

Characterizing Gum Natural Rubber Samples Through Advanced Techniques

Jean L. Leblanc,¹ Jean-François Pilard,² Ekkawit Pianhanuruk,² Irene Campistron,² Jean-Yves Buzaré³

¹Paris-Sorbonne Université (Paris 6), Polymer Rheology and Processing, F-94408 Vitry-sur-Seine, France

²Université du Maine, UCO2M UMR CNRS 6011, F-72085 Le Mans, France

³Université du Maine, LPEC UMR CNRS 6086, F-72085 Le Mans, France

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ABSTRACT: Owing to its origin, Natural Rubber exhibits more variation than synthetic polymers. If, over the years, NR specifications have evolved from mere visual inspections towards the more complex Technically Specified Rubber (TSR) schema, industrial practice shows that, even for typical TSR grades, significant variations still exist within each shipment, especially in regard to processability. It follows that mastication is quite systematically needed in industrial operations, without or with processing aids or so-called peptizers. Typical NR compounding operations consume therefore time and mixer capacity, a situation, which obviously calls both better characterization methods of (gum) natural rubber and eventually improved grades. There are nowadays promising new techniques to analyze and characterize polymer materials, some of which are a priori attractive for a better specification of NR grades. One such technique is the so-called

Fourier Transform rheometry, a dynamic testing method to investigate both the linear and the non-linear viscoelastic domains of polymer materials. Other are spectroscopic methods like solid Nuclear Magnetic Resonance (NMR), either liquid or solid, whose results might be complemented by Size Exclusion Chromatography with special detection techniques, e.g. SEC-MALS, and Differential Scanning Calorimetry (DSC). The purpose of the work reported here was to investigate a series of gum NR grades using such techniques, with the objectives not only to demonstrate their interest but also to cross-validate their results. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 3058–3071, 2011

Key words: rheology; rubber; NMR; viscoelastic properties; microstructure

INTRODUCTION

Despite its industrial success, production specifications of Natural Rubber (NR) remain relatively poor, when compared to synthetics, as only the so-called technically specified (i.e., TSR) grades are characterized with respect to basic rubber test techniques, such as the Mooney viscosity, the (Wallace) Plasticity (P_0), and the Plasticity Retention Index (PRI).¹ Other popular grades, such as ribbed smoked sheets (RSS) for instance are still classified with respect to visual inspection criteria only.²

NR exhibits larger variation than synthetic elastomers, because around 50 different clones of *Hevea Brasiliensis* are nowadays in use, therefore introducing inevitable production differences, further enhanced by climate, soil and other local effects, plus obviously seasonal influences on tapping. The composition of (dry) NR is rather complex, with up to 3% proteins, 2% acetone-soluble resins, minor quantities

of sugar and inorganic salts, and even traces of minerals such as copper and manganese. Over the years, NR specifications have evolved from the mere visual inspection still in usage for RSS grades to the more complex TSR-schemes which include certain values on P_0 , PRI, N_2 content, etc., expectedly to guarantee a certain quality and consistency. However, practice shows that, even for typical TSR grades, a lot of variation still exists especially with respect to processability, for which specifications based on Mooney viscosity³ and on basic elasticity related measurements [e.g., plasticity number and recovery value^{4*}] do not warrant an easy processing and hence constant rheological properties of final compounds. On the factory floor, rubber engineers know well that qualitatively the best NR grades have also the highest initial viscosity and, consequently, are the most difficult to process, requiring for instance premastication, without or with processing aids or so-called peptizers, a practice which obviously consumes both time and mixer

Correspondence to: J. L. Leblanc (jean.leblanc@ifoca.com).

*Note that ISO 2007 : 1991, Rubber, unvulcanized - Determination of plasticity - Rapid-plastimeter method, uses a principle similar to this test method but the apparatus, test conditions, and procedure are somewhat different.

capacity. There is thus a need for both better characterization methods of (gum) natural rubber grades.

Most rubber processing operations occur at high rate of strain, and therefore it is essentially the nonlinear viscoelastic response of rubber materials that is of interest, whilst all current test methods in use for NR grades characterization are essentially (near) linear viscoelastic methods, e.g., Mooney viscosity, P_0 , and PRI. Not many instruments or test techniques allow the nonlinear viscoelastic domain to be investigated in confidence, and in what harmonic testing methods are concerned, only closed test cavity torsional dynamic rheometers proved to give reproducible and meaningful results. To extend its capabilities, a commercial dynamic rheometer was purposely modified to develop what has been called "Fourier Transform" (FT) rheometry.^{5,6} The capabilities of this technique in delivering data likely related with macromolecular characteristics have so far been approached with a number of polymer materials⁷⁻⁹ and the aims of this article are to offer a further demonstration by comparing advanced molecular characterization results with FT rheometry data, using a series of typical Natural Rubber samples.

MACROMOLECULAR CHARACTERIZATION TECHNIQUES

Differential scanning calorimetry

Differential scanning calorimetry (DSC) determination was performed on a Perkin-Elmer DSC-7 with a heating rate of 10°C/min under nitrogen atmosphere. The sample weight was about 5–10 mg. Calibration was achieved with indium as reference material.

Nuclear magnetic resonance

¹H NMR liquid state spectra were recorded at room temperature on a Bruker 400 Fourier Transform spectrometer at 400.13 MHz in CDCl₃ solution using tetramethylsilane (TMS) as internal standard. Solid-state NMR experiments were carried out at room temperature on a Bruker Avance 300 MHz wide bore spectrometer at 75.47 MHz using Cross-Polarization (CP) combined with Magic Angle Spinning (MAS). The spectra were recorded at spinning frequencies equal to 5 kHz. Chemical shifts are expressed in ppm downfield from TMS used as an external reference. For CP-MAS experiments, we chose the ¹H radio frequency field strength such as the $\pi/2$ -pulse duration was equal to 4 μ s. The frequency field phase is switched to $\pi/2$ simultaneously to the application of a frequency field to the carbons matching the so-called Hartmann-Hahn condition during the contact time t_{CP} . A high power proton decoupling is applied during acquisition. The reconstruction of the spectra was performed with the

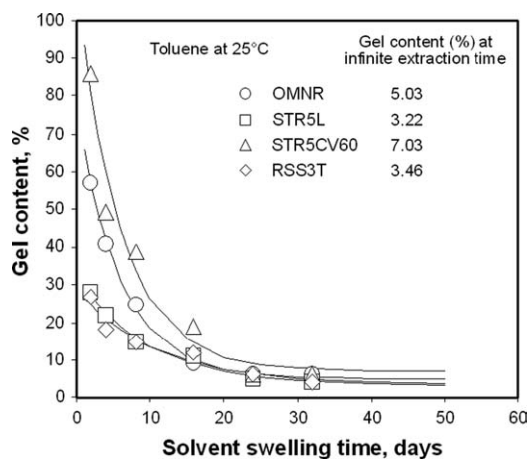


Figure 1 Assessing the gel content through a solvent swelling kinetic method.

DMFit2006 software using four adjustable parameters for each NMR line: isotropic chemical shift, line width, line-shape, and line intensity¹⁰ The ¹³C CP magnetization curves versus contact time of each carbon of the epoxy resin were built-up from line intensities.

Gel content through solvent swelling

It is widely accepted that dry natural rubber samples can have a gel component, defined as the proportion that does not dissolve in a good solvent of the gum rubber. Many methods have been reported¹¹⁻¹⁴ for assessing the gel content but none is so far well established because results remain sensitive to the choice of solvent, the time allowed for solubilizing, and of course the temperature. The following simple procedure was therefore used that focuses on swelling kinetics. A sample of around 1 gm is cut in small pieces and poured in 50 mL of toluene at room temperature. The rubber solvent system is gently agitated for a few minutes before allowing the dissolution to proceed undisturbed for selected periods (e.g., 2 days, 4 days, 8 days, etc. until equilibrium time is likely reached). The swollen rubber pieces sediment at the bottom of the flask so that, after each period, 10 mL of supernatant solution are carefully drawn out using a fine-tipped pipette. The dissolved rubber in the supernatant sample is recovered by evaporating the solvent under vacuum at 50°C for 24 h. The sol and gel fractions, i.e., Φ_{sol} and Φ_{gel} are calculated using:

$$\Phi_{sol} = \frac{W_i V_1}{W_1 V_2} \quad \text{and} \quad \Phi_{gel} = 1 - \Phi_{sol}$$

Where W_1 is the initial weight of rubber, W_i is the weight of rubber in the 10 mL supernatant solution at time i , V_1 the overall volume (i.e., 50 mL) and $V_2 = 10$ mL. This procedure yields gel fractions after various

period so that the fraction for an infinite solubilizing time is easily obtained by extrapolation, using a single three parameters exponential decay equation, as illustrated in Figure 1. As can be seen, relatively minor differences are seen between the NR samples, providing an “infinite” extraction time is considered. Large gel contents are observed only for less than 10 days dwell time in the solvent but the results are transient. Such results suggest that an alternative method consists in assessing the supernatant rubber content after some 50 days swelling time.

