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Thermooxidative study of raw natural rubber from Brazilian IAC 300 series clones

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ABSTRACT

The improvement of rubber tree species is of key importance due to the worldwide market demand of this renewable material essential for several types of industries. The thermal performance of natural rubber produced from new clones of IAC 300 series, and the Malaysian RRIM 600 clone (used as control) have been evaluated using DSC and TGA/DTG techniques in air and nitrogen atmospheres. The results have shown that in oxidative atmosphere, the thermal stability of the Brazilian clones was slightly better than that of the Malaysian clone RRIM 600, and that, in an inert atmosphere, there are no significant differences in the thermal behavior among them. The natural rubbers from IAC clones have shown good thermal stability up to 300 °C in inert and oxidative atmospheres, which is important for several industrial applications. The decomposition changes from a one step process to a three step process, when moving from an inert to an oxidative atmosphere. The index of thermal stability has shown that the natural rubbers have higher thermal stability in inert atmosphere.

1. Introduction

Due to its high mechanical performance, good elasticity, and unique properties, natural rubber is an important renewable material for production of tires and a large number of other industrial products [1]. Currently, the largest commercial source of natural rubber is *Hevea brasiliensis* (Willd. ex Adr. de Juss.) Muell.-Arg. *Hevea* is traditionally cultivated in humid tropics within 10° north and south of the equator, where the quantity and distribution of rainfall and the ambient temperature are suited for its growth. In Brazil, attempts have been made to extend rubber cultivation to the non-traditional regions of the country, where similar tropical climatic conditions exist [2,3]. The efforts to establish new zones for rubber cropping in Brazil, demonstrating the potential for rubber production in regions such as São Paulo, Mato Grosso and Bahia states have been extremely important. The Agronomic Institute (IAC) and the Embrapa Agricultural Instrumentation Research Center (Embrapa/CNPDIA) have improved and evaluated new *Hevea* varieties (clones), the IAC series, in order to increase the production and quality of the natural rubber more appropriate to the Brazilian soil and climate. The main goal of the genetic improvement program of the *H. brasiliensis* is to develop species which are resistant to diseases, more productive and which can produce high quality rubber. Currently, field tests of the new IAC series clones are being carried out in São Paulo state, southeastern region of Brazil [3–6]. Some works have been reporting the study of physical properties, agronomical characteristics such as latex production, wind damage, resistance to anthracnose panel canker, and thermal degradation behavior of the newly developed clones from the IAC series in order to recommend these clones to be cultivated on a large scale in São Paulo state [3,4,6–11].

The thermal performance of the rubber is of key importance for industrial applications since the processing temperatures used to produce rubber-based products are usually high and close to their degradation temperature. Raw rubber, cis-1,4 polyisoprene, is an unsaturated cross-linkable (vulcanizable) polymer with elastic-rubber properties at room temperature. At higher temperatures or under the influence of deforming forces, raw rubber exhibits increasing viscous flow, so that it can be molded under suitable conditions, therefore, being a starting material for the production of elastomers [12]. One of the most widely accepted methods for

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Table 1
Parentage and estimates of annual yield of dry rubber per hectare (mean of 6 years) of IAC 300 series clones [7]

Clones	Parentage	Mean yield (kg ha^{-1} year^{-1})
IAC[a] 300	RRIM[b] 605 (Tjir[c] 1 × PB[d] 49) × AVROS[e] 363	1921
IAC[a] 301	RRIM[b] 501 (Pil[f] 49 × Lun[g] N) × AVROS[e] 1518	1827
IAC[a] 302	RRIM[b] 501 (Pil[f] A 49 × Lun[g] N) × AVROS[e] 353	1713
IAC[a] 303	RRIM[b] 511 (Pil[f] B 84 × Pil[f] A 44) × AVROS[e] 1218 (AVROS[e] 214 × AVROS[e] 216)	1607
RRIM[b] 600	Tjir[c] 1 × PB[d] 86	1493

[a] IAC: Agronomic Institute of Campinas.
[b] RRIM: Rubber Research Institute of Malaysia.
[c] Tjir: Tjirandji.
[d] PB: Prang Besar.
[e] AVROS: Algemeine Vereinigung Rubber Planters Oostkust Sumatra.
[f] Pil: Pilmoor.
[g] Lun: Lunderston.

studying the thermal properties of polymeric materials is thermogravimetry. Thermogravimetric data provides information on thermal breakdown, mass loss of the material in different stages, threshold temperature, and the nature and the extent of the degradation of the material [13]. The aim of this work is to study the thermal properties of the natural rubber from new Brazilian clones of the IAC 300 series using thermogravimetric analysis (TGA), differential thermogravimetric analysis (DTG) and differential scanning calorimetry (DSC).

