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Studies on thermal–oxidative degradation behaviours of raw natural rubber: PRI and thermogravimetry analysis

P. Danielle Galiani*¹, J. Antonio Malmonge², B. Guenther Soares¹ and L. Henrique Capparelli Mattoso³

Thermal–oxidative degradation behaviours of raw natural rubber (NR) have been investigated by using thermogravimetry analysis in inert and oxidative atmospheres and the plasticity retention index (PRI). The activation energy E_a , was calculated using Horowitz–Metzger and Coats–Redfern methods and compared with PRI. The E_a values obtained by each method were in good agreement with each other. The June samples are the least stable rubbers among the studied ones, whereas February samples exhibited the highest values of activation energy, therefore in agreement with the PRI behaviour, which indicates that the thermo-oxidative stability of the June samples are the poorest during the thermo-oxidative degradation reaction. Natural rubber is a product of biological origin, and thus these variations in the values of thermal behaviour and PRI might be related to the genetic differences and alterations of climatic conditions that act directly on the synthesis of non-rubber constituents, which are generally reflected in latex and rubber properties.

Keywords: Natural rubber, Thermogravimetry analysis, PRI, Degradation

Introduction

Natural rubber (NR) is used in >40 000 consumer products, including >400 medical devices, due to its unique properties, which include resilience, elasticity, abrasion and impact resistance, efficient heat dispersion, and malleability at cold temperatures.¹ The sole commercial source, at present, is NR harvested from the Brazilian rubber tree, *Hevea brasiliensis*.² About 10% of the latex harvested from *Hevea* trees is manufactured into latex products. The remaining 90% of latex is coagulated and converted into dry rubber. Most of the dry NR is used in tires, especially those which call for high performance, notably aircraft and truck tires.

Natural rubber is susceptible to oxidation, which may affect both the processing qualities of the rubber and also the final compounded rubber mechanical properties. The quality of a rubber manufactured product depends on the raw rubber quality. It is known that several factors influence the NR physical–chemicals properties; moreover, industries are increasingly demanding for quality and uniformity of the NR produced in the country. The

plasticity retention index (PRI) is a measure which reflects the resistance of NR to thermal oxidation.³ This index is a property widely used by manufacturers, mainly tire industry that is the major NR user. The parameters required by Brazilian Standard NBR 11597⁴ specify 60% as the minimum acceptable value for all rubber categories.

Knowledge of degradation and mode of decomposition under the influence of heat is highly recommendable in the processing and fabrication procedures.⁵ Thermogravimetric analysis (TGA) has proved to be a highly successful technique for determining the thermal stability of polymeric systems. Thermal stability can be regarded as the ability to maintain the required properties of materials at a desired temperature. To study how the decomposition temperature is related to the structure of materials, TGA is widely used to determine the range of service temperature due to its simplicity to analyse the information obtained from a simple thermogram.⁶ Because thermal stability is related to both the initial degradation temperature and the degradation rate of a polymer, the determination of activation energy is very important.^{7,8}

Degradation and stabilisation of polymers have been studied from both fundamental and practical points of view for a long time.⁹ The derivation of kinetic data in the study of polymer decomposition has received increasing attention in the last decade. Flynn–Wall–Ozawa, Horowitz–Metzger and Coats–Redfern methods are commonly used to determine the kinetic parameters as activation energy.^{10–16}

In this paper, the thermal–oxidative degradation of raw NR samples collected in February and June, from

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GT1 and PR255 clones, has been studied in detail by TGA under oxidative and inert atmospheres. The purpose is to evaluate the thermal and thermo-oxidative degradation behaviours and compare to the PRI (%) data for each clone. The kinetic parameter (activation energy E_a) was calculated using two relations: Horowitz–Metzger and Coats–Redfern.

