

A comparative study of the non-isothermal degradation of natural rubber from Mangabeira (*Hancornia speciosa* Gomes) and Seringueira (*Hevea brasiliensis*)

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Abstract Due to the increasing search for alternative sources of natural rubber (NR) whose properties are similar to *Hevea brasiliensis*, several sources have been studied in the past few years. Among them, Mangabeira (*Hancornia speciosa* Gomes), which is native to Amazon rainforest and other regions of Brazil, has a potential as another viable rubber source. As a continuation of a series of comparative studies between *Hancornia* and *Hevea* (clone RRIM 600) these two species by our research team, their thermal behavior was analyzed by thermogravimetry (TG) using Flynn–Wall–Ozawa’s approach in order to obtain kinetic parameters (reaction order, pre-exponential factor and activation energy) of the decomposition process. Results indicated that the thermal behavior of NR from *Hancornia* was comparable to *Hevea* with some differences observed as follows: reaction order for *Hancornia* was higher than for *Hevea* at the beginning of degradation

and very close for temperatures over 350 °C; activation energy and pre-exponential factor had the same trend, i.e., increased with increasing degree of conversion remaining almost constant between 20 and 70% and then increasing for higher degrees, although *Hevea* was slightly more thermally stable than *Hancornia*. These major influences in the degradation process in the early stage are attributed to differences in non-rubber constituents present in these two species.

Keywords Natural rubber · Thermal behavior · *Hevea brasiliensis* and *Hancornia speciosa* Gomes · Mangabeira

Introduction

For the past few years, there has been an increasing search for materials from ecologically friendly materials from renewable resources due to the growing need to reduce residue accumulation from synthetic polymers [1–5]. In this context, natural rubber (NR) has been increasingly replacing synthetic ones in many applications favored by its unique properties such as elasticity, flexibility and resilience. Furthermore, NR has a wide range of commercial applications in various products that require superior properties, including high-performance tires used in aircraft and automotive industries [1, 6–8].

NR is a natural polymer, high-molecular-mass *cis*-1,4-polyisoprene, which can be obtained from over 2,500 different species of plants [1, 3]. However, the most economically important source of NR is the Pará rubber tree (*Hevea brasiliensis*) due to its facility of plantation and adaptation to different climates, high productivity and rubber content in the latex (ca. 30–36%), high molecular

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mass of the polymer, and good chemical and thermal resistance of the cured products [6–9].

Several rubber-producing plants such as Guayule (*Parthenium argentatum*), dandelion (*Taraxacum koksaghy*), golden rod (*Solidago canadensis*) and Mangaba tree (*Hancornia speciosa* Gomes) have emerged in the search for new alternative sources of rubber [4, 5]. The most important feature that must be displayed by these sources, in addition to high productivity, feasibility of cultivation and harvesting, is high molecular mass, which is the main factor determining ultimate properties and applications [5, 7, 8].

Hancornia speciosa Gomes, a member of Apocynacea family commonly known as “mangabeira”, is a plant native to Amazon rainforest, Caatinga, and Cerrado vegetations in Brazil that grows more than 10 m tall and is not only well known for its uses in local cuisine and in traditional medicine—mangabeira fruits can be eaten fresh or consumed as juice, jellies, confectionery, ice cream, and liquors, and its latex has been used in treatments for gastrointestinal disorders and tuberculosis [4]—but also has attracted attention of scientists for its potential use as an alternative source of rubber [10–12]. However, only recently have the technological (nitrogen, ash content, plasticity retention index, Wallace plasticity, Mooney viscosity, dry rubber content and acetone extract) and structural (protein content, molecular mass, FTIR, NMR) properties of its rubber been characterized [11, 12]. The low protein content of *Hancornia*, when compared to *Hevea* latex, was one of the most remarkable findings, suggesting its potential in nonallergic applications.

In addition to the above-mentioned properties, understanding of the thermal behavior is of key importance to rubber industries because both processing and maximum end-use temperatures depend on this behavior, i.e., in order to process any rubber product, one needs to know its thermal behavior so that degradation during and after processing is minimized. Moreover, the durability of any finished rubber product depends, among several other factors, on the end-use temperature since the higher this temperature the shorter its durability. In this work, rubber from *Hancornia speciosa* Gomes was analyzed by TG in combination with Flynn–Wall–Ozawa approach, which was used due to its good reproducibility and relative simplicity of execution, to assess kinetics parameters in order to compare the thermal behavior of *Hancornia* with “standard” NR from *Hevea brasiliensis* (clone RRIM 600).

