Evolution in the Natural Rubber Native Structure and Plasticity Retention Index from the First Tapping of Clonal Trees

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ABSTRACT: This study was carried out with five rubber clones planted in Côte d'Ivoire from the first tapping up to the 18th month of tree tapping (1 tapping/4 days). Changes in the natural rubber native mesostructure (macromolecular structure, macrogel, and microgel) of films prepared from fresh field latex were monitored. At the same time, the evolution of the thermooxidation sensitivity of raw rubber samples [grade 10 technically specified rubber (TSR10)] was also monitored with the plasticity retention index (PRI). The substantial initial macrogel rate (70–86%, depending on the clone) fell during the first 18 months of tree tapping to reach a few percent. However, during the same period, the initially low microgel rate (5–15%) increased and then remain stabilized around 55% rubber. The macromolecular structure [weight-average molecular weight (M_w) and molar mass distribution (MMD)] also changed after tree opening. M_w increased and stabilized after 7.5 months of tapping. The bimodal MMD primarily involved short chains (molar mass < 400 kg/mol) at the opening of the trees. The TSR10 samples, prepared with latex from virgin trees, showed high PRIs and, therefore, low sensitivity to thermooxidation. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 903–909, 2005

Key words: gels; rubber; structure

INTRODUCTION

Natural rubber (NR) with its specificities offers undeniable advantages over its synthetic counterparts, notably for the production of tires and certain technical items used in shock absorption. However, this agricultural product has one major disadvantage from a manufacturer's point of view: lack of consistency in its technological properties and, therefore, in its processability, which is currently sometimes difficult to predict with the available criteria.[1–3] To predict the performance of NR, it is absolutely necessary to understand how its structure, more complex than that of its synthetic counterparts, affects its properties and how its structure evolves during processes. To study the NR structure, four domains should be defined: the macrostructure (raw rubber), mesostructure (macrogel[4] and microgel[5] and interactions between polyisoprene chains and non-isoprene compounds), microstructure (or macromolecular structure), and nanostructure (or chemical structure). The macrogel (macroaggregates) is the part of NR that is visible and insoluble in a conventional polyisoprene solvent and that can be eliminated by centrifugation. The microgel (microaggregates), contained in the soluble part, can be eliminated not by centrifugation but by filtration (porosity ≤ 1 μm). NR is an agricultural product (agro-material), and its structure and, therefore, its properties will depend on agronomic factors (clone,[6] tapping system, etc.) and the season.[7] It is very important to know the impact of these factors to control them as well as possible. One step toward this process is determining the evolution of the native structure of NR during the first 18 months of tapping The native structure is the structure not modified by any physicochemical treatment (e.g., drying) or biological treatment (e.g., maturation); it is the structure of NR as it leaves the tree.

In that field, Sekhar[8] showed that NR obtained from the tapping of virgin trees contained a large amount of gel. In fact, he did not make a distinction between the microgel and macrogel but quantified the total gel by filtration. The quantity of gel decreased during successive tappings, becoming constant. Sakdapipanich et al.,[9] who did not study the microgel, showed that NR from virgin mature trees (10–16 years old), tapped for the first time, contained as much as 80% gel (or macrogel). The amount of the macrogel fell from 80 to about 3% after 6 days of tapping (tapping every day). At the same time, the weight-average molar mass (M_w) increased from 262 to 2530 kg/mol (polystyrene equivalent), the latter being the value obtained with trees tapped regularly for around 10 years. Unfortunately, the tapping system used

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by Sakdapipanich et al. (every day or D1) is not realistic because farmers tap once every other day (or D2), sometimes once every 3 days (D3), and for industrial plantations once every 3 days (or D3 6D/7, not on Sunday). It is thus important to evaluate the evolution of the structure of NR of virgin trees with an operating system usually used by professionals. In addition, the trees are usually opened after they are 6 or 7 years old, not 10 or 16 years old. In these two extreme cases (D1, trees more than 10 years old, and D3 6D/7, trees 7 years old), it is probable that the dynamics of the renewal of latex within the tree are different. Moreover, our study of virgin Hevea trees is the first to focus on both the evolution of all essential components of the NR structure (the macromolecular structure, macrogel, and especially microgel) and the concomitant evolution of sensitivity to thermooxidation [plasticity retention index (PRI)] for several clones for an 18-month period of tapping.

