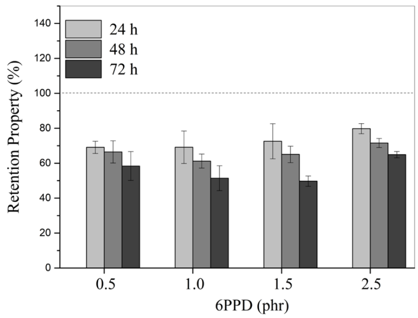

Figure 7. Retention of tear strength for oven thermal-oxidative aging comprising 1.0 phr of TMQ in combination with different 6PPD contents.

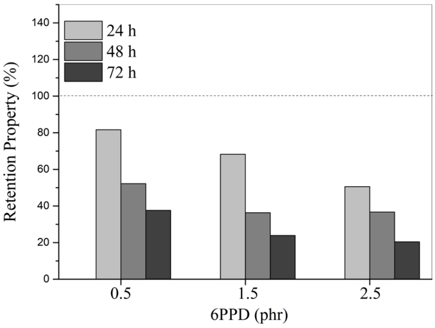

Figure 8. Retention of 6PPD in oven thermo-oxidative aging comprising 1.5 phr of TMQ in combination with different 6PPD contents.

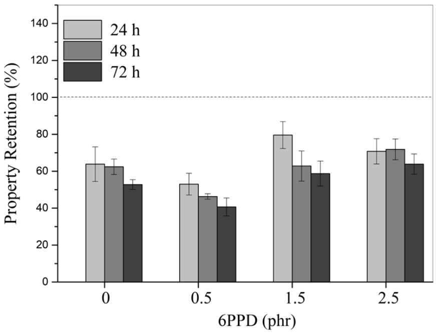

Figure 9. Retention of tear strength for oven thermal-oxidative aging comprising 1.5 phr of TMQ in combination with different 6PPD contents.

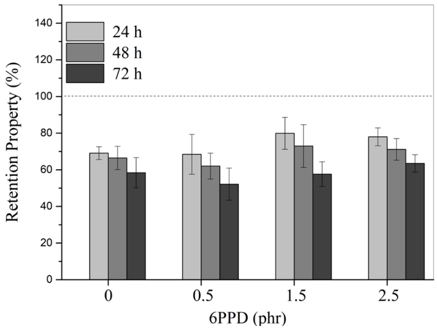

Figure 10. Retention of tensile strength in oven thermal-oxidative aging comprising 1.5 phr of TMQ in combination with different 6PPD contents.

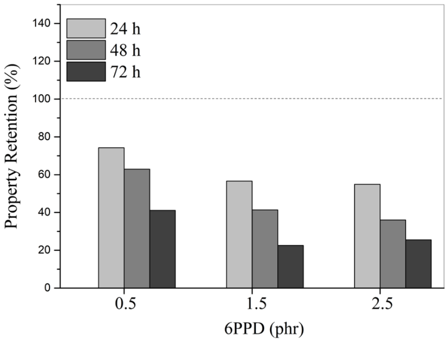

Figure 11. Retention of 6PPD in oven thermo-oxidative aging comprising 1.5 phr of TMQ in combination with different 6PPD contents.

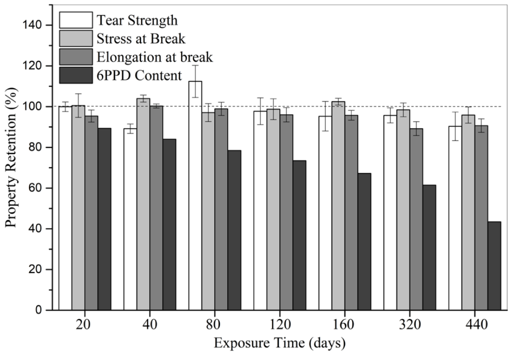

Figure 12. Retention of property in environmental aging of the composition comprising 2.5 phr of 6PPD and 1.0 phr of TMQ.

that the best property retention was found with 2.5 phr of 6PPD, reaching 70%.

On the other hand, Figure 8 shows the retention of 6PPD in oven thermo-oxidative aging using 1.0 phr of TMQ in combination with different 6PPD contents. We observed that the best retention of the property occurred with 0.5 phr, which reached approximately 40%.

Tear strength retention for oven thermal-oxidative aging using 1.5 phr of TMQ in combination with different 6PPD contents is shown in Figure 9. We observed that the best retention of the property was found at 2.5 phr 6PPD, which reached 78%.

Figure 10 shows the stress at break retention for oven thermo-oxidative aging using 1.5 phr of TMQ in combination with different 6PPD contents. We observed the best retention of the property with 2.5 phr of 6PPD, reaching 70%.

