

# Comparative Study on the Technological Properties of Latex and Natural Rubber from *Hancornia speciosa* Gomes and *Hevea brasiliensis*

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**ABSTRACT:** This work reports a systematic comparative study of the technological properties of natural latices and rubbers extracted from *Hancornia speciosa* Gomes and *Hevea brasiliensis* [(Willd. ex Adr. de Juss.) Muell.-Arg.] (clone RRIM 600) trees from 11 collections in Brazil throughout 2004. Natural rubber latex particle sizes and distributions were quite similar with an average diameter around 1  $\mu\text{m}$ . Molecular weight, Wallace plasticity, and Mooney viscosity values were approximately the same for both rubbers. Fourier transform infrared spectroscopy peaks characteristic of natural rubber were observed for both *Hancornia* and *Hevea*. The measured differences in

technological properties included lower values for *Hancornia* dry rubber content, % ash, % nitrogen, and plasticity retention index but higher value for acetone extract. Interestingly, nitrogen and protein content were much lower in *Hancornia*, suggesting that it may have important applications in nonallergic rubber uses. This represents the first report of laticifer-produced low-protein natural rubber. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2986–2991, 2009

**Key words:** latex; natural rubber; *cis*-1-4-polyisoprene; *Hancornia speciosa* Gomes; *Hevea brasiliensis*

## INTRODUCTION

Natural rubber has a wide range of commercial applications because of its superior elasticity, flexibility, and resilience. This material is a biopolymer consisting of isoprene units linked together in a 1,4-*cis* conformation. Among more than 2500 species<sup>1</sup> of plants that produce rubber, *Hevea brasiliensis* [(Willd. ex Adr. de Juss.) Muell.-Arg.], the Brazilian rubber tree, is by far the largest commercial source, because of its excellent quality, high rubber content, and production capability.

*Hancornia speciosa* Gomes (member of Apocynaceae), a native Brazilian plant popularly known as “mangabeira,” is a tree that grows more than 10 m tall in the Amazon, North-East, and Center-East of Brazil. It is also found in Venezuela, Colombia, and Peru. Its fruit, known in Brazil as mangaba, can be

eaten fresh or consumed as juice, ice cream, jellies, confectionery, and liquor.<sup>2</sup> The growth of commercial uses for the fruit, mainly in the north and north-east of Brazil, has aroused the interest of researchers<sup>3–6</sup> in increasing the productivity and improving the characteristics of the fruit.

*Hancornia* also produces white latex that can be tapped from the tree similarly to *Hevea*. This latex has been used in traditional medicine to protect against gastric disorders and tuberculosis<sup>2</sup> and as a source of rubber during times of emergency. It is therefore possible to obtain both fruit and latex from the same plant. Although the literature<sup>7,8</sup> reports that *Hancornia* rubber has comparable molecular weight and microstructure to *Hevea* rubber, no systematic study has been done covering a wide range of physical and chemical properties, especially those of interest for the tire industry, nor throughout the year.

In the present study we investigated the quality of the latex and rubber extracted from *Hancornia speciosa* Gomes trees in 11 collections conducted during 1 year compared with that of *Hevea brasiliensis* (clone RRIM 600) using standard methods of technological interest.

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## EXPERIMENTAL

### Sample collection

The lattices were collected and pooled from 25 trees of *Hevea* (RRIM 600) and 60 trees of *Hancornia* from the same location [Experimental Farm of the University of São Paulo State (UNESP), campus of Ilha Solteira, located at 20° 22' S latitude, 51° 22' W longitude, and 335 m altitude] and stabilized in a commercial solution of ammonium hydroxide. This region's soil is predominantly Rhodic Haplustox and the climate is predominantly tropical pluvius. The trees, *Hevea* and *Hancornia*, were planted in 1997 with spacing of 5 m along the plantation lines and 3 m between plants. Latex collection took place for 11 months, starting in February 2004. For each collection, trees were tapped over 3 consecutive days. The temperature data represent the average of 15 days before the date of each collection and the precipitation is the sum of all precipitation occurring 15 days before each collection. The pooled latex samples were thoroughly mixed, coagulated with 3N acetic acid, and dried at 40°C. A separate latex collection in April 2007 was conducted to secure fresh latex for particle size, protein, and molecular weight evaluations.