Gel permeation chromatography with MALS detection (SEC-MALS)

Macromolecular characteristics were assessed in CIRAD (Montpellier, France) using size exclusion chromatography coupled with multiangle light scattering (SEC-MALS). The SEC-MALS equipment consists of an online degasser (Elite™, Alltech Associates, Deerfield, IL), a Waters 515 pump, a refractive index detector (Waters 2410) and a multiangle light scattering detector (Dawn DSP, Wyatt Technology, Santa Barbara, CA). Three PLgel-Mixed-A (Polymer Laboratories, Varian, Palo Alto, CA) mixed bed columns (20 mm, 300 mm × 7.8 mm internal diameter) with a guard column were used. The columns were maintained at 45°C and THF (tetrahydrofuran) was used as mobile phase with a flow rate of 0.65 mL/min; the injected volume was 150 mL. The data from MALS detectors were analyzed with the Astra software, V 5.3.2.22 (Wyatt Technology) using either the Berry or the Zimm method. Test solutions were prepared by dissolving 25 ± 5 mg of rubber in 40 mL THF (HPLC grade) stabilized with 2,6-di-*tert*-butyl-4-methylphenol. After 1-week storage in darkness at 30°C, solutions were filtered through 1 μm, glass fiber paper (Pall Co, Port Washington, NY), so that with respect to the polymer concentration before and after filtration the gel content was assessed. Kim et al. have published details of the technique.^{15,16}

RHEOLOGICAL CHARACTERIZATION TECHNIQUES

Mooney viscometer

Mooney torque ML(1+4) was assessed using a standard instrument, according to ASTM D 1646-03a test method.^{17,18} A large rotor (diameter: 19.05 mm; thickness: 5.54 mm) was used.

Fourier transform rheometry

Principle of the technique

Fourier Transform (FT) rheometry is a technique that documents the nonlinear viscoelastic behavior of polymer materials through performing large am-

plitude oscillatory strain (LAOS) experiments. No commercial instruments are yet available but the technique is easily implemented on appropriate instruments. Essentially, Fourier transform rheometry consists in capturing strain and torque signals during dynamic testing and in using the appropriate calculation algorithm to resolve it into their harmonic components.

FT is simply a mathematical treatment of harmonic signals that resolves the information gathered in the time domain into a representation of the measured material property in the frequency domain, as a spectrum of harmonic components. If the response of the material is strictly linear, then proportionality between (applied) strain and (measured) torque is kept, the torque signal is a simple sinusoid and consequently the torque spectrum consists of a single peak at the applied frequency. A nonlinear response is thus characterized by a number of additional peaks at odd multiples of the applied strain frequency. At high strain, a nonlinear response is observed so that the torque signal becomes distorted, which reflects a lack of proportionality between the applied strain (perfectly sinusoidal) and the measured torque. FT can also be applied on the strain signal to quantify its quality.

Wilhelm et al.^{5,19} demonstrated that only odd torque harmonics are significant in terms of material's response. Indeed, if a shear strain of maximum strain amplitude γ_0 (rad) is applied at a frequency ω (rad/s) to a viscoelastic material, the strain varies with time t (s) according to $\gamma(t) = \gamma_0 \sin(\omega t)$ and the shear stress response can be expected to be given by a series of odd harmonics, i.e.:

$$\sigma(t) = \sum_{j=1,3,5,\dots}^{\infty} \sigma_j \sin(j\omega t + \delta_j) \quad (1)$$

providing one assumes that, over the whole viscoelastic domain (i.e., linear and nonlinear), the viscosity function $\eta = f(\dot{\gamma})$ can be approximated by a polynomial series with respect to the shear rate. If the tested material exhibits a pure linear viscoelastic response, eq. (1) reduces to the first term of the series, as considered in most standard dynamic test methods.

Up-dating a torsional dynamic tester for Fourier transform rheometry

Any commercial torsional dynamic tester can be conveniently updated for Fourier transform rheometry, but conventional open gap rheometers, for instance parallel disks and cone-and-plate instruments have been shown to be limited to relatively low strain amplitude experiments²⁰ on materials exhibiting a relatively modest elasticity. Indeed laboratory practice shows that open gap rheometers give poorly reproducible results with very stiff and/or highly elastic

materials, essentially because it is nearly impossible to reproducibly position such materials in the testing gap. Because they were designed for easy handling of very stiff materials, such as filled rubber compounds, closed cavity torsional testers are particularly suitable for Fourier transform rheometry and, therefore, the appropriate modifications were brought to a Rubber Process Analyzer, RPA 2000® (Alpha Technologies, now a division of Dynisco LLC, Franklin, MA) to capture strain and torque signals. Details on the modification and the measuring technique were previously reported.²¹ Essentially, strain and torque signals, as provided by the instrument, are collected by means of an electronic analogic – digital conversion card. Test results consist thus in data files of actual harmonic strain and stress readings versus time. Proprietary data handling programs are then used to perform Fourier transform calculations and other data treatments. Through simultaneous FT treatment of both the torque and strain signals, it has been demonstrated that, at large strain amplitude, the RPA submits materials to a nearly pure strain sinusoidal signal.⁹ However, strain signal quality degenerates as strain angle decreases and a correction method had to be developed, as explained below.

Fourier Transform analysis yields essentially two types of information: (1) the main signal component, i.e., the peak in the FT spectrum that corresponds to the applied frequency [hereafter noted either $T(1\omega)$ or $S(1\omega)$ with respect to the torque or strain signals respectively], (2) the harmonics, with the third (i.e., the peak at 3 times the applied frequency) the most intense one. A specific calculation program, written using the FT algorithm available in MathCad 8.0® (MathSoft Inc.), is used to obtain the amplitude of the main stress and strain components (corresponding the test frequency) and the relative magnitudes (in %) of the odd-harmonic components, i.e., $I(n \times \omega_1)/I(\omega_1)$. Note that we used $I(n\omega_1)/I(\omega_1)$ or the abridged form $I(n/1)$, to describe the n th relative harmonic component of any harmonic signal; $S(n\omega_1)/S(\omega_1)$ or $S(n/1)$ specifically means that a strain signal is considered; $T(n\omega_1)/T(\omega_1)$ or $T(n/1)$ is used for the Torque signal.

Strain sweep test protocols for nonlinear viscoelasticity investigations

When submitting pure polymers to harmonic strain, nonlinear viscoelastic behavior occurs at high strain amplitude and, therefore, strain sweep test is the method of choice to investigate nonlinearity. The appropriate test protocols were developed, which essentially consist in performing strain sweep experiments through two subsequent runs separated by a resting period of 2 min. At least two samples of the same material are tested (more if results reveal test material heterogeneity), in such a manner that, through inversion of the strain sequences (i.e., Run 1 and Run

2), sample fatigue effects are detected, if any. Differences are expected between Runs 1 and 2 for materials exhibiting strain memory effects. With the RPA, the maximum applicable strain angle depends on the frequency, for instance around 68° ($\approx 950\%$) at 0.5 Hz, considerably larger than with open cavity cone-plan or parallel disks torsional rheometers. Whatever the frequency, the lower strain angle limit is 0.5° (6.98%) below which the harmonic content of the strain signal becomes so high that measured torque is excessively scattered and likely meaningless. Test protocols at 0.5 Hz were designed to probe the material's viscoelastic response within the 0.5° to 68° range, with up to 20 strain angles investigated.

FT analysis of the strain (i.e., applied) signal allows its quality to be precisely documented and, if needed, the appropriate correction to be brought on torque harmonics, according to²²:

$$T(n\omega/1\omega)_{\text{corr}} = T(n\omega/1\omega)_{\text{TF}} - \text{CF} \times S(n\omega/1\omega)_{\text{TF}} \quad (2)$$

where $T(n\omega/1\omega)_{\text{TF}}$ and $S(n\omega/1\omega)_{\text{TF}}$ are the n th relative harmonic components of the torque and strain signals, respectively. CF is the correction factor, as derived from a plot of $T(n\omega/1\omega)$ vs. $S(n\omega/1\omega)$. The correction applies also when considering the so-called "total torque harmonic content" (TTHC), i.e., the sum $\sum T(n\omega/1\omega)$ of all the odd harmonics up to the 15th.