EXPERIMENTAL

Samples

The clones used for this study were GT1, VM515, PB312, RRIC121, and PB330. All trees were tapped with the same system (stimulation frequency = 4 times/year). The trees were planted in 1992 and opened in April 1999 in ½ S D3 6D/7, where S = spiral, D3 = every three days, and 6D/7 = six days on seven, not on Sunday.

Latex sampled a few hours after tapping, collected from 10 trees, was used after thorough homogenization; 15 mL was taken immediately to prepare the films, and then the rest of the latex was used to prepare three cup coagula to make grade 10 technically specified rubber (TSR10) samples. The films were used to analyze the native mesostructure of NR, and the TSR10 samples were used to measure PRI. TSR10 is a normalized type of commercial dry rubber made after granulation, creping, granulation again, and drying.[10]

Film preparation

Around 2 mL of fresh field latex was deposited onto a glass plate. The latex was spread with a glass slide and then blown dry with compressed air for 30 min at room temperature. The films were washed by immersion in deionized water at 50°C for 30 min and dried again with compressed air for 30 min and then in a vacuum oven at 40°C for 4 h. The films were placed overnight in a desiccator containing silica gel.

The films were stored in vials under nitrogen and kept in the dark before the solution preparation.

Preparation of TSR10 samples

Cote d'Ivoire produces mainly technically specified rubber (TSR)10 and TSR20 commercial NR grades because farmers collect rubber in the coagulum (cup lump) form, not the latex form. PRI variation is an important problem for this type of commercial rubber in Cote d'Ivoire, as it is in some other countries.

After maturation for 15 days (3 days in the cup and 12 days on a tray), the cup coagula were creped (12 double passes under water), crumbed (rotary cutter with 0.5-in. mesh), and dried (2.5 h, 120°C, and 1.5 m/s air flow).

Macrogel quantification

The samples (60 mg) were dissolved in cyclohexane (30 mL) stabilized with 2,6-di-*tert*-butyl-4-methylphenol (BHT). The solutions were gently stirred for 1 h/day for 14 days and then centrifuged (35,000 g, 1 h, and 17°C). The quantity of macrogel (MG) was determined by the weighing of the centrifugation residue after drying (4 h at 50°C in a vacuum oven).

Microgel quantification

With UV detection with steric exclusion chromatography (SEC), the Beer–Lambert law implies that the area of the rubber peak, in a given chromatogram, is proportional to the concentration of the injected solution:

$$A = \varepsilon l C \quad (1)$$

where A is the absorbance, ε is the molar extinction coefficient, l is the cell length (cm), and C is the concentration (mg/mL). For a given sample injected into the SEC apparatus, a calibration curve, $S = f(C)$ (where S is the area of the rubber peak and C is the concentration of the injected solution), gave the concentration of the solution after filtration. $S = f(C)$ was obtained from polyisoprene standards. Thus, the concentration of the solution was known before and after filtration; the fraction eliminated by filtration, that is, the percentage of microgel, could be determined.

SEC analysis

The samples (60 mg) were dissolved in cyclohexane (30 mL) stabilized with BHT. The solutions were gently stirred for 1 h/day for 14 days, centrifuged (35,000 g, 1 h, and 17°C), diluted to 0.2 mg/mL, filtered (1 μm), and injected into the SEC apparatus. The chromatograph consisted of an Erma (Wellington, New Zealand) ERC-3112 solvent gas remover, a Waters (Milford, MA) 510 pump, an automatic injector, a Waters 486 UV detector (220 nm), and two PLgel 30-cm mixed columns with a porosity of 20 μm (Polymer Laboratories, Amherst, MA). The entire installation was computer-controlled by Maxima-Waters (Milford, MA) software. The column temperature was fixed at 65°C. The cyclohexane flow rate was 0.8 mL/