### Physical and chemical characterization

Technological properties of the lattices and dry natural rubber were evaluated by the standard methods for determining the dry rubber content (% DRC), nitrogen content (% N), ash content (% ash), acetone extract (% AE), Wallace plasticity ( $P_0$ ), Mooney viscosity ( $V_R$ ), and plasticity retention index [PRI (%)], using standard procedures described by the Brazilian Association of Standard Methods (ABNT)<sup>9</sup> which are consistent with those from ISO 2859-1 and ISO/ID 3951. All tests were performed in triplicate.

The Wallace plasticity was obtained using a Plastimeter model PG-2000AX (GRAMMA). In this case, 10 samples of 10 cm diameter and 3.6 mm height were die cut from a rubber sheet; five samples used to measure initial plasticity ( $P_0$ ) and five to measure plasticity after oven aging at 140°C for 30 min ( $P_{30}$ ). The % PRI is calculated as follows<sup>10</sup>:

$$\% \text{ PRI} = (P_{30}/P_0) \times 100 \quad (1)$$

The Mooney viscosity was obtained using a Mooney Viscometer model MVG-2000AX (GRAMMA). Two samples of 50 mm diameter and 6 mm thickness with a central hole of 8 mm in diameter were used for each test. The chamber was maintained at 100°C ( $\pm 0.5^\circ\text{C}$ ).

Molecular weights and their distributions were determined by gel permeation chromatography of rubber solutions ( $\sim 7$  mg/mL) prepared from dried latex dissolved overnight in tetrahydrofuran. The

soluble fraction was filtered through 1.6- $\mu\text{m}$  poly(tetrafluoroethylene) (PTFE) syringe filters (Millipore, Burlington, MA) into autosampler vials with silicone/PTFE lined septa. A 50  $\mu\text{L}$  aliquot of solution was injected into a Hewlett-Packard 1100 series HPLC, coupled to multiangle laser light scattering (DAWN DSP laser photometer; Wyatt Technologies, Santa Barbara, CA), and a multiple refractive index (HP107) detector (Agilent Technologies, Palo Alto, CA) using a Phenogel 5- $\mu\text{m}$  Linear/Mixed Guard Column (Agilent Technologies) and a PL gel 10- $\mu\text{m}$  Mixed-B size exclusion column maintained at 35°C. Molecular weight averages were normalized to a  $1.2 \times 10^6 M_w$  polyisoprene standard.

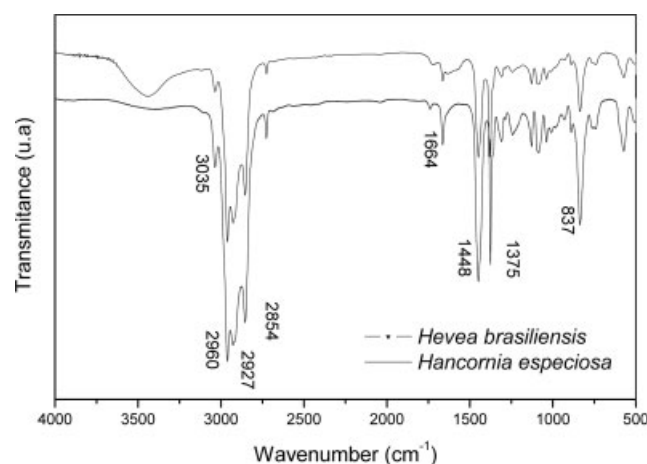
The particle size distribution of the lattices was determined from dilute latex suspensions using a Horiba LA-900 Laser Light Scattering Particle Size Distribution Analyzer according to the manufacturer's instructions.

