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Variation of technological properties of field natural rubber lattices from *Hevea brasiliensis* clones and natural rubber-based compounds

Diego Hernán Giraldo-Vásquez [a] & Sandra Milena Velásquez-Restrepo [b]

[a] *Departamento de Ingeniería Metalúrgica y de Materiales, Universidad de Antioquia, Medellín, Colombia. dhernan.giraldo@udea.edu.co*
[b] *Grupo BIOMATIC - Biomecánica, Materiales, TIC, Diseño y Calidad para el sector cuero, plástico, caucho y sus cadenas productivas, Centro de Diseño y Manufactura del Cuero del SENA, Itagüí, Colombia. smvelasquez@sena.edu.co*

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Abstract

Natural rubber (NR) is a widely used biopolymer, but the variability of its properties is a great disadvantage. In this work, variation during a 6-month period of total solids (TSC), dry rubber (DRC), ash, volatile-matter, and nitrogen content of field natural rubber (NR) lattices and mechanical properties of NR solid sheets-based compounds was studied. NR samples were collected from IAN 710, IAN 873 and FX 3864 clones of *Hevea brasiliensis* at a plantation within the state of Antioquia, Colombia. Rainfall, environmental temperature, relative humidity, and sunlight hours were daily registered. NR sheets-based compounds were manufactured and their rheometric and mechanical properties were measured. Significant variations ($p<0.05$) among clones and tappings for most of the measured properties were found. Leaf senescence was the phenological stage that presented the greatest influence on NR properties. Some recommendations to control the variation of properties of raw NR during manufacturing of rubber goods were stated.

Keywords: Natural rubber; process control; variability in raw materials; rubber testing.

Variación de las propiedades tecnológicas de látex de campo de caucho natural de variedades clonales de *Hevea brasiliensis* y de compuestos de caucho natural

Resumen

El caucho natural (NR) es un biopolímero ampliamente usado, pero la variabilidad de sus propiedades es una gran desventaja. En este trabajo se estudió la variación del contenido de caucho seco (DRC), total de sólidos (TSC), cenizas, material volátil y nitrógeno de látex de campo de NR, así como de las propiedades mecánicas de compuestos basados en láminas sólidas de NR, evaluando muestras recolectadas durante 6 meses. Las muestras se obtuvieron de tres variedades clonales de *Hevea brasiliensis* -IAN 710, IAN 873 and FX 3864- cultivadas en una plantación en Antioquia, Colombia. En el cultivo donde se recolectó el látex se monitorearon diariamente pluviosidad, temperatura ambiente, humedad relativa y horas de sol. Se moldearon compuestos emplenado láminas de NR, determinando sus parámetros reométricos y sus propiedades mecánicas. Se encontraron diferencias estadísticamente significativas ($p<0.01$) para la mayoría de las propiedades evaluadas como efecto de la variedad clonal y la época de recolección. La defoliación fue la etapa fenológica que presentó la mayor influencia sobre las propiedades del NR. Se presentan algunas recomendaciones para controlar la variación de las propiedades del NR durante la fabricación de artículos con este material.

Palabras clave: caucho natural; control de procesos; variabilidad en materias primas; ensayos a cauchos.

1. Introduction

Natural rubber (NR) is a highly demanded raw material for manufacturing a wide range of products. Most of the NR used in industrial processes is obtained by tapping the latex of *Hevea brasiliensis trees*, followed by preserving the NR latex in liquid form or crumbing and drying it to produce its coagula [1]. Since NR lattices tapping and collection involves many manual-labors, NR production is a high impact alternative for the socio-economic development of agricultural communities in Asia, Africa, and South America [1,2]. Projections of the International Rubber Study Group -

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IRSG indicate that the world NR demand is forecasted to grow to 12.5 million tons in 2016, increasing to 16.0 million tons in 2024, continuing the upward trend of recent years [3]. As an alternative for the improvement of farmers' incomes, almost six thousands of them have established and harvested small NR plantations in Colombia in the last two decades.

Productivity of NR plantations has been improved by incorporating new genetic varieties of *Hevea brasiliensis* and evaluating the properties of the NR obtained from the existing ones; several studies on the properties of NR obtained from RRIM 600, WG 1, GT 1, IAN 873, FX 3864, and PB 235 clonal varieties harvested in Brazil have been carried out [4-9].

As a natural raw material, properties of NR strongly depend on the tree clone type, tapping frequency, weather, and season. These yields to variability in NR properties, what generates loss of materials and energy during the various stages of industrial processes [10]. Variations can be explained because NR latex is a very complex colloidal system. NR particles comprise 30–45% of the latex weight, but lipids, proteins, and sugars are also latex biochemical constituents; type and ratio of each substance contribute to rubber specific properties. During the drying process of NR sheets, thermo-oxidation and storage hardening may result in changes of NR bulk properties [7].

