Sustainable Natural Rubber Compounds: Naphthenic Oil Exchange for another Alternative from Renewable Source

Aline Zanchet[1*], Pamela S. Garcia[1], Regina C. R. Nunes[2], Janaina S. Crespo[3] And Carlos H. Scuracchio[4]

[1]*Center of Applied Engineering, Modeling and Social Sciences – Federal University of ABC, Santo André – SP, Brazil*
[2]*Instituto de Macromoléculas Professora Eloísa Mano (IMA) Federal University of Rio de Janeiro (UFRJ), Rio de Janeiro, RJ, Brazil*
[3]*University of Caxias do Sul, 95070-560, Caxias do Sul – RS, Brazil*
[4]*Materials Engineering Department – Federal University of São Carlos – SP, Brazil*

Abstract: Because of the high viscosity of rubber compounds, the use of processing aids is essential in these materials formulations. Despite most of these additives currently used are derived from petroleum, there are a number of attempts to replace them with similar renewable sources, aiming to make rubber formulations more environmentally friendly. In this work, the natural rubber compounds were prepared and the vulcanization characteristics, dynamic mechanical properties and morphology of compounds containing the natural oil were compared with those of the vulcanized standard, which was prepared by using naphthenic oil. The results indicated that the substitution of naphthenic oil by soybean oil induced variations in all properties; this natural oil showed to be a good alternative as a processing aid instead of petroleum-based oils. However, the results of Atomic Force Microscopy (AFM) showed that the use the soybean oil in formulations with silanized silica altered the dispersion of these fillers.

Keywords: Natural rubber, silanized silica, soybean oil.

I. INTRODUCTION

Processing aids are organic substances that, when added to the polymers, improve their flexibility and their processability. They are largely used to reduce the viscosity and the elasticity of the pre-vulcanized materials, so the capacity of mixing with other additives into elastomeric matrix and their fluidity during molding are enhanced [1]. Processing aids are classified in two different categories: the plasticizers, which act towards reducing intermolecular interactions, implying a reduction in the glass transition temperature (Tg) of the elastomer; and the lubricating agents, which reduce the compound viscosity with no changes in the Tg's values. Regarding the known processing aids, such as the paraffinic, aromatic and naphthenic oils, the latter is the most widely used due to good compatibility with most elastomers [2].

However, the growing use of these oil derivatives may generate serious environmental problems, mainly when they are disposed of in landfills and dumps. Thus, some studies have been conducted in order to develop environmentally correct compounds, using materials from natural sources [2-6].

Since January 2010, a European Directive, EEC n. 1272/2008, established that pneumatic manufacturers should reduce the amount of oils with high contents of polycyclic aromatic compounds (PAC), to avoid contaminating the environment [3–5]. Therefore, non-pollutant and biodegradable vegetable oils deriving from renewable sources have been an alternative to be used as replacements for plasticizers/lubricants for rubber compounds. The literature presents some studies about processing aids, such as oils from: soybean [3,5], castor [6], palm [7], coconut [8], peanutand liseed [9] in elastomeric compound, where these same ones showed satisfactory results. It is known that this compound is predominantly composed of triglycerides, which are products deriving from the condensation between glycerol and fatty acids.

When a new component is added to a rubber compound, attention must be played about its influence on the vulcanization reaction. Since accelerated vulcanization is a complex process, any change, such as in the pH or compounds that can participate of the reaction and alter the mobility of the chains, can have a drastic influence on its kinetics and results. Dasgupta et al. [10] analyzed compounds of natural rubber with different types of oils, such as vegetable oils, aromatic, naphthenic and paraffinic oils. They observed that some mechanical properties were influenced, mainly with the use of soybean oil, showing an increase in tensile strength.

Ismail et al. [7] studied the effect of fatty acid present in palm oil as a vulcanization activator in carbon black filled natural rubber compounds. They observed that the cure time (t_{90}) and the process safety time (t_{s2}) increased with the increased concentration of the palm oil fatty acid, retarding the vulcanization process.

