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Evaluation of thermal behavior of latex membranes from genetically improved rubber tree (*Hevea brasiliensis*)

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Abstract

Thermal stability, thermal decomposition process, residual mass, temperature of glass transition (T_g) and temperature dependence of storage modulus (E'), were determined for latex membranes prepared from six clones of *Hevea brasiliensis*: IAC 331, IAC 332, IAC 333 and IAC 334 grown at experimental plantations of Instituto Agronômico de Campinas (IAC) in Votuporanga, São Paulo State, Brazil. Latex membranes from GT1 and RRIM 600 Asian matrix clones were used as references. The thermal behavior of latex membranes from genetically improved rubber trees was characterized using thermogravimetry/derivative thermogravimetry (TG/DTG), differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The thermal behavior of latex from clones studied in the present work showed similar features of the clones previously reported (IAC 40, IAC 300, IAC 301, IAC 328, IAC 329 and IAC 330), with mass loss in four consecutive steps, except IAC 333, which showed an additional mass loss step.

Keywords: Latex; Clone; Thermal analysis; TG/DTG; DSC; DMA

1. Introduction

Latex, a natural rubber, is a polymer of *cis*-1,4-polyisoprene, produced by more than four hundred different species of plants, but the main source is *Hevea brasiliensis* [(Willd ex Adr. de Juss.) Muell-Arg.] [1]. Although this tree is indigenous to the Amazon Basin in South America, currently it is mainly grown in southeast Asia. Due to latex's many application in automobile, pharmaceutical, and more recently biopolymer industries, latex has a valuable and essential place in the international market. Recent studies have also shown that latex can also be successfully used as a temporary substitute of skin [2,3].

The genetic improvement of the rubber tree aims to obtain plants with increased yields, disease resistance, and adaptation to different environments. All these improvements have been achieved by researchers from Instituto Agronômico de Campinas, IAC (Campinas, São Paulo State, Brazil), whose studies have resulted in several clones of *H. brasiliensis* [4–6], which were grown up at experimental and commercial plantations in the plateau region in the state of São Paulo, Brazil.

Latex yield is not the only important parameter to consider in a breeding program. Knowledge of the latex's properties are essential, since these data are integral to applications of this natural polymer. Recently, the results of studies concerning the thermal stability and the thermal decomposition process of natural rubber extracted from clones of *H. brasiliensis*, developed by IAC, called IAC 40, IAC 300, IAC 301, IAC 328, IAC 329 and IAC 330 were reported [7,8]. The Asiatic matrix clones GT1 and RRIM 600 were used as baseline references since these matrices are the main cultivated clones of the rubber tree in the world. These studies showed that comparative data can be used to ensure the quality of latex sources developed by IAC. The present work evaluates the thermal behavior of the latex for the

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clones IAC 331, IAC 332, IAC 333 and IAC 334 using TG/DTG, DSC and DMA.

2. Experimental method

All plants were grown up at experimental plantations of IAC, located in Votuporanga, São Paulo State, Brazil. Latex samples were collected from IAC 331, IAC 332, IAC 333 and IAC 334 clones which were obtained by selection breeding procedures [9], and the standards of the Asiatic matrix clones GT1 and RRIM 600. Latex extracted from 10 trees of each clone were homogenized and kept in 100 mL flasks containing 10 mL of concentrated ammonia (28% m/m, $d = 0.90$ g/cm^3) at room temperature (ca. 25 °C) [10,11]. Before testing the membranes were prepared by putting 5 mL of latex solution (latex + concentrated ammonia), into a Petri dish followed by drying in a hot-air-oven at 50 °C for ca. 24 h [12]. In order to more easily remove the membranes, the Petri dishes were previously coated with a film of silicon, which was produced by spreading a thin layer of silicon paste that was then heated in an oven at 125–150 °C for 2–3 h. After the Petri dishes cooled down the surfaces were washed with liquid soap using a scouring pad, and left to dry at room temperature.