The objective of this study is to assess the variation of NR latex of three clones that are planted in Colombia and Brazil, during a six month period. Mechanical properties of compounds manufactured with NR sheets from coagula of the same plantations were also evaluated.

2. Methodology

IAN 710, IAN 873 and FX 3864 are *Hevea brasiliensis* clones developed in Brazil by crossing original Brazilian species with the Asian clone PB 86. These three clones are widely harvested in Brazil and they are the most planted *Hevea* clones in Colombia [11]. FX 3864 has presented good resistance to South American Leaf Blight (SALB) due to the attack by *Microcyclus ulei*, while IAN 873 exhibits better productivity and denser foliage than IAN 710 and FX 3864 [11,12].

In this study, NR lattices from IAN 710, IAN 873 and FX 3864 clones were collected and evaluated over a 6-month period (February–July 2012). During this study, leaf senescence occurred between late January and February, leaf development between late February and March; from late March to July, mature leaf was the phenological stage. The trees selected for collecting samples were 14 years old and 8 years of tapping. Latex tapping was carried out every two days (D2 system), to 36 trees of each clonal series. Trees with similar diameter trunks were chosen. Plantation is located at Tarazá municipality, Antioquia, Colombia.

A randomized complete block design was used for NR collection from each clone, for lattices and for sheets and their compounds. An analysis of variance (ANOVA) was carried out for each test condition, using a significance level of 0.01. Tukey's test was used for each test condition to identify differences among means.

Rainfall, environmental temperature, relative humidity, and sunlight hours at plantation were daily registered during the study.

Field latex samples were monthly collected and stabilized prior to their analysis in laboratory. Dry rubber (DRC), total solids (TSC), ash content, volatile-matter content, and nitrogen content were measured for each sample according to ASTM D1278 [13]. Reference values for the properties were taken from ASTM D 2227 [14].

TSC tests were carried out in an oven at 100 °C for 2 hours using about 2.5 ± 0.5 g of liquid field latex. Mass was determined by an analytical balance. TSC was calculated by eq. (1):

$$\% \, TSC = \frac{C - A}{B - A} * 100 \tag{1}$$

where: A is the petri dish mass in grams, B is the petri dish mass plus the original sample in grams, and C is the petri dish mass plus the dry sample in grams.

For determining DRC, a co-precipitation of some constituents which did not include the rubber was made during the latex acid coagulation. DRC was calculated by eq. (2):

$$\% \, DRC = \frac{dry\ mass\ of\ coagulum}{mass\ of\ the\ wet\ sample} * 100 \tag{2}$$

Ash content tests were carried out in a muffle furnace at a temperature up to 550 ° C, with approximately 5 g of dry rubber per sample. The final mass of residual ashes in the crucible was weighted by using an analytical balance and the final ash content was determined by eq. (3):

$$\% \, Ash\ content = \frac{C - B}{D} * 100 \tag{3}$$

where: D is the sample mass, B is the empty crucible, and C is the crucible plus the ash mass.

To determine the volatile-matter content, about 10 to 12 grams of rubber were placed on a watch glass and heated in a muffle furnace at a temperature of 100 ± 5 °C until getting a constant weight. Samples were placed in a desiccator until these were cooled at room temperature; samples were weighted after cooling. Volatile-matter content was calculated by eq. (4):

$$V = \left[\left(\frac{A - B}{A} \right) - \left(\frac{C - D}{C} \right) \right] * 100 \tag{4}$$

where: V is the volatile-matter content, A is the sample mass at the beginning, B is the sample mass after its homogenization in the mill, C is the sample mass before drying in the muffle furnace, and D is the sample mass after drying in the muffle furnace.

Measuring of DRC, TSC, ash and volatile-matter content was carried out in triplicate for each test condition. Nitrogen (N) content was measured by the Kjeldahl process applied to 2 gr of each sample cutted into small pieces, as stated in ASTM D1278 standard [13]. N content measure was carried out once for each test condition.

NR sheets were obtained every two months at the plantation. Field lattices were coagulated for 24 hours using an acetic acid solution diluted in water at 1% v/v. After coagulation, the samples were washed to remove residual acetic acid and rolled using an open rolls mill. Finally, the sheets were outdoors dried for 8 days, under a roof top.