The same authors [7] studied the effects of fatty acids derived from palm oil in different elastomeric compounds (natural rubber and epoxidized natural rubber). In this study, the authors describe that larger amount of acid acts as an activator in the vulcanization process and reduces the reversal process due to the formation of more stable connections.

Nonetheless, these investigations have been limited to palm oil and to compositions without filler, or those containing carbon black or calcium carbonate. In turn, the use of these oils with silanized silica, which is a filler increasingly more used in rubber compounds, has not yet received due attention [12,13].

The aim of this study is to investigate the influence of soybean oil addition on the vulcanization characteristics, dynamic mechanical properties and on the morphology of a compound reinforced with silanized silica, and comparing to the use of petroleum-derived naphthenic oil.

II. MATERIALS AND METHODS

2.1. Materials

The materials used in this study are: Natural Rubber (NR) from Lanxess (Duque de Caxias, RJ, Brazil); zinc oxide (ZnO with 80 wt% of Zn) (Agrozinco Indústria and Comércio Ltd., Ferraz de Vasconcelos, SP, Brazil); stearic acid (Proquitec Indústria de Produtos Chemical S/A, Vargem Grande Paulista, SP, Brazil); naphthenic oil Agecom 600 N (Agecom Produtos de Petroleum Ltd., Mauá, SP, Brazil); sulfur (Basile Chemical Indústria and Comércio Ltda., São Paulo, SP, Brazil); 2-mercaptobenzothiazole (MBT) (Interchemical Comércio and Indústria de Produtos Chemical Ltd.); and tetramethyl thiuram disulphide (TMTD) (Interchemical Comércio and Indústria de Produtos Chemical Ltd.). Silanized silica (GR COUPSIL®113/8113 - ULTRASIL® VN3/Si9® Bis(triethoxysilylpropyl)tetrasulfide - Evonik Industries) was used as the filler [14]. The soybean oil was provided by Química Madater Indústria e Comércio Ltda. (EstânciaVelha, RS, Brazil). Soybean oil has acidity of 0.859 (mg KOH /g) and a relative density at 25 °C in 0.9225g/cm^3.

2.2 Characterization of soybean oil (SO) and naphthenic oil (NO)

To better understand the influence of soybean oil (a substituent of the naphthenic oil) in the proposed formulations, some tests were conducted in order to understand their chemical composition and structure.

2.2.1 Thermogravimetric analysis of soybean and naphthenic oil

Thermogravimetric (TGA) analyses were conducted to provide information about the composition and thermal stability of soybean and naphthenic oil. This analysis was performed by a TGA Q500 (TA Instruments, New Castle, DE, USA) device. About 6-7 mg of each sample was heated from room temperature up to 700 °C under nitrogen atmosphere at heating rate of 10 °C/min. All the measurements were made in duplicate.

2.3. Rubber compound preparation

The elastomeric compositions were prepared with the following proportions in parts per hundred of rubber (phr): NR (100), ZnO (5), stearic acid (1), Silanized silica (50), naphthenic oil (5), sulfur (2,5), MBT (1), and TMTD (1). The naphthenic oil was replaced with the soybean, and we used the following nomenclature: NO-5 (5 phr of naphthenic oil); SO-5 (5 phr soybean oil); SO-10 (10 phr soybean oil) and SO-15 (15 phr soybean oil). Most of the additives were mixed using a Banbury mixer (Copé trademark), with an amount of 1.20 kg by mixing, using speed of 50 rpm rotors with a discharge temperature of 125° C. After the first mixing step, the accelerated vulcanization components were incorporated (sulfur and accelerator) in a two-roll mill.

2.4. Cure characteristics

The cure characteristics were determined using a *Rubber Process Analyzer (*RPA 2000, Alpha Technologies) at the vulcanization temperature of 160 °C, according to ASTM D2084. The calculated cure parameters include: cure time t_{90} (90% of the maximum torque); scorch time t_{s1} (indicating the process safety time); maximum torque M_H (related to the molecular stiffness); minimum torque M_L (proportional to the initial viscosity); and $\Delta M = M_H - M_L$ (which it can be correlated with the crosslink density). The effect of reversion in the compositions was also calculated, according to Ismail et al. [7]. The percentage reversion R is defined as:

$$R = \frac{(M_{max} - M_t).100}{(M_{max} - M_{min})}$$

Equation 1

where: M_{max} is the maximum torque, M_t is the torque at time t (60 min), M_{min} is the minimum torque, and CRI (Cure Rate Index) values were calculated by using Equation (2) on the RPA:

$$CRI = \frac{100}{t_{90} - ts_1} \quad \text{Equation 2}$$

2.5. Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) measurements were performed using a TA Instruments DMA Q800. The compression molded samples with dimensions of (35x13x3) mm^3 were tested on a dual-cantilever fixture. The temperature used in the experiments ranged from −100 to 100 °C, at a heating rate of 3 °C/min and frequency of 1 Hz. The strain was set at 25 µm. The storage modulus (E') and loss modulus (E'') were calculated as a function of temperature and the glass transition temperature (Tg) was determined from the maximum of the E'' curves.

2.6. Atomic force microscopy

Atomic force microscopy (AFM; NX10, Park systems, Suwon, Korea) was used to investigate the surface morphology of the samples. Phase images were recorded in the tapping mode using a silicon tip. The probe oscillated at a resonance frequency of approximately 320 kHz with spring constant of 48 N/m.

2.7. Payne effect

The difference (ΔG') between elastic modulus at low strain (G'0) and high strain (G'∞) is a measurement of Payne effect attributed to the filler structure. It can be understood as physical bonds of the filler interaggregates (van der Waals - London forces) which are broken at high strains. This technique was used to evaluate filler-filler interactions in the compounds using the Rubber Processing Analyser - RPA 2000. The elastic modulus was obtained according to the variation of strain from 1 to 300% for the calculation of the Payne effect in unvulcanized compositions at 100°C.

III. RESULTS AND DISCUSSION

3.1 TGA characterization of soybean and naphthenic oils

Figure 1 shows that the soybean oil is more thermostable than naphthenic oil. The soybean oil started to lose mass above 300°C [15], while naphthenic oil started to degrade above 160°C [16]. According to the literature, the superior thermal stability of soybean oil occurs due to the presence of natural antioxidants, which retard the degradation of this oil [17].
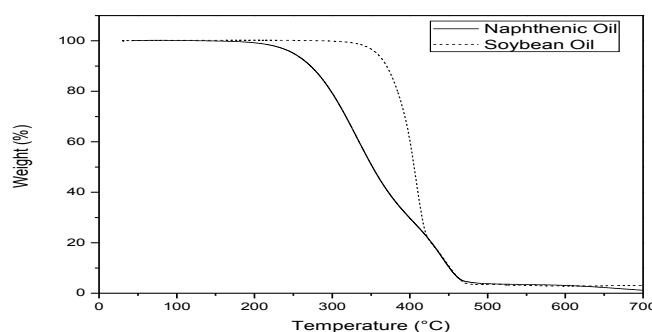

Figure 1. TGA curves of the Naphthenic and Soybean oils.

3.3 Characterization of the compounds
Cure Characteristics

Table 1 shows the results of the RPA analyses, in which the scorch time (t_{s1}), vulcanization time (t_{90}), minimum torque (M_L), maximum torque (M_H), torque values difference (ΔM) and cure rate index (CRI) were evaluated.

Table 1: Cure characteristics of the compositions.

Sample	t_{s1} (min)	t_{90} (min)	M_L (dNm)	M_H (dNm)	ΔM (dNm)	(CRI) (min^{-1})
(NO-5)	0.28	1.19	13.36	22.24	8.88	109.89

(SO-5)	0.69	1.87	10.90	21.74	10.84	84.74
(SO-10)	0.66	1.86	10.91	21.67	10.76	83.33
(SO-15)	0.99	2.19	6.86	15.60	8.74	83.27

According to the results, the substitution of naphthenic oil by soybean oil caused changes in all the cure parameters (t_{s1}, t_{90}, M_H, M_L, ΔM and CRI) of the NR compound. The pre-cure time (t_{s1}) values show that, for samples NO-5 and SO-5, which contain the same amount of oil in phr, the simple substitution of naphthenic oil by soybean oil led to an increase in the t_{s1} value, delaying the beginning of the vulcanization reactions. The SO-10 and SO-15 samples exhibited the same behavior. Ismail et al. [7] reported the same behavior when using palm oil. The authors proved that the fatty acid concentration in the palm oil had caused an increase in the safety time (t_{s1}), having a very similar behavior to other retarders, such as benzoic acid.