Experimental

Material

Natural rubber

Natural rubber (*Hevea brasiliensis*) lattices from GT1 and PR255 clones were collected from different trees, in summer (February) and winter (June), in the region of Mato Grosso State, Brazil. These clones were chosen to represent good clones available in Brazil. The trees were planted in 1989 (i.e. they were 19 years old at the beginning of the experiment). The samples were prepared in a rubber processing factory. In order to obtain dry rubber, all cup lumps were then granulated, washed and dried in an air dryer at $120 \pm 2^\circ\text{C}$ for 4 h under the same processing conditions to avoid between-batch variations.

Methods

Plasticity retention index

Plasticity retention index analysis¹⁷ consists of determining the Wallace plasticity P_0 of a standardized NR specimen (thickness 3–3.8 mm) before and after 30 min aging at 140°C , in an oven with controlled air circulation. The PRI, percentage of Wallace plasticity retained, is then given by equation (1)

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

where P_{30} is the plasticity after aging in the oven, and P_0 is the plasticity before aging in the oven.

Thermogravimetric analysis

The thermal degradation parameters of rubber samples from GT1 and PR255 clones were evaluated using the TA instrument thermoanalyser Q500, and thermogravimetric (TG) scans were carried out with 10 ± 1 mg of the samples in platinum pans, heated from room temperature up to 600°C at a rate of $10^\circ\text{C min}^{-1}$ in oxidative and inert atmospheres with a flow rate of 40 mL min^{-1} . The TG curves were analysed as percentage weight loss as a function of temperature. The decomposition stages were identified using a derivative of the TG curves. Several

methods have been developed in order to investigate the thermal stability of rubbers.¹⁸ The kinetic parameters evaluated for each stage of degradation processes are carried out by using the integral methods for the kinetic analysis of the single thermogravimetric curve data. Several approaches have been proposed in literature for the integral of the Arrhenius equation in order to determine the activation energy from experimental integer data.¹⁹

In this paper, the activation energy for decomposition E_a has been calculated from the slopes of the best fit straight lines obtained when the plots using two models, namely, Horowitz–Metzger²⁰ and Coats–Redfern²¹ methods, which are the most acceptable and commonly are used to obtain kinetic data.^{7,14,16,19,22} Nevertheless, there are still some doubts about their accuracy for determining the kinetic parameters¹⁹ because their lack of accuracy in the estimation of the temperature integral. However, the most common application of these approximations is the determination of the activation energy and not the computation of the temperature integral.¹⁹

Table 1 presents the relation used to evaluate the degradation kinetics for each model.

Results and discussion

The thermal decomposition temperatures of the polymers were evaluated by TGA and derivative thermogravimetric (DTG) analysis in inert and oxidative atmospheres. Additionally, there is a significant dependence on the thermal decomposition of NR samples under the test atmosphere, as can be seen in Figs. 1 and 2. The mean features of the thermograms are characterised by a decrease in the maximum degradation temperature ($\sim 30^\circ\text{C}$) observed in the thermograms obtained for both clones under the oxidative atmosphere.