Experimental

Lattices were collected and pooled from 25 trees of *Hevea* (RRIM 600) and 60 trees of *Hancornia* and stabilized in

commercial ammonia solutions. These samples were collected from the same location [Experimental farm of the São Paulo State University (UNESP), campus of Ilha Solteira, Brazil, located at 20°22' S of latitude, 51°22' W of longitude and 335 m of altitude], which is a region with a characteristic tropical pluvius climate and a predominantly Rhodic Haplustox soil.

TG analyses were carried out on a thermoanalyzer model Q 500 (TA Instruments, USA). Dynamic scans were conducted in a temperature range of 25–600 °C, at constant heating rates of 5, 10, 15 and 20 °C min⁻¹, under nitrogen atmosphere at a flux rate of 40 mL min⁻¹. For sample preparation, about 10 mg of NR was used in an Al₂O₃ crucible. Experiments were carried out under inert (nitrogen) atmosphere to minimize the effect of oxygen in the thermal degradation process since oxygen causes side reactions that make the kinetic process extremely difficult to be comparatively analyzed.

In order to obtain the kinetic parameters of rubber degradation, thermogravimetric curves were analyzed according to Flynn–Wall–Ozawa’s approach [13–18]. In summary, when solid polymeric material undergoes non-isothermal decomposition at constant heating rate ($\beta = dT/dt$) thermal decomposition events can be described by

$$\frac{d\alpha(t)}{dt} = \beta \frac{d\alpha(T)}{dT} = f(\alpha)A \exp\left(\frac{-E}{RT}\right) \quad (1)$$

where $d\alpha(t)/dt$ is the time rate of consumption of polymer (α being the fraction that undergoes decomposition or the conversion degree), A is the pre-exponential factor, E is the activation energy of the degradation process, R the gas constant, and T is the absolute temperature.

By means of a series of mathematical steps [19–21], Eq. 1 results in the following expression

$$\ln \beta = \ln\left(\frac{AE}{R}\right) - 5.3305 - 1.0516\frac{E}{RT} - \ln(F(\alpha)) \quad (2)$$

where $F(\alpha)$ is a power series expansion for the integration of the exponential term of Eq. 1. Therefore, for a constant degree of conversion ($\alpha = \text{constant}$), the plot of $\ln(\beta)$ versus $1/T$, obtained from TG curves recorded at several constant heating rates (β) should result in a straight line whose slope is approximately $-1.0516E/R$ and intercept yields the pre-exponential factor.

In order to determine reaction order (n), also known as the Flynn–Wall–Ozawa’s exponent, Avrami’s theory [22] was extended for non-isothermal conditions giving

$$\alpha(T) = 1 - \exp\left[\frac{-k(T)}{\beta^n}\right] \quad (3)$$

By taking double logarithm in both sides of Eq. 3 with $k(T) = A \exp\left(\frac{-E}{RT}\right)$, the following expression is obtained:

$$\ln\{-\ln[1 - \alpha(T)]\} = \ln(A) - \frac{E}{RT} - n \ln(\beta) \quad (4)$$

Therefore, a plot of $\ln[-\ln(1 - \alpha(T))]$ versus $\ln(\beta)$, which is obtained at the same temperature from a number of isotherms taken at different heating rates, should yield straight lines whose slopes will have the value of the reaction order [20–22].

Results and discussion

Figure 1 shows the thermogravimetric (TG) and first derivative (DTG) curves for rubber obtained from *Hevea* and *Hancornia* samples at heating rates of 5, 10, 15 and 20 °C min⁻¹. The onset of thermal decomposition occurred between 290 and 300 °C, almost independently from the heating rate. As the decomposition takes place the maximum of DTG curves shifts from 360 to 395 °C as the heating rate increases from 5 to 20 °C min⁻¹ for both species. The end of thermal decomposition process occurred up to 490 °C with about 1–3% of char yield. Moreover, the similarity between the TG curves for these two species studied is an indication that the decomposition mechanisms may be the same. This is somewhat expected since both *Hevea* and *Hancornia* species produces essentially *cis*-1.4-polyisoprene with little changes in latex composition [11]. On the other hand, when molecular mass and latex composition are very different, thermal stability may give rise to different thermal behaviors.

Figure 2 shows the plots of $\ln\{-\ln[1 - \alpha(T)]\}$ versus $\ln(\beta)$ for the calculation of the reaction order as a function of the temperature in the active pyrolysis region. The values of reaction order, calculated from the slopes of the straight lines in Fig. 2, are shown in Fig. 3 as a function of the temperature.

It can be seen that reaction order increased with increasing temperature up to 1.24 and, subsequently, decreased to a lower value near zero at the completion of the reaction. This indicates that both the early and the latter stages of rubber degradation follow zero order kinetics, whereas the intermediate stages follow a first order kinetics as reported in our previous works [20, 21].