2. Experimental methods

Natural rubber latices from different clones of the IAC 300 series (IAC 300, 301, 302 and 303) and from RRIM 600, an old popular clone (used as a control), were obtained from Northwest Regional Pole in Votuporanga city, an IAC experimental plantation. Table 1 shows the parentage and the mean yields per hectare in the first 6 years of the new Brazilian clones, which were obtained by selective hybridization between two superior clones, followed by selection of an ortets within the progenies, and vegetative multiplication and evaluation [7]. The clones were grown in the plateau region of São Paulo state/Brazil, whose coordinates and ecological conditions are [4]: 20°25′S, 49°50′W, altitude 450 m; mean temperature during growing season 32 °C; mean annual rainfall 1480 mm, with a hot wet summer and a dry winter with low temperature and rainfall; Paleudalf soil, with average nutrient status and poor physical structure. Natural rubber trees were tapped, and the stabilization of the samples was made using 4.7 mL of NH_4OH for 100 mL of latex. The samples were coagulated with 3 mol L^{-1} acetic acid solution and dried.

Thermogravimetric analysis was obtained in a TA Instruments model Q500, in the temperature range from 25 °C to 800 °C, at a heating rate is 10 °C/min in inert (nitrogen) and oxidative (synthetic air) atmospheres, with a flow rate of 40 mL min^{-1}. Approximately 10 mg of each sample were used for each sample preparation.

The glass-transition temperature (T_g) of the samples (ca. 6 mg) was measured using a TA Instruments model Q100 DSC. The instrument was calibrated with an indium standard. The T_g was defined as the inflection point of the jump heat capacity using a scan rate of 10 °C/min within the temperature range from −80 °C to 100 °C, and determined from the second scan. All measurements were conducted under a nitrogen atmosphere.

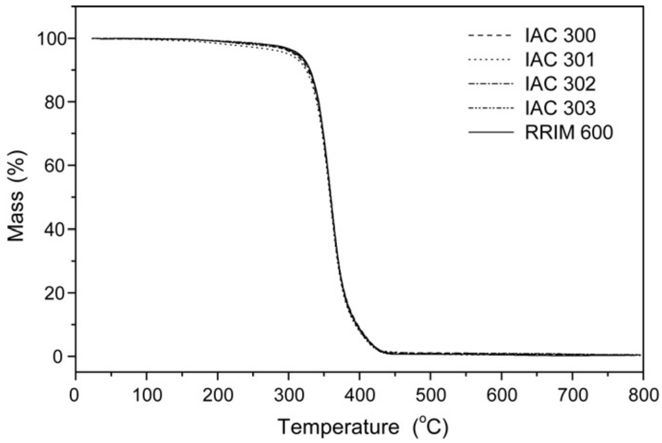

Fig. 1. TG curves of the IAC 300 series clones in inert atmosphere (10 °C/min).

Molecular weights of rubber in solution were determined by Size Exclusion Chromatography with Multi-Angle Laser Light Scattering (SEC-MALLS). Fifteen microliters liquid latex was dissolved overnight in 3 mL of 0.2 m filtered THF in 8 mL borosilicate vials with Teflon coated lids. The sample solution was then filtered through 1.6 μm GF/A w/GMF Whatman syringe filter into a 12 mm × 32 mm clear borosilicate screw-cap vials with a PTFE septum. Molecular weights and their distributions were determined using a Hewlett-Packard 1100 series HPLC, coupled to a Wyatt Dawn DSP laser photometer and a HP 1047 refractive index detector. For each sample, following a THF blank run, a 50 μL subsample was injected and run through a Phenogel 5 μm Linear/Mixed Guard Column (Phenomenex) and a PLgel 10 μm mixed-B exclusion column. The flow rate used was 1 mL/min, column temperature 35 °C, and the wavelength 632.8 nm. SEC-MALLS chromatograms were analyzed using Astra version 4.73 software. Measurements were performed in triplicate.