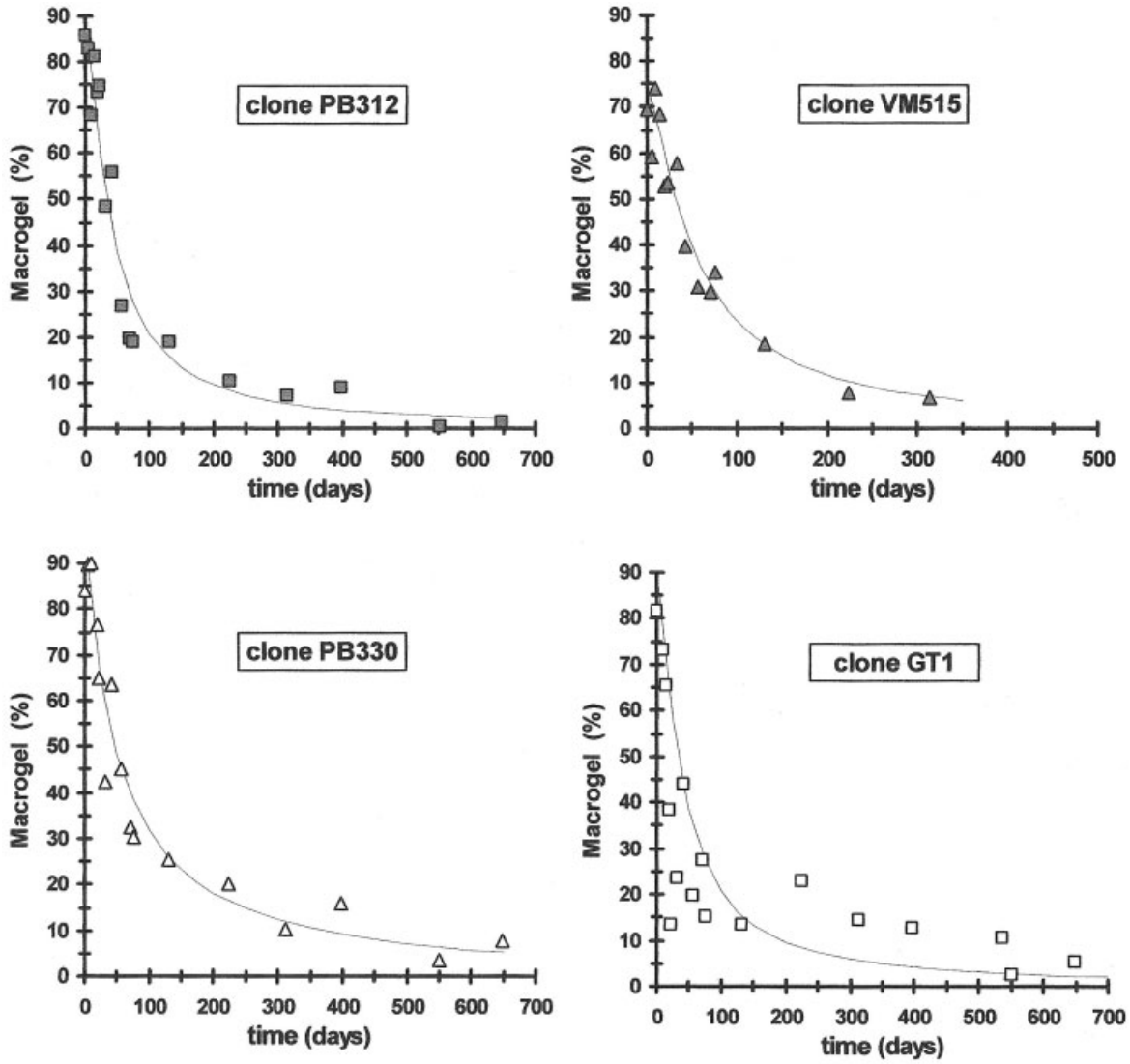

Figure 1 Variation in the macrogel percentage over 18 months of tapping for the four clones studied (first tapping at time = 0).

min. Calibration was carried out with synthetic poly(*cis*-1,4-isoprene) with molar masses ranging from 1310 to 1.2 million g/mol.

PRI determination

The method given in standard ISO2930 was followed. The PRI method consists of determining the (Wallace) plasticity of a disc of NR with standardized dimensions (thickness = 3.2–3.8 mm) before and after aging for 30 min at 140°C in a Wallace oven with controlled air circulation. The PRI, the percentage of Wallace plasticity retained, is then given by the following relation:

$$\mathrm{PRI} = \left(\frac{P_{30}}{P_0}\right) \times 100 \qquad (2)$$

where P_{30} is the plasticity after aging in the oven and P_0 is the plasticity before aging in the oven. Thus, the higher the PRI is, the better the resistance is of the analyzed NR to thermal oxidation.