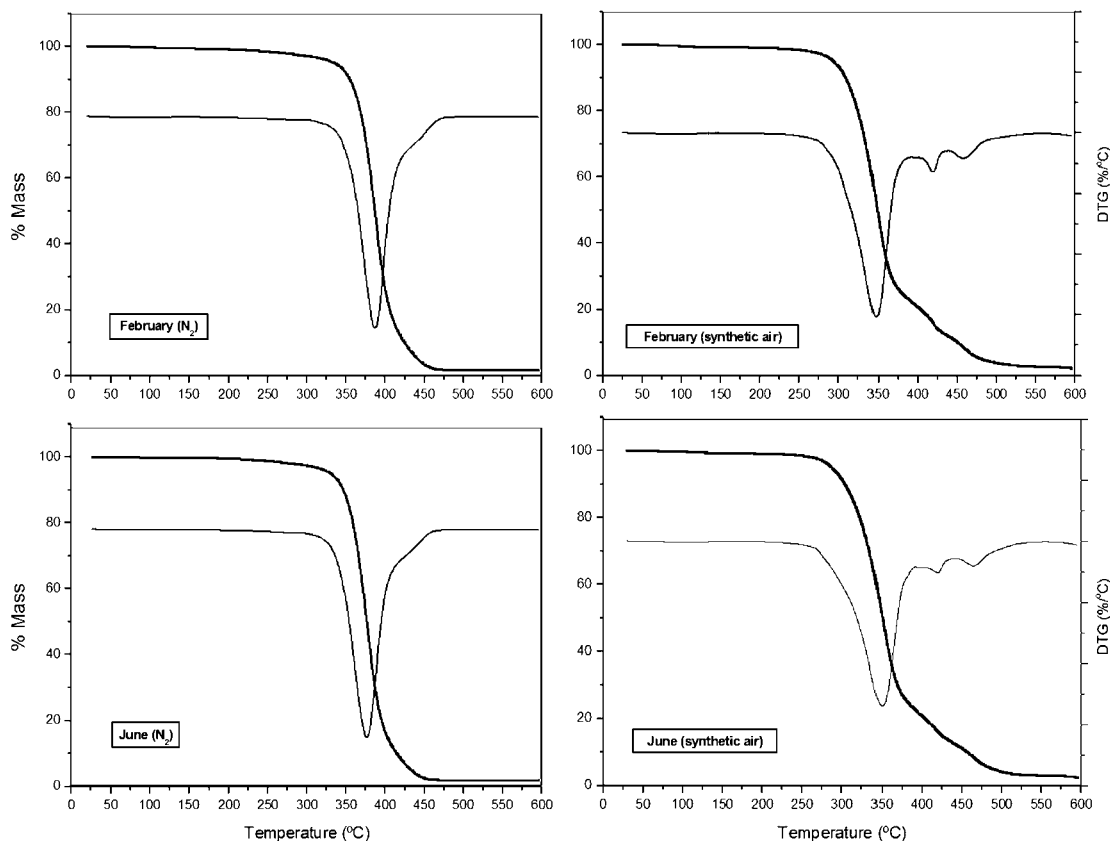
The decomposition stages were identified using a derivative of the TG curves, and thus, Tables 2 and 3 show the maximum temperature of each stage of degradation and the percentage of loss mass in oxidative atmosphere for GT1 and PR255 clones respectively.

Natural rubber has a chemical structure [poly(*cis*-1,4-isoprene)], based around a double bond building unit that makes it susceptible to oxidation, which can be caused by light, high temperatures, atmospheric oxidants (O_2 , O_3 , etc.) or excessive physical stresses.¹⁷ Thermal oxidation of this polymer, in its solid state, is a complex process in which two competing phenomena occur: scission and cross-linking, resulting in the

Table 1 Relation used for each model*

Model	Equation	Where
Horowitz–Metzger	$\log[-\log(1-\alpha)] = \frac{E_a \theta}{2.303RT_m^2}$	α is the decomposed fraction, E_a is the activation energy of decomposition, T_m is the temperature at the maximum rate of weight loss, θ is the value of $T-T_m$ and R is the gas constant. From the plots of $\log[-\log(1-\alpha)]$ versus θ , the activation energy E_a for decomposition can be determined from the slope of the straight line of the plots.
Coats–Redfern	$\log\left[\frac{-\log(1-\alpha)}{T^2}\right] = \log\frac{AR}{\beta E} \left[1 - \frac{2RT}{E_a}\right] - \frac{E_a}{2.303RT}$	α is the fraction of sample decomposed at the time T , T is the derivative peak temperature, A is the frequency factor, E_a is the activation energy and R is the gas constant. A plot of $\log[-\log(1-\alpha)/T^2]$ versus $1/T$ gives the slope for evaluation of the activation energy most appropriately, for $n=1$.