NR sheets were mixed with sulfur as vulcanizing agent, stearic acid, and zinc oxide as activators, N-tert-butyl-2-benzothiazole sulfenamide (TBBS) as accelerator and carbon black as reinforcing filler. Only the type of NR was varied among compounds, seeking to evaluate the variation of properties related to the origin of NR. Accelerator/sulfur ratio and sulfur content were chosen to obtain a conventional vulcanization system.

Mixing was carried out in an open rolls mill. Rheometric cure curves at 160 °C for the compounds were obtained according to ASTM D 5289 [15,16]. From rheometric tests, the optimum vulcanization times (t90) were determined. Specimens for tensile, uniaxial compression, and compression-set test were manufactured by compression molding. Shore A hardness was determined for cured cylindrical specimens. Uniaxial compression tests of samples after compression-set tests were also carried out.

Tensile tests and hardness measurements were carried out in quintuplet for each test condition, and uniaxial compression and compression-set tests were carried out in triplicate for each test condition

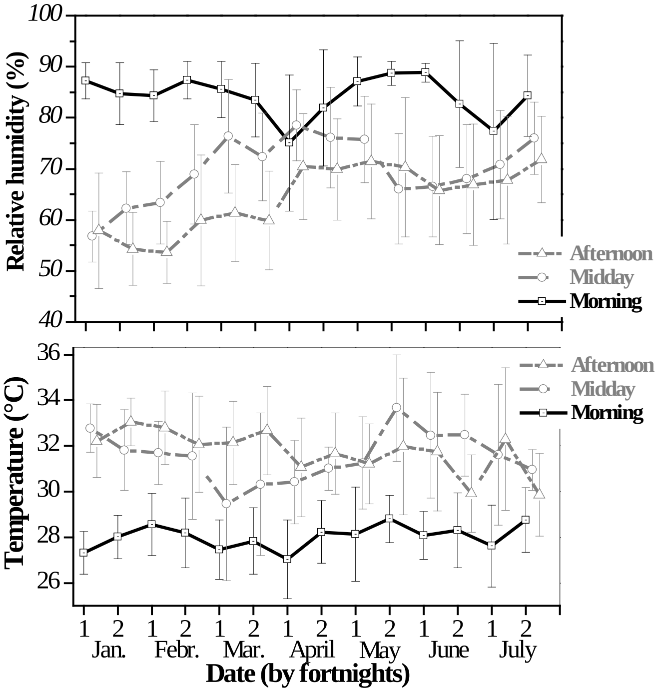

Figure 1. Temperature and relative humidity at plantation where NR lattices were collected. Average and standard deviation are plotted. Data were horizontally shifted in order to facilitate the visualization of results.
Source: The authors.

3. Results and discussion

3.1. Climatic variables

As mentioned before, climatic conditions at plantation could influence the NR properties. Seeking to identify if there is any relationship between climatic variables and NR lattices and sheets studied in this work, measures of climatic variables are shown in Figs. 1 and 2. Data were taken daily, but results were grouped by fortnights in order to facilitate the visualization of each variable behavior.

It can be observed that dry season occurs between January and February, with some rainy days since April to July. As expected, relative humidity at midday and afternoon were related to rainfall and sun hours per day. Rainfall reached the highest values among all the measures during the second fortnight of May. It is important to notice that relative humidity was generally higher at morning, when tapping was carried out.

The influence of climate variables behavior on NR properties will be discussed in next sections.

3.2. Technological properties of lattices

Monthly variation of dry rubber content (DRC) and total solids content (TSC) by clonal series is shown in Figs. 3 and 4, respectively. It must be taken into account that TSC and DRC are strongly related because TSC represents the amount of all nonvolatile materials present in latex; these nonvolatile materials include rubber itself. It is well known that in *Hevea brasiliensis* latex, rubber contains more than 90% of poly (*cis*-1, 4-isoprene) [5], therefore, DRC and TSC values are usually very close. DRC values are related with the physiological response of the tree because it is an indicator of the biosynthetic activity of lactiferous vessels [4, 6].

