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Non-linear Viscoelastic Characterization of Natural Rubber Gum through Large Amplitude Harmonic Experiments

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Standard dynamic testing requires strict proportionality between stress and strain for valid resolution of the (measured) complex modulus into its elastic and viscous components. Thus, it is restricted to material and/or testing conditions that correspond to linear viscoelastic behaviour; otherwise 'apparent' results are obtained, with therefore limited meaning, if any, in terms of material science. Correct non-linear harmonic testing under large amplitude oscillatory strain is however feasible today using purposely modified torsional rheometers to capture full strain and torque signals which are appropriately treated in order to extract pertinent and useful information. Harmonic techniques that require signal processing to convert the response of the material in the time domain into a material property in the frequency domain are usually referred to as Fourier Transform (FT) rheometry, i.e. a development of the so-called dynamic (or harmonic) testing to investigate both the linear and the non-linear viscoelastic domains of polymer materials. It consists essentially of considering the frequency spectrum of the torque signal obtained when submitting a material to high strain. Contrary to standard dynamic testing, no validity condition is needed for FT rheometry. In principle, any dynamic rheometer can conveniently be modified for FT testing, but implementation of the technique on a commercial torsional rheometer, operating with a closed test cavity, proved to give repeatable and reliable results on a number of polymer systems. A series of natural rubber gum samples were tested in order to further illustrate the capabilities of the technique.

Key words: Natural rubber; non-linear; viscoelasticity; harmonic testing; Fourier Transform rheometry; linear; strain; stress; torque

With a world consumption roughly matching the ones of overall synthetic elastomers, natural rubber (NR) is the most important elastic material used in manufacturing numerous products such as tyres, conveyor belts, hoses and other engineered parts. When compared to synthetics however, production specifications of NR remain relatively poor since only the so-called technically specified grades (TSR) must be characterized with respect to basic rubber test techniques, such as the Mooney viscosity, the Wallace Plasticity (P_O) and the Plasticity Retention Index (PRI)[1]. Other popular grades, such as ribbed smoked sheets (RSS) are classified with respect to visual inspection only[2].

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By nature, NR exhibits more variation than synthetic polymers. About fifty different clones of *Hevea brasiliensis* are grown, therefore introducing inevitable production differences, further enhanced by climate, soil and other local effects, as well as seasonal effects 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 described by the Rubber Manufacturers Association[2] to the more complex TSR-schemes which include certain values on P_O, PRI, N_2 content etc., expected to guarantee a certain quality and consistency. However, practice shows that, even for typical TSR grades, a lot of variation still exists within each shipment although they are perfectly within specifications. These variations are especially pronounced in regards to processability; including viscosity (e.g. Mooney viscometer[3]) and elasticity (e.g. Plasticity Number and Recovery value[4]) readings which surely help to a certain degree in specifying NR grades. However, even if there is a rough correlation between low shear viscosity and molecular weight on one hand, and between plasticity or recovery numbers and molecular weight distribution on the other hand, selecting materials according to current specifications does not warrant easy processing and constant rheological properties of final compounds. In addition, rubber engineers know well that qualitatively the best NR grade has also the highest initial viscosity and consequently, is the most difficult to process. The current solution is mastication, with or without processing aids or so-called peptizers, but it consumes both time and mixer capacity. There is thus a need for both better characterization methods of (gum) NR and improved NR grades.

Most rubber processing operations occur at a high rate of strain, and therefore it is essentially the non-linear viscoelastic response of rubber materials that is of interest. Not all instruments or test techniques allow the non-linear viscoelastic domain to be investigated and, when specific harmonic testing methods are concerned, only a few torsional dynamic rheometers, with a closed test cavity, i.e. the 'Rubber Process Analyzer', RPA 2000®, or the 'Production Process Analyzer', PPA® (Alpha Technologies, now a Dynisco company), proved to provide very reproducible and meaningful results under high strain conditions. These instruments are essentially rotorless rheometers and meet all the requirements for standard measurements of rheological properties of unvulcanized rubber[5]. The measuring principle of the RPA has been studied in detail and validated through extensive experiments and numerical simulations[6,7]. In order to extend its capabilities, such an instrument was purposely modified in our laboratory with the objective of developing what has been called 'Fourier Transform' (FT) rheometry[8,9]. The capabilities of FT rheometry in delivering data likely related with macromolecular characteristics have so far been demonstrated with a number of polymer materials[10–12] and the aim of this paper is to further extend this demonstration to NR grades.

FOURIER TRANSFORM RHEOMETRY

Principle of the Technique

Fourier Transform (FT) rheometry is a powerful technique to document the non-linear viscoelastic behaviour of polymer materials as observed when performing large amplitude oscillatory strain (LAOS) experiments. No commercial instruments are yet available but the technique is easily implemented on appropriate instruments. Any simple polymer can exhibit non-linear viscoelastic properties

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when submitted to sufficiently large strains; in such case the observed behaviour is so-called extrinsic non-linear viscoelasticity, owing to external factors (i.e. the applied strain). Complex polymer systems, such as filled rubber compounds, appear to be intrinsically non-linear, since their response to applied strain has an internal origin, i.e. their morphology, and superposes to the non-linearity associated with large strains.