Polymer degradation is a complex phenomenon involving many reactions that are difficult to analyze separately. During the early stages of degradation random scission occurs along the main chains with simultaneous crosslinking, and therefore becomes an autocatalytic process with the reaction course. As the reaction proceeds, the increase in mass fraction of decomposed sample, crosslinked compounds and volatiles liberation contribute to a reduction in reaction order until it reaches a minimum at higher degrees of conversion [20, 21]. Therefore, explaining the bell-

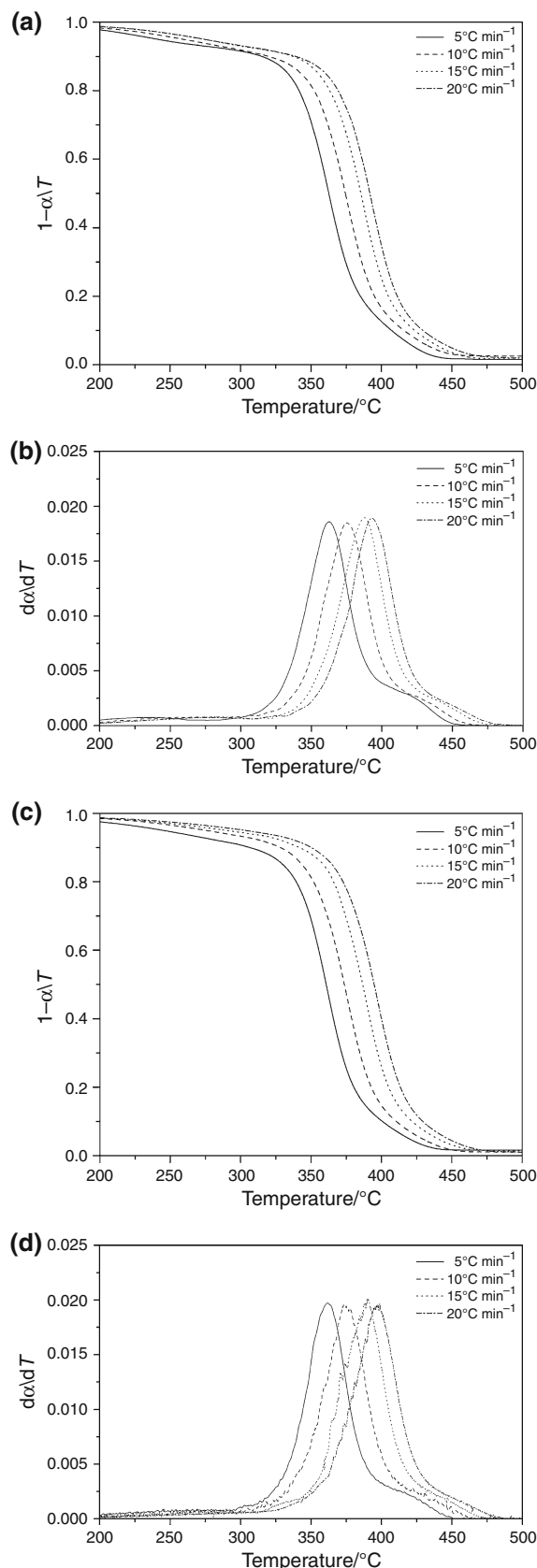


Fig. 1 Plots of $1 - \alpha(T)$ versus T and $d\alpha(T)/dT$ versus T for **a, b** *Hevea* and **c, d** *Hancornia*

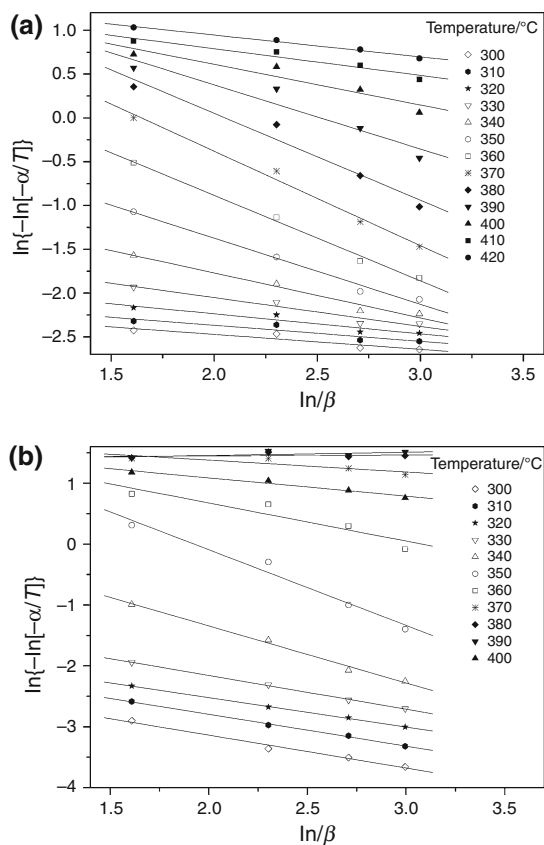


Fig. 2 $\ln\{-\ln[1 - \alpha(T)]\}$ versus $\ln(\beta)$ for a *Hevea* and b *Hancornia*