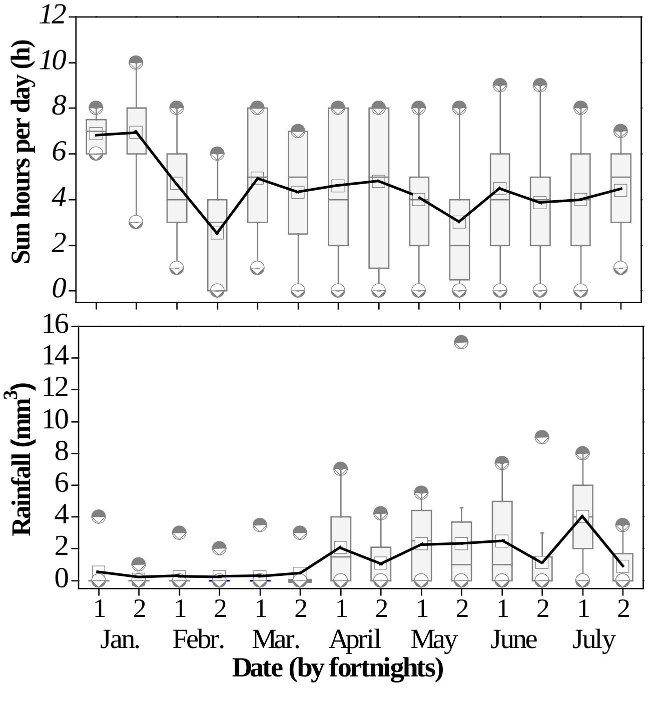

Figure 2. Boxplot of rainfall and sun hours per day at plantation were NR lattices were collected. Lines connecting the average values are showed to facilitate the visualization.
Source: The authors.

The highest TSC and DRC occur in February-March period and the lowest values occur in May for IAN 873 and FX 3864 clones. For IAN 710 clone, the highest TSC and DRC occur only in February and the lowest values occur in April. Lower values of the percentage of DRC and TSC generally match the few sun hours, high rainfall and relative humidity at midday and afternoon. This agrees with the description in several studies of Moreno et al. [4, 6]. DRC and TSC values are related to a decrease in the biosynthesis of the rubber tree between January and February when the foliation and flowering senescence begin. It is significant to notice that DRC and TSC for the three clonal varieties studied in this work are above the average values that are reported in literature [4-8].

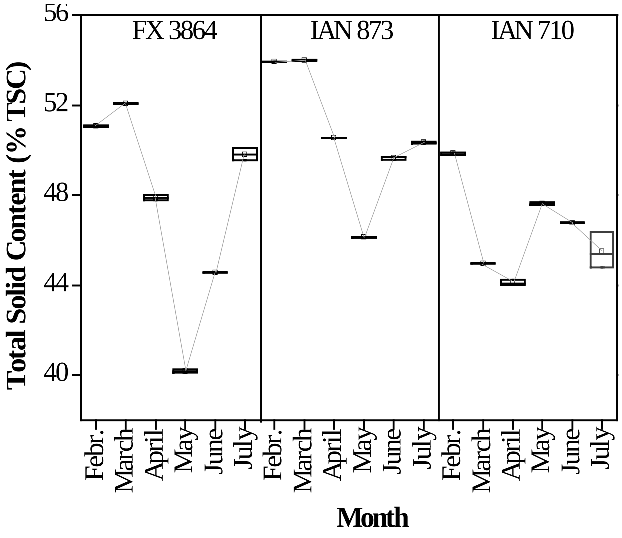

Figure 3. Monthly variations in TSC of field latex.
Source: The authors.

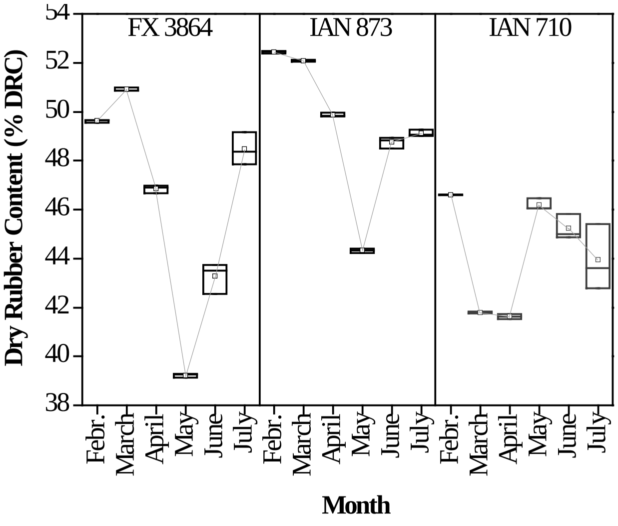

Figure 4. Monthly variations in DRC of field latex.
Source: The authors.