RESULTS AND DISCUSSION

As for the seedlings, the quantity of macrogel MG was substantial upon tree opening for the five studied clones; it was between 70 and 86%, depending on the clone (Fig. 1). The MG percentage fell rapidly, almost linearly, during the first 10 weeks of tapping. After 10 weeks of tapping, the MG rates were still around 20–30%, depending on the clone. Unlike seedlings, it took around 10 months of tapping to reach MG rates (1–5%) comparable to those of trees regularly tapped for several years.[9,11]

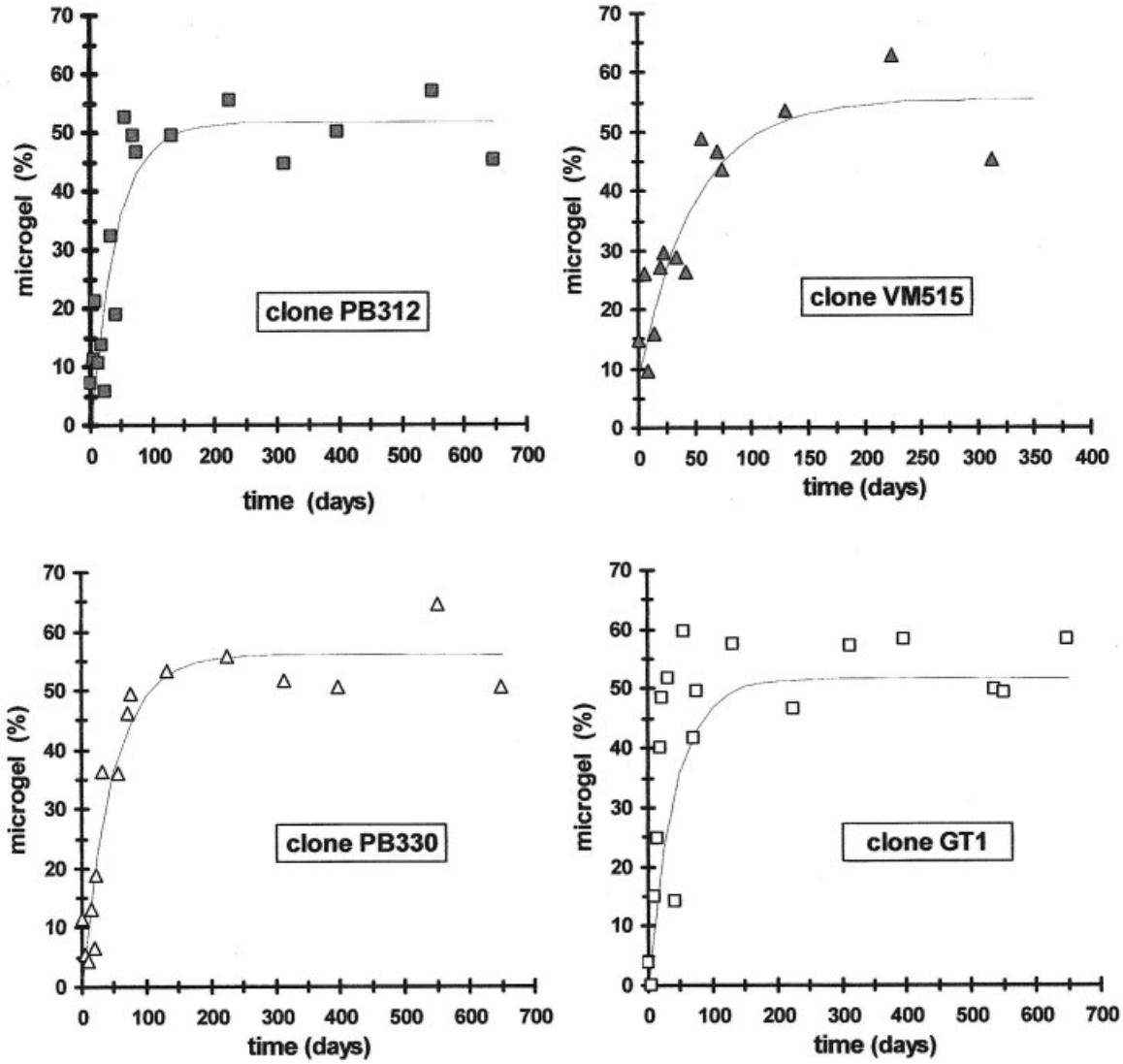

Figure 2 Variation in the microgel percentage over 18 months of tapping for the four clones studied (first tapping at time = 0).