3. Results and discussion

Figs. 1 and 2 show typical TG and DTG curves obtained for the raw rubber from the IAC 300 series clones in inert atmosphere, respectively. TG and DTG curves of all clones evaluated have shown the same general shape, suggesting that the decomposition mechanisms are similar. All samples studied exhibited an initial small mass loss attributed to the elimination of volatile components such as water, and ammonia residue (added to the latex to stabilize it

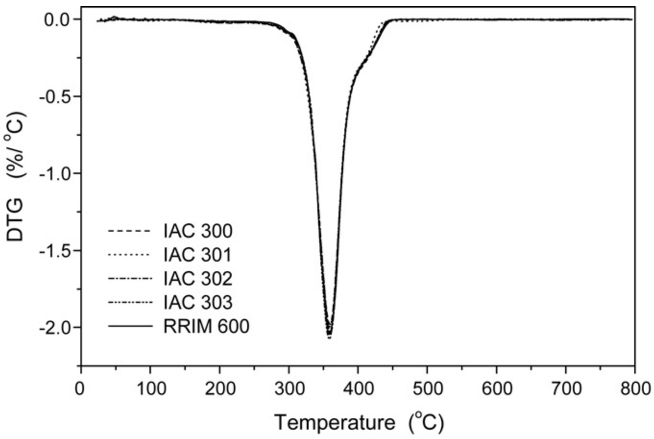

Fig. 2. DTG curves of the IAC 300 series clones in inert atmosphere (10 °C/min).

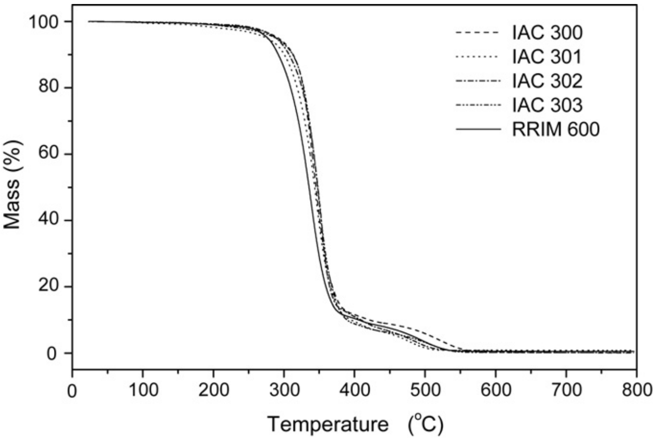

Fig. 3. TG curves of the IAC 300 series clones in air atmosphere (10 °C/min).

during the transportation, and to avoid coagulation) [9]. According to the traces, natural rubber from all the new clones was quite stable up to 300 °C. It can be seen that the TG curves have only one large plateau and the DTG curve has one primary degradation peak, indicating that thermal degradation of the raw natural rubber from the IAC clones is mostly a one-stage process. The decomposition ranged from approximately 300 °C to 450 °C with a mass loss of about 95%, which can be assigned to the thermal decomposition of the natural rubber into monomers, dimers, trimers, etc., in inert atmosphere. A small shoulder can be observed in the DTG curves at approximately 420 °C attributed to the crosslinked and cyclized networks, which degrade at higher temperature [15,16]. The temperature of the maximum mass loss rate or the peak temperature of the DTG curves, Fig. 2, is around 360 °C for all samples.

The temperature at which 50% decomposition occurs is generally considered as an index of thermal stability [14]. Our results have shown that this temperature is about 360 °C for the rubber from IAC clones, as well as for the control, RRIM 600 clone, indicating that the new clones have thermal stability comparable to the well-established Malaysian clone, RRIM 600. The raw natural rubber suffered almost complete decomposition. At 800 °C, the content of residues was insignificant for all clones, about 0.3%. This lower content of residues indicates that few impurities were added during the extraction process of the latex in the plantation. Basically, the same behavior has been obtained for all samples.

