

DSC Valuation of PRI of Raw Natural Rubber

F. BONFILS,¹ J. C. LAIGNEAU,¹ S. SYLLA,² J. SAINTE BEUVE¹

¹ CIRAD-CP, 2477 Avenue du Val de Montferrand, BP5035, 34032 Montpellier Cedex 1, France

² CNRA, B. P. 1536, Abidjan 01, Côte d'Ivoire

Received 21 January 2000; accepted 19 June 2000

ABSTRACT: Thermal oxidation of raw natural rubber from *Hevea brasiliensis* was analyzed by differential scanning calorimetry (DSC) in dynamic mode. The results obtained revealed a linear relation between the PRI and onset temperature obtained by DSC ($r^2 = 0.91$), for PRI values <70. On the other hand, when the natural rubber PRI was over 70, DSC was unable to assess that criterion accurately. This was probably because the two techniques were not equivalent regarding the phenomenon measured. Oxidation primarily results in chain scissions during PRI measurement. In DSC, the transition seen during thermal oxidation was associated with crosslinking. In fact, thermo-oxidation is in the initial phase when PRI is measured, but in the terminal phase at the onset of transition in DSC. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 2354–2359, 2001

Key words: natural rubber; NR; plasticity retention index; PRI; differential scanning calorimetry; DSC; thermo-oxidation

INTRODUCTION

Given its physico-chemical properties, which are as yet unrivalled, raw natural rubber remains the world's leading elastomer. Nevertheless, manufacturers consider that this agricultural material still reveals too great a variability, leading to rejects for manufactured articles and higher production costs. There are several quality criteria that can be measured at the production site, which enable natural rubber specification and, in theory, show how it will perform during processing.

Among them, the Plasticity Retention Index (PRI) is used to rapidly assess the susceptibility of a raw natural rubber sample to thermal oxidation. Indeed, although raw NR contains natural antioxidants, it has a chemical structure [poly-

(*cis*-1,4-isoprene)] that makes it susceptible to thermal oxidation in the presence of molecular oxygen. Thermal oxidation of this polymer, in its solid state, is a complex process in which two competing phenomena occur: scission and crosslinking.

The PRI standardized method¹ (ISO2930) consists in determining the (Wallace) plasticity of a disc of natural rubber with standardized dimensions (thickness: 3.2 to 3.8 mm) before and after aging for 30 min at 140°C in an oven with controlled air circulation. The PRI, percentage of Wallace plasticity retained, is then given by the relation:

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

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

Correspondence to: F. Bonfils.

Journal of Applied Polymer Science, Vol. 79, 2354–2359 (2001)
© 2001 John Wiley & Sons, Inc.

Thus, the higher the PRI, the better the resistance of the natural rubber analysed to thermal oxidation.

However, this criterion is fairly controversial. In fact, it is used more as a safety net by industrialists, due to its low correlation to changes in natural rubber in an internal mixer, for example.² This is probably partly due to PRI definition, a ratio, on the one hand, and on the other hand to the fact that other parameters, such as physical degradation, are involved in an internal mixer. Moreover, PRI determination requires at least 30 g of rubber. Thus, in some applications, having a few hundred mg of rubber is not enough to measure PRI, and hence, its susceptibility to thermal oxidation. For that reason, Differential Scanning Calorimetry (DSC), an analytical technique used to study thermal oxidation of elastomers,³⁻⁵ seemed to be the ideal tool for assessing the PRI of natural rubber. DSC has also been widely applied to study thermal oxidation of natural rubber,⁶⁻⁸ or its stabilization by certain antioxidants.⁹⁻¹¹ Work by Goh^{8,12} revealed the equivalence of isothermal and dynamic modes for analyzing the oxidation of natural rubber, provided a moderate heating rate was used (<20°C/min). We, therefore, opted for the dynamic mode, which offers the advantage of analyzing a sample in under 20 min, irrespective of its PRI.

The results described in this article show that it is important to use a sample weight as constant as possible to ensure good repeatability of onset temperature measurement (T_o). Under the conditions used, the latter was well correlated to the PRI of a natural rubber sample, but only for PRI values <70. Measurements by Size Exclusion Chromatography (SEC) during a DSC cycle revealed that the transition observed in DSC was associated with crosslinking of the material and not chain scissions.

MATERIALS AND METHODS

Materials

The specificities of the natural rubber samples studied (clonal origin, maturation time, etc.) are given in Table I. Two types of raw material were studied—the first collected in cup lump form (natural latex coagulation in the field), the second collected in latex form and coagulated artificially with acid (off-latex rubber).

