

Seasonal and Clonal Variations in Technological and Thermal Properties of Raw *Hevea* Natural Rubber

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ABSTRACT: This study was undertaken over a 10-month period under environmental conditions within the state of Mato Grosso, Brazil, to evaluate the causes of variation in the technological and thermal properties of raw natural rubber (NR) from different clones of *Hevea brasiliensis* (GT 1, PR 255, FX 3864, and RRIM 600). These clones were chosen to represent good clones available in Brazil. The technological properties of raw NR were evaluated in terms of their dry rubber content (DRC), Wallace plasticity, plasticity retention index (PRI), and Mooney viscosity. The thermal performance was evaluated with the thermogravimetry (TG)/differential thermogravimetry

(DTG) technique. There were significant variations ($p < 0.01$ and $p < 0.05$) between clones and tappings for all technological properties, except for the percentage DRC among the clones. Of the clones studied, clone PR 255 presented the highest sensitivity to thermooxidation, as measured by its PRI value. The clone type and period of the year did not significantly influence the thermal behavior (TG/DTG under a nitrogen atmosphere) among the four clones evaluated. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2749–2755, 2011

Key words: crosslinking; rubber; thermal properties

INTRODUCTION

Fresh *Hevea* latex is a heterogeneous system in which negatively charged particles are suspended in cellular cytosol (C-serum). The major particle groups are the rubber particles, lutoids, and Frey–Wyssling complexes. Rubber particles, the primary constituent, comprise 30–45% of the weight of the solids of *Hevea* latex. Other biochemical constituents of the latex (lipids, proteins, sugars, etc.) contribute to specific properties of the rubber.¹

Rubber particles in *Hevea* latex are obtained, after tapping, in liquid form or as coagula. For the manufacturing process, coagula have to be dried after crumbing. During the drying process, two phenomena may result in changes to the structure and, consequently, to the bulk properties of natural rubber (NR): thermooxidation and storage hardening.²

NR is an agricultural raw material whose quality strongly depends on agronomic factors such as the clone type, soil, weather, and season. This is often a major inconvenience during the manufacturing process because of the variability in properties and, consequently, the mixing behavior, which, in certain cases, remains difficult to predict with the available criteria.³ NR is susceptible to oxidation; this can affect both the processing qualities of the rubber and also the final mechanical properties of the compounded rubber.

Natural antioxidants offer protection from the degradation of *Hevea* NR. Thus, the higher the plasticity retention index (PRI) is, the better the resistance of NR to thermal oxidation is. The main chain unsaturation of the NR poly(*cis*-1,4-isoprene) makes it susceptible to degradation, which can be caused by light, high temperatures, atmospheric oxidants (O₂, O₃, etc.), or excessive physical stresses.⁴ Thermal oxidation of this polymer, in its solid state, is a complex process in which two competing phenomena occur: scission and crosslinking. This results in the deterioration of its chemical and physical properties.

This study was the result of a cooperation between Embrapa Agricultural Instrumentation (Brazilian Agricultural Research Corp.) and Plantation Edouard Michelin (Brazil), with the objective of evaluating and monitoring some clonal and seasonal variations of NR from trees of four of its most planted clones in Brazil.

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EXPERIMENTAL

NR (*Hevea brasiliensis*) lattices from different clones (GT 1, PR 255, FX 3864, and RRIM 600, a widely reported clone of Malaysian origin used as a reference) from Plantation Edouard Michelin (Mato Grosso, Brazil) were evaluated over a 10-month period (October 2007–July 2008). The trees were planted in 1989 (i.e., they were 18 years old at the beginning of the experiment). Latex tapping was carried out on 60 trees of each of the four clones. The material was transported to a rubber processing factory where all cuplumps were then granulated, washed, and dried in an air dryer at $120 \pm 2^\circ\text{C}$ for 4 h under the same processing conditions.