*For solid state reactions $f(\alpha)=(1-\alpha)^n$, where n is the order of reaction, for many pyrolysis processes, $n=1$, i.e. first order reaction.²²



1 Curves (TG/DTG) of NR samples collected in February and June from GT1 clone heated from room temperature to 600°C at rate of 10°C min⁻¹, under nitrogen and oxidative (synthetic air) atmosphere

deterioration of the chemical and physical properties.²³ According to Tangpakdee and Tanaka,²⁴ variations in these properties occur due to a larger or smaller quantity of non-rubber constituents that will influence rubber characteristics, such as, for instance, in the formation of cross-linking, and molecular mass variations and its distribution.

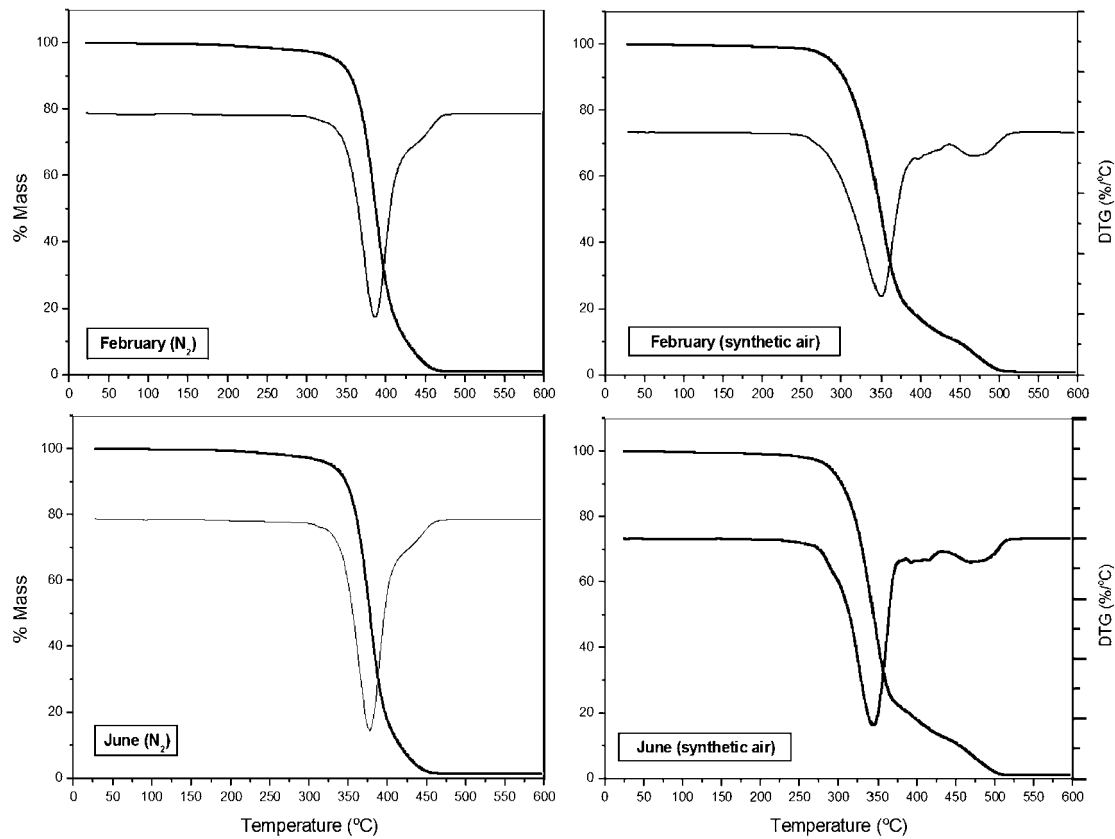
GT1 and PR255 clones showed similar decomposition behaviour in inert atmosphere (Figs. 1 and 2 respectively), indicating that thermal degradation of the raw NR from the GT1 and PR255 clones is mostly a one stage process. The decomposition ranged from ~315 to 450°C with a mass loss of ~96%, which can be assigned to the thermal decomposition of the NR into monomers, dimers, trimers, etc. A small shoulder can be observed at ~430°C attributed to the cross-linked and cyclized networks, which degrade at a higher temperature.²⁵