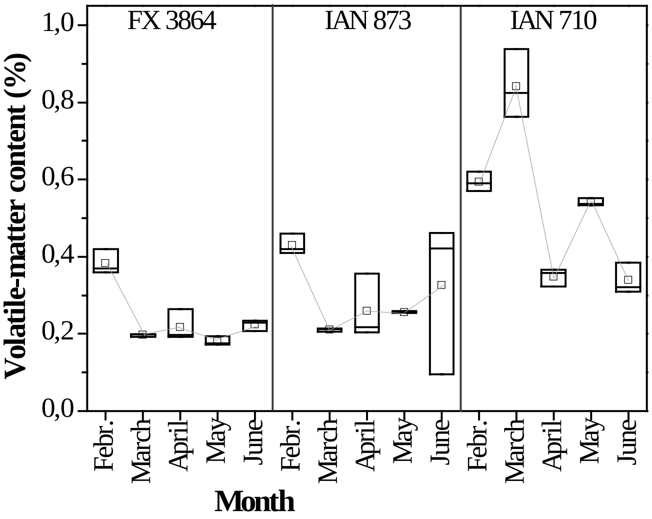

Figure 5. Monthly variations in volatile-matter content of field latex.
Source: The authors.

In Fig. 5, the variation of volatile-matter content is shown. Volatile-matter in NR latex is related to high amounts of moisture, as well as contamination with volatile substances during coagulation of rubber sheets. Volatile-matter content for most of the samples was less than the 0.8%, which is the maximum percentage allowed by ASTM D 2227; just in March the values were higher than the limit for IAN 710 clone. The variance in some samples of a same clone at the same collection time is due to the lack of greater control over the collection and processing of rubber carried out by farmers during tapping.

Highly significant variations ($p < 0.01$) among season and the clones were observed for TSC, DRC, and volatile-matter content. Season-clones interaction was also significant ($p < 0.01$) for these properties. Comparison of all the possible pairs of clones means through Tukey tests indicated that there were significant differences in TSC, DRC, and volatile-matter content. Variations of lattices properties suggested different performances among clones even at the same agronomic and climatic conditions, as reported in other studies on Brazilian and African NR [4-6,14].

Fig. 6 shows the variation of ash content. Ashes in NR latex are related to nonvolatile mineral fraction, including minerals inherent in the rubbery substance such as Ca and Mg [4,6]. Ash content of all the samples was below 0.60%, the maximum specified in ASTM D2227 standard [9]. ANOVA and Tukey tests indicated that no significant differences were observed among clones, or over the period of the study. N, P, K, Na, Cl and S are mobile in *Heveas*, while Zn, Cu, Mn, Fe, and Mg are partially mobile. When nutrients are absorbed by a process of constant reutilization, as occurs during leaf senescence, ash content tends to decrease, as observed in February for IAN 873 and IAN 710 [4,6].

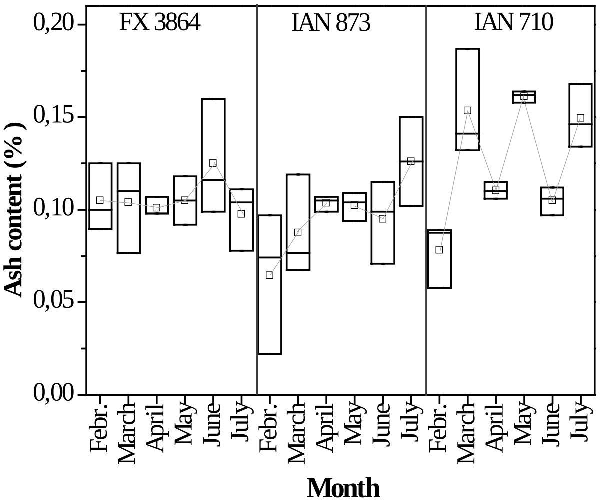

Figure 6. Monthly variations in ash content of field latex.
Source: The authors.

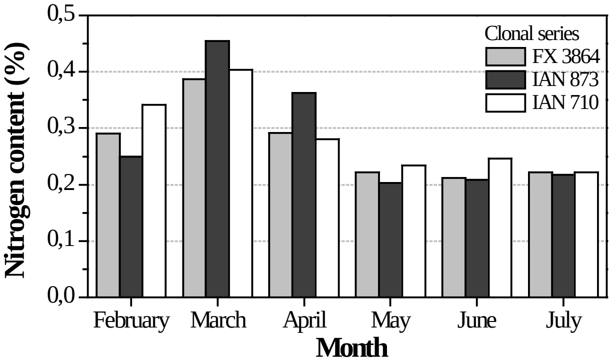

Figure 7. Monthly variations in nitrogen content of field latex.
Source: The authors.