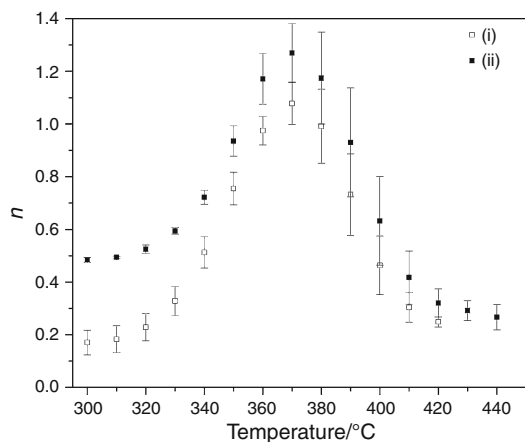


Fig. 3 Order of reaction (n) as a function of the temperature for (i) *Hevea* and (ii) *Hancornia* rubbers

shaped curve of the variation of reaction order with the temperature (Fig. 3).

It can be also observed that the reaction order for *Hevea* rubber was considerably lower than for *Hancornia* at the beginning of the degradation and assumed similar values for temperature over 350 °C. For temperatures over 350 °C, which lie in the active pyrolysis region (300–475 °C), a significant reduction in non-rubber components

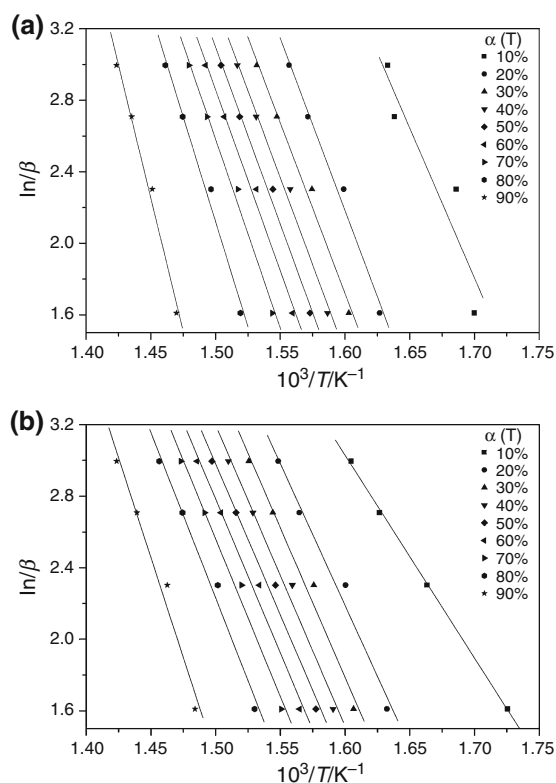


Fig. 4 Plots of $\ln(\beta)$ versus $1/T$ for a *Hevea* and b *Hancornia*

and molecular mass due to chain scission has already taken place. Thus, the possible differences between the two sources of rubber due to factors such as non-rubber constituents and molecular mass differences can no longer be taken into account, and the partly degraded rubbers might have similar thermal behaviors.

It is well known in the literature that besides polyisoprene, its major component, natural rubber contains carbohydrates, proteins, lipids, heavy metals and other components [23–26]. The quantities of these components depend on clones, seasonal variation and climate, and influence on the properties of dry rubber, including mechanical, thermal and industrial ones [11, 20, 21, 23, 27]. However, the major influence of the non-rubber components on the thermal behavior may take place in the early stage of the degradation process, at low temperatures, where they are not yet totally decomposed.