In terms of the microgel quantity (μg), a reverse phenomenon was found (Fig. 2): the microgel rate was very low when the trees were opened (5% $<$ μg $<$ 15%, depending on the clone). It increased during the following tappings and stabilized after about 3 months of tapping at approximately 55%, regardless of the clone. It might be thought that such a proportion of the microgel was due to the use of cyclohexane. In tetrahydrofuran (THF), μg would be much smaller, even nothing. However, Shiibashi[12] discovered the presence of 49% microgel (called the filtration gel) in a sample of NR (RSS1) solubilized in THF. After 18 months of tree tapping, regardless of the clone, the total gel percentage (G_T = MG + μg) was substantial (ca. 55–60%; Fig. 3) and primarily consisted of the microgel.

Sakdapipanich et al.[9] showed that the macrogel upon tree opening (first tapping at time = 0) was not modified by transesterification, unlike the macrogel present in rubber from regularly tapped trees. The latter became soluble after transesterification. This macrogel upon tree opening was due to covalent crosslinking of polyisoprene macromolecules within the rubber particles.[9] Such crosslinking reactions are catalyzed by toxic oxygen species ($O_2 \cdot^-$, OH $\cdot$, etc.) present in the laticiferous cells.[9] Rubber particles in these cells appear to trap radicals because of the absence of antioxidants and, as such, compensate for the classical physiological mechanisms of cell protection. The raw rubber (TSR10) obtained from latex from the 2 or 3 first tappings should present very high sensitivity to thermooxidation, comparable to that of a synthetic polyisoprene without an antioxidant (PRI = 0). PRI is greater the more NR resists thermooxidation. The PRI values of the TSR10 samples were high (PRI $>$ 60) for the 1st month of tapping for clones