The dry NR samples were first evaluated for their dry rubber content (DRC), Wallace plasticity (P_0), Mooney viscosity (V_R), and PRI according to standard ABNT-NBR 11597 methods.⁵ PRI analysis⁴ consisted of determining the P_0 of a standardized NR specimen before and after oven-aging in air (30 min at 140°C with controlled air circulation). The PRI was then given as the percentage ratio of the plasticity after oven-aging to the plasticity before oven-aging (P_0). The parameters required by Brazilian Standard NBR 11597⁵ specify 60% as the minimum acceptable value for all rubber categories.

Thermogravimetric analysis was performed on samples of dry raw NR with a TA Instruments (New Castle, Delaware) Thermo-Analyzer Q500. Scans were carried out with 10 ± 1 mg samples in platinum pans, which were heated from room temperature up to 600°C at a rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere with a flow rate of 40 mL/min. The initial decomposition temperature (T_i) and final decomposition temperature (T_f) were obtained from the thermogravimetry (TG) curves. The maximum decomposition temperature at the maximum mass loss rate (T_{max}) was also recorded.

Fourier transform infrared (FTIR)–attenuated total reflectance (ATR) spectra were recorded with a PerkinElmer (Waltham, Massachusetts) (model Paragon 1000) spectrophotometer in a range from 4000 to 400 cm^{-1} with films cast from toluene solution on ZnSe crystals (the sampling surface was pressed into intimate optical contact with the top surface of the crystal).

The molecular weights of the rubber were determined by size exclusion chromatography (SEC) with multiangle laser light scattering. Approximately 5–10 mg of dry NR was dissolved overnight in 3 mL of 0.2-m-filtered tetrahydrofuran in 8 mL borosilicate vials with Teflon-coated lids. The sample solution was then filtered through a 1.6- μm Glass microfibre media allowing filtration of difficult samples with less hand pressure (GF/A w/GMF) Whatman syringe filter into $12 \times 32\text{ mm}^2$ clear borosilicate screw-cap vials with polytetrafluoroethylene septa. The molecular weights were determined with a Hewlett-Packard 1100 series High-performance liquid chromatography (HPLC),

coupled to a Wyatt Dawn DSP laser photometer (containing 18 light scattering detectors and a 632.8-nm wavelength laser) and an HP1047 refractive-index detector. A PLgel 10- μm mixed-B size exclusion column (Hewlett Packard) and a Phenogel 5- μm linear/mixed guard column (Phenomenex) were used with a column compartment temperature of 35°C . The chromatograms were analyzed with Astra software (Wyatt Technologies). Measurements were performed in triplicate.

RESULTS AND DISCUSSION

In this study, relevant NR properties, such as DRC, P_0 , V_R , and PRI, in different clones were investigated. The results of the technological properties and environmental variants (temperature and rainfall) are shown in Figure 1.

DRC is a physiological parameter of the latex and an indicator of the biosynthetic activity in latex vessels.⁶ DRC, a measure of productivity, showed no variation between clones. Generally, DRC tends to decrease in latex extraction in May and July, corresponding to the beginning of the dry season.⁷ In this period, the trees begin to lose their leaves, and there is a decrease in precipitation and an increase in heat-stroke. The latter factors may cause DRC to decrease, probably because they diminish photosynthesis and the consequent biosynthetic activity of the rubber tree. This hypothesis was corroborated by Ferreira et al.⁷

In this study, the DRC values [Fig. 1(d)] were higher in October and November; this corresponded to the period of intense insolation when the trees had a larger amount of leaves. Compared with other clones, GT 1 presented the least resistance to climatic variations.

V_R and P_0 are related to the polyisoprene chain length; P_0 provides a picture of the microstructure of the raw material.⁸ Highly significant variations ($p < 0.01$) among the clones were observed for P_0 and V_R . Clones PR 255 and RRIM 600 showed the largest ($x = 49.5$) and the smallest average ($x = 35.6$) P_0 's, respectively. From October to March, all clones presented P_0 values higher than 30 units; below this value, rubbers are considered too soft.⁹ It is noteworthy that clone PR 255 produced rubber with over 30 units P_0 for all tappings. Many significant variations among tappings were observed for P_0 ($p < 0.01$) than for V_R ($p < 0.05$).