Total protein [ $\mu\text{g/g}$  dry weight (dw) latex] was measured according to ASTM D 5712, a modified Lowry protein assay. Values reported are the average of three determinations and represent all detectable protein in latex after solubilization in 1% sodium dodecylsulfate and 50 mM sodium phosphate buffer.

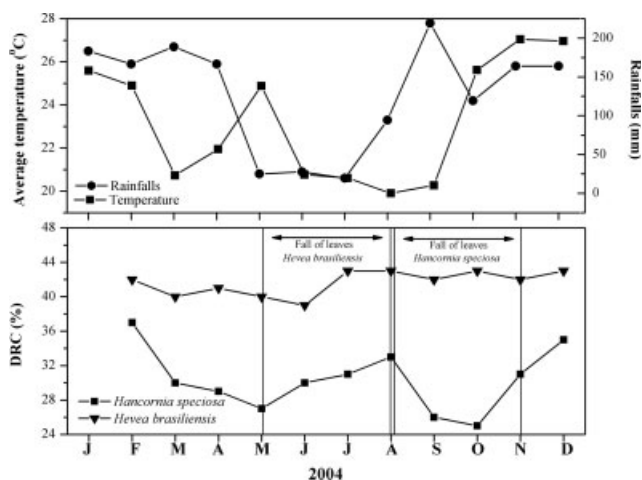
Fourier transform infrared (FTIR) spectra were recorded with a NEXUS 670 spectrophotometer from Nicolet Instrument (Madison, WI). Purified lattices (centrifuged at 12,500 rpm for 20 min at 4°C) were coagulated with 3N acetic acid and dissolved in toluene. The solutions were cast on glass slides, placed in an oven with air circulation, and then the temperature was increased to 60°C for 24 h. Thin films ( $<15$   $\mu\text{m}$ ) were peeled from the glass surfaces and analyzed by FTIR.

## RESULTS AND DISCUSSION

The FTIR spectra for *Hancornia* and *Hevea* (Fig. 1), indicate characteristic polyisoprene bands as described



**Figure 1** FTIR spectra of the rubber extracted from *Hancornia* and *Hevea* trees.



**Figure 2** Variation of DRC for *Hancornia* and *Hevea* latex and the climatic conditions during 2004.

in the literature.<sup>11–14</sup> Primary cis-1,4 microstructure of rubber from *Hancornia* has been reported from NMR determinations.<sup>8</sup>

DRC is a physiological parameter of the latex, which is influenced by seasonal and clonal variation. It is a measure of the amount of rubber in latex and also reflects the photosynthetic activity in the tree's laticiferous vessels. Latex production and more precisely the latex flow can be influenced by high DRC because of viscosity effects.<sup>15</sup> Besides the variation among trees and clones, DRC can be influenced by other factors such as: tapping systems, climatic phenological variation throughout the year, and stimulation.<sup>16,17</sup> In this study, *Hevea* DRC was higher and more stable throughout the year than *Hancornia* DRC (Fig. 2). On average, *Hevea* DRC was 28% higher than that of *Hancornia* (Table I). This is not entirely surprising, since *Hevea* has been bred primarily for rubber production. Moreover, literature values for *Hevea* DRC are normally lower than that found here.<sup>16,18–20</sup> This can be explained by the low

frequency of tapping of the trees, since the seringal studied in the present work were used for research only.

The lowest values of DRC were, in general, obtained during the leaf senescence period, as observed in *Hevea* by Ortolani et al.<sup>21</sup> and Moreno et al.<sup>18,19</sup> The lowest DRC values found in this study were from May to August for *Hevea* and from August to November for *Hancornia* (Fig. 2) which correspond to the leaf senescence periods for *Hevea* and *Hancornia*, respectively.

The % N is a technological estimation of the protein content in dry rubber.<sup>16,22</sup> Remarkably, *Hancornia* rubber showed much lower % N than *Hevea* rubber; although in both cases, % N is below the 0.6% that corresponds to the maximum content recommended by the Brazilian Standards NBR 11597.<sup>9</sup> No significant variation in % N was observed during the 11 months of this study (Fig. 3).