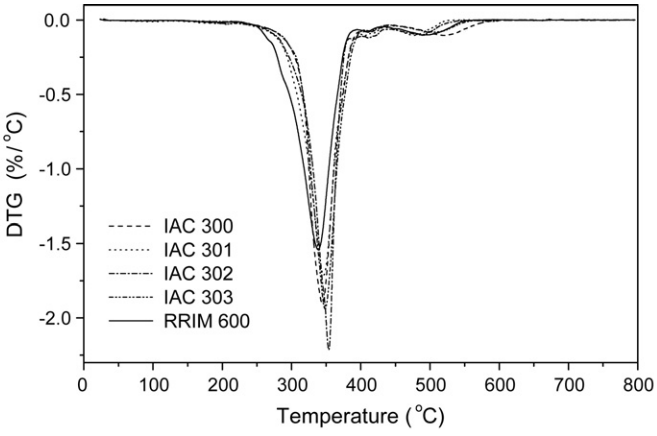

Fig. 4. DTG curves of the IAC 300 series clones in air atmosphere (10 °C/min).

Table 2
Weight-average molecular weight ($\bar{M}_w$), number-average molecular weight ($\bar{M}_n$), and polydispersity ($\bar{M}_w/\bar{M}_n$) of IAC 300 series clones

Clones	$\bar{M}_w$ (g/mol)	$\bar{M}_n$ (g/mol)	$\bar{M}_w/\bar{M}_n$
IAC 300	1,661,000	730,400	2.27
IAC 301	1,697,000	1,376,000	1.23
IAC 302	1,645,000	1,097,000	1.50
IAC 303	1,612,000	1,060,000	1.52
RRIM 600	1,537,000	842,000	1.83

For the oxidative atmosphere, TG and DTG curves for the IAC 300 series clones are shown in Figs. 3 and 4, respectively. In this study, all samples again exhibited an initial small mass loss associated to the elimination of volatile substances, as seen in the nitrogen atmosphere. The scans illustrate that thermal degradation of the Hevea rubber samples started at around 250 °C. The thermal degradation of natural rubber in air is not a simple random chain scission process, but it has some side reactions that occur simultaneously [17]. During early degradation (up to 300 °C), oxidation, crosslinking, and chain scission may occur at the same time, the main reactions being oxidation and crosslinking. In this study, the results have shown that the thermal degradation of natural rubber in synthetic air occurred in three consecutive mass losses. The first step of degradation started at around 250 °C, and was completed at 400 °C, the mass loss is about 87%, which can be attributed to the thermal decomposition of the natural rubber. At these temperatures, the main reaction was an oxidative degradation, accompanied by the occurrence of mass loss, which is more time dependent and intense as temperature increases than it normally occurs for experiments carried out under nitrogen atmosphere [17,18]. The second mass loss peak, about 3%, ranges from approximately 400 °C to 450 °C can be attributed to the final thermal decomposition of the natural rubber. For the third mass loss peak, the mass loss is around 6%, and it ranges from approximately 450 °C to 600 °C, and was associated with the thermal decomposition of the carbonaceous residues from the rubber. The occurrence of two or more peaks in the DTG curves in air atmosphere indicates the formation of thermally stable intermediate products, and the absence of these peaks in nitrogen atmosphere may be due to the absence of intermediate products formed in the presence of air, Figs. 1 and 2 [14,16,19].

The residue remaining after the thermooxidative degradation at 600 °C can be associated to the ash naturally present as a component of the latex or impurities added to the latex during the extraction and coagulation process at the plantation [9]. The residue content, approximately 0.5%, does not vary among the different clones investigated.

The temperature at which 50% decomposition occurs for the rubber from IAC clones is about 345 °C and for the control, RRIM 600 clone, is around 335 °C, indicating that in oxidative atmosphere, the thermal stability of the IAC clones is slightly better than that of the RRIM 600 clone, what might be due the intrinsic genetic characteristic of this new clone series. The index of thermal stability has shown that the natural rubbers from IAC clones have higher thermal stability in inert atmosphere than in oxidative one, as expected, and the decomposition process changes from one step to three steps depending on the atmosphere used.

The molecular weight (MW) of natural rubber is of great importance since it influences the properties and processability of rubber products [20,21]. Physical properties, such as modulus, tensile strength, and tear strength are largely dependent on the MW and the molecular weight distribution [22]. Table 2 shows the molecular characterization results. All samples present high molecular weights, in the order of 1 million g/mol, indicating a rubber high quality [20,21,23]. The natural rubber from IAC clones present, in almost all cases, higher weight and number average molecular weights than that of RRIM 600 clone, indicating that the high