In Figure 11, we show the retention of the 6PPD in oven thermo-oxidative aging using 1.5 phr of TMQ in combination with different 6PPD contents. We observed that the best retention of the property was found at 0.5 phr, which reached 40%. In the results related to Figures 4 to 11, we observed that the highest consumption of 6PPD was for the composition with 1.5 phr of TMQ.

By evaluating the results, the combination of the stabilizing additives presented in Figure 6 (1.0 phr of TMQ) was selected to continue this study, since retention property of the tear resistance is important for the tire sidewall.

3.2 Environmental aging

The environmental aging testing took place in the periods of 20, 40, 80, 120, 160, 320 and 440 days. After each period, the samples were subjected to mechanical testing and quantification of 6PPD content (Figure 12).

It can be observed that up to 440 days the mechanical properties showed that the reduction of tear and tensile strength, as well as elongation at break, was less than 10%. Additionally, there was a gradual reduction in 6PPD content by approximately 56% after 440 days of exposure time.

Apparently, the consumption of the stabilizing additive is not directly related to the loss of tear and tensile strength as well as the elongation at break. This observation is possibly, indicating that the elastomeric matrix has not yet started the degradation process.

The specimens aged at the environment were exposed to the ozone, UV radiation and oxygen combined with variations of weather conditions of temperature and humidity. Therefore, after 440 days the specimens experienced chain scission of the cross-linking on the surface and also within the material.

Thus, the consumption of 6PPD was significant, since the test started in November of 2011 until February 2013, with temperature variation from 7.3 °C to 29.3 °C, comprising two summer seasons with temperature variations between 17 °C and 29.3 °C[27]. In such a climate, the surface temperature of rubber specimens reaches as high as 50°C under direct sunlight[28]. Since temperature increases, the heat may contribute to the stabilizing additive to migrate to the surface and subsequently reacting with the oxygen in the outer region of the elastomer[29], being consumed. On the other hand, it must also be considered that the increase in temperature increases the solubility of the additive in the matrix, which leads to a reduction in its consumption. In this study, the results indicate that consumption appears to be associated with the migration of the additive to the surface.

However, 6PPD content that remained in the samples in combination with the TMQ was sufficient to maintain the properties of the elastomeric matrix. The combination of the additives might be the reason for better withstanding property in natural weathering[30]. The antioxidant can deactivate the absorbed light, thereby reducing radical formation, which also resulted in the reduction of photooxidation[28,30].

3.3 Aging in an ozone chamber

The aging in the ozone chamber was performed for periods of 80, 160 and 320 h (Figure 13) without any strain. There was approximately 18% drop in tear strength after 80 h of exposure test and thereafter the mechanical properties remained constant.

It was also observed that the elongation at break did not change and stress at break decreased by 12% after 320 h of exposure test. There was a gradual consumption of 6PPD, reaching up to 10%. This accelerated aging was less aggressive because just caused little variations in the mechanical properties of the compositions. It occurred because only tensioned elastomers are attacked by ozone, resulting in deep cracks perpendicularly to the applied tension[5]. Probably, during the aging test, the composition's tear strength was more affected by the elastomeric chain scission than the changes in crosslinking density[31].

3.4 Photochemical aging in UV chamber

The accelerated aging test in the UV chamber occurred at 120, 240 and 480 h. The results showed that the stabilizing additives had a protective effect in the compositions (Figure 14).

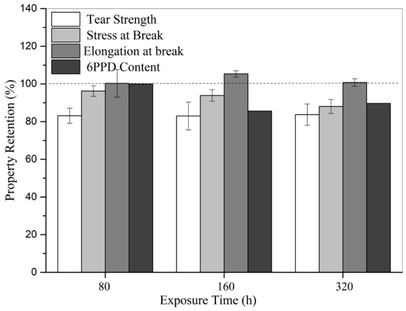

Figure 13. Retention of mechanical properties aged in the ozone chamber of the compositions comprising 2.5 phr of 6PPD and 1.0 phr of TMQ.

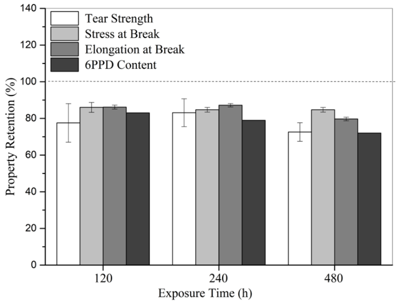

Figure 14. Retention of mechanical property in UV chamber photochemical aging of the compositions comprising 2.5 phr of 6PPD and 1.0 phr of TMQ.