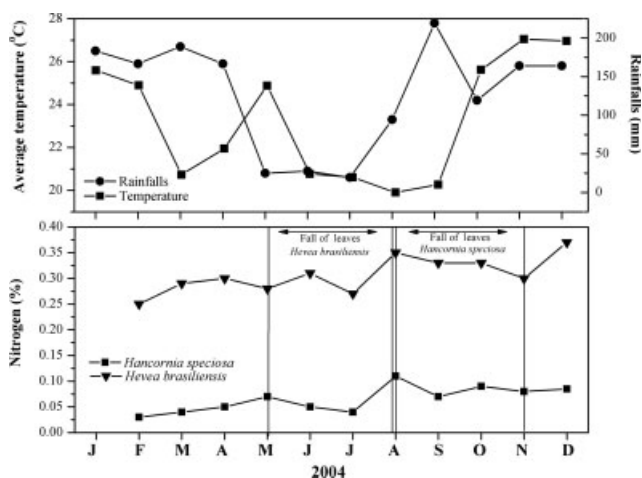
Total protein content of latex collected from both species on April 2007 was determined as described earlier. Fresh *Hevea* latex total protein was  $32,300 \pm 167 \mu\text{g/g}$  dw latex, and *Hancornia*  $1900 \pm 32 \mu\text{g/g}$  dw latex. So the lower %N is indeed related to lower protein, as expected. The ASTM D 1076-06 specification for protein content of a Category 4 Latex (safe for people with Type I latex allergy) is under  $200 \mu\text{g/g}$  dry wt. rubber (and no detectable antigenic proteins). Nevertheless, the low initial value for protein in fresh *Hancornia* latex is encouraging and additional studies are warranted. Moreover, the dramatic difference in latex protein content between two laticifer-forming species, grown under the same climatic and edaphic conditions, suggests it is neither the laticifer structure *per se* nor the tapping process that is responsible for the protein content of *Hevea* latex but rather the basic biology of the plants.

The %AE of the rubber is the organic acetone-soluble fraction whose main components are lipids.<sup>16</sup> These lipids are integral to the latex particle

**TABLE I**  
Technological Properties of Latex-Rubber Extract from *Hancornia speciosa* Gomes and *Hevea brasiliensis* (Clone RRIM 600) Measured Over 11 Months

Technological properties	<i>Hancornia</i>			<i>Hevea</i>		
	$\bar{x}$	s	CV (%)	$\bar{x}$	s	CV (%)
DRC (%)	30.3	3.67	12.08	41.6	1.43	3.44
N (%)	0.065	0.025	38.46	0.31	0.035	11.40
Ash (%)	0.105	0.0752	71.415	0.144	0.0430	29.778
Acetone extract (%)	6.90	0.89	12.9	2.59	0.55	21.06
$P_0$	42	6	15	40	5	13
PRI (%)	64	9	13	79	9	11
$V_R$	89	17	19	89	6	7

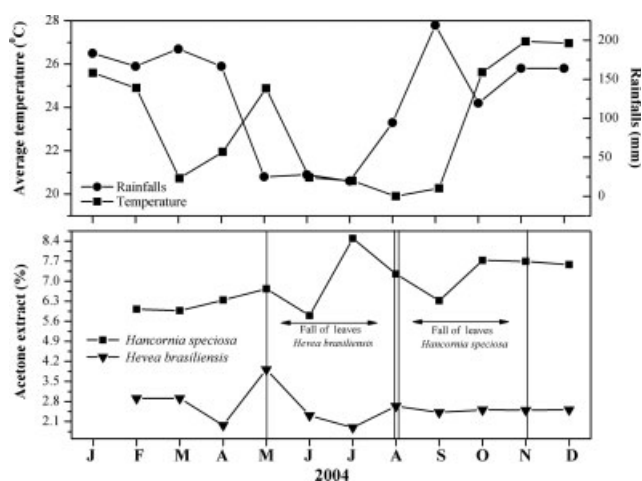
Averages ( $\bar{x}$ ), standard deviations (s), and coefficients of variation [CV (%)] for the technological properties [dry rubber content (DRC), nitrogen content, ash, acetone extract, Wallace plasticity ( $P_0$ ), plasticity retention index (PRI), and Mooney viscosity ( $V_R$ )].