Modeling the effect of strain amplitude on FT rheometry results

According to strain sweep test protocols described above, RPA-FT experiments and data treatment yield essentially two types of information, which reflects how the main torque component, i.e., $T(1\omega)$, and the relative torque harmonics vary with strain amplitude. Such variations can conveniently be modeled with simple mathematical relationships.

The ratio of the main torque component over the strain, i.e., $T(1\omega)/\gamma$ has obviously the meaning of a complex modulus, i.e., $G^* = 12.335 \times \frac{T(1\omega)}{\gamma}$ [with G^* in kPa, $T(1\omega)$ in arbitrary unit and γ in %] and, for a material exhibiting linear viscoelasticity within the experimental window, a plot of G^* vs. γ shows the most familiar picture of a plateau region at low strain, then a typical strain dependence. Such a behavior is well captured with the following equation:

$$G^*(\gamma) = G_f^* + \left[\frac{G_0^* - G_f^*}{1 + (A\gamma)^B} \right] \quad (3)$$

where G_0^* is the modulus in the linear region, G_f^* the final modulus, A the reverse of a critical strain for a mid modulus value to be reached, and B a parameter describing the strain sensitivity of the material.

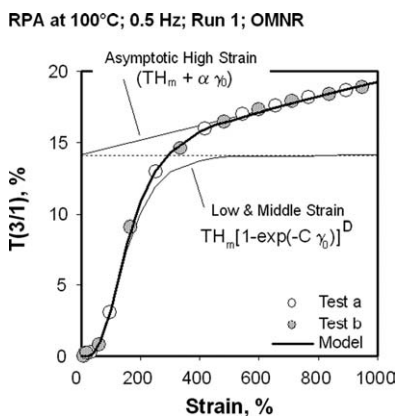


Figure 2 Modeling the variation of relative torque harmonics with strain amplitude; note that for the sake of clarity, the low and middle strain component of the model has been multiplied by TH_m ; otherwise this component plateaus out at 1.

Odd torque harmonics become significant as strain increases and are therefore considered as the nonlinear viscoelastic “signature” of tested materials, only available through Fourier Transform rheometry. Numerous experiments on various pure, unfilled polymers have shown that relative torque harmonics vary with strain amplitude in such a manner that an initial S-shape curve appears bounded by a simple linear variation at high strain. Accordingly, the following model was successfully developed to fit results obtained on simple polymer systems:

$$TH(\gamma) = (TH_m + \alpha\gamma_0) \times [1 - \exp(-C\gamma_0)]^D \quad (4)$$

where γ_0 is the strain magnitude, TH_m , α , C , and D parameters of the model. The member $(TH_m + \alpha\gamma_0)$ expresses an asymptotic linear variation of harmonics in the high strain region, while the member $[1 - \exp(-C\gamma_0)]^D$ describes the onset and the development of the nonlinear viscoelastic response, obviously occurring in the low and middle strain regions, as illustrated in Figure 2.

The physical meaning of parameters TH_m and α is obvious; parameter D somewhat reflects the extent of the linear viscoelastic region (i.e., where no harmonics are detected), while parameter C indicates the strain sensitivity of the nonlinear character. As the strain γ is

smaller and smaller, in other words in the linear viscoelastic region, eq. (4) corresponds to asymptotically zero harmonics, in complete agreement with theory. It is worth noting that in using eq. (4), one may express the deformation (or strain) γ either in degree angle or in %. Obviously all parameters remain the same except C , whose value depends on the unit for γ . The following equality applies for the conversion: $C(\gamma, \text{deg}) = \frac{180\alpha}{100\pi} \times C(\gamma, \%)$, where $\alpha = 0.125$ rad.

EXPERIMENTAL RESULTS AND DISCUSSION

Test materials

With the objective to cover a representative range with a limited number of samples, a series of Natural Rubber grades were collected, thanks to the courtesy of the Rubber Research Program of Thailand. Except wrapping in dark plastic sheets, no particular precaution were observed in sampling and transporting the sample, so that any atmosphere, temperature and other effects, if any, are considered to have affected the test materials in the same manner. A NR grade commercially available in France was included in the study and a commercial high cis-1,4 polybutadiene as typical high elasticity synthetic material. Table I gives a description of the samples and a few characterization results (suppliers’ data).

STR 5L is a technically specified light color rubber grade, obtained by coagulating freshly collected high quality latex. Wet crumbs are then placed in open trays and dried in a forced air dryer at a temperature of 110–125°C, before testing at a certified TSR laboratory. Rubber passing the TSR L specifications has a maximum 0.04% dirt content, maximum 0.4% ash content, a maximum 0.6 nitrogen content, an initial plasticity $P_0 = 35$ (minimum) and a minimum plasticity retention index of 60.

Whole field latex is used to produce RSS. Collected latex is first diluted to 15% solids, and then coagulated for around 16 h with dilute formic acid. Coagulated material is then milled, water removed, and sheeted with a rough surface to facilitate drying. Sheets are dried in a smokehouse for one to seven days. RSS grades consist of deliberately coagulated rubber sheets and graded according to their color, consistency and observed impurities. RSS3F and

TABLE I
Test Samples

Sample code	Material description	Origin	Mooney ML(1+4) _{100°C}
STR 5L	Natural rubber, Standard Thai rubber, 5L grade	Thailand	70
STR 5CV60	Natural rubber, constant viscosity grade	Thailand (Jana)	63
RSS3F	Natural rubber, rib smoked sheet #3	Safic-Alcan, France	75
RSS3T	Natural rubber, rib smoked sheet #3	Thailand	67
OMNR	Natural rubber, optimized molecular weight	Thailand	60.
BR40	98% cis-1,4 Polybutadiene, NeoCis BR40	Polimeri, Italy	43

TABLE II
Mooney Results, Gel Content, and Macromolecular Characteristics

NR sample	Mooney ML(1+4) 100°C	SEC—MALS results				
		Gel content (%)	M_n (Kg/mol)	M_w (Kg/mol)	M_z (Kg/mol)	MWD
STR 5L	70	23.96 ± 1.44	679 ± 31	1278 ± 11	2375 ± 21	1.88
STR 5CV60	63	16.87 ± 1.91	491 ± 2	1323 ± 3	2779 ± 140	2.69
RSS3F	75	34.47 ± 1.39	1051 ± 43	1755 ± 34	2934 ± 60	1.67
RSS3T	67	45.28 ± 0.95	1143 ± 27	1685 ± 29	2597 ± 84	1.47
OMNR	60	15.72 ± 4.29	464 ± 18	1130 ± 73	2407 ± 284	2.43
BR40 ^a	43	0	142	493	N/A	3.2

^a Source : Univ. P. & M. Curie—Polymer Rheology & Processing; molecular weights by GPC.

RSS3T meet the following specifications: 0.20 dirt content maximum, 1.00% ash content (maximum), 0.60% maximum nitrogen content, $P_0 = 30$ (minimum) and PRI = 50 (minimum).

STR 5CV60 is a technically specified “constant viscosity” grade, produced from field latex, whose Mooney viscosity is stabilized to a specified value [i.e., ML(1+4)100°C = 60 ± 5], through the addition of a suitable chemical. Dirt, ash, and N₂ contents (%) are maximum 0.05, 0.6, and 0.6 respectively. PRI is minimum 60. On storage this grade is expected to remain within eight hardness units.

Optimized Molecular Weight Natural Rubber (OMNR) is a new grade currently developed in Thailand, through coagulation of selected field latex products; the viscosity is reduced and stabilized through the addition of a (undisclosed) chemical. No stabilizer or oil is added. OMNR is relatively similar to TSR CV60 but is expected to show no variation on ageing.

Used for comparison purposes, Europrene NeoCis BR40 is a 98% cis-1,4 polybutadiene from a Ziegler-Natta process with a neodymium salt as catalyst, commercially available from Polimeri Europa (Italy).

Mooney, gel content and SEC-MALS data

Table II gives the Mooney results, the gel content and the SEC-MALS data, as kindly provided by CIRAD-Montpellier; data on 98% cis-1,4 polybutadiene are also included.