P_0 and V_R are used to evaluate NR behavior during development and use in industry. Their relationship, however, is dependent on the history of the rubber samples involved because differences in the processing, drying conditions, and mastication can affect the values. P_0 and V_R show, in general, a linear correlation,⁹ which was confirmed by this study (Fig. 2). Variations in this property seem to occur because of variable quantities of nonrubber constituents, which influence the formation of crosslinking, molar masses, their distributions, and so on.¹⁰

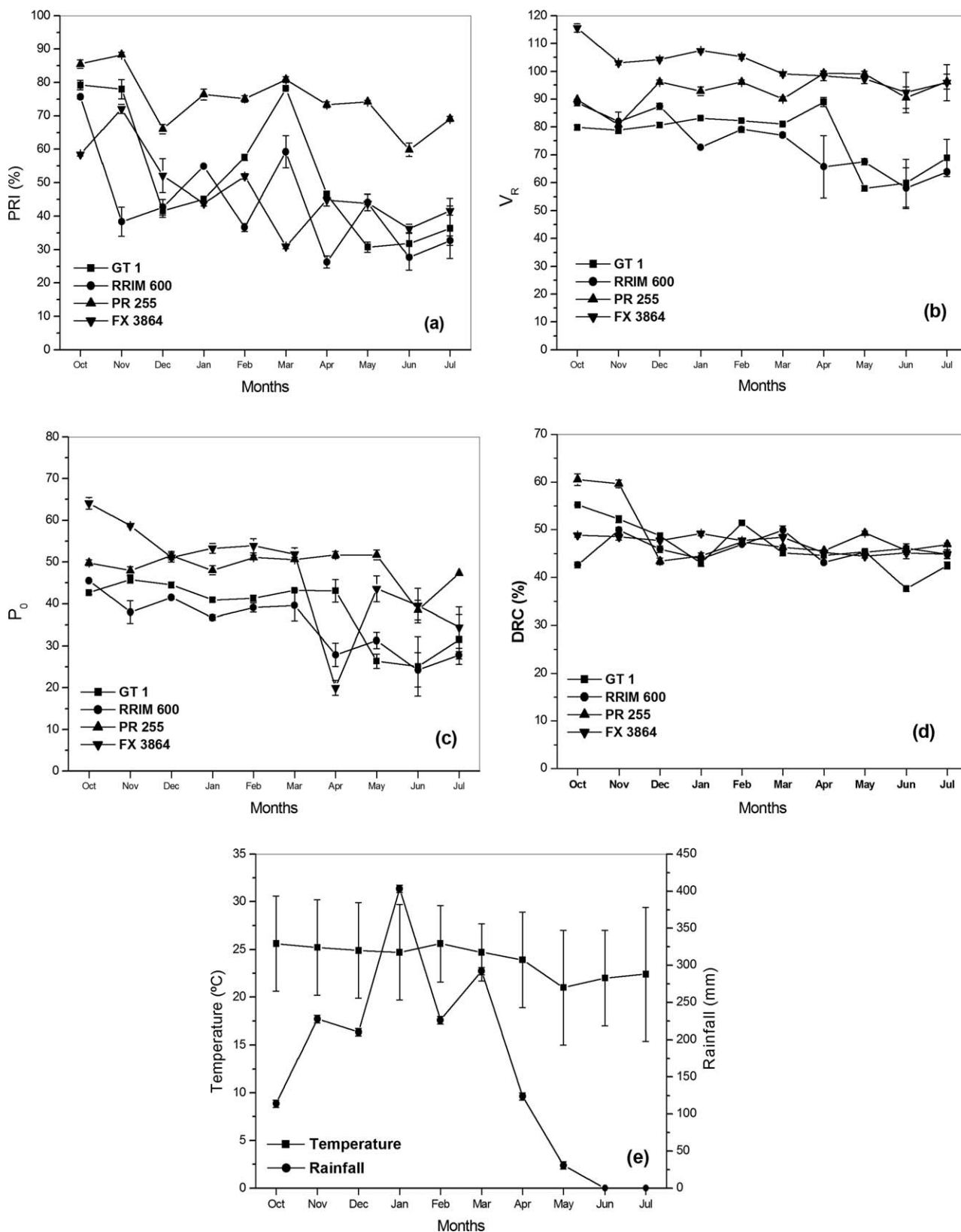


Figure 1 Monthly variations in the technological properties of NR and some climatic data.