Prior to any DSC or PRI analysis, the samples were homogenized in accordance with standard ISO1796, and sheeted by three passes through the mill rollers at 27°C.

Sample Preparation

As a general rule, natural rubber is dissolved in a given solvent and the resulting solution is then placed in the DSC cell and the solvent evaporated off. We did not use that method, which has the drawbacks of modifying the raw material structure (used for PRI measurement) and of only allowing analysis of the soluble part of the material. In fact, natural rubber is never completely dissolved, and it can contain up to 50% gel in some cases.^{13,14} For this reason, a given weight ($1 < w < 1.5$ mg) of the natural rubber sample was directly pressed in the DSC cell, in an oven at 90°C, for 40 min.

Methods

DSC Analysis

A Perkin-Elmer DSC-7 differential scanning calorimeter was used. The instrument was purged with air at a flow rate of 35 mL/min during operation. Heating scans were run at 20°C/min from 50 to 130°C, at 10°C/min from 130 to 150°C and at 5°C/min from 150 to 250°C. Standard two-hole vented pan covers were used over each heating unit, which were recommended to prevent disruptions linked to the difference in thermal emissivity between the sample and the reference pan.¹⁵

SEC Analysis

The samples were dissolved in cyclohexane stabilized with 2,6-ditertbutyl-4-methylphenol (BHT), at a rate of 3 DSC pans for 10 mL of solvent (initial concentration about 0.3 mg/mL). The solutions, stored at 30°C, were gently stirred for one hour periodically for 14 days, then filtered (porosity 1 μ m) and injected into the SEC apparatus.

The chromatograph used consisted of an ERMA ERC-3112 solvent gas remover, a Waters 510 pump, an automatic injector, a Waters 486 UV detector (220 nm), and two PLGEL 30-cm mixed columns with a porosity of 20 μ m (Polymer Laboratories). The column temperature was fixed at 65°C. The cyclohexane flow rate was 0.8 mL/min, the injected volume 100 μ L, for the natural rubber samples, and 25 μ L for the standard solutions. Calibration was carried out with synthetic

Table I Specifications, PRI, and Onset Temperature Values for the Analyzed Samples

No. Sample	Type	Clone	Maturation (Days)	Onset (°C)	PRI
B3	cup lumps	PB217	3	198.9	73.1
HA5	cup lumps	PB217	6	208.3	80.9
M1	cup lumps	PB217	15	194.4	22.2
M3	cup lumps	Mixture	15	194.8	25.9
M5	cup lumps	Mixture	15	197.3	32.2
M6	cup lumps	Mixture	15	194.8	42.2
M7	cup lumps	Mixture	15	199.5	57.8
M9	cup lumps	Mixture	15	199.2	53.9
M13	cup lumps	mixture	15	201.1	60.4
R2	cup lumps	PR107	2	202.7	80.8
R5	cup lumps	PR107	5	200.8	72.7
R6	cup lumps	PR107	6	201.2	78.9
R10	cup lumps	PR107	10	201.7	68.9
R15	cup lumps	PR107	15	199.6	58.1
M8	cup lumps	PR107	15	200.7	62
60FQ5	cup lumps	GT1	6	194.9	33.5
17CE	off-latex	GT1	16 h	—	74
13CE	off-latex	GT1	16 h	210.5	83.9
20LB	off-latex	GT1	16 h	203.5	68.2
20F	cup lumps	PB235	6	196.4	25.1
17F	cup lumps	PB235	6	195.3	30.5
301L	off-latex/industrial	Unknown	Unknown	198.8	73.4
5WFA	off-latex/industrial	Unknown	Unknown	200.5	71.2
NAT10IA	cup lumps/industrial	Unknown	Unknown	198.5	53.1
NAT10VA	cup lumps/industrial	Unknown	Unknown	200.9	61.3
NAT10VB	cup lumps/industrial	Unknown	Unknown	200.7	63
CP14	off-latex/industrial	Unknown	Unknown	202.6	64.2

poly(*cis*-isoprenes) with molecular weights of 1310, 3030, 8000, 32,400, 71,950, 97,200, 295,000, 452,000, and 1.2 million (expressed in g/mol).