TABLE III
Differential Scanning Calorimetry Results of Various Sample NR Gums

Sample code	Gum sample T_g (°C)	CH ₂ Cl ₂ extraction		THF extraction	
		Uns Soluble %	Extracted sample T_g (°C)	Uns Soluble %	Extracted sample T_g (°C)
STR 5L	-63	10	-63	17	-63
STR 5CV60	-63	21	-62	24	-63
RSS3F	-64	18	-62	26	-62
RSS3T	-63	11	-62	8	-63
OMNR	-64	6	-63	4	-62

As can be seen the gel content data obtained through the solvent swelling kinetic method on NR samples (Fig. 1) do not correspond at all with the data obtained by the CIRAD but it must be noted that the latter were obtained only after 1 week solubilizing and using a filtration technique. Figure 1 above showed that after 1 week the solubilizing process is still far from equilibrium and furthermore, using a 1 μm mesh filter is likely retaining grossly swollen but not (naturally) networked macromolecules. One would conclude that gel content data associated with SEC-MALS measurements are not reliable information. One notes however a nearly perfect linear relationship between the gel content and the number average molecular weight as determined by SEC-MALS. It is also worth underlining that there is no correlation between Mooney results and macromolecular dimensions, either M_n or M_w .

An interesting observation is the larger molecular weight distribution of the two constant viscosity grades (i.e., STR 5CV60 and OMNR) when compared with the RSS and the field latex grades. A careful analysis of the data given in Table II reveals in fact that the chemicals used to stabilize the viscosity do reduce more the number average than the weight average molecular weight, hence the larger (nearly double) MWD. Owing to the limited number of samples studied here, such an observation might be fortuitous and calls for further investigations.

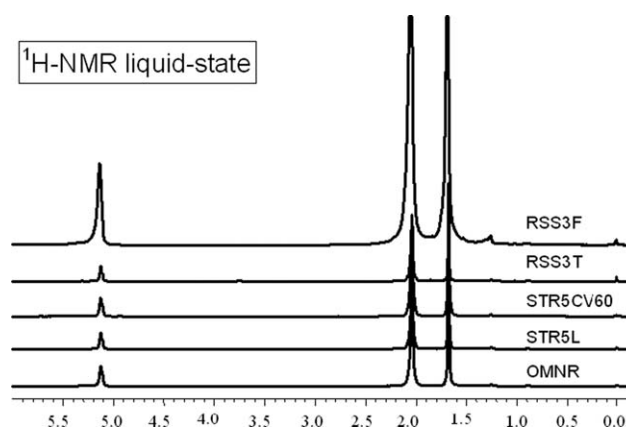


Figure 3 ¹H-NMR liquid-state of natural rubber samples.

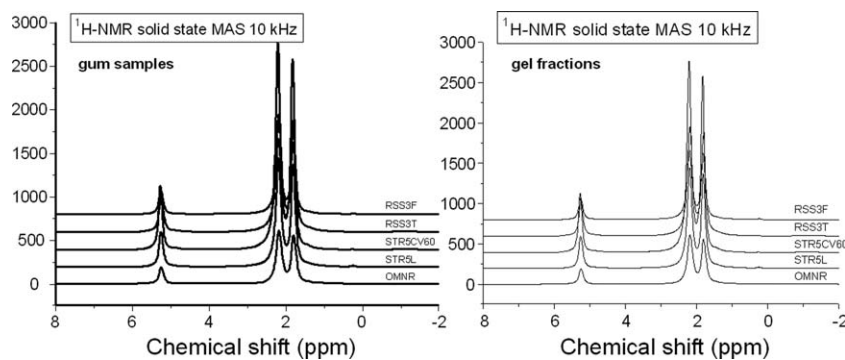


Figure 4 ^1H -NMR solid MAS 10 kHz on gum natural rubber samples (left) compared to gel fractions (right).

Differential scanning calorimetry results

Glass transition temperature T_g was assessed by DSC on dry gum samples as received and on samples after 72 h Soxhlet extraction with either CH_2Cl_2 or THF. T_g was measured on the second heating thermogram to avoid thermal history effects, if any. Table III tends to show that, though OMNR is known to present by far the lowest level of nonrubber components, no significant difference is observed as seen in T_g values for all the samples, either with or without nonrubber ingredients. Note that the polybutadiene sample was found totally soluble either in CH_2Cl_2 or THF and has a T_g of -108°C .

NMR analysis

^1H NMR analysis was firstly performed in liquid state after Soxhlet extraction. As shown in Figure 3, ^1H -NMR spectra exhibit three main characteristic signals: the first one centered at 5.25 ppm corresponds to the alkene proton, the next two signals centered respectively at 2.18 and 1.80 ppm can be related to the methylene and the methyl protons. Similar results are obtained when performing the experiments in solid state. Moreover, no difference

was noticed when analyzing either the soluble or the gel fraction of the various grades of NR gums (Fig. 4). Indeed, for all NR grades investigated, no significant chemical shift was observed whatever the percentage of insoluble fraction in the gum rubber (from OMNR to STR 5CV60 see Table III).

Complementary ^{13}C solid NMR experiments performed on samples either of the soluble or the gel fraction gave expected spectra (Fig. 5). Indeed specific signals centered at 134.8, 125.3, 32.5, 26.7, and 23.6 ppm corresponding respectively to carbon signals $=\text{C}-$ (2), $=\text{CH}-$ (3), $-\text{CH}_2-$ (1), and $-\text{CH}_3$ (5), were observed. No significant chemical shift difference was noticed between the various NR grades. In addition, similar spectra were obtained from the analysis of both the soluble and the gel fractions of each sample.

To further document the analysis, a cross polarization magic angle spinning (CP-MAS) technique was performed as it has been well documented that it gives precious information especially about the amount of mobile regions versus rigid ones in NR gums.²³ A comparison stack plot of ^{13}C -NMR solid CP-MAS of all NR grades investigated in the C-4 region (25–30 ppm width) is given in Figure 6 as it gives the best separation performance.²⁴ The line widths of CP-MAS spectra in this range correspond indeed to immobile and mobile components of the polyisoprene chains. A curve fitting (DMFit2006 software) was used to simulate the

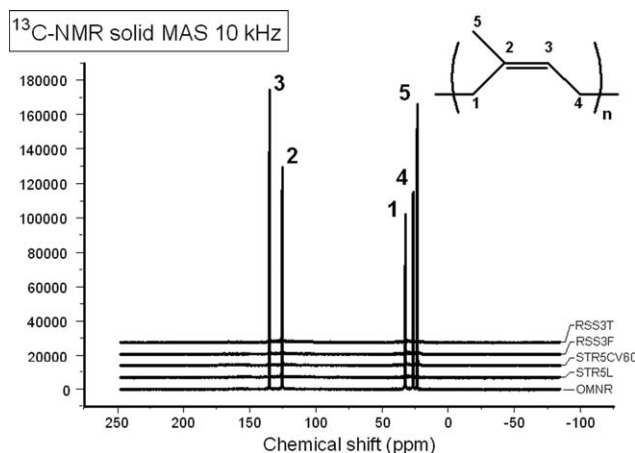


Figure 5 ^{13}C -NMR solid MAS 10 kHz of natural rubber samples.

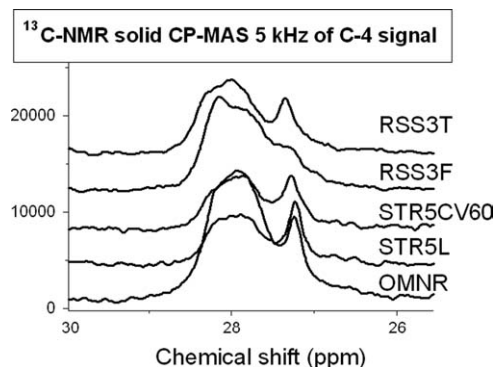


Figure 6 ^{13}C -NMR solid CP-MAS 5 kHz of C-4 signal of natural rubbers.

TABLE IV
 ^{13}C -NMR Solid CP-MAS 5 kHz; Ratio "Immobile/
 Mobile" Contributions to the Signal Intensity in the C-4
 Region

Sample	Mobile component (%)	Immobile component (%)	Ratio immobile/mobile
STR5L	28	72	2.6
STR5CV60	27	73	2.7
RSS3T	18	82	4.6
RSS3F	8	92	12.3
OMNR	22	78	2.9
BR40	100	0	–

line width and the integrated area of each carbon signal. The different percentages of the mobile and immobile fraction and the ratio "immobile/mobile" are thus obtained. It must be noted however that CP-MAS experiments do not really give absolutely quantitative data because rigid regions are overestimated, whilst perfectly evidenced. However, as all reported experiments were performed in exactly the same conditions, results given in Table IV can be considered as valuable (relative) information.