Highly significant variations ($p < 0.01$) in PRI were observed among clones and among tappings. These could have been due to genetic differences among the

clones and climatic variations that affected the *in situ* synthesis of some nonrubber constituents (tocopherols, proteins, amino acids, etc.), whose strong

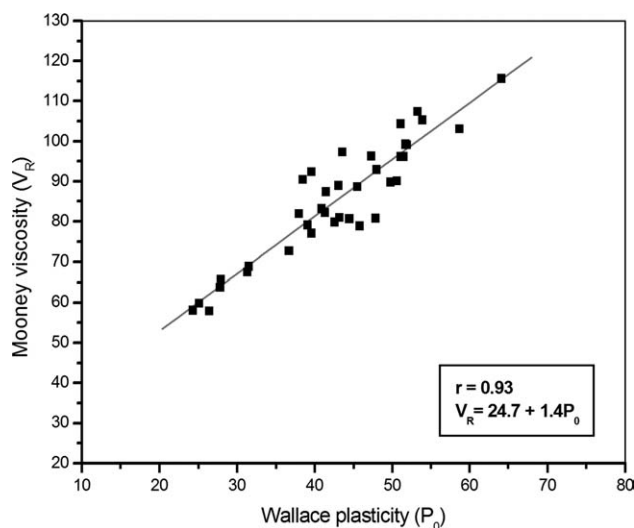


Figure 2 Correlation between V_R and P_0 .

antioxidant actions^{11–13} protect rubber from degradation. From the PRI results [Fig. 1(a)], clone PR 255 showed the lowest variation and highest values (average of ~75%) than the others and was the only clone that met the requirements of the standard ABNT/NBR 115975 (minimum 60%) throughout. The statistically significant variations in the PRI properties among tappings were observed in October–April, October–May, October–June, October–July, November–June, and November–July. Such a high variation in PRI was previously reported in *Hevea*.¹⁴ At times, the differences in PRI among the clones were dramatic (e.g., collections in June and November).¹⁴

According to the literature,^{6,15} the technological properties of NR vary by age (shelf-life estimation), type of coagulant, period of the year, and clonal origin. The chemical and physical properties of the polymers, including density, glass-transition temperature, chemical reactivity, solubility, and the like, depend essentially on the chemical structure (molecular scale).³

Thermogravimetric analysis provides information on thermal degradation, mass loss of the material in different stages, threshold temperature, and nature and extent of material degradation.¹⁶ Figure 3 shows the T_i , T_{max} , and T_f decomposition temperatures of NR obtained from the TG curves in an inert atmosphere (for the characterization of material response at high temperature without oxygen effects). The inert atmosphere was used to separate the thermal degradation processes from the thermooxidative processes, as measured by PRI.

All of the differential thermogravimetry (DTG) curves had one degradation peak; this indicated that thermal degradation of the raw NR from different clones was a one-stage reaction in the range from 315 to 450°C. Although PRI values of the samples showed variation among the tappings and the clones, they showed similar thermal behavior, and

all of the clones were quite stable up to 300°C. This suggests oxidative processes, not thermal ones, were mainly responsible for the PRI differences. T_i , as reported in Figure 3, ranged from approximately 317 to 340°C; this indicated that the thermal stability in an inert atmosphere was quite good. The T_i values decreased from 5 to 30°C for all clones collected in July compared with those collected in February, so NR produced during periods of high biosynthetic activity may have been more thermally stable. Clone GT 1 produced the most thermally stable NR ($T_i = 330^\circ\text{C}$) in the July tappings.