For the oxidative atmosphere, the nature of TG curves indicates that the rubber samples degrade in three stages, except for the sample collected in February from PR255 clone (Fig. 2), which show two stages of degradation. The results showed that degradation did not occur in a single stage, and around the main peak there are some small peaks. These peaks could not be separated completely, but overlap each other, indicating that the degradation consists of several reactions.²⁶ The occurrence of two or more peaks in the thermogram indicates the formation of thermally stable intermediate products;^{25,27} this behaviour is an evidence of the multiple stage degradation that occurs in NR.²⁸ Li *et al.*²⁹ reported that the thermal degradation of NR in air is not a simple random chain scission process, but

also has some side reactions that are carried out simultaneously. In addition, the process of degradation is an exothermic reaction.

From the results in Table 2, it can be seen that the first stage ranges from 265 to 395°C and the second one ranges from 395 to 438°C. The third decomposition process, appearing at the highest temperatures, ranges from 439 to 493°C. For PR255 clone (Table 3), the scans illustrate that thermal degradation of the rubber samples presented the first stage ranges from 271 to 398°C and the second one ranges from 384 to 517°C. The third decomposition process ranges from 432 to 521°C, appearing only for the sample collected in June.

The first stage of degradation of the rubber samples started at ~260°C and was completed at 400°C, and the mass loss is ~50%, which can be attributed to the thermal decomposition of the NR. 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.^{25,29,30} The second mass loss peak, between 80 and 94%, temperature up to 385°C can be attributed to the final thermal decomposition of the NR. For the third mass loss peak, the mass loss is ~95%, and it ranges from ~430 to 600°C, associated with the thermal decomposition of the carbonaceous residues from the rubber. During the propagation stage, polymer radicals formed by chain scission combine with oxygen to yield peroxy radicals. Moreover, the oxidation process may be accelerated by further decomposition of the hydroperoxides to generate free radicals.^{28,31}



2 Curves TG/DTG of NR samples collected in February and June from PR255 clone heated from room temperature to 600°C at rate of 10°C min⁻¹, under nitrogen and oxidative (synthetic air) atmosphere

Further information on the thermal degradation of the rubber samples were obtained from the kinetic parameter (activation energy E_a) calculated by the Horowitz–Metzger and Coats–Redfern methods. In this paper the E_a values of the rubber samples in nitrogen were compared with those found in air for each method. The authors also investigated the relationship of the E_a and PRI (resistance to thermal degradation) results among the tappings (February and June) and clonal origin.

The linear dependence of thermal degradation of NR samples as a function of temperature, as per Coats–Redfern and Horowitz–Metzger methods in oxidative and inert atmospheres, was obtained. The linear plot with concurrency value R^2 around 0.98 was chosen for all methods. The activation energy was calculated by regression analysis and the results obtained in oxidative and inert atmospheres are presented in Figs. 3 and 4 respectively.

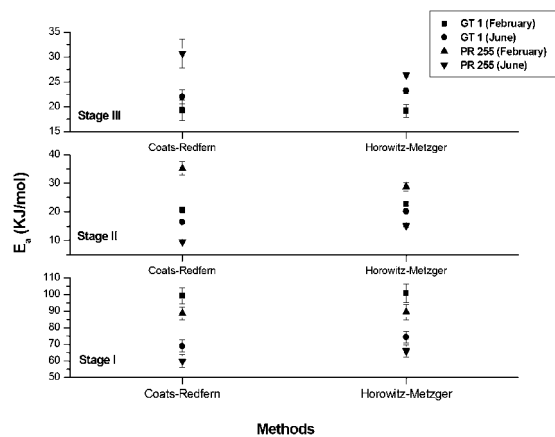
Table 2 Maximum degradation temperature T_{max} for each degradation stage for GT1 clone under oxidant atmosphere and respective mass loss