It can be seen that, in comparison with a synthetic elastomer such as high cis-1,4 polybutadiene (Neo-Cis BR40), all NR samples exhibit a high percentage of rigid fraction. This is somewhat unexpected with respect to the structural differences between high cis-1,4 polyisoprene and high cis-1,4 polybutadiene and this observation tends to evidence a strong heterogeneity of the macromolecular structure of Natu-

ral Rubber. In addition two groups of NR can be distinguished: on one hand OMNR, STR5L, and STRCV60 with very little difference, if any, between them, and on the other hand, the smoked sheet grades, RSS3T, and RSS3F, with the latter showing a higher ratio immobile/mobile than the former. If one compares the data in Table IV with the macromolecular characterization by SEC-MALS (Table II), a (weak) relationship is seen between the mobile component content (or the immobile/mobile ratio) and either the gel content or the number average molecular weight, essentially because the two smoked sheet grades are very different from the other ones. A larger sampling of NR grades would however be needed to reinforce this observation.

Experiments with the RPA

With respect to its testing principle, the RPA must be loaded with a volume excess of test material. Numerous experiments on various systems have shown that a tight control of sample volume and shape is essential for accurate and reproducible results. Therefore, before testing, samples were compression molded at 100°C in a 3 cm³ mould mimicking the RPA test cavity geometry (i.e., 0.125 radian reciprocal cone; 20.625 mm radius), in such a manner that the instrument was loaded with test samples having a 5% excess volume. At least two samples of the same material were tested (more if results reveal anomalies). As described above, strain sweep test protocols at 0.5 Hz were used.

RPA at 100°C ; 0.5 Hz

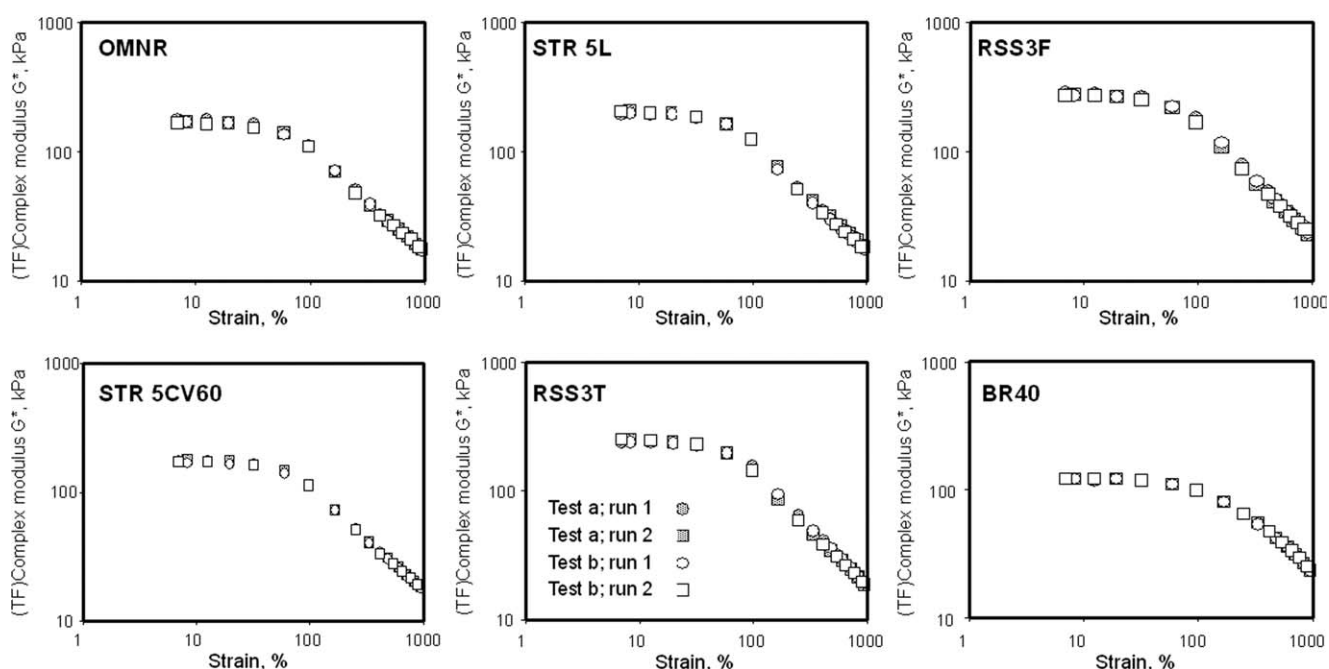


Figure 7 RPA-FT at 100°C on gum Natural Rubber samples; complex modulus G^* vs. strain; strain sweep tests at 0.5 Hz.

TABLE V
RPA-FT Strain Sweep Experiments at 100°C and 0.5 Hz;
Fit Parameters of eq. (3)

Frequency (Hz): 0.5						
Sample	Run (a&b)	G_0^* (kPa)	G_f^* (kPa)	1/A %	B	r^2
STR 5L	1	200.2	14.6	131.1	1.776	0.9993
	2	205.2	17.3	116.7	1.877	0.9992
STR 5CV60	1	181.0	13.1	118.2	1.792	0.9999
	2	180.1	16.1	110.1	1.989	0.9997
RSS3T	1	225.4	15.2	122.5	1.766	0.9998
	2	234.1	18.3	109.2	1.883	0.9997
RSS3F	1	275.3	16.5	127.5	1.721	0.9989
	2	266.3	18.1	121.2	1.758	0.9999
OMNR	1	171.2	12.0	119.2	1.668	0.9999
	2	165.2	15.5	117.0	1.893	0.9998
BR40	1	122.8	12.4	248.8	1.511	0.9998
	2	124.2	11.1	250.4	1.468	0.9998

(RPA-FT) Complex modulus vs. strain

Complex modulus G^* versus strain curves are shown in Figure 7. In all cases, the two tested samples (a & b) give identical results thus demonstrating the excellent homogeneity of tested materials and the reproducibility of the testing method. For all materials no differences are seen between Run 1 and Run 2 data, which

indicates that either there are no significant strain history effects or that strain effects are immediately recovered during the 2 min resting period between runs. It is worth underlining here that G^* data are derived from the main component of the torque signal, as obtained through FT analysis. Qualitatively similar graphs are obtained when using G^* values from the standard RPA (built in capabilities) but with an error by excess, particularly in the nonlinear region.

Figure 7 clearly shows that all tested materials do exhibit a linear region, whose limit depends on the material. NR samples remain linear up to around 20% strain, whilst BR exhibits no strain effect up to around 50% strain.

Fit parameters of eq. (3) are given in Table V from RPA-FT results at 0.5 Hz. As can be seen, the r^2 values reveal that the fitting is excellent in all cases. Modeling G^* vs. strain experiments with eq. (3) yields three parameters, whose physical meaning is immediate, and which allow a direct comparison between test materials (Fig. 8).

G_0^* is the (extrapolated) "linear" modulus. The two stabilized grades, i.e., OMNR and STR 5CV60 exhibit similar values, significantly higher than for polybutadiene BR40. RSS3F has the highest complex modulus, followed by RSS3T, then STR 5L, which is slightly