Variation of nitrogen content is presented in Fig. 7. It can be observed that nitrogen content increased during leaf development (March). This is because during this phenological stage, the demand for nitrogen changes according to biosynthetic activity for latex production. Nitrogen content for all the samples was within the ASTM 2227 standard specification for industrial processes [14], regarding that the maximum value recommended is 0.6%. Latex from IAN 710 clone showed some differences in nitrogen content when compared to lattices from the other two clonal series. Aristizabal et al. reported that the higher DRC corresponds to the lower nitrogen content, which is related to the phenological stage [9]. In our work, this behavior was not observed.

3.3. Properties of NR sheets-based compounds

Figs. 8 and 9 show the variation in processing times according to rheometric tests. Compounds with NR tapped in April showed the highest processing times for the three clonal series. Differences in t90 and scorch time of clones could be related to changes in rubber plasticity and viscosity, due to the fact that of NR particles in latex are surrounded by a complex mixture of proteins, lipids, and fatty acids that can form long chains and interact with elastomer chains [16].

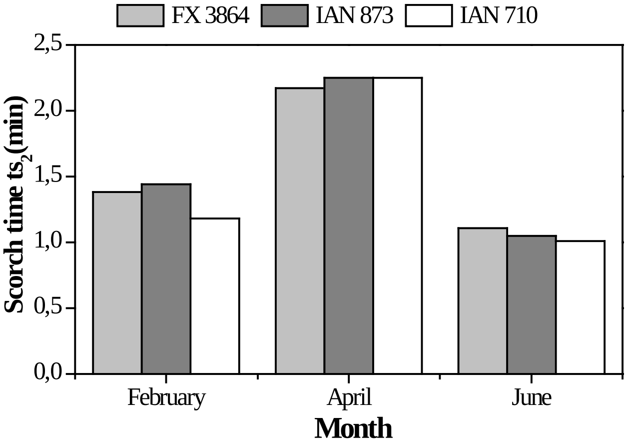

Figure 8. Variation in vulcanization induction times according to rheometric tests.
Source: The authors.

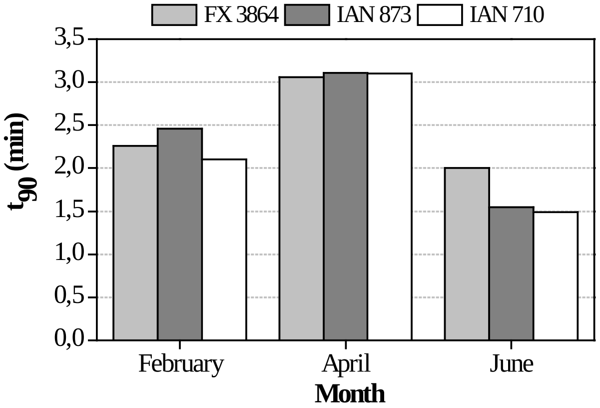

Figure 9. Variation in vulcanization times according to rheometric tests.
Source: The authors.

Another probable cause of variations is that drying and chewing are not rigorously controlled in small plantations. It has been reported that molecular weight and gel content in NR vary markedly with the drying conditions after washing with water, because storage hardening takes place after drying even if the natural rubber is left to stand at room temperature [10].

Moduli at 100 and 300 % of elongation in tensile tests for specimens cured according to rheometric tests are reported in Figs. 10 and 11, respectively. Compounds based on tapped NR in April showed the highest values of tensile moduli for the three clones. IAN 873 NR-based compounds had higher properties than the other clones. Some differences in tensile properties were observed over the time for each clone.

Fig. 12 shows the variation in Shore A hardness for specimens cured according to rheometric tests.

ANOVA demonstrated that hardness varied over the time for FX 3864 and IAN 873 clones. No variation in hardness was observed over the time for IAN 710 compounds. Compounds based on IAN 710 NR showed the lowest values of hardness, but for FX 3864 and IAN 873 compounds the hardness varied even in a same month.

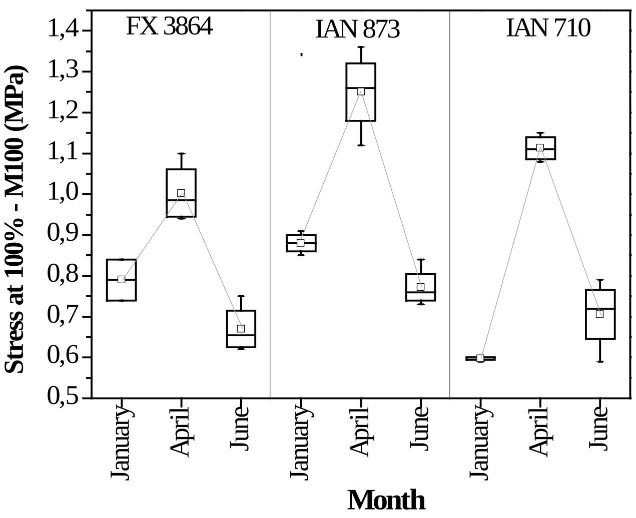

Figure 10. Tensile moduli at 100% (M100) of NR-based compounds.
Source: The authors.