Thermal behavior of the latex films was analyzed using TG/DTG, DSC and DMA curves. All samples were performed three or four times for each technique. TG/DTG and DSC curves were obtained in a simultaneous thermoanalyzer modulus SDTQ600 (TA Instruments), with a continuous air flow of 100 mL/min, at a heating rate of 20 °C/min. The temperatures ranged from ca. 20 to 900 °C. The samples were cut from the original latex membranes into small pieces weighing 6–15 mg and placed in alumina crucibles without a lid. Before performing the experiments the thermal analyzer equipment was calibrated, using metallic indium, zinc and aluminum for temperature; alumina standards for weight adjustment; sapphire for DSC heat flow, and metallic zinc for DSC cell constant.

Data from DMA were not presented in the previous studies [7,8], but considering the viscoelastic features of latex, this evaluation was used in the current study to provide important information about temperature and time effects on its dynamic–mechanical properties of latex. The DMA curves were obtained with a Netzsch 242C apparatus in tensile mode, at a heating rate of 5 °C/min, with temperatures ranging from −120 to 180 °C controlled with liquid nitrogen, and a frequency of 10 Hz. Latex membranes samples were cut with sections size of ca. 4.45 mm × 1.95 mm, and 10.78 mm distance between clamps. Glass transition temperature was detected as the maximum at phase angle (tan δ) peak, which is obtained by the ratio between the storage modulus (E'') and the loss modulus (E') [13].

3. Results and discussion

The TG/DTG curves of latex from matrix clones GT1 and RRIM 600, and IAC 331, IAC 332, IAC 333 and IAC 334 clones are presented in Figs. 1 and 2, respectively. These curves

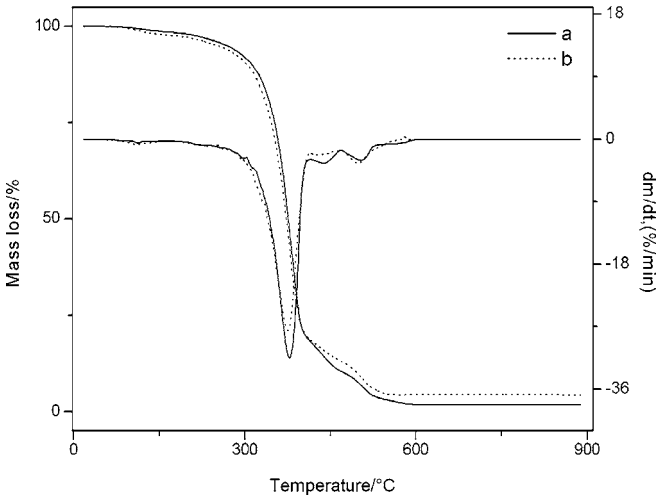

Fig. 1. TG/DTG curves of: (a) GT1 and (b) RRIM 600 clones.

revealed mass loss in four steps for clones: GT1, RRIM 600, IAC 331, IAC 332 and IAC 334, and five steps for the IAC 333 clone. Thermal stability, temperature range, mass loss and percent residue of thermal decomposition from each of the clones are presented in Table 1. Almost all membranes evaluated exhibited thermal decomposition in four stages from room temperature up to 580 °C. The exception was IAC 333, which exhibited an additional mass loss up to 857 °C. This additional step was probably related to pyrolysis of carbonaceous residue [14]. The behavior of latex from IAC 333 is unique among all the IAC clones reported to date [7,8]. These data suggested that the clones with the largest and the smallest thermal stability are IAC 331 and IAC 333, respectively. The first mass loss is detected between room temperature and 179 °C for both IAC 331 and IAC 333, and it is attributed to the elimination of volatile compounds, including water and probably ammonium residue added to latex after extraction to avoid coagulation [10,11]. The second step began at 156 and 179 °C, followed by the third and fourth consecutively step detected from 409 and 425 °C for 331 and 333, respectively. These steps are related to the decomposition of