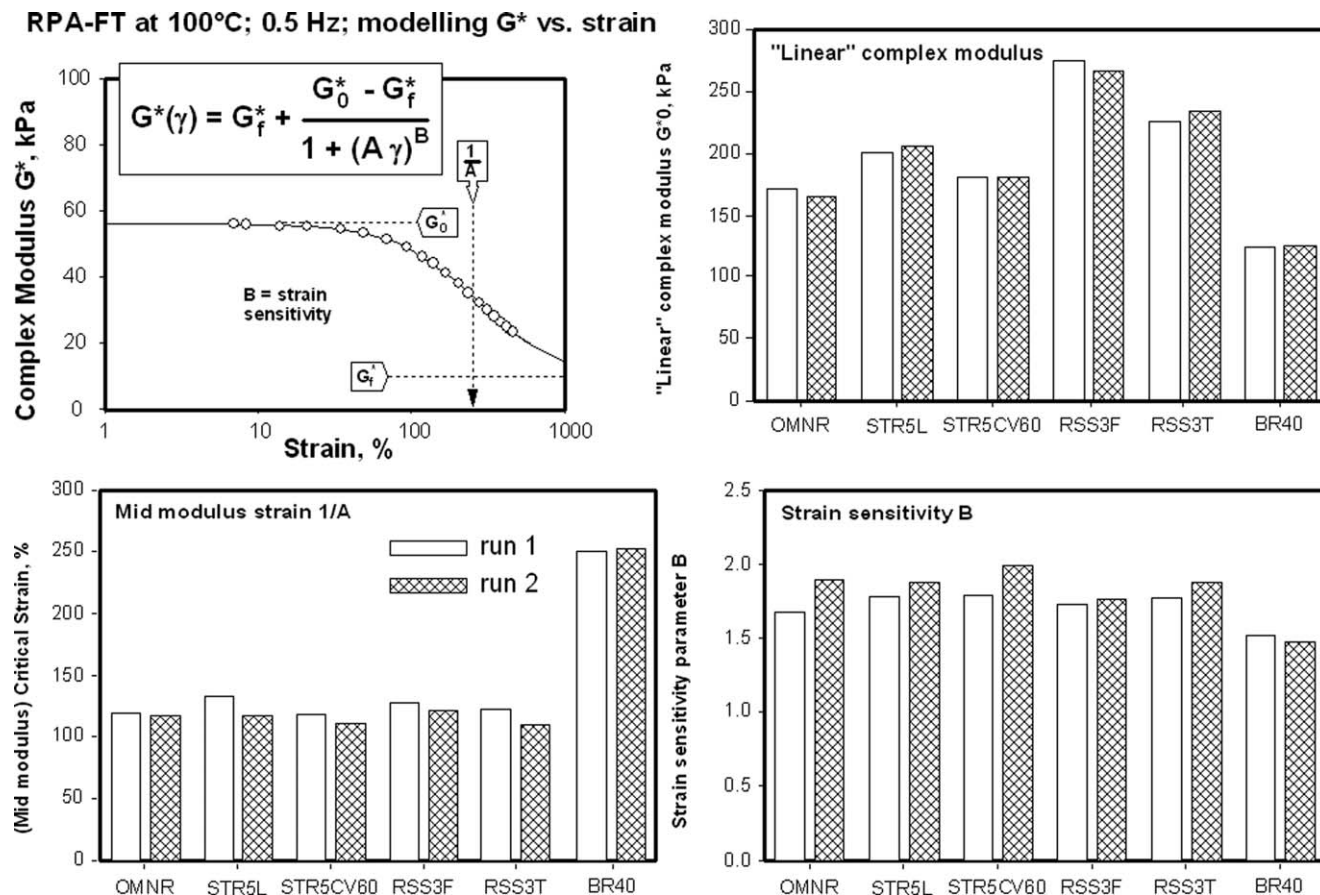


Figure 8 Comparing test materials through parameters of eq. (3).

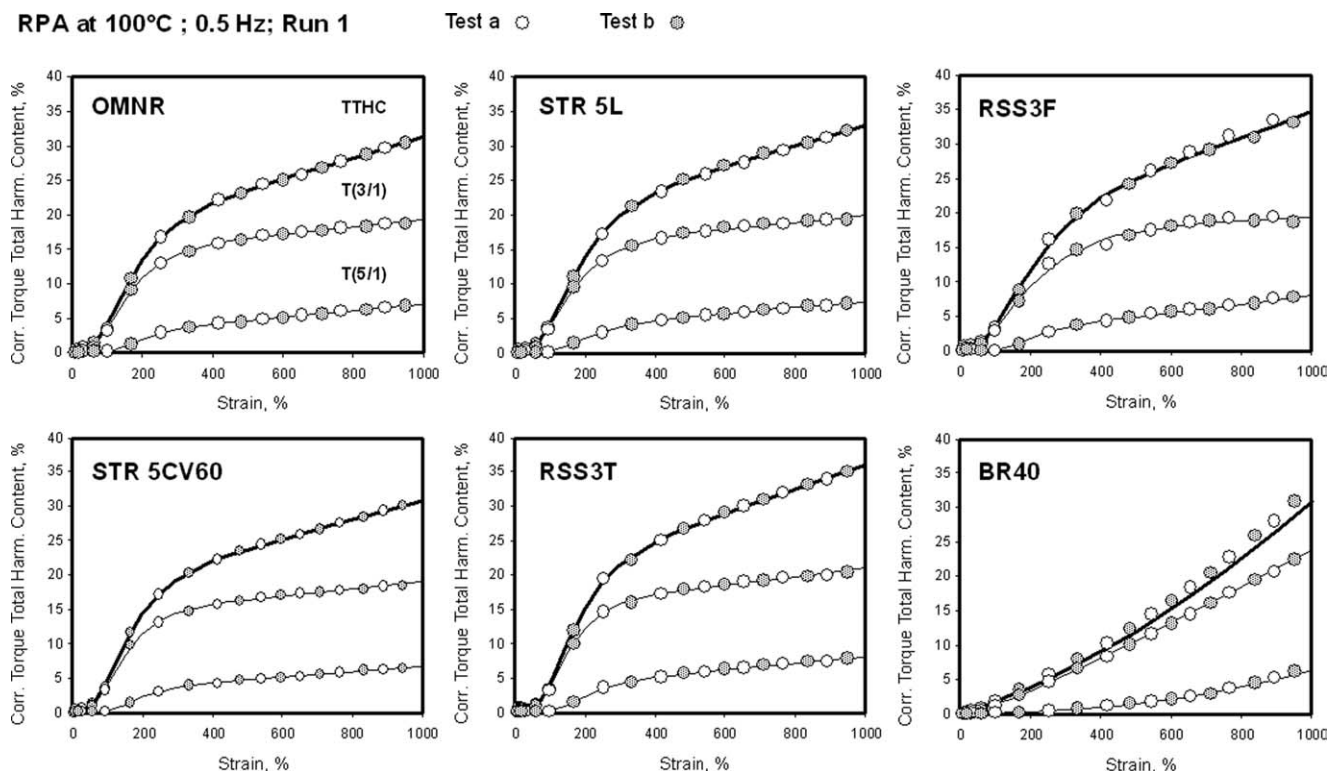


Figure 9 RPA-FT; torque harmonics vs. strain; 5th relative torque harmonic T(5/1); 3rd relative torque harmonic T(3/1); total torque harmonic content TTHC.

stiffer than OMNR and STR 5CV60. The (number averaged) molecular weight is expected to be the prime macromolecular character affecting the complex modulus of polymer on the rubbery and in the terminal flow regions and indeed G^*_0 is directly commensurable with the available characterizing information (Table II). The midmodulus critical strain ($1/A$) is somewhat related with the extent of the linear viscoelastic region and, as shown in the lower left graph of Figure 8, all NR samples are similar, but very different from polybutadiene. The strain sensitivity parameter B is original information, revealing little, if any, differences between the NR grades tested, but larger strain sensitivity that polybutadiene. Differences between run 1 and run 2 data are not large enough to be really significant; one notes however that all NR samples exhibit slightly larger strain sensitivity during Run 2, contrary to polybutadiene.

(RPA-FT) Torque harmonics vs. strain

Figure 9 shows how the torque harmonics varies with increasing strain amplitude for all the samples tested, at 0.5 Hz frequency. Data are well reproducible with no difference between tests a and b. Run 1 data are given but there is hardly any difference with Run 2 data, which indicates that torque harmonics of the series of gum rubber are insensitive to strain history. Drawn curves correspond to fit obtained with eq. (4) and, as expected, the overall

torque harmonic content (TTHC) curve envelopes the single harmonic ones, here T(3/1) and T(5/1). There is a marked difference between NR samples and synthetic polybutadiene, as the latter exhibits harmonics, which varies differently with strain amplitude. NR samples clearly exhibit the S-shape of the model which, at large strain, appears to be converging toward a linear variation with strain. Polybutadiene data might exhibit the same pattern but neither the end of the transition region nor the asymptotic high strain behavior is observed within the experimental strain window of the instrument. In term of chain structure, high cis-1,4 polybutadiene differs from NR only by the absence of pending methyl group and only this difference is sufficient to completely change the “nonlinear viscoelastic signature”. Such a marked difference between the two types of rubber is therefore worth noting.

Fit parameters for TTHC, T(3/1), and T(5/1) vs. strain are given in Table VI.