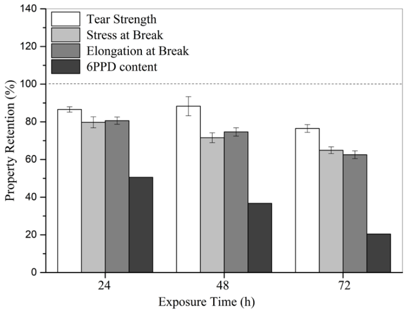

Figure 15. Retention of properties in oven thermo-oxidative aging of the composition comprising 2.5 phr of 6PPD and 1.0 phr of TMQ.

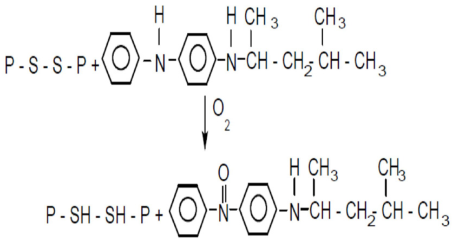

Figure 16. Redox mechanism between stabilizer and elastomer[30].

The results for 120 h of testing showed a decrease of up to 20% in the tear strength and around 15% in the elongation at break. The properties maintenance occurred over time considering the standard deviation. The consumption of 6PPD content was gradually reaching up to 25% and it seems to be associated with the decreased in mechanical properties. For these specimens, probably the cross-linking formation, as well as chain scission, occurred in the highest proportion than in the ozone chamber. According to Douminge et al.[32], the competition among sulfur bonds and chain scission during degradation lead to physical modifications of the macromolecular chains. These modifications may be associated with a decrease of mechanical properties (as tear resistance, stress and elongation at break) when exposed to photochemical aging.

3.5 Thermo-oxidative aging in oven

The retention of properties after the forced-air oven heat-oxidative aging test decreased gradually at 24, 48 and 72 h (Figure 15).

The mechanical properties, stress and elongation at break decreased up to 37% for 72 h of exposure. In turn, tear strength decreased by up to 22% with 72 h of exposure. The consumption of 6PPD was gradual, reaching 80% and is related to the reduction of mechanical properties. The aging mechanism in this scenario is caused by temperature[32]. The stress and elongation at break of aged specimens were reduced by thermal aging[33] and the phenomenon can be attributed to the scission of poly and disulfide bonds and the formation of additional monosulfide bonds. The scission of poly and disulfide bonds is caused by the stabilizer hydrogen atoms in a condition, where the vulcanized elastomer and the stabilizer form a redox system, as shown in Figure 16[33].

3.6 Dynamic mechanical thermal analysis (DMTA)

The aged specimens were submitted to DMTA test to evaluate if aging influences the glass transition of the rubber compositions. The loss factor (tan δ) is the quotient between loss modulus (viscous component) and the storage modulus (elastic component) response of the polymeric material (E''/E')[33,34]. As shown in Figure 17, in the range of -60 °C and -40 °C there is a transition region, characterized by the maximum peak of the tan δ curve. Additionally, it defines the glass transition temperature (*Tg*) of the compositions studied.

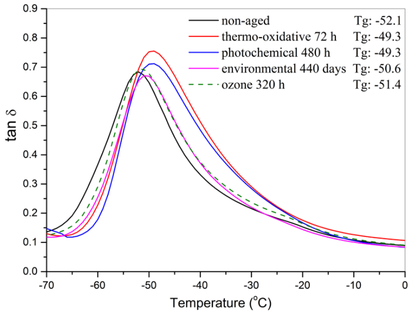

Figure 17. Aging effect on tan δ behavior as a function of temperature in compositions comprising 2.5 phr of 6PPD and 1.0 phr of TMQ (standard deviation in the temperature determination is ±0.5 ºC).

From the results, it was found that the oven thermo-oxidative aging resulted in the displacement of *Tg* values to higher temperatures compared to the non-aged sample. This change is associated with the reduction of the polymeric chain's mobility as a result of the increased crosslinking density after aging[35].

4. Conclusions

From this research, it was possible to indicate that the stabilizing additives used in the compositions helped to maintain the integrity of the mechanical properties after aging tests. The most suitable concentration of stabilizing additives to maintain the mechanical properties of the studied compositions was 2.5 phr of 6PPD and 1.0 phr of TMQ. The use of higher TMQ contents did not contribute to improving mechanical properties.

From all the aging tests performed in this research, the most significant change related to the compositions' molecular structure and consequently the loss of properties and consumption of 6PPD occurred in the oven thermo-oxidative aging.

During the aging test, temperature showed to be the determining factor that contributed to accelerating the degradation and significant reduction of the 6PPD content, which occurs basically by the chemical reaction with oxygen. Therefore, it is the most suitable aging in order to evaluate the effects promoted by the stabilizing additives.

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