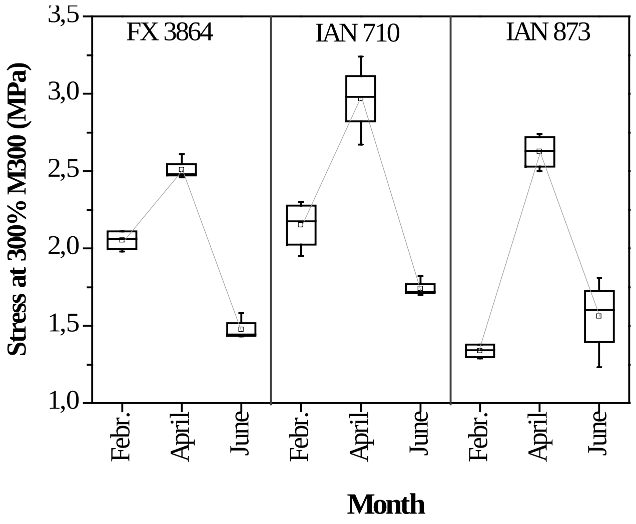

Figure 11. Tensile moduli at 300% (M300) of NR-based compounds.
Source: The authors.

Uniaxial compressive moduli for specimens cured according to rheometric tests are reported in Fig. 13. Compounds based on tapped NR in April showed the highest values of compressive moduli for the three clones. For the other test conditions, some differences in compressive moduli were observed over the time and among clones. Compression-set for specimens cured according to rheometric tests are reported in Fig. 14. The best compression-set values were presented during April for the three clones. IAN 710 compounds showed the worst compression-set of the three clones. Uniaxial compression tests after compression-set were carried out for comparing the resistance to change the mechanical properties under the effect of time and temperature.

Uniaxial compressive moduli after compression-set tests are reported in Fig. 15. All the specimens showed a decrease in compressive moduli, as an effect of the thermal aging

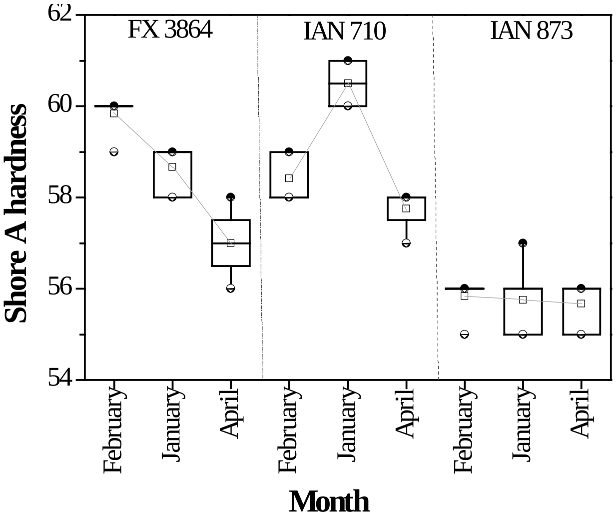

Figure 12. Shore A hardness of NR-based compounds.
Source: The authors.

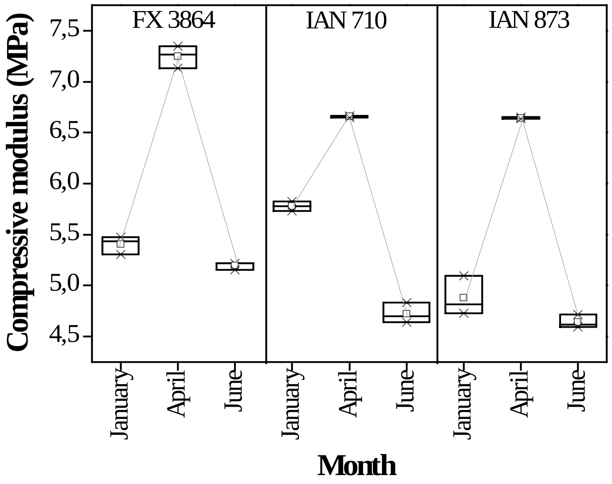

Figure 13. Uniaxial compressive moduli of NR-based compounds.
Source: The authors.