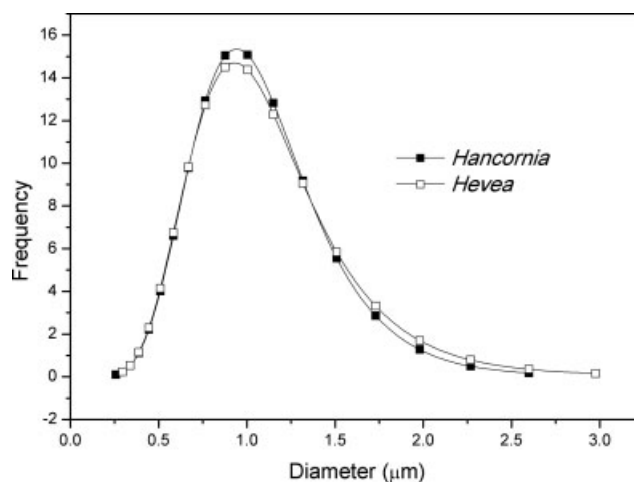
**Figure 3** Variation of nitrogen content for *Hancornia* and *Hevea* natural rubber and the climatic conditions during 2004.

membranes and they influence mechanical stability during storage in ammonia.<sup>23</sup> The average value (6.90%) for *Hancornia* was higher than that found for *Hevea* (2.59%) (Fig. 4). Note also that FTIR spectra show a more pronounced  $\text{—OH}$  stretch around  $3300\text{ cm}^{-1}$ , probably because of free fatty acids and/or alcohols in *Hancornia* (Fig. 1). The % acetone extracts considered appropriate for industrial use of natural rubber is between 2 and 5%,<sup>9</sup> which is lower than that found for *Hancornia*. High lipid content in natural rubber may increase gel (insolubles) content and/or adversely affect green compound tack and appearance.<sup>24</sup>

Plants produce rubber encapsulated in  $\sim 1\text{-}\mu\text{m}$  diameter latex particles with phospholipid monolayer membranes consisting of species-specific fatty acids, proteins, and lipids.<sup>25</sup> The differences in acetone extracts observed here may in fact be due to inter-



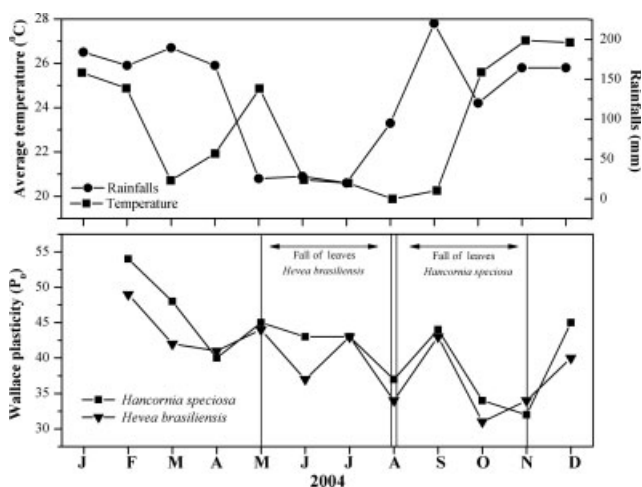
**Figure 4** Variation for extract acetone of *Hancornia* and *Hevea* latex and the climatic condition of 2004.