Regarding the optimum cure time (t_{90}) values, the NO-5 and SO-5 samples exhibited distinct vulcanization times. The samples with soybean oil presented an increase in vulcanization time, especially those with higher oil concentrations (ex: SO-15). These results are supposed to reflect the effect of the chemical composition of the different oils. According to Bezerra et al. [18] and Costa el al. [19], soybean oil presents unsaturated fatty acids (oleic and linolenic acids) in their structure; this makes their active centers favor unexpected lateral reactions and instability in the zinc complex, which to retards the vulcanization time.

The M_L (minimum torque) values showed that by substituting naphthenic oil by soybean oil (NO-5 → SO-5) promoted a reduction in these values, confirming its more efficient plasticizer and/or lubricant action than NO. This reduction is also verified for compositions with greater soybean oil (SO-10 and SO-15) contents. Here, this decrease in viscosity was already expected due to the increase in the amount of oil, favoring the increase in space between chains, facilitating sliding between them when the shear stress is applied during the test [3,5, 20].

The results of the maximum torque (M_H) showed that the NO-5 and SO-5 samples presented similar values. However, the sample with a higher amount of soybean oil (SO-15) presented a significant decrease in this value. Probably 15 phr of soybean oil was the amount that favored the increase in free volume between the NR chains. Hence, SO-15 sample presented an increase in the number of freedom degrees for the different conformations of the molecular structure, which decreased its resistance to flow (of the non-crosslinked fraction) and also reduced the "stiffness" of the cured material (reduction in torque amplitude - M_H) [21].

Table 1 also show the data of ΔM, which represents the degree of crosslinking of each sample. It is noticed that samples with 5 to 10 phr of soybean oil exhibited the highest ΔM values. Probably, these samples presented better interactions at the interface between filler and rubber. Assuming that the value of torque obtained from the vulcanization curve was proportional to the final number of crosslinks, it was noticed that the samples 5 and 10 phr soybean oil have very similar amounts of crosslink [22,23,24], this will be applied to the DMA analysis.

Regarding the CRI results, samples with soybean oil were vulcanized in longer times; consequently, these samples presented smaller CRI values. These results were expected due primarily to the acidity of soybean oil, which could have delayed the onset of vulcanization reactions. However, there was a decrease in the vulcanization speeds.

Figure 2 show the curves torque versus time, where it is possible to observed the reversion processes. From Figure 2 and using the equation 1, the reversal percentage of each sample was obtained (see Table 2). The results show that the reversion processes decrease in two conditions: when the soyben oil was embedded into NR compounds; and when the soybean oil content was increased in each composition. According to the literature [21], reversal is a term generally used to loss of non-oxidative heat aging network structures. It can be the result of a long vulcanization time (overcure) or aging hotter sections. It is most severe at temperatures above about 155 °C. It occurs in vulcanizates containing a large number of polyssulfidic crosslinks. Regarding the results, two hypotheses may be raised: (1) The soybean oil can have prevented the occurrence of non-oxidative degradation reactions, protecting the crosslinks and the main chains of rubbers; (2) this vulcanization system can be semi efficient, where the presence of fewer polysulfidic bonds can have favored the thermal resistance of the rubber compositions. The crosslinks formed during the vulcanization process with soybean oil are more stable.
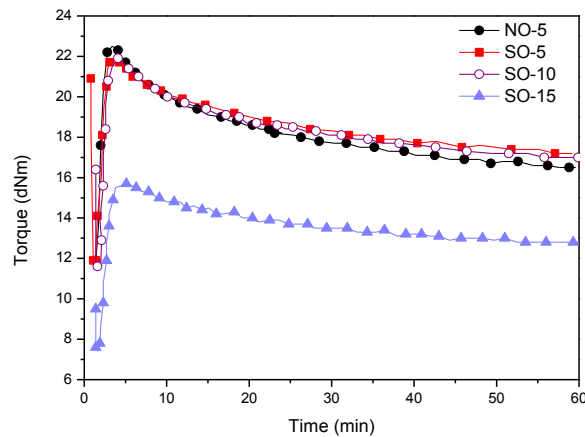
Figure 2: Torque versus time graph.