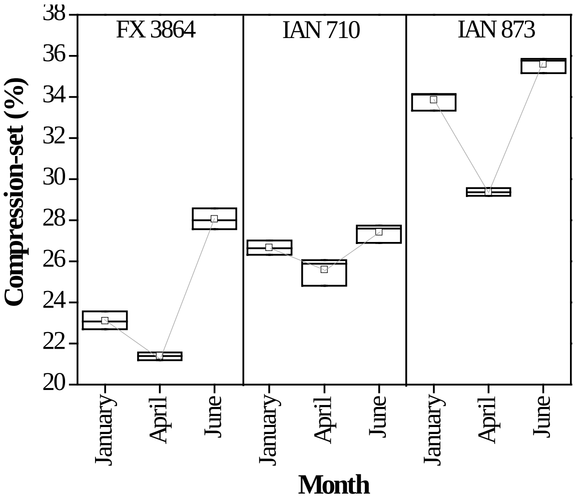

Figure 14. Compression-set of NR-based compounds.
Source: The authors.

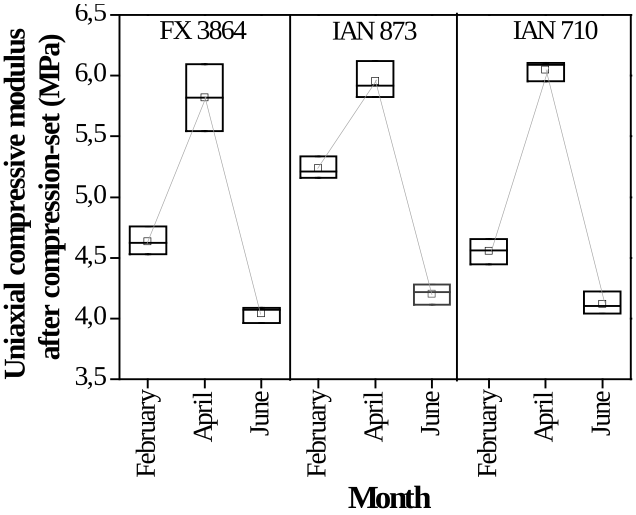

Figure 15. Uniaxial compressive moduli after compression-set tests.
Source: The authors.

during compression-set tests. However, the lower variation of compressive moduli was observed for IAN 873 and IAN 710 compounds.

Mechanical properties of NR sheets-based compounds studied in this work showed significant variations ($p < 0.01$) among tapings. Highly significant variations ($p < 0.01$) among clones were observed for Shore A hardness and compression-set, however, this behavior was not found for the other mechanical properties. The difference in the way how mechanical properties varied is attributed to the role of activators, sulfur and accelerator on the mechanical properties of vulcanized NR [16].

4. Conclusions

Technological properties of NR lattices and NR sheets-based compounds showed highly variability with season, except for ash content in lattices. Significant variations were observed among the clones for almost all of the lattices properties evaluated over the time of this study. Hardness, compression-set and viscosity-related rheometric properties presented significant variations among clones, but vulcanization times, tensile and compressive properties of NR sheets-based compounds did not show significant variation among clones, which is explained by to the role of vulcanization system on these properties for vulcanized NR.

Although rainfall and sun hours per day may have influenced the variations of the properties of the NR evaluated, each clone presented different responses to climatic variations, which is attributed to its intrinsic characteristics. It was observed that the phenological stage seems to influence NR properties, specially the leaf senescence. New researches over a major time of lattices and coagula are needed in order to achieve a better understanding on performance of materials studies here.

NR is a complex biopolymer with an intrinsic variability in composition and properties, but in this work it was detected that better NR tapping, collecting, and drying practices at plantations must be carried out seeking to reduce the variation of NR properties.

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D.H. Giraldo, received the BSc. Eng in Mechanical Engineering in 2000 from the Universidad Nacional de Colombia, Medellin, Colombia, and the MSc. degree in Engineering in 2003 from the Universidade de Sao Paulo, Sao Paulo, Brazil. Since 2004 he is a full professor in the Departamento de Ingeniería Metalúrgica y de Materiales, Facultad de Ingeniería, Universidad de Antioquia, Colombia. His research interests include polymer processing, mechanical behavior of materials and reverse engineering.
ORCID: 0000-0002-4306-9978

S.M. Velásquez, received the BSc. Eng in Bioengineering in 2008 and MSc. degree in Engineering in 2011, all of them from Universidad de Antioquia, Medellin, Colombia. From 2009 to 2011, she worked for rubber and plastic manufacturing companies as manager. Since 2011 she has been a researcher at Servicio Nacional de Aprendizaje – SENA. His research interests include innovation and applied research in industrial processes.
ORCID: 0000-0002-6697-2801