**Figure 5** Particle size distribution for rubber particles from *Hancornia* and *Hevea*.

specific variation of the particle composition. Systematic differences in particle size between species have also been reported.<sup>26</sup> However, the mean rubber particle size distribution profiles for *Hancornia* and *Hevea* rubbers are quite similar (Fig. 5). The average particle size was approximately the same, i.e.,  $\sim 1\text{ }\mu\text{m}$  for both species. The higher lipid content in *Hancornia* then highlights important differences in rubber particle composition. Siler et al.<sup>25</sup> quantified the lipid content of natural rubber particles in four species and found insufficient membrane lipid for a complete monolayer, suggesting that the rubber particle surface is a mosaic of protein, conventional membrane lipids and other components.<sup>25</sup> In *Hancornia* higher acetone extracts, fatty acids may be needed to stabilize a membrane that is inherently lower in protein. Similar characteristics have been reported for guayule latex particles.<sup>25</sup>

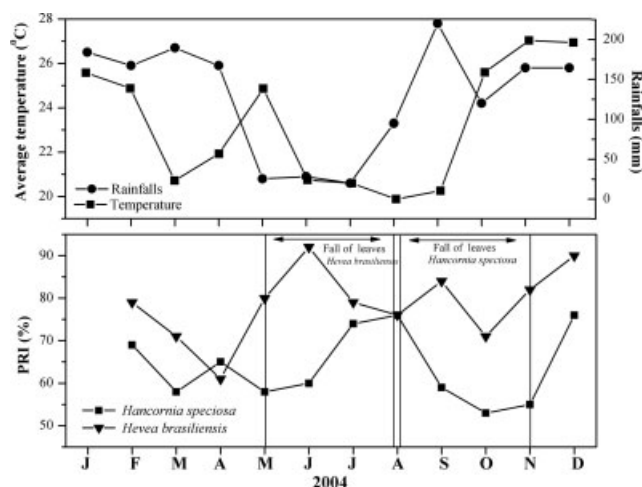
$P_0$  and  $V_R$  are the main properties considered in the evaluation of the processability of natural rubber by the tire industry as well as other industry sectors. Excessively hard rubbers, i.e., high  $P_0$  and  $V_R$  values, are not always preferred because of the high consumption of energy, labor, and time for their processing.<sup>16</sup>  $P_0$  values were approximately the same for both rubbers (Fig. 6) and remain above 30, below which the rubbers are considered very soft.<sup>27</sup> No significant variation in  $P_0$  was observed during the year. The same average value for  $V_R$  was found for *Hancornia* (89) and *Hevea* (89) (Table I) with higher variation for *Hancornia* (Fig. 7). The molecular weights and distributions for *Hancornia* and *Hevea* rubbers (April 2007) are comparable:  $M_w$  was  $1.13 \times 10^6\text{ g/mol}$  with polydispersity of 1.24 and  $1.00 \times 10^6\text{ g/mol}$  with polydispersity of 1.24 for *Hancornia* and *Hevea*, respectively. Therefore, the three key indicators of polymer structure, namely  $V_R$ ,  $P_0$ , and  $M_w$ , suggest that *Hancornia* natural rubber is similar to



**Figure 6** Variation of plasticity ( $P_0$ ) for *Hancornia* and *Hevea* natural rubber and the climatic conditions during 2004.

*Hevea* natural rubber for practical use; i.e., the degree of polymerization and microstructure are the same.