T_{max} (Fig. 3), or the peak temperature on the DTG curves, was around 380°C for all of the samples. They showed similar patterns, indicating a similar decomposition mechanism for all tappings, although the thermal stability of the clones studied appeared to be higher than that reported elsewhere.^{16–18} The shoulder observed at about 430°C, similar to previous reports, could have been due to crosslinked and cyclized networks, which degrade at high temperature.¹⁶ It could be concluded that the NR thermal stability may have been dependent on season and on clone. In the light of these results, the thermal stability and molecular weight measurements were made on samples of clones GT 1 and PR 255 collected during different seasons—February (summer), May (transition) and June (winter)—and subjected to different durations of storage hardening.

For this study, GPC was performed on NR samples (after processing) during a period of approximately 13, 10, and 9 months after collection in February, May, and June, respectively. The dry rubber samples were stored inside plastic boxes in the laboratory at room temperature (25–30°C). Molecular weight averages ranged from 650 to 1100 kg/mol, as seen in Table I.

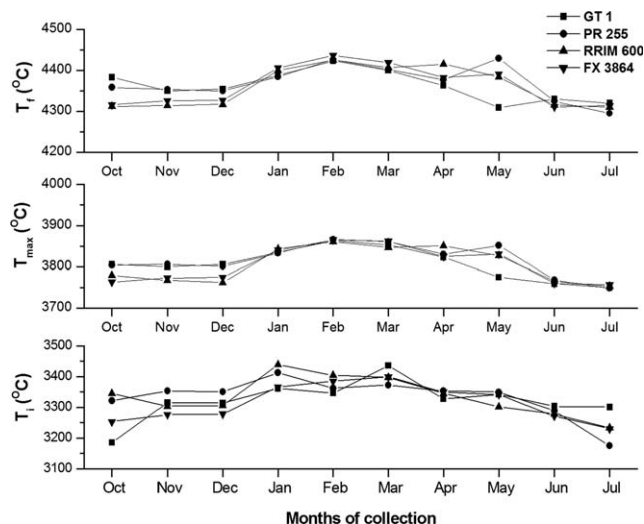


Figure 3 T_i , T_{max} , and T_f for four clones evaluated.

TABLE I
 M_w , M_n , and Polydispersity (M_w/M_n) of the Dry NR for the PR 255 and GT 1 Clones

Clone	Month	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n
GT 1	February	810	980	1.21
	May	700	883	1.26
	June	657	821	1.25
PR 255	February	920	1,077	1.17
	May	926	1,093	1.18
	June	744	915	1.23

In this set of *Hevea* NR samples, PR 255 had a slightly higher weight-average molar mass (M_w) and number-average molar mass (M_n ; 4–5%) than GT 1 (Table I). The lowest values of molecular weight were found in the June samples for both clones. Depending on the metabolic activity of the biological source (the *Hevea* tree), NR could be more or less disposed to degradation.¹⁹ The differences in molecular weight values were a result of either clonal and seasonal effects, changes in storage, or both. Ehabe et al.¹⁹ showed that M_n and M_w of rubber from clones GT 1 and PB 217 were not affected by 45 days of cuplump maturation and storage. However, these parameters decreased with the maturation of clone PB 235 rubber. It is possible that the chain-scission process was more pronounced in clone PB 235 rubber because of insufficient natural antioxidants.