Table 2. Reversion (%) data.

Samples	R (%)
NO-5	58.55
SO-5	41.92
SO-10	43.40
SO-15	32.03

Dynamic Mechanical Analysis

The dynamic mechanical analysis (DMA) is one of the most important techniques that can be used to quantify the viscoelastic behavior of elastomers. Storage modulus (E') and loss modulus (E") were analyzed in the present work [25]. This behavior can be attributed to the molecular mobility increase of the polymer chains above the T_g. Figure 3 shows the storage modulus curves. Analyzing the data before Tg, it was observed that the sample containing 5 phr of naphthenic oil (NO-5 sample) presented a greater reduction of the stiffness in relation to the SO-5 sample. For samples with 10 and 15 phr of soybean oil, the stiffness has decreased when compared to SO-5 sample. It was already expected, once these oil contents promoted a greater movement of some segments of the chains. So, the higher the concentration of oil in the compound, the higher the mobility of the segments of the chains presented in the NR. In the glass transition region, the mechanical behavior of amorphous polymers varied from typical behavior of a rigid material to an elastomeric material [26,27]. Concerning the rubber plateau (above T_g), which is related to the crosslink, it may be noted that the samples containing the same amount of oil (NO-5 and SO-5) exhited higher E' values (i.e., higher crosslink) as compared to other samples (SO-10 and SO-15), corroborating to the ΔM values (as seen before).
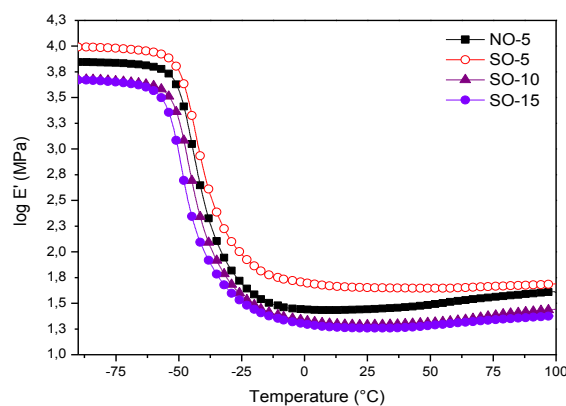

Figure 3. Storage modulus (E') as a function of temperature.

Figure 4 shows the loss modulus *versus* temperature curves, where the glass transition temperature (T_g) of each sample was determined in the maximum point of the curves (see Table 3). According to the data from

Table 3, the samples containing the same amount of oils from different sources (NO-5 and SO-5) had very similar values of T_g. This was already expected, since they present similar amounts of crosslink as previously seen in Figure 3. However, the samples with higher amounts of soybean oil showed a trend to shift their T_gs to lower temperatures, particularly the SO-10 sample. These results indicate that above 10 phr of soybean oil, NR chains have acquired sufficient energy and they were able to move at lower temperatures. In these cases, the variation of Tg reflected the crosslink density of these samples, attributing to their lower crosslink densities (reflected in the storage module measures).
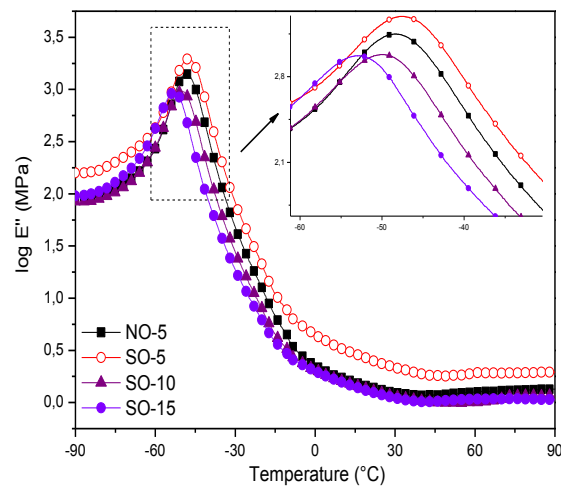

Figure 4. Loss modulus (E'') as a function of temperature.