The number-average molecular weight (M_n) was used to calculate the average number of chain scissions per poly(isoprene) molecule (S), which was obtained as follows:

$$S = \left(\frac{DP_0}{DP_t} \right) - 1 \quad (2)$$

where DP_0 is the initial degree of polymerization and DP_t the degree of polymerization at time t , which is equivalent to:

$$S = \left(\frac{M_{n0}}{M_{nt}} \right) - 1 \quad (3)$$

where M_{n0} is the initial number-average molar mass and M_{nt} number-average molar mass at time t .

RESULTS AND DISCUSSION

It is very important for good result repeatability to use a weight of rubber as constant as possible. Indeed, increasing the sample size led to an increase in the oxidation onset temperature (T_o) (Fig. 1). Under the conditions used, rubber weighing between 1 and 1.5 mg, the standard deviation from the onset temperature (T_o) varied between 0.2 and 0.7°C for three replicates of the same sample.

The relation between onset temperature and PRI for the set of samples studied is shown in Figure 2(a). This relation can be described by a linear model, though the correlation between the two parameters is relatively moderate ($r^2 = 0.68$). That was partly linked to certain samples whose PRI was over 70 (301L, B2, R6, HA5, and 13CE). If only the samples in zone 1 [$20 < \text{PRI} < 70$; Fig. 2(b)] were taken into account, the correlation between PRI and T_o was much better ($r^2 = 0.91$). In the second zone (PRI > 70), the correlation be-

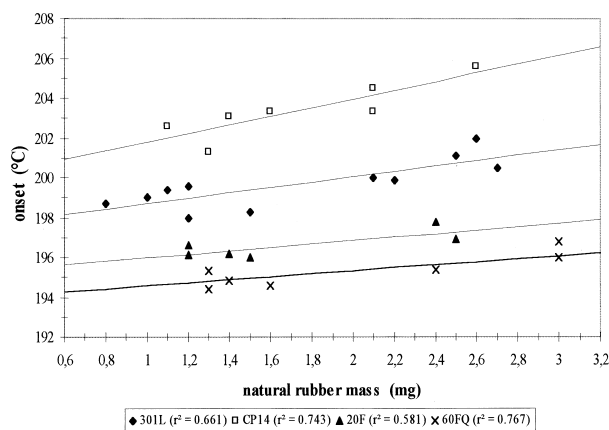


Figure 1 Effect of sample weight on the onset temperature value.

tween T_o and PRI was very poor, due to two types of behavior. In some cases, the onset temperature for certain samples (301L or B2) was much lower than suggested by the model; in other cases it was the opposite; the onset temperature was much higher than forecast by the model (13CE or HA5). In fact, in zone 2, samples with the same PRI had onset temperatures that differed by almost 6°C, whereas the standard deviations were equal to or lower than 0.7°C.

The lack of precision in DSC determination of PRI values over 70 could be linked to the different mechanisms involved in the two measurements. In the case of PRI, chain scissions are largely in the majority compared to crosslinking (Fig. 3). Regarding the transition seen in DSC, it is reasonable to assume that it is related to crosslinking. Indeed, in theory, the formation of a bond is always exothermic, whereas its dissociation is endothermic. Chih-Yu Kao et al.,¹⁶ in their study of polyethylene terephthalate hydrolysis by DSC, did obtain endothermic transitions. In addition, Smith and Stephens⁵ following studies on SBR and polybutadiene, showed that two exothermic reactions occurred with unsaturated elastomers. They attributed the first exothermic reaction (180–200°C) to the oxidative crosslinking reaction.

It, therefore, seems important at the outset, to identify the cause (scission and/or crosslinking) of the transition observed in DSC for natural rubber. To monitor changes in the macromolecular structure during a thermo-oxidation cycle in DSC, two criteria were measured by SEC. The first was the average chain scission rate (S), the other was NR concentration ($[NR]$) in the solution injected

into the SEC. The latter was assessed from the peak surface relative to natural rubber on the chromatogram. Indeed, the more the NR crosslinked in the DSC pan, the lower was the $[NR]$ in the solution injected into the SEC. Figure 4, describing the changes in S during a thermo-oxidation cycle in DSC, shows that chain scissions began early before onset temperature, but were practically stationary just after onset temperature. Chain scissions, which ought to have resulted in endothermic transition, are therefore not visible in DSC. Figure 5, which gives the solubilized NR concentration as a function of the degree of thermo-oxidation in DSC, reveals that crosslinking was just beginning before onset, and continued well beyond it. The transition observed in DSC, during natural rubber oxidation, is therefore indeed associated with crosslinking reactions.