Clone	Stage I		Stage II		Stage III	
	$\Delta T/^\circ\text{C}$ and $T_{max}/^\circ\text{C}$	%mass loss in T_{max}	$\Delta T/^\circ\text{C}$ and $T_{max}/^\circ\text{C}$	%mass loss in T_{max}	$\Delta T/^\circ\text{C}$ and $T_{max}/^\circ\text{C}$	%mass loss in T_{max}
February	280–390	49.3 ± 0.1	401–438	84.4 ± 0.1	439–493	91.0 ± 0.1
	347	...	421	...	458	...
June	265–395	50.2 ± 0.1	395–435	84.1 ± 0.1	448–483	92.2 ± 0.1
	349	...	420	...	466	...

Table 3 Maximum degradation temperature T_{max} for each degradation stage for PR255 clone under oxidant atmosphere and respective mass loss

Clone	Stage I		Stage II		Stage III	
	$\Delta T/^\circ\text{C}$ and $T_{max}/^\circ\text{C}$	%mass loss in T_{max}	$\Delta T/^\circ\text{C}$ and $T_{max}/^\circ\text{C}$	%mass loss in T_{max}	$\Delta T/^\circ\text{C}$ and $T_{max}/^\circ\text{C}$	%mass loss in T_{max}
PR255	280–398	52.2 ± 0.1	442–517	94.2 ± 0.1
	351	...	472
June	271–383	48.3 ± 0.1	384–430	83.2 ± 0.1	432–521	94.4 ± 0.1
	346	...	405	...	478	...

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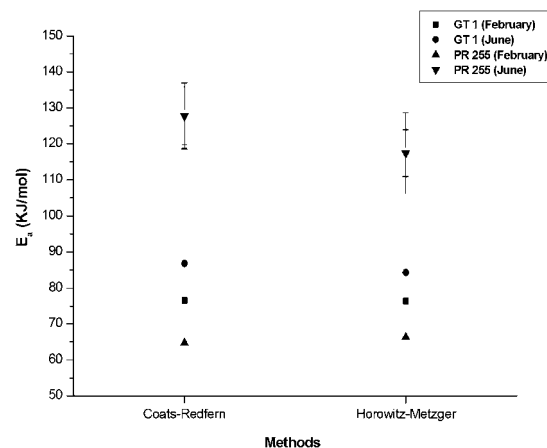
3 Activation energy E_a of thermal decomposition curve (in oxidative atmosphere) for NR samples obtained for different methods at different degradation stages

The results obtained by the Coats–Redfern method were in agreement with the results of Horowitz–Metzger method. In the first stage, attributed to the thermal decomposition of the NR, the E_a values varied between 55 and 105 kJ mol⁻¹; this stage presents higher activation energy in oxidative atmosphere. It is well known that the carbon–carbon double bond disassociation energy is greater than that of single bond, and thus single bond scission occurs first.⁹

Stages I and II (Fig. 3) clearly gave evidence that in the activation energy of rubber samples, the resistance to thermal degradation decreased with increasing temperature in oxidative atmosphere when compared with step I. The third stage of degradation for sample collected in June, a small increase in the activation energy was observed compared to the second stage. This variation was already expected because when more than one degradation mechanism is occurring, the activation energy will not always be constant.¹⁰

According to the literature,³⁰ polymer degradation is a complex phenomenon involving many reactions that are difficult to analyse separately. During the early stages of degradation random scission occurs along the main chains with simultaneous oxidation and cross-linking and therefore becomes an autocatalytic process with the reaction course. As the reaction proceeds, the increasing weight fraction of decomposed sample was observed as well as many concurrent degradation processes such as oxygen uptake, peroxide formation and cross-linking. Besides that the thermal degradation behaviour of NR also depends on the type of rubber *Hevea* clones as verified by Moreno *et al.*²⁸ and Medeiros *et al.*³⁰