Torque harmonics quantify the nonlinear viscoelastic behavior and how they vary with increasing strain amplitude is likely reflecting how macromolecular characteristics of polymers monitor the strain response. The third relative torque harmonics T(3/1) is the largest and indeed does capture the essential of the nonlinear behavior, as shown in Figure 9 above. The model [eq. (4)] parameters are consequently reflecting subtle macromolecular differences

TABLE VI
RPA-FT at 100°C; 0.5 Hz on NR Samples; Modeling Relative Harmonics vs. Strain with eq. (4)

Sample		TTHC		T (3/1)		T (5/1)	
		Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
STR 5L	TH _m	18.29	16.34	15.11	14.57	3.06	2.43
	α	0.0147	0.0178	0.0047	0.0058	0.0043	0.0054
	C	0.0115	0.0151	0.0127	0.015	0.0138	0.0222
	D	4.12	5.02	4.41	4.65	10.80	29.09
	r ²	0.9999	0.9998	0.9998	0.9998	0.9995	0.9991
STR 5CV60	TH _m	16.85	15.64	13.86	13.59	2.77	2.33
	α	0.0139	0.0158	0.005	0.0055	0.0039	0.0046
	C	0.0134	0.0151	0.0147	0.0153	0.0163	0.0199
	D	4.75	4.65	5.22	4.54	12.78	18.73
	r ²	0.9998	0.9999	0.9997	0.9998	0.9996	0.9994
RSS3T	TH _m	18.13	19.47	14.89	15.59	3.19	3.44
	α	0.0178	0.0168	0.0059	0.0057	0.0048	0.0047
	C	0.0135	0.0129	0.0157	0.0156	0.0163	0.0183
	D	5.46	3.62	6.52	4.42	16.12	15.18
	r ²	0.9998	0.9997	0.9998	0.9995	0.9998	0.9988
RSS3F	TH _m	16.72	20.93	16.4	17.1	1.80	4.18
	α	0.0176	0.0176	0.0030	0.0036	0.0062	0.0053
	C	0.0093	0.0109	0.0083	0.0123	0.0172	0.0146
	D	3.25	3.05	2.91	3.30	17.53	10.36
	r ²	0.9993	0.9986	0.9989	0.9987	0.9989	0.9980
OMNR	TH _m	16.14	15.28	14.06	13.62	2.37	2.19
	α	0.0152	0.0168	0.0052	0.006	0.0046	0.0051
	C	0.0128	0.0143	0.0135	0.0153	0.0172	0.0173
	D	4.50	4.71	4.84	5.37	17.49	14.82
	r ²	0.9998	0.9997	0.9998	0.9999	0.9994	0.9995
BR40	TH _m ^a	102.90	51.22	23.59	26.03	107.50	63.19
	α ^a	0.0860	0.0754	0.0149	0.0143	0.2061	0.1383
	C	0.0002	0.0003	0.0012	0.0011	0.0001	0.0001
	D	1.06	0.90	1.34	1.32	1.65	1.59
	r ²	0.9999	0.9998	0.9999	0.9998	0.9980	0.9973

^a Since the high strain asymptotic behavior is not observed in the experimental windows, fit parameters for the polybutadiene sample must be considered with care.

between the NR samples considered (see Table VI). As shown in Figure 10, RSS3F and RSS3T are clearly different, as would be expected with respect to their highest molecular weight, and likely their higher gel content. OMNR and STR5CV60 are close but not identical. Such results call obviously for further investigations.

Quarter torque signal integration

As shown above, FT analysis of strain signal allows clearly quantifying the nonlinear response of viscoelastic materials submitted to high strain, but experiments with various polymer systems have revealed that, at high strain, the torque signal can be distorted either "on the left" or "on the right", with respect to a vertical axis drawn at the first quarter of the cycle. Such differences do not reflect in the FT spectrum. Therefore, to supplement FT analysis, quarter cycle integration was developed as an easy data treatment technique to distinguish both types of distortion. The ratio of the first to second quarters torque signal integration, i.e., Q1/Q2 allows clearly distinguishing the nonlinear response of certain materials, between

the strain amplitude effect on a pure and a complex polymer materials. With most pure polymer, Q1/Q2 ratio is always higher than one and increases with strain amplitude; in such a case the torque signal is always distorted "on the left" (i.e., Q1 > Q2). With certain (complex) systems, Q1/Q2 is generally higher than one at (very) low strain, and then quickly passes below one as γ increases. It is believed that Q1/Q2 lower than one is reflecting either some structural character or heterogeneities in materials, which enhances their nonlinearity.

When polymer materials have a sufficient, sizeable level of heterogeneity, they are complex systems which exhibit morphology-induced effects, which superimpose to both time and strain induced effects. We call this behavior intra (or morphology-induced) nonlinear viscoelasticity (because owing to the internal morphology of the material).

Figure 11 shows Q1/Q2 ratio vs. strain amplitude for all samples. The polybutadiene, the stabilized NR grades, i.e., OMNR and STR5CV60, do conform to the expected behavior for pure polymers, i.e., Q1/Q2 always higher than one, thus reflecting essentially a distortion "on the left" of the measured

RPA at 100°C ; 0.5 Hz ; T(3/1) vs Strain

$$TH(\gamma) = (TH_m + \alpha \gamma) [1 - \exp(-C \gamma)]^D$$

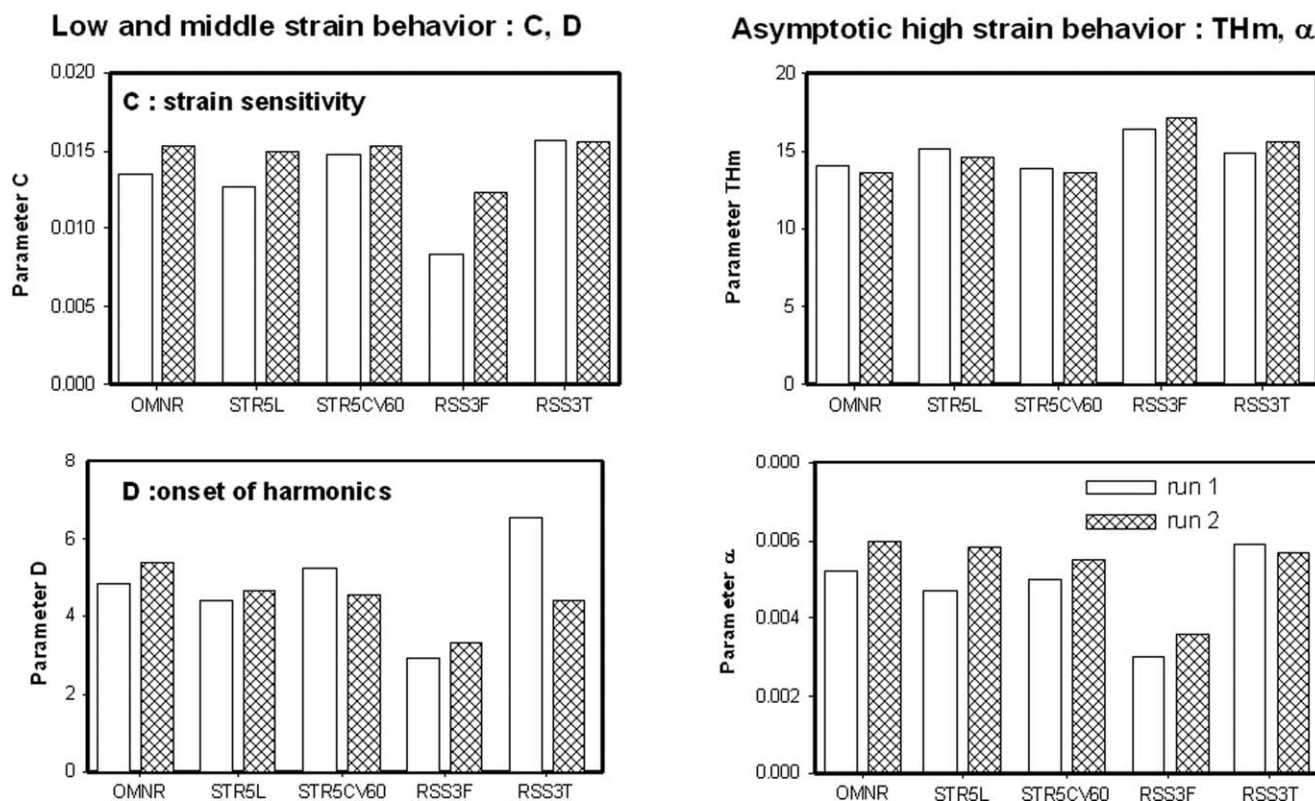


Figure 10 Nonlinear viscoelastic signatures of NR samples; comparing materials through parameters of eq. (4).

torque signal. For such materials, the nonlinearity occurs through the application of a sufficiently large strain, and their behavior is therefore said extra nonlinear viscoelasticity (or “strain-induced”). When polymer materials have a sufficient, sizeable level of heterogeneity, they exhibit morphology-induced effects, which superimpose to both time and strain induced effects. We call this behavior intra (or “morphology-induced”) nonlinear viscoelasticity. It is quite interesting to observe that RSS3F, and partially RSS3T and STR5L, show “intra nonlinearity”, which would reflect an heterogeneous structure, possibly due to semipermanent aggregates of many molecules that would reflect in so-called gel content. Half a century ago, M. Melvin expressed similar views,²⁵ in a theory for the viscosity of raw rubbers. Briefly, he postulated that microscopic rheological units, like small, tacky and elastic solid particles do affect the macroscopic flow of the rubber, through their relative movement and slippage. The number of temporary attachment points per unit area and the mean life of these attachments were key parameters of the theory. As a matter of facts, contemporary views about the likely structure of Natural Rubber^{26–30} supports the existence of such rheological units in grades with a significant amount of gel. Indeed, chain terminal groups of various chemistry appears

to play a key role in the so-called “green strength” of the material, and in other bulk viscosity dependent properties. Through such terminal groups, rubber chains would assemble and form pseudo-crosslinked structures. Dispersed in a gel-free matrix, such units would somewhat give the bulk rubber some of the characteristics of heterogeneous polymer systems, namely the capability to exhibit morphology-induced effects, i.e., $Q1/Q2 < 1$ in dynamic strain sweep experiments, as indeed observed with RSS3F, RSS3T, and STR5L. Conversely OMNR and STR5CV60 (and of course synthetic polybutadiene BRN40), which are reported “gel free,” show essentially extra nonlinearity. One notes incidentally that $Q1/Q2$ tends to be higher in run 2 experiments, except with BR40.