Table 3. Glass transitions of the compositions.

Samples	T_g (°C)
(NO-5)	-48
(SO-5)	-47
(SO-10)	-50
(SO-15)	-53

Atomic force microscopy (AFM)

The AFM analysis provided phase images (Figure 5), where different components present in each sample were observed. Garcia et al. [29] described that the morphology can be analyzed by the different color in the images, where these differences represent the hardness scale. Since the samples are mostly composed of natural rubber, silica and oils, depending on the formulation, 2 or 3 color scales were observed. As the fillers present a spherical shape, it was concluded that the lighter areas represent the stiffer materials (silica), the areas with intermediary shades represent the NR and the processing oil (if the oils are between the rubber chains), and the darker areas (less rigid materials or "soft" materials), which represent segregation of processing oils in NR. For sample NO-5, which contains 5 phr of naphthenic oil, greater homogeneity and better dispersion of silanized silica in NR were observed.

This results were not verified in the samples with soybean oil. The greater the amount of soybean oil added to NR, the worse was the dispersion of the fillers in the elastomer. It was also possible to observe segregation of the soybean oils in the rubber matrix (represented in Figure 6 by an arrow). Despite the use the silanized silica (as filler) improves its compatibility with the elastomeric matrix, the silanized molecules may have hindered the dispersion of the fillers, favoring their aggregation. Some works in the literature [30, 31] have showed that the use of natural oils improved the dispersion and distribution of fillers (as carbon black) in the elastomer, since there is some interaction between oil/filler and oil/elastomeric matrix. One of these works reported the morphology and the interactions between NR, carbon black and vegetable oil [31]. In this work, the authors proved the presence of interactions between the long chains of unsaturated fatty acid esters of the vegetal oil with the polar groups of the carbon black present on their surface (phenol, carboxyl and lactones) and also the interactions between the non-polar parts of these oils with the NR molecules. However, as seen previously, the silanized silica into the mixture did not favor these interactions. It is known that the silica surface contains silane (non-polar), which has a chemical affinity with the natural rubber (non-polar).
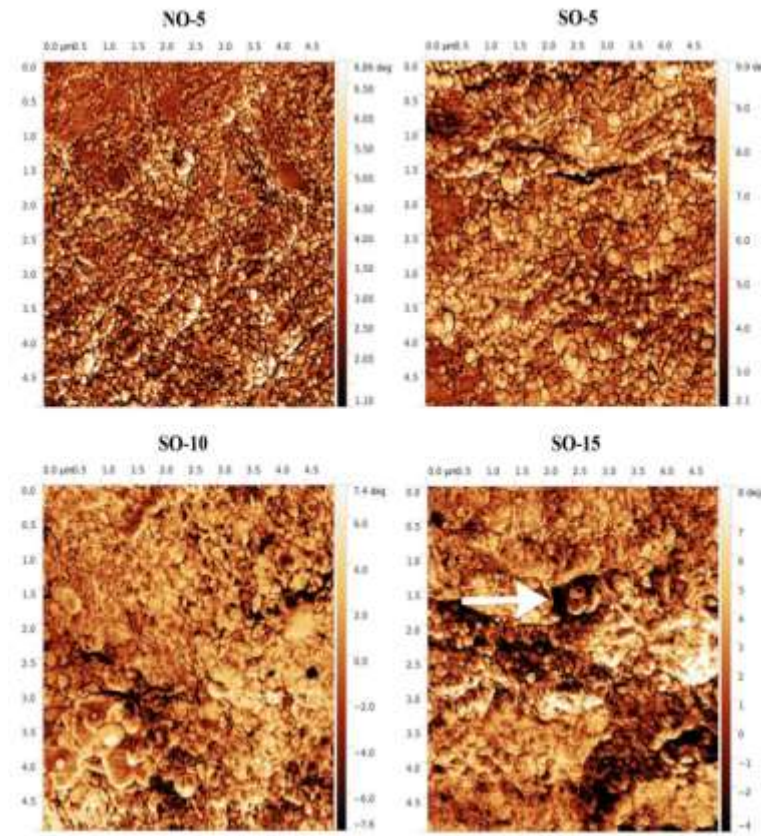
Figure 5. Tapping mode AFM phase images of the samples