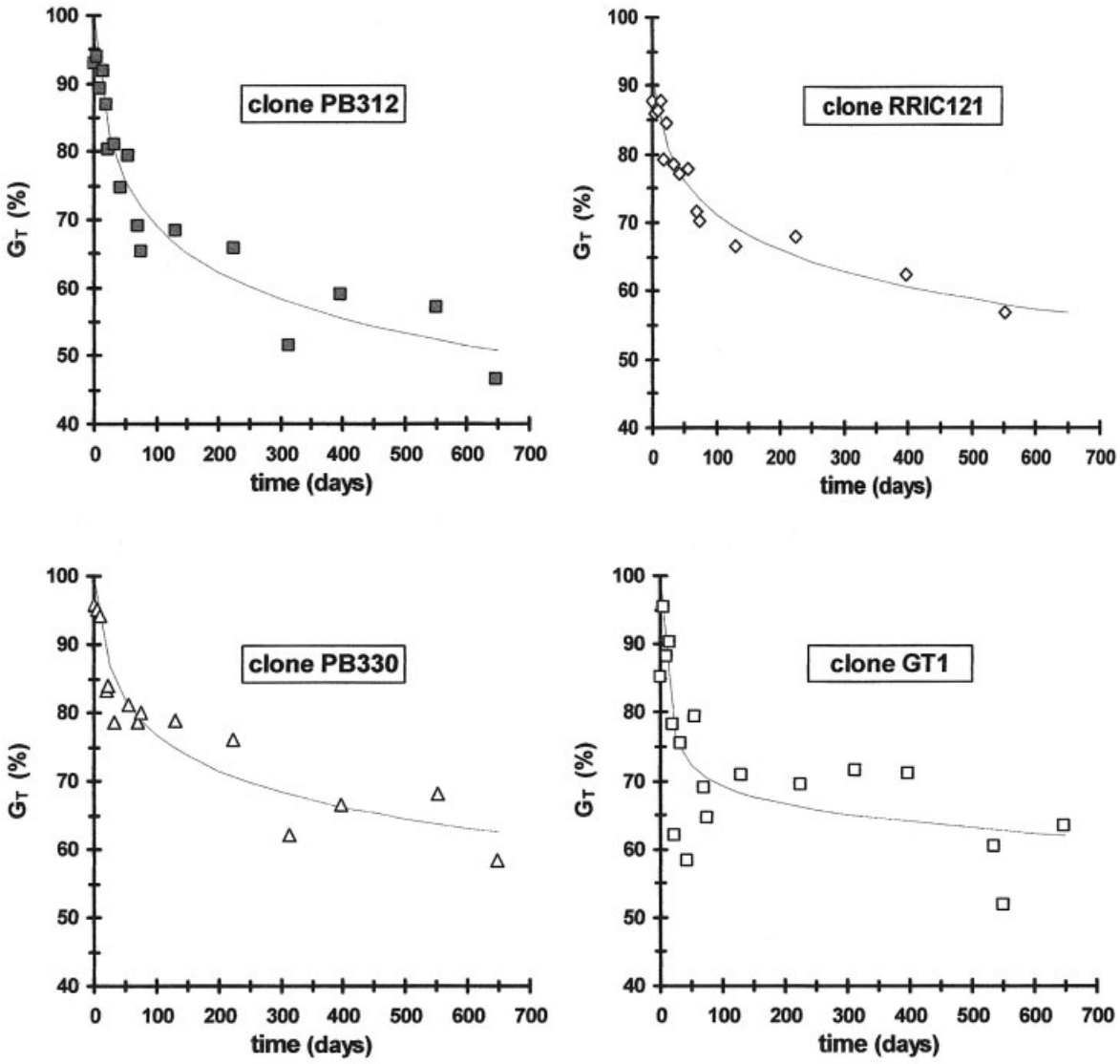

Figure 3 Variation in G_T over the first 18 months of tapping (first tapping at time = 0).

RRIC121 and VM515, for example (Fig. 4). Then, PRI decreased more or less according to the clone over the following tappings (Fig. 4). The TSR10 samples prepared with latex from the first tapping had a PRI of approximately 60. Such a PRI is a sign of a sample that resists thermooxidation well. It is therefore very likely that there were antioxidants in the initial latex and in the rubber obtained. The drop in PRI after 2 months (several tappings; Fig. 4) can be explained by a decrease in the quantity of the antioxidant in the laticiferous cells or probably instead by a change in the balance of antioxidants and prooxidants.[13] In fact, a seasonal variation in PRI is often found.[7] The drop in PRI could also probably be due to complex biochemical phenomena taking place during coagulum maturation in relation to bacterial development in the medium.[14]

The macromolecular structure of NR also changed over successive tappings. M_w, around 300–600 kg/

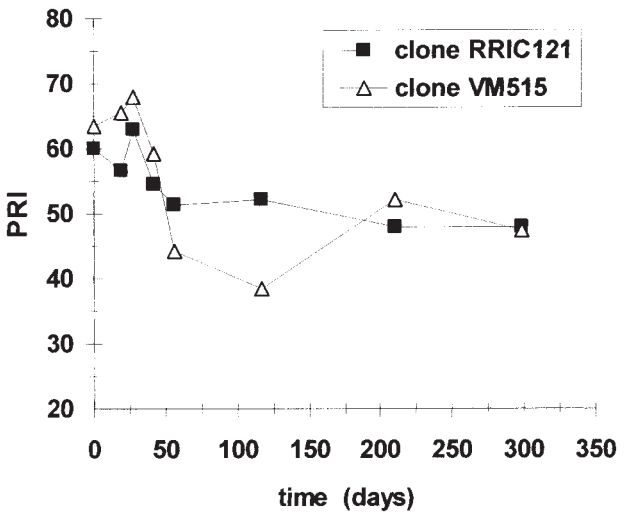

Figure 4 Variation in PRI over the first 10 months of tapping for clones VM515 and RRIC121.