CONCLUSIONS

A set of interesting characterization data has been obtained on a representative but limited series of Natural Rubber samples. Differential scanning calorimetry and spectroscopic investigations yielded relatively expected results, essentially in line with the cis-1.4 polyisoprene macromolecular structure but with little differences, if any, between the various NR grades considered. Macromolecular size

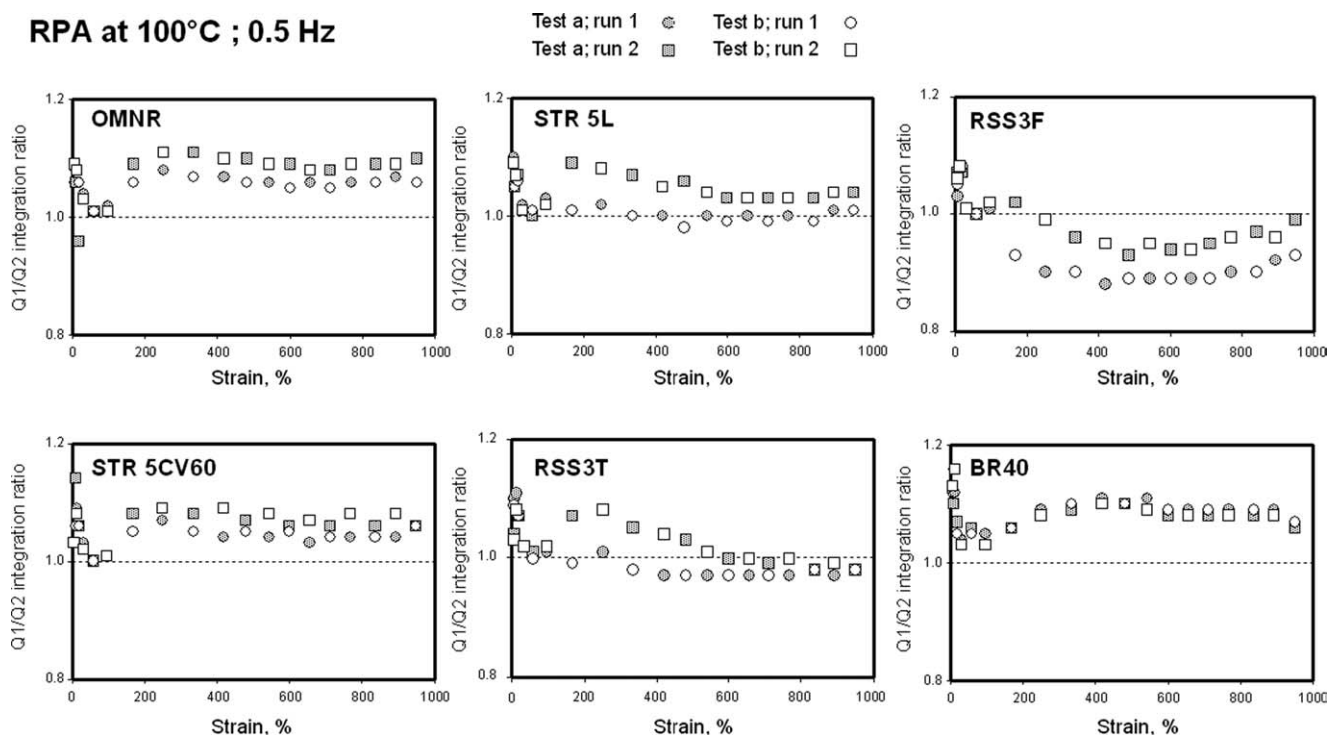


Figure 11 Assessing extrinsic/intrinsic nonlinear viscoelastic character through quarter cycle torque integration.

measurement by SEC-MALS ranked the various grades in the expected order and revealed that CV grades have a broader molecular weight distribution than grades directly coagulated from fresh latex. Because the easier processing associated with (relatively) broad MWD is well-known for synthetic elastomers, this side effect of the viscosity stabilizing chemicals might be the real benefit in using CV grades.

Fourier Transform rheometry is a fast and comprehensive characterization technique, allowing the selected NR grades to be sorted out without ambiguity. Both the linear and the nonlinear domains are conveniently investigated and, through the appropriate data handling and modeling techniques, quite a large set of complementary information is obtained. The linear complex modulus is expectedly related with the macromolecular size but the extent of the linear domain is practically the same for all NR grades, up to around 120% strain at 100°C. It is however the nonlinear viscoelastic behavior, as documented through torque harmonics, that reveals subtle macromolecular differences between the various NR samples. Whilst in principle equivalent, the two RSS grades studied are clearly different, somewhat in line with their high molecular weight, and likely their higher gel content. Conversely, the two CV grades are close but not identical. Quarter cycle integration, as a complementary LAOS data treatment, shows that the RSS and the field latex grades exhibit “intra nonlinearity,” which likely reflects an

heterogeneous structure, possibly due to semipermanent aggregates of many molecules. It is remarkable that an advanced solid NMR technique, such as the cross polarization magic angle spinning (CP-MAS) analysis leads to a similar conclusion, in term of ratio of “immobile/mobile” components of the polyisoprene chain. All NR samples exhibit a high percentage of rigid fraction, an unexpected result with respect to structural differences between high cis-1,4 polyisoprene and polybutadiene. Natural Rubber has thus a strong heterogeneity of its macromolecular structure and two groups can be clearly distinguished: the CV grades on one hand and the smoked sheet grades on the other hand. Such results obviously call for further investigations with a broader sampling.

With respect to the most recent views about the structure of natural rubber, a coherent picture emerges from both the spectroscopic characterization and the nonlinear rheological analysis in the present report. Indeed, FT rheometry demonstrates “intra nonlinearity” with RSS and the field latex grades that is assigned to a heterogeneous structure of the elastomer, possibly due to semipermanent aggregates (or “rheological units”) of many molecules. Contemporary views about the likely structure of natural rubber supports the existence of such rheological units in grades that are not chemically treated for viscosity stabilization. Indeed, chain terminal groups of various chemistry appears to play a key role in the so-called “green strength” of the material, and in other bulk

viscosity dependent properties. Through such terminal groups, rubber chains assemble and form pseudo-crosslinked structures. Dispersed in a gel-free matrix, such units somewhat give the bulk rubber some of the characteristics of heterogeneous polymer systems, namely the capability to exhibit morphology-induced effects.

Whilst not really an objective of the reported work, all the above results can eventually be discussed with respect to present NR grade selection criteria. Notwithstanding the precise information about macromolecular size and features provided by SEC-MALS, DSC, and NMR techniques, it is obvious that such approaches are laboratory methods whose implementation on NR producing sites would likely meet tremendous difficulties, not to mention the necessary investment. In comparison, experiments with torsional dynamic rheometers are no more difficult to perform than Mooney viscometer or Parallel plate tests, require less or equivalent time, and the same sample preparation. Dynamic tests however have the capability to yield a number of significant parameters, some of which directly commensurable with macromolecular weight (e.g., complex modulus) and others likely giving a deep insight in macromolecular features (e.g., harmonics from Fourier Transform experiments) and their role in the processing behavior. The TSR schema is more than 30 years old and essentially reflects available technical capabilities in the late 1980's. With respect to the small and arbitrary series of tested NR samples, the above reported results are obviously limited in scope, but they surely advocate for a reconsideration of the manner technical specified rubber grades are sorting out, with the advantage that RSS grades could also be included in the technical specifications.

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