The use of the SEC–multiangle laser light scattering technique in studies of NR has received increasing attention in the last decade.^{20–22} Subramaniam²³ was the first to characterize the macromolecular structure of NR by SEC. M_w of NR from *H. brasiliensis* ranges from 500 kg/mol to more than 1000 kg/mol (depending on the samples studied^{24,25}) because of the interactions of nonrubber compounds, such as proteins and lipids, with the polyisoprene chains. This associative structure is partly destroyed when the polyisoprene is dissolved in a solvent. However, in many cases and in this study, a portion of the NR remains as an insoluble gel.⁸

NR is a product of biological origin, this gives rise to a particularly complex structure that varies with agronomic parameters.²⁴ In addition, coagulation of the latex and maturation of the coagulum obtained will modify the macromolecular structure of NR.²⁴ The manner in which the NR latex is coagulated, dried, processed, and stored can increase the gel content of the rubber.^{26,27} This is of significant concern to rubber processors.²⁰ These increases in gel content are associated with so-called storage hardening or rises in NR viscosity during storage.² Storage hardening has been attributed to crosslinking associated with various mechanisms or interactions between so-called abnormal groups of the NR polyisoprene molecule and certain nonrubber compounds in latex, specifically proteins and lipids.

Sources of NR can differ in their susceptibility to this storage hardening.^{2,26} These differences can be associated with processing history and may be a clonal characteristic of the latex itself.

In this study, linear correlations were observed between the variables P_0 and M_w ($r = 0.96$), which were significant at $p < 0.01$. Li et al.²⁸ showed that P_0 was correlated with M_w for an NR sample after accelerated storage. P_0 and M_w were measured on NR samples from different origins.⁸ The clonal origin, type of tapping, maturation time, and type of processing had a highly significant effect on the $P = f(M_w)$ relations observed and, hence, at first, on the technological properties of NR. This study showed that two samples of NR can be identical in terms of plasticity but very different in terms of the average polyisoprene chain length or M_w .⁸

The relationship between the molecular chain breakdown and the decrease in viscosity after maturation and storage could arise from the fact that the slower the metabolism of the tree is, the more efficiently rubber is synthesized.¹⁹ However, because the biological environment characterizing NR coagulation and maturation is very complex, a change in the serum activity with maturation should be associated with the selective activation of antioxidants from their less reactive forms.¹⁹

Investigation of the chemical structure of the NR samples with FTIR spectroscopy showed, obviously, that peaks characteristic of NR were observed in the spectra of both *Hevea* clones studied and regardless of the season (Fig. 4).

In the spectrum obtained for the clone GT 1 sample collected in June, three new absorption bands

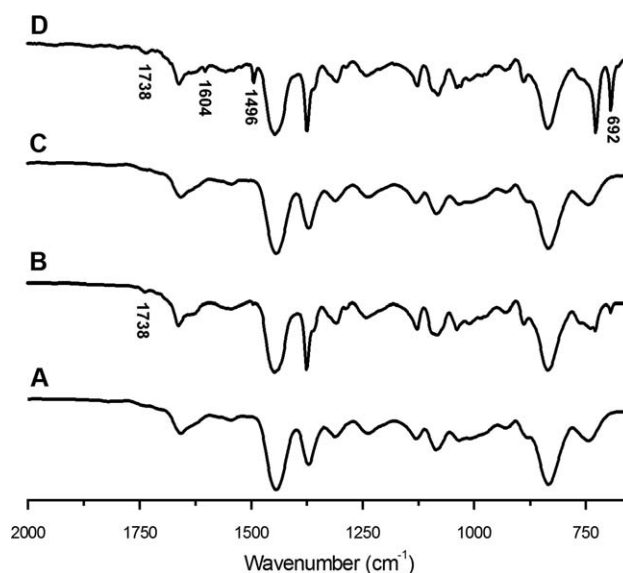


Figure 4 FTIR–ATR spectra for the rubber samples collected in different seasons of the year: (A) clone PR 255 (February), (B) clone PR 255 (June), (C) clone GT 1 (February), and (D) clone GT 1 (June).