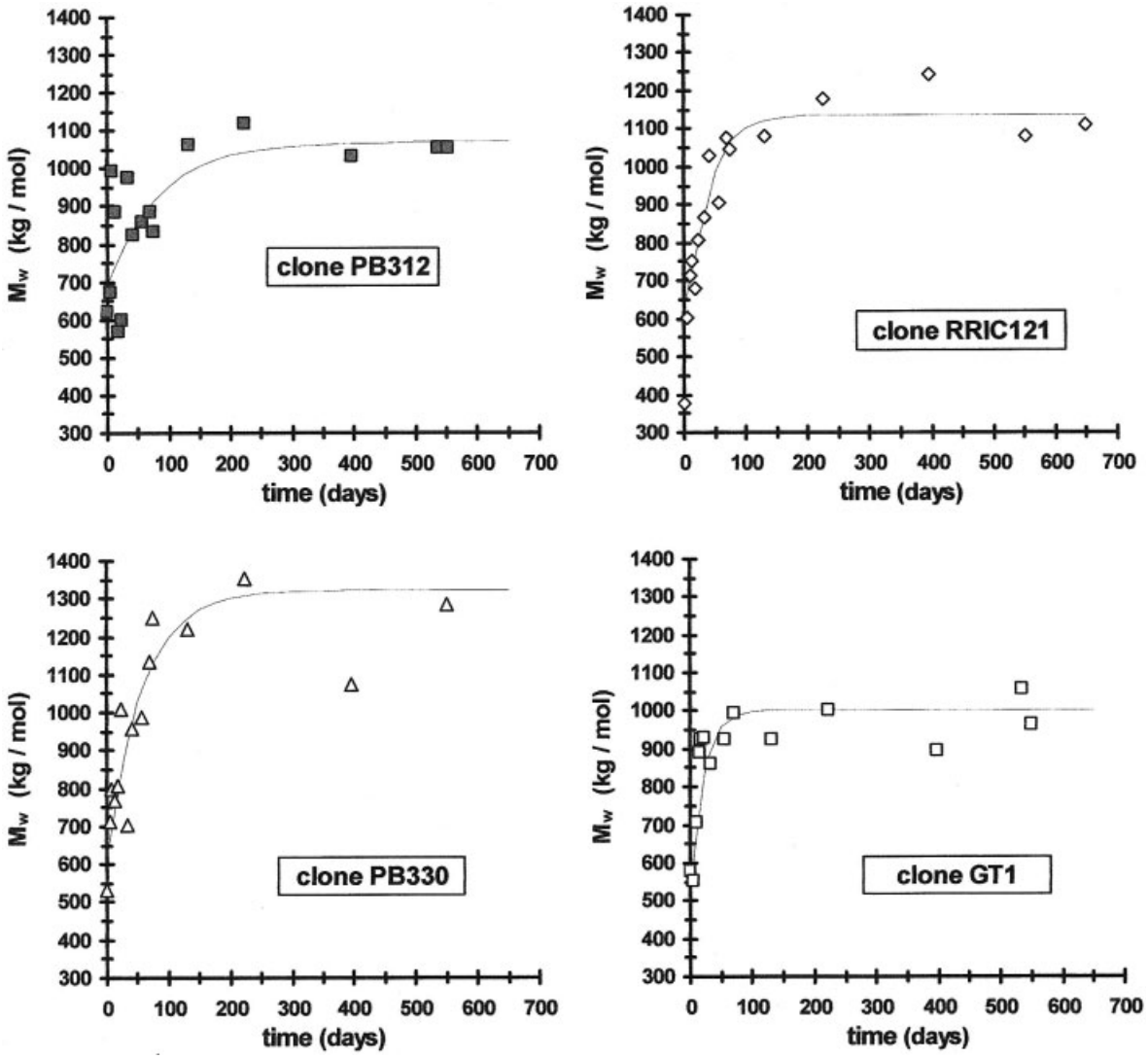

Figure 5 Variation in M_w over the first 18 months of tapping (first tapping at time = 0).

mol (polyisoprene equivalent) when the trees were opened, gradually increased over successive tappings, reaching 1000–1300 kg/mol, depending on the clone (Fig. 5). As tapping progressed, the quantity of rubber soluble in cyclohexane increased as the total gel decreased (Fig. 3) and the molar mass distribution (MMD) changed (Fig. 6). This MMD could be considered to consist of two populations: one of short chains (molar mass $<$ 400 kg/mol) and another of long chains (molar mass $>$ 400 kg/mol). This change was reflected in a decrease in the short-chain population ($<$400 kg/mol) and an increase in the long-chain population ($>$400 kg/mol; Fig. 6).

CONCLUSIONS

When the mesostructure of NR is studied, the microgel must not be neglected. Indeed, a given sample may have a macrogel content approaching 0 but a microgel content of almost 50%. The mesostructure of NR evolves considerably between the moment at which a tree is opened and successive tappings (not only gels but also M_w and MMD). Our results for the macromolecular structure and macrogel are consistent with the results of Sakdapipanich et al.,[9] excepted for the time to reach equilibrium: about 18 months in our case and 6 days for Sakdapipanich et al. This difference probably lies in the different systems studied: tapping in D1 (trees more than 10 years old) for Sakdapipanich et al. and tapping in D3 6D/7 (stimulation of trees; trees 7 years old) for our study.