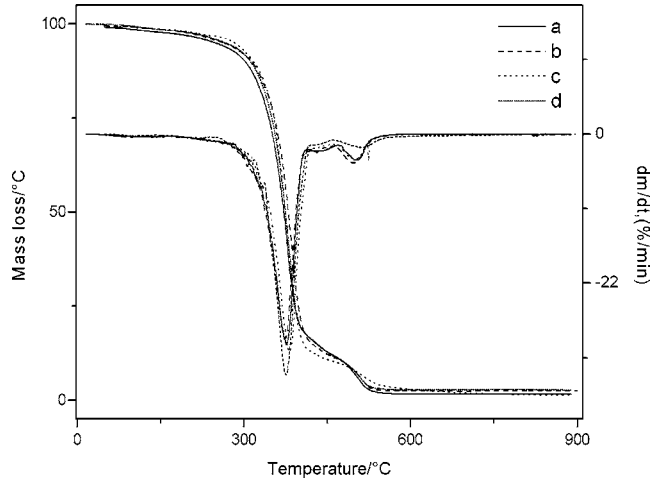

Fig. 2. TG/DTG curves of: (a) IAC 331, (b) IAC 332, (c) IAC 333 and (d) IAC 334 clones.

Table 1
Thermal stability, temperature range and mass losses of thermal decomposition process of natural rubber from *Hevea brasiliensis* clones

Clones *m_i	Temperature range (°C)	Mass loss (%)	Attribution	Residue (%)
GT1	20–170	1.5	Volatile	
12.304 mg	170–585	96.5	Thermal decomposition	2.0
RRIM 600	20–165	2.3	Volatile	
7.687 mg	165–559	93.3	Thermal decomposition	4.4
IAC 331	20–156	1.5	Volatile	
9.3570 mg	156–555	95.9	Thermal decomposition	1.8
IAC 332	20–169	1.3	Volatile	
14.325 mg	169–541	95.5	Thermal decomposition	2.7
IAC 333	20–179	2.3	Volatile	
8.300 mg	179–576	93.4	Thermal decomposition	
	576–850	2.3	Carbonaceous residue	2.0
IAC 334	20–158	1.6	Volatile	
10.038 mg	158–549	95.5	Thermal decomposition	3.0

* Starting mass sample.

the constituents of latex poly-*cis*-1,4-isoprene and other organic substances in minor quantities.

The residue remaining after thermal decomposition to temperatures up to 850 °C, varied between 1.8 and 4.4%, and are attributed to the ashes naturally present as constituent of latex [15] or impurities, inadvertently added to latex during to extraction process at the field [10,11]. Considering the results presented here to the data for all clones from IAC evaluated so far [7,8], there appears to be no relationship between the amount of residue and thermal stability.

The corresponding DSC curves generated for the Asiatic reference clones and IAC clones are presented in Figs. 3 and 4, respectively, and all data about differential scanning calorimetry are shown in Table 2. The results show an initial tendency to deviate from base line in the endothermic direction, but without

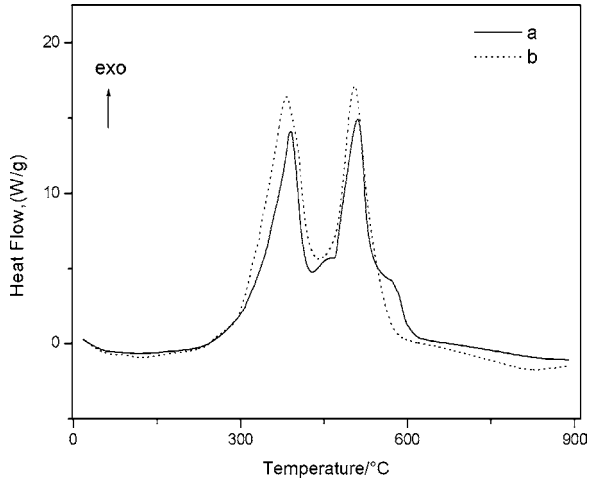

Fig. 3. DSC curves of: (a) GT1 and (b) RRIM 600 clones.