Malmonge et al. [11] studying technological properties (dry rubber, ashes, nitrogen and protein content, Wallace plasticity, plasticity retention index and Mooney viscosity and rubber/latex acetone extract) of latexes and natural rubbers from *Hancornia* and *Hevea* found that the protein content of *Hancornia* is much lower than *Hevea*, therefore in agreement with the differences found for the thermal behavior of these two sources of rubber. Moreover, as pointed out by these authors and corroborated by the

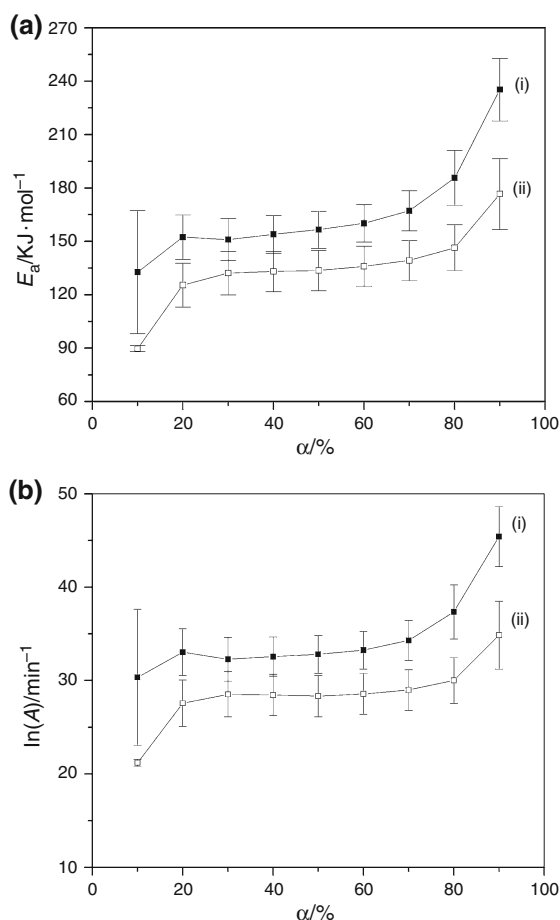


Fig. 5 **a** Activation energy of (E_a) and **b** natural logarithm of the pre-exponential factor, $\ln(A)$, versus the degree of conversion for (i) *Hevea* and (ii) *Hancornia* rubbers

literature [28, 29], despite not being beneficial for the thermal behavior, a low protein content rubber can be very useful in non-allergic applications.

Figure 4 shows the plots of $\ln(\beta)$ versus $10^3/T$ for the calculation of the activation energy (E) as a function of the conversion degree, $\alpha(T)$. The values of the activation energy as a function of the conversion degree and the pre-exponential factor, $\ln(A)$, measured as the intercept of the straight lines of the plots of $\ln(\beta)$ versus $10^3/T$, are shown in Fig. 5.

Figure 5 shows that both the activation energy and pre-exponential factor increased with increasing degree of conversion remaining almost constant for degrees of conversion between 20 and 70% and then increasing for higher degrees. This variation in activation energy values was already expected because when more than one degradation mechanism is occurring the activation energy will not always be constant [20, 21]. It can also be observed that, in agreement with the Flynn–Wall–Ozawa's exponent values in Fig. 3, rubber extracted from *H. brasiliensis* is slightly

more thermally stable than the one from *H. speciosa*. Since previous results [11] showed that *Hancornia* has a molecular mass somewhat higher ($1.13 \times 10^6 \text{ g mol}^{-1}$) than *Hevea* ($1.00 \times 10^6 \text{ g mol}^{-1}$), which would be expected to confer an opposite thermal behavior, the main factor that must have contributed to this apparently opposite trend was the presence of non-rubber constituents, especially the higher amount of proteins in *Hevea*. The influence of non-rubber components on thermal behavior of the two species is currently under investigation.

Conclusions

Results showed that rubbers extracted from *H. speciosa* and *H. brasiliensis* had a similar thermal behavior. Reaction order indicated a multi-step degradation process for both rubbers. It was also observed that the reaction order for *Hevea* rubber was considerably lower than for *Hancornia* at the beginning of the degradation and assumed similar values for temperatures over $350 \text{ }^\circ\text{C}$. Activation energy and pre-exponential factor increased with increasing degree of conversion remaining almost constant between 20 and 70% and then increasing for higher degrees, therefore in agreement with the reaction order values. This indicated that rubber extracted from *H. brasiliensis* was slightly more thermally stable than the one from *H. speciosa*. The major influence of the non-rubber constituents on the thermal behavior took place in the early stage of the degradation process, at temperatures below $350 \text{ }^\circ\text{C}$, where they were not yet totally decomposed. Meanwhile, for temperatures higher than $350 \text{ }^\circ\text{C}$, possible differences between the two sources of rubber due to factors such as non-rubber constituents and molecular mass could no longer account for thermal stability due to their partly or totally degraded nature as well as partial rubber decomposition. This study therefore shows the potential of *Hancornia* as another alternative source of rubber whose thermal properties can be comparable to rubber from *H. brasiliensis*.

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