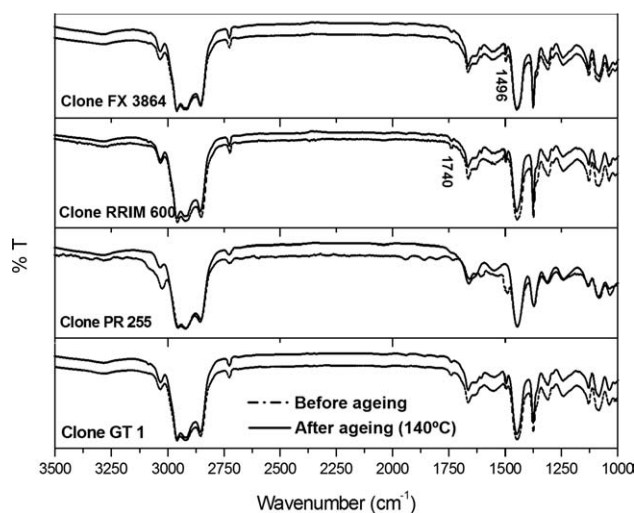
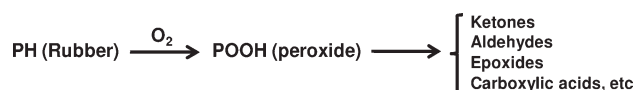


Figure 5 FTIR-ATR spectra for GT 1, PR 255, RRIM 600, and FX 3864 clones before and after 30 min of aging at 140°C.

were detected at 1604 cm^{-1} , which were characteristic of the coupled asymmetric axial deformation of conjugated double bonds ($\text{C}=\text{C}-\text{C}=\text{C}$). The development of double bonds in the polymer main chain usually leads to condensation-forming crosslinks between chains: at 1496 cm^{-1} , the axial deformation of the $\text{C}=\text{C}$ ring, and at 692 cm^{-1} , the angular deformation outside the bond plans $\text{C}=\text{C}$ of the ring.²⁹ The absorption signal at 1738 cm^{-1} , characteristic of $\text{C}=\text{O}$, was observed for samples collected in June from both clones.

Unsaturated fatty acids may undergo auto-oxidation, caused by the same factors that promote oxidation of the rubber and leading to the formation of hydroperoxides, also called *primary oxidation products*, which then degrade and also produce aldehydes, ketones, alcohols, carboxylic acids, esters, and so on as secondary products. The mechanism of thermal oxidation can be summarized as follows:³⁰



Actually, for polyisoprene in its solid state, the balance between scission and crosslinking depends on available oxygen diffusion in the material.²

Therefore, oxidation is monitored as an increase in oxygen-containing groups (e.g., $\text{C}=\text{O}$ and OH) and a decrease in oxidizable groups (e.g., $\text{C}=\text{C}$ and CH_3).³¹ The region among 1710–1745 cm^{-1} is attributed to the carbonilic compounds, such as esters, ketones, aldehydes, and so on.³²

To investigate the effect of temperature on the thermooxidation of NR, samples from different clones were submitted to a thermal treatment at 140°C for 30 min, equivalent to the temperature and time used in the PRI assay. Figure 5 comprises FTIR

spectra obtained for NR samples with and without thermal treatment at 140°C for 30 min for clones GT 1, PR 255, FX 3864, and RRIM 600.

For clone PR 255, no structural change occurred from the thermal treatment. However, for clones GT 1, RRIM 600, and FX 3864, absorption bands appeared at 1496 cm^{-1} and approximately 1738 cm^{-1} for the samples thermally treated for 30 min of aging at 140°C; this indicated that these clones were more susceptible to thermooxidation. These results were in agreement with the results obtained from the PRI analysis.

CONCLUSIONS

The results indicate distinct behaviors in the properties of rubbers for all clones studied, which showed high variability throughout the year. Significant variations ($p < 0.01$) were observed among the clones for all of the properties evaluated, except for DRC. On average, clone PR 255 had the highest PRI values (75%) and the most stable values over the 10-month period from October 2007 to July 2008.

The technological properties of NR varied with the period of the year and clonal origin of samples. Although environmental changes (temperature and rainfall) may have influenced the variations of the technological properties of the clones evaluated, ultimately the intrinsic characteristics of each clone elicited different responses to climatic variations. The results for T_{max} show that the all samples had a high thermal stability in an inert atmosphere. The clones showed similar patterns; this indicated a similar decomposition mechanism for all tappings.

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