Payne Effect

The study of the Payne effect is a valuable rheological tool to understand the reinforcement mechanism of rubber compounds with active fillers [32]. It is based on the nonlinear viscoelastic behavior of the compound at high strains and it is a measure of the particle-particle interaction in a reinforced polymer.
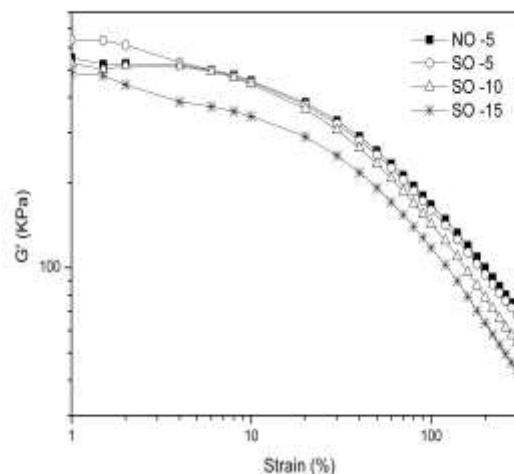

Figure 6. G' of the compositions developed at high deformations.

Figure 6 shows this non-linear viscoelastic behavior in all samples, where the values at low strain modulus (G' 1%) are higher than the values at high strain modulus (G' 300%), as expected. As mentioned in literature [32,33,34], filler-filler interaction may restrict the motion of the elastomeric chain under strain, increasing the G' values. Regarding our work, it is necessary to understand the reason of the results in the Figure

6. Parameters related to dispersion and distribution of the filler can change the dynamic properties of each sample, and the presence of soybean oil and its amount may have contributed with these results.

At low strains, the samples with 5 phr exhibited distinct results for the different oils. The SO-5 sample presented the higher stiffness compared to the NO-5 sample, and this behavior is maintained in higher SO content. These results may be attributed to different affinities between the oils and the fillers. Because the silanized silica has little affinity with the soybean oil, it was not able to reduce the filler-filler interaction, and thus it was forced to migrate to the regions among the particles

At higher strains, there was the breakdown of the filler network, i.e., disruption of the interaggregate bonding of the fillers. The difference between G'1% and G'300% (ΔG '= G'1% - G'300%), reported in Table 4, is higher for SO-5 composition. This result indicates a higher amount of broken filler agglomerates, which were effectively contributing to the performance of the compound.

Table 4. Payne Effect of natural rubber compositions with silanized silica and naphthenic oil (NO) or soybean oil (SO) in different ratios.

Samples	Payne Effect (KPa) ($\Delta G' = G'1\% - G'300\%$)
NO-5	481.31
SO-5	571.49
SO-10	473.59
SO-15	444.43

IV.   CONCLUSION

In this work, the performance of soybean oil as well as naphthenic oil in compositions with natural rubber were evaluated. For low content addition, the properties measured may be compared to naphthenic oil. However, substantial changes were observed when the soybean oil was incorporated in elastomeric compositions: the TGA analysis confirms the higher thermostability of vegetable oil due to the presence of possible natural antioxidants. According to the curing properties, the use of soybean oil promoted an increase in the vulcanization and in the scorch time, maybe reflecting the acidity of this compound. Also, the results showed that the soybean oil favored the formation of stable chemical bonds. The AFM analysis presented an interesting and effective tool helping to monitor changes in the compositions morphology. Additionally, this method allowed to observe the segregation of the soybean oil within the compositions, including formulations up to 15 phr of SO. The Payne effect corroborates with these results, since the composition with lowest amount of soybean oil presented the biggest difference in the modulus at high and low strain, which indicates higher filler-filler interactions breakup.

ACKNOWLEDGEMENTS

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