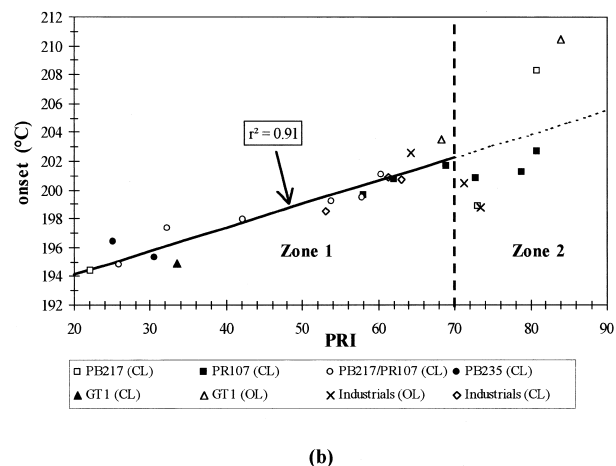
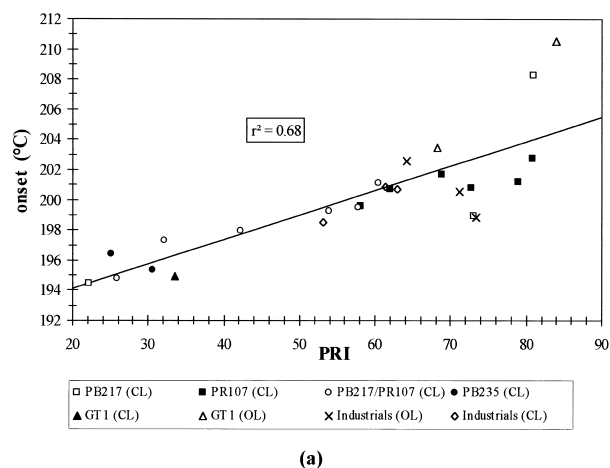


Figure 2 Relation between onset temperature and PRI for several sets of natural rubber samples (CL: cup lump, OL: off-latex).

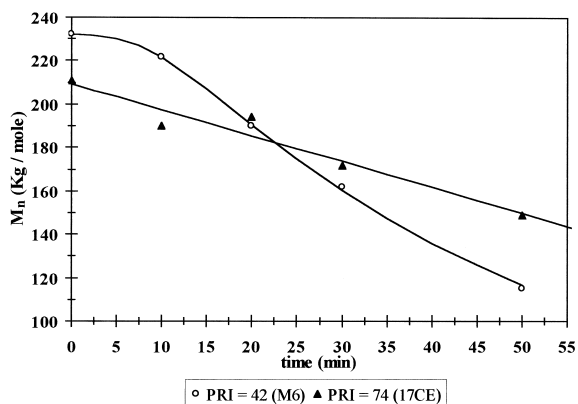


Figure 3 Changes in number-average molar mass (M_n) during thermo-oxidation of natural rubber samples in a PRI oven.

It should also be noted that at the onset of transition in DSC, oxidation had reached a much greater degree ($S \approx 8$, Fig. 4) than for a PRI measurement ($S \approx 0.5$, Fig. 6), for the same sample.

The results obtained therefore show that, although the two methods used enabled measurement of natural rubber susceptibility to thermo-oxidation, they do not reveal the same physico-chemical phenomena. Thermo-oxidation of natural rubber is measured at an early stage (primarily chain scissions) by PRI, and in the terminal phase (primarily crosslinking) by DSC. That may indirectly explain why, for PRI samples < 70 , two samples with the same PRI can have very different T_o values (Fig. 2). The direct reason that enables DSC to distinguish between two samples with the same PRI is much more complex. It is most certainly linked to the intrinsic microstructure of the samples involved and requires further studies.

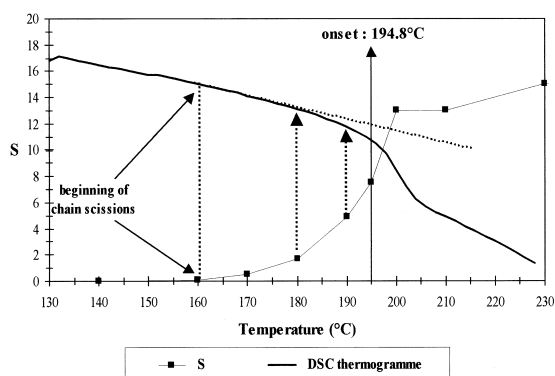


Figure 4 Variation in the mean chain scission rate (S) during the DSC thermal oxidation run (sample M6).