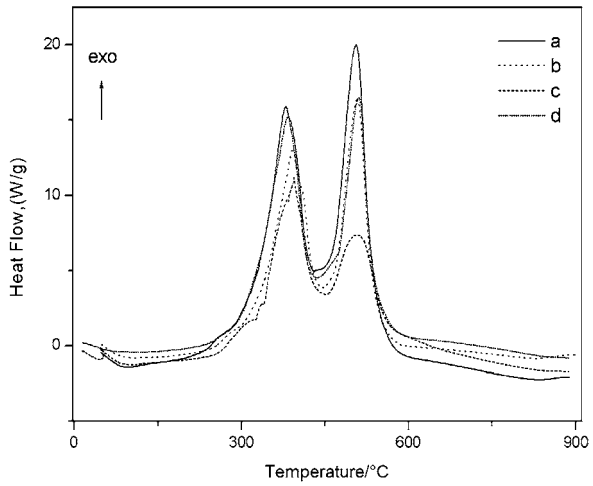

Fig. 4. DSC curves of: (a) IAC 331, (b) IAC 332, (c) IAC 333 and (d) IAC 334 clones.

a characterizing broad endotherm. This endothermic trend can be associated with the elimination of volatile compounds, which occurs with little heat flow. Next it is observed two exotherms at temperatures corresponding to the temperatures observed in the thermal decomposition process provided by TG/DTG data. The first exotherm exhibits a maximum at temperatures between 378 and 391 °C, with heat flow varying from 1.7 to 2.6 kJ/g, which corresponds to the second step of thermal decomposition. The second exotherm occurs at temperatures between 506 and 512 °C, with heat flow varying from 0.8 to 2.6 kJ/g. This exotherm corresponds to the last steps of thermal decomposition. The DSC curve shape of GT1 and IAC 333 clones suggests that thermal decomposition occurs in more than four consecutive steps. It was observed that exotherms and exothermic peaks of the DSC curves obtained from Shimadzu and Netzsch DSC apparatus for the previously data reported [7,8], show a different behavior from those performed by SDTQ600 apparatus.

Table 2
Temperature range, peak temperature and heat flow for the thermal decomposition process of natural rubber from *Hevea brasiliensis* clones

Clones *m_i	Temperature range (°C)	Temperature maximum (°C)	Heat flow (kJ/g)	Characteristic
GT1	240–430	388.6	2.1	Exo
12.304 mg	430–629	512.1	2.2	Exo
RRIM 600	253–443	380.3	2.8	Exo
7.687 mg	443–600	507.0	2.2	Exo
IAC 331	227–431	378.1	2.7	Exo
9.357 mg	431–615	508.1	2.7	Exo
IAC 332	276–445	391.1	2.0	Exo
14.325 mg	445–604	509.9	2.0	Exo
IAC 333	268–450	385.1	1.7	Exo
8.300 mg	450–599	511.8	0.9	Exo
IAC 334	266–436	383.9	2.3	Exo
10.038 mg	436–603	512.3	1.9	Exo

* Starting mass sample.

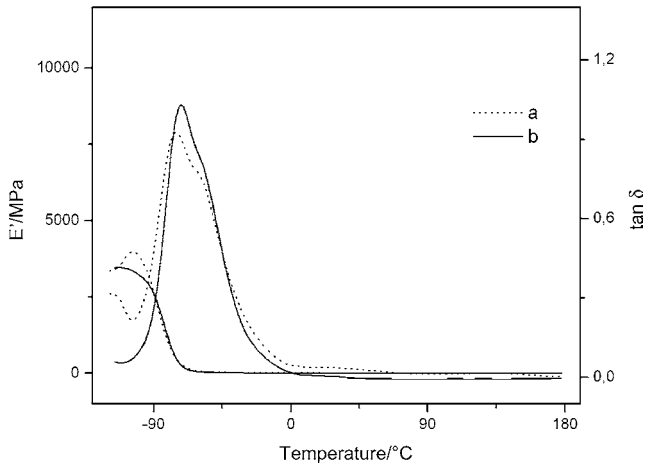

Fig. 5. DMA curves (storage modulus and tan δ) of: (a) GT1 and (b) RRIM 600 clones.