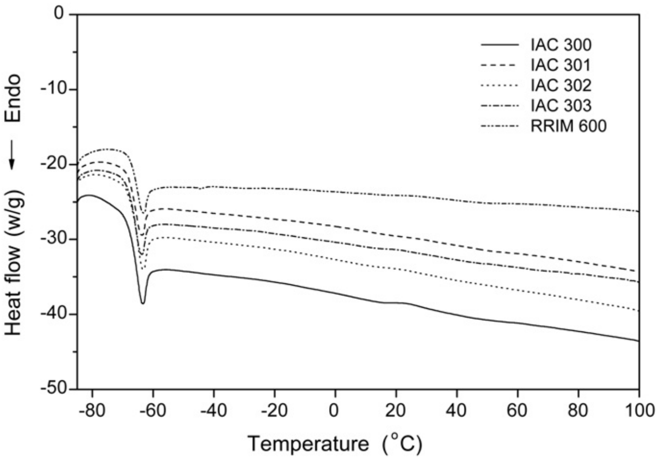

Fig. 5. DSC curves of the IAC 300 series clones (10 °C/min).

molecular weight of natural rubber from these clones may lead to excellent material performance [21–23].

Polydispersity or molecular weight distribution values were estimated by dividing the weight-average molecular weight by number-average molecular weight. A ratio of 1.0 would indicate a sample containing molecules of one size. Higher ratios indicate a greater variance in the size of the large rubber molecules [21,23]. Polydispersity results showed that all clones studied have narrow range of values, ranging from about 1.5 to 2.3 (Table 2), in agreement with the monomodal chromatograms (not shown) obtained. According to the literature, it is generally considered that with other structural factors remaining constant, a decrease in polydispersity leads to an increase in impact strength, tensile strength, softening point, environment stress cracking, etc. [21,24].

The glass transition temperature (T_g) is an important parameter in polymeric applications, because it defines how the polymer behaves under ambient conditions. Many of the important technical properties of elastomers such as resilience and abrasion resilience can be correlated to T_g. This phenomenon is characterized by the temperature at which the material changes from the glassy to the rubbery state. Elastomers have glass transition temperatures below room temperature. Thus, elastomeric materials are rubber-like polymers at room temperatures, but below their glass transition temperature they will become rigid and lose their rubbery characteristics [19,25].

DSC provides information concerning the enthalpy change accompanying a physical or chemical event within a material. The glass transition is a second order event, which manifests itself in a DSC curve as a step change corresponding to the change in the heat capacity of the system [19]. Fig. 5 shows DSC curves measured from the natural rubber from IAC 300 series clones, and RRIM 600 clone during the second heating scan. The curves exhibited changes in baseline in the temperature of approximately −63 °C, which are attributed to the glass transition temperature of natural rubber. The results of the T_g values are summarized in Table 3. There are not significant differences among the T_g values of the different Brazilian clones in relation to the Malaysian clone RRIM 600, which is way below the room temperature, and that is important for several technological applications. Fox and Flory [26,27] first established the existence of a linear relationship between T_g and the inverse of the number average molar mass ($\bar{M}_n$). However, Kow et al. [28] showed that, in the case of polyisoprenes, this behavior is only observed below M_n of around 5000. Since in the present case $\bar{M}_n$ values obtained were in the order of 10^6 such a relationship was not observed, in agreement with other works in the literature [29].

Table 3
Glass transition temperature (T_g) of the raw natural rubber from different clones

Clones	T_g (°C)
IAC 300	−63
IAC 301	−64
IAC 302	−63
IAC 303	−64
RRIM 600	−63

4. Conclusions

The natural rubbers from the Brazilian clones of the IAC 300 series have shown good thermal stability up to 300 °C in inert and oxidative atmospheres. This work showed that the decomposition process changes from one step to three steps when moving from a inert to an air atmosphere, and the index of thermal stability shows, as expected, that the natural rubbers have higher thermal stability in inert atmosphere. In oxidative atmosphere, the thermal stability of the IAC clones was slightly better than that of the RRIM 600 clone, whereas in inert atmosphere, their thermal behavior was equivalent to the RRIM 600 clone. All samples have high molecular weights, greater than 1 million g/mol. The natural rubber from IAC clones present slightly higher molecular weight than that of the RRIM 600 clone. The glass transition temperature obtained by DSC of the new clones was approximately −63 °C. The results have shown that there are no significant differences in the thermal behavior among the different Brazilian clones studied, and they present thermal stability, molecular weights and glass transition suitable for many technological applications.

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