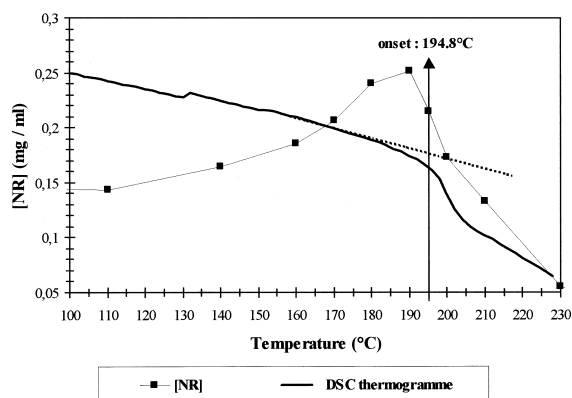


Figure 5 Variation in the quantity of soluble NR (NR) during the DSC thermal oxidation run (sample M6).

CONCLUSION

It is important to use a sample weight as constant as possible to ensure good onset temperature (T_o) repeatability. Under the conditions used, DSC was able to accurately assess the PRI of a natural rubber sample, but only for PRI values < 70 . For PRI > 70 , two samples with the same PRI can have very different T_o . This may be linked to the fact that the two measurements do not account for thermo-oxidation of the material to the same degree. Indeed, during PRI measurement, oxidation is in the initial phase and is primarily reflected in chain scissions. In DSC, the transition is due to crosslinking, and material oxidation is in its final phase when transition occurs.

The results obtained prompt a question: why are chain scission reactions not revealed by DSC? In theory, they account for as many elementary reactions and radicals as crosslinking reactions.

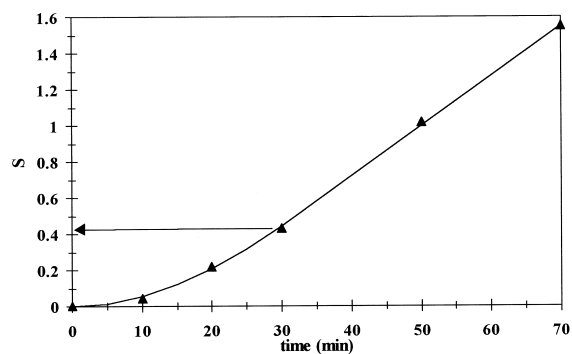


Figure 6 Variation in the mean chain scission rate (S) during the PRI thermal oxidation run (sample M6).

There should be equivalence, at least from an energy point of view.

REFERENCES

1. Norme ISO2930, Raw natural rubber—Determination of plasticity retention index (1995).
2. Bristow, G. W.; Sears, A. G. *NR Technol* 1984, 15, 1.
3. Brazier, D. W. *Rubber Chem Technol* 1980, 53, 437.
4. Gonzalez, V. *Rubber Chem Technol* 1981, 54, 134.
5. Smith, R. C.; Stephens, H. L. *J Elastomers Plast* 1975, 7(4), 156.
6. Ponce-Vélez, M. A.; Campos-Lopez, E. *J Appl Polym Sci* 1978, 22, 2485.
7. Keller, R. W.; Stephens, H. L. *Rubber Chem Technol* 1982, 55, 161.
8. Goh, S. H. *Thermochim Acta* 1984, 77, 275.
9. Goh, S. H. *J Elastomers Plast* 1977, 9, 186.
10. Goh, S. H.; Lee, S. Y.; Seah, C. L. *Thermochim Acta* 1988, 126, 149.
11. Stenberg, B.; Björk F. *J Appl Polym Sci* 1986, 31, 487.
12. Goh S. H. *Thermochim Acta* 1984, 75, 323.
13. Allen, P. W.; Bristow, G. M. *J Appl Polym Sci* 1963, 7, 603.
14. Bonfils, F.; Koman Achi, A.; Sainte Beuve, J.; Sylla, S.; Allet Don, A.; Laigneau, J. C. *J Nat Rubber Res* 1995, 10, 143.
15. Mc Naughton, J. L.; Mortimer, C. T. In *IRS. Physical Chemistry Series 2*; Butterworths: London, 1975, vol. 10.
16. Chih-Yu, K.; Wu-Hsun, C.; Ben-Zu, W. *J Appl Polym Sci* 1998, 70, 1939.