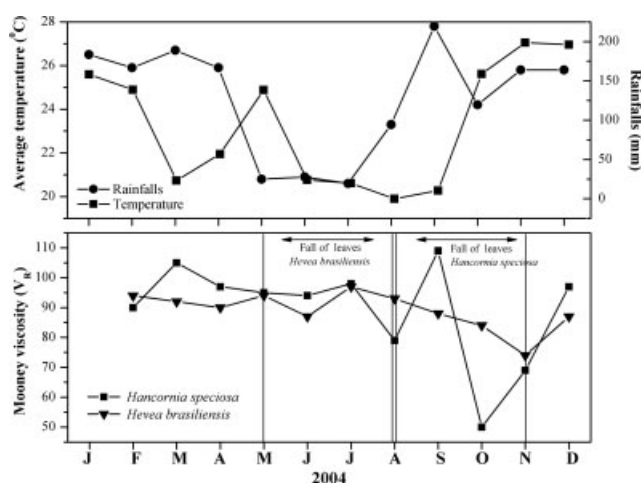
Another important technological property of rubber, % PRI, is an estimate of the resistance to thermo-oxidative degradation of natural rubber.<sup>16,27</sup> PRI is used as a technological tool for prediction of processability of natural rubber; it varies with clonal origin, type of collection, maturation time, process, etc., in *Hevea*.<sup>28</sup> The standard NBR 11597<sup>9</sup> specifies 60% as a necessary minimum value for all rubber types. In this study, *Hevea* averaged 79% over the collection period (Table I). The average PRI for *Hancornia* was 64% and above the minimum value. However, significant variation was observed during the year for both rubbers (Fig. 8), including five values below 60% for *Hancornia*. High variation in PRI has been previously noted for *Hevea*.<sup>19,29</sup> However, at times the differences in PRI between the species



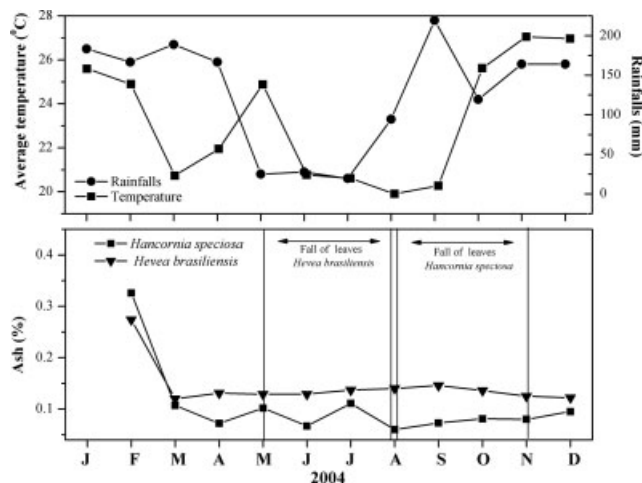
**Figure 8** Variation of PRI for *Hancornia* and *Hevea* natural rubber and the climatic conditions during 2004.

was dramatic (e.g., collections in June and November). Since *Hancornia* rubber was more sensitive to oxidative degradation, as measured by PRI, it may be expected to undergo greater viscosity reduction during processing. Tuampoemsab and Sakdapipaich<sup>30</sup> recently studied the effect of nonrubber constituents on PRI and found that while extraction of proteins or lipids reduces PRI, the effect of proteins is more pronounced. Mitigation of heat oxidative aging of raw rubber in *Hevea* by natural proteins was supported by molecular weight measurements after heat aging. Lower PRI reported here for *Hancornia* rubber might then be related to lower protein levels. The mechanism is complex, however, in that the same study suggested isolated lipids with free fatty acid promote the oxidative degradation of natural rubber.<sup>30</sup>

Low variation in % ash was observed in both rubbers except for February, which was the first



**Figure 7** Variation of Mooney viscosity ( $V_R$ ) for *Hancornia* and *Hevea* natural rubber and the climatic conditions during 2004.



**Figure 9** Variation of ash percentage for *Hancornia* and *Hevea* natural rubber and the climatic conditions during 2004.

collection after a long period without tapping (Fig. 9). The average values found here were 0.105% and 0.144% for *Hancornia* and *Hevea*, respectively, with *Hancornia* apparently more susceptible to variation from environmental and/or biological causes than *Hevea*. All % ash values lie within the established specification NBR 11597.<sup>9</sup>

### CONCLUSIONS

*Hancornia* trees produce natural latex containing high-molecular-weight *cis*-1,4-polyisoprene with many technological properties comparable to natural rubber from *Hevea*, which suggest it is suitable for use in industrial applications. The key differences in physical/chemical properties and temporal variation were also identified. The low protein characteristic of *Hancornia* latex is most remarkable, suggesting its technological potential in nonallergic applications. Further studies are needed to fully evaluate the commercial potential of this material, including determination of the properties of cured rubber.

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