The raw rubber samples (type TSR10) obtained from the three first tappings of the virgin trees presented low sensitivity to thermo oxidation (PRI $\geq$ 60). These results show that the latex from virgin trees, as for the latex from mature Hevea, contains natural antioxidants. Studies are in progress to evaluate the antioxi-

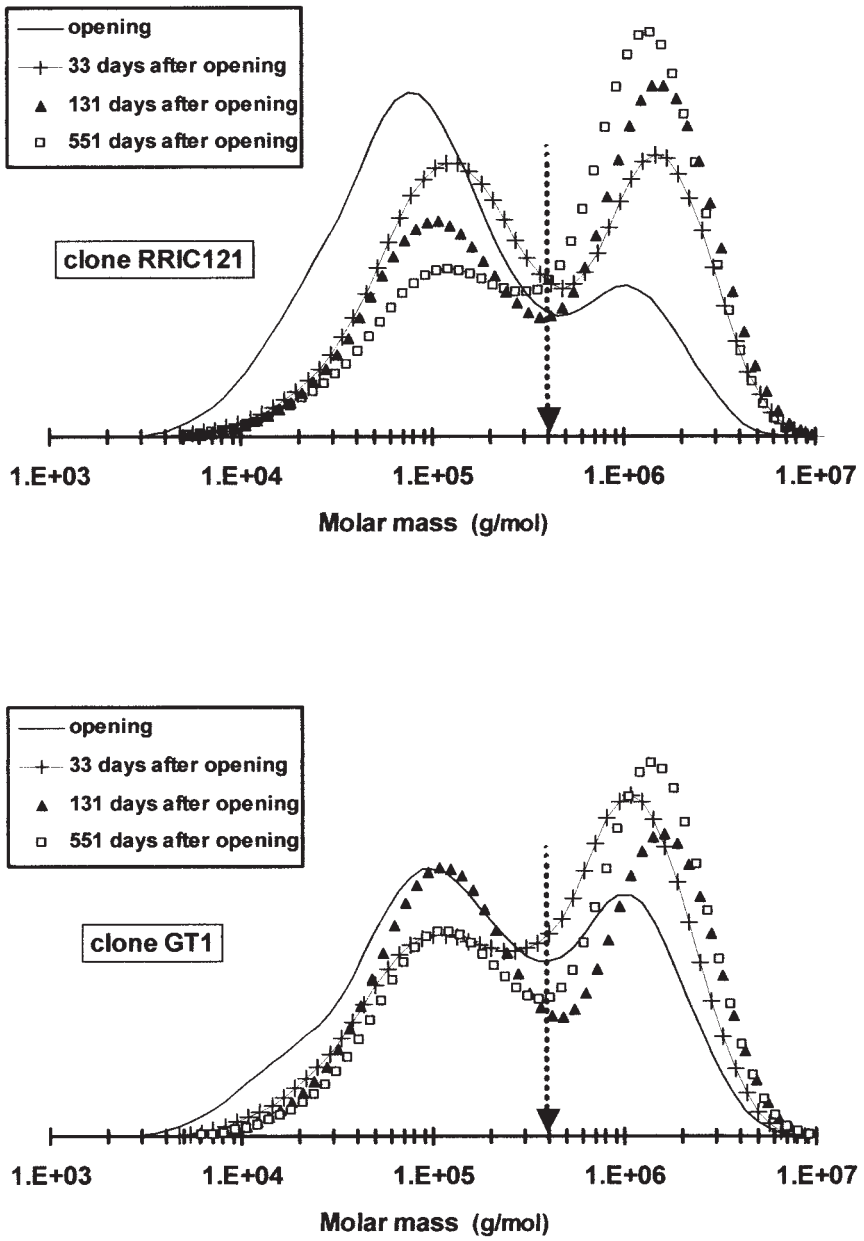

Figure 6 Variation in the native MMD during tapping for clones RRIC121 and GT1.

dant power of latex extracts from virgin Hevea trees and its evolution during harvesting of the trees.

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