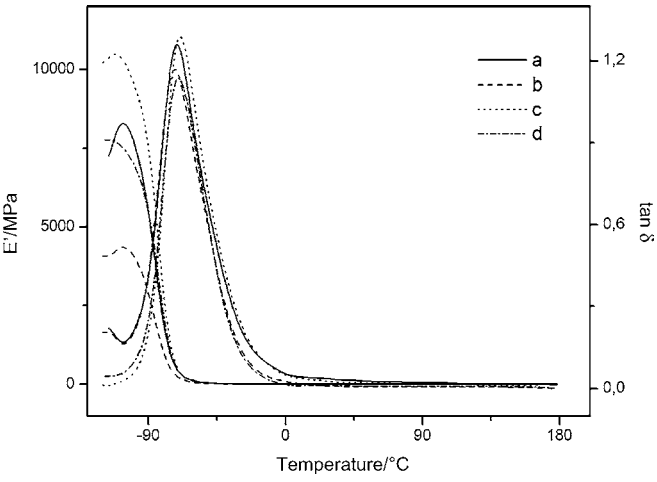

Fig. 6. DMA curves (storage modulus and tan δ) of: (a) IAC 331, (b) IAC 332, (c) IAC 333 and (d) IAC 334 clones.

According to WENDLANT [16] these variations are due to the differences in the assembly of oven and sensor equipment.

The DMA curves of the latex films are presented in Fig. 5 (GT1, RRIM 600 clones) and in Fig. 6 (IAC 331, IAC 332, IAC 333 and IAC 334 clones). In these figures, the storage modulus (E') and loss factor ($\tan\delta = E''/E'$) are plotted as a function of the temperature, which is used to calculate the glass transition temperatures (T_g). Table 3 shows data from the DMA analysis of the Asiatic and IAC clones. The glass transition temperature of GT1 matrix clones was detected at −75.8 and −72.5 °C for RRIM 600. IAC clones T_g ranged from −71.8 to −69.0 °C. A direct relationship between the values of storage modulus (E') and tan δ (E''/E') values was observed for all clones and increased in the following order IAC 333, IAC 334, IAC 331, IAC 332, RRIM 600 and GT1 clones.

Table 3
Cross section (width × thickness), distance between clamps (length), initial value of storage modulus (E') and T_g peak temperature of tan δ from *Hevea brasiliensis* clones

Clone	Cross section (mm)	Length (mm)	Storage modulus (E') (MPa)	T_g (°C)
GT1	4.1	10.3	3355	−75.8
RRIM 600	5.2	10.8	3454	−72.5
IAC 331	6.4	9.8	7306	−71.0
IAC 332	6.9	10.7	4068	−71.8
IAC 333	6.8	12.2	10227	−69.0
IAC 334	4.9	10.9	7739	−70.0

4. Conclusions

The TG/DTG curves (SDTQ600 apparatus) demonstrate that the thermal decomposition behavior of evaluated clones, except for IAC 333, is similar to the other materials from IAC and Asiatic clones previously analyzed, and the Asiatic matrix clones included in this analysis. The DSC curves showed endo and exothermic events which correspond to the mass loss observed by TG/DTG curves, with a good definition.

The T_g temperatures of latex membranes were obtained through DMA curves, and ranged from −75.8 to −69.0 °C.

Data obtained by thermal analysis techniques suggest that latex membranes from the studied clones can be employed at the range of temperature from −69 to 156 °C, without considering a safety range, to keep their viscoelastic properties.

Data provided by these techniques show a great potential on the characterization of latex membranes due their repeatability and reproducibility verified by the assays performed.

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