Plasticity retention index (%) values are presented in Fig. 5. According to the months of collection, it was observed that only the results obtained for clone PR255 met the requirements of the standards ABNT/NBR11597 (minimum 60%).⁴ All clones have shown a decrease around 20% for samples collected in June compared with February. In this set of *Hevea* samples, it can be seen that PR255 had higher PRI than GT1 clone. According to the literature,^{32,33} PRI variations in NR are influenced by genetic differences among clones and by alterations of climatic conditions that act directly on the synthesis of non-rubber constituents from the latex



4 Results of activation energy E_a of thermal decomposition curve (in inert atmosphere) for NR samples by different methods

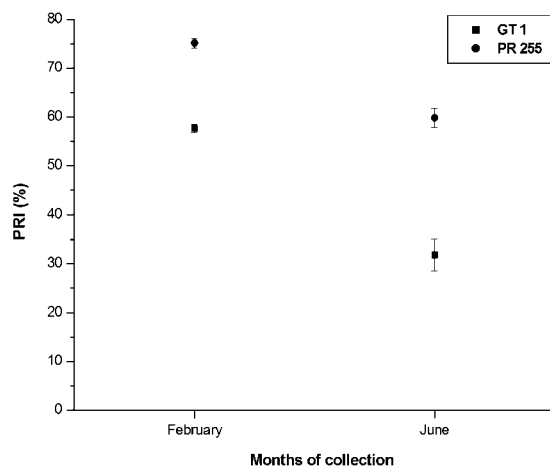
obtained by tappings, mainly tocopherols, presenting a strong antioxidant action.

Since E_a provide measure of the resistance to thermal degradation (a higher E_a indicates a more stable material), it was observed that the values of activation energy ranged between the most and the least thermally stable clones (in the first stage of degradation), i.e. the June samples are the least stable rubbers among the studied ones, whereas February samples exhibited the highest values of activation energy (Fig. 3). Oxygen generally tends to act as an oxidising agent promoting, therefore oxidative degradation, which is more time dependent and more accentuated with increasing temperature than normally occurs for experiments carried out under the nitrogen atmosphere. Actually, for polyisoprene in its solid state, the balance between scission and cross-linking depends on available oxygen diffusing in the material.²³

Thermogravimetric data provide 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.²⁵ The clones showed similar and different thermal behaviours in inert and oxidative atmospheres respectively. PRI values of the samples have shown variation among the tappings (February and June). Regarding the clonal origin, PR255 clone collected in June had a very higher PRI value compared to GT1 clone collected in June (Fig. 5) and the lower E_a (calculated from TG curves) in stage I (Fig. 3), this was probably because the two techniques were not equivalent regarding the phenomenon measured. Therefore, these results also suggest that different conditions, not thermal ones, were mainly responsible for the PRI differences.

Conclusions

This study indicated that the thermostability of raw rubber samples, from GT1 and PR255 clones, in air is substantially lower than that in nitrogen and the decomposition mechanism is more complex. The decomposition changes from a one stage process to a three stage process, when moving from an inert to an oxidative atmosphere. The activation energy values obtained by Horowitz–Metzger and Coats–Redfern methods were in good agreement with each other. The samples collected in



5 Plasticity retention index values of NR samples from GT1 and PR255 clones

June are the least stable rubbers among the studied ones, whereas samples collected in February exhibited the highest values of activation energy and PRI, which indicates that the thermo-oxidative stability of the June samples is the poorest during the thermo-oxidative degradation reaction, and that of the February samples are the best. The composition and chemical structure of raw NR samples change in each pyrolysis stage, due to complicated chemical structure as a result of the interactions of non-rubber compounds, such as proteins and lipids, with the polyisoprene chains. The variations in the thermal behaviour, activation energy E_a and PRI's measures, therefore, were expected because of the genetic differences, intrinsic to each clone type, which are generally reflected in latex and rubber properties.

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