Essentially, FT rheometry consists of capturing strain and torque signals during dynamic testing and using FT calculation algorithms to resolve them into their harmonic components. *Figure 1* illustrates the principle of the test technique, with data gathered when submitting, a gum SMR CV 60 sample to a harmonic strain of 12.0 degree (or 168%) amplitude at 100ºC and 1 Hz frequency.

FT is nothing more than 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 the 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, for instance 1 Hz, in the case of the experiment displayed in the figure. A non-linear response is characterized by a number of additional peaks at odd multiples of the applied strain frequency, as clearly shown in the middle left part of the figure (torque spectrum). At 168% strain, gum SMR CV 60 clearly exhibits a non-linear response, as shown by the distortion of the torque signal 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 in order to quantify its quality. As shown in the middle right inset, there are some peaks at odd multiples of the frequency which are slightly higher than the noise. As a logarithmic scale is used, their importance is however exaggerated as demonstrated by their actual relative values displayed in the lower inset table (built with the appropriate signal analysis software). For instance, the 3rd relative torque harmonic is 10.26%, quite significant indeed, whilst the 3rd relative strain harmonic is only 0.61%. Through simultaneous FT treatment of both the torque and strain signals, it has been demonstrated that, at large strain amplitudes, the RPA submits materials to a nearly pure strain sinusoidal signal[10]. However, strain signal quality degenerates as the strain angle decreases and a correction method had to be developed, as explained below.

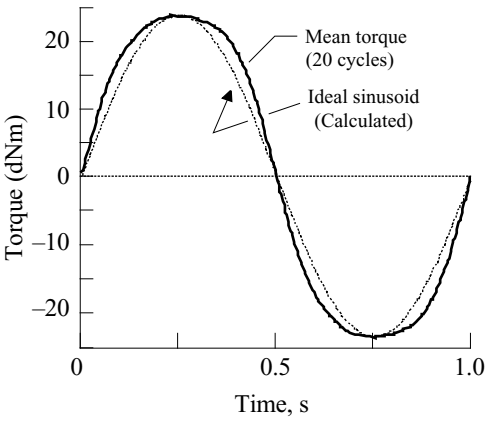
As demonstrated by Wilhelm *et al.*[8,13] only odd torque harmonics are significant in terms of material's response. Indeed, if a shear strain of maximum strain amplitude, γ_0 (rad) is applied at a frequency, ω (rad/s) to a viscoelastic material, the strain varies with time, t (s) according to $\gamma(t) = \gamma_0 \sin(\omega t)$and the shear stress response can be expected to be given by a series of odd harmonics, i.e.:

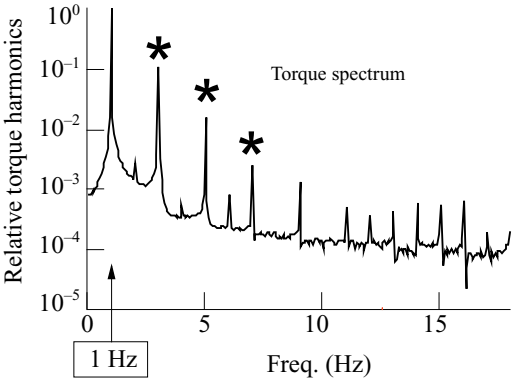
$$\sigma(t) = \sum_{j=1,3,5}^{\infty} \sigma_j \sin(j\omega t + \delta_j) \qquad \ldots 1$$

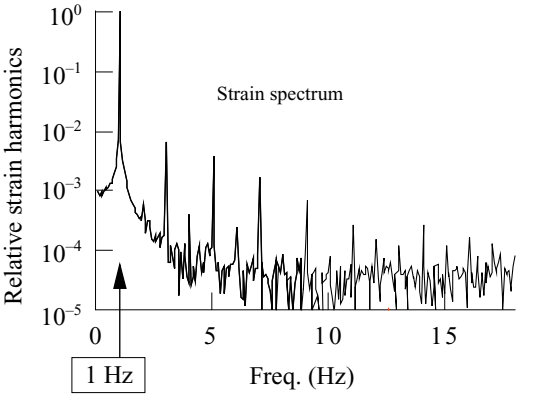
providing one assumes that, over the whole viscoelastic domain (i.e. linear and non-linear), the viscosity function, $\eta = f(\dot{\gamma})$ can be approximated by a polynomial series with respect to the shear rate ($\dot{\gamma}$). If the tested material exhibits a pure linear viscoelastic response,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

With a simple homogeneous polymer material, non-linearity occurs with the application of high strain. The distortion is generally more severe with compounded

SMR CV 60 - RPA-FT at 100ºC; 1 Hz; 12º (167.6%)







Fourier Transform spectra; odd harmonic components analysis

Nr pts	Freq. resol	Main freq.	3rd harm.	5th harm.	7th harm.	9th harm.	11th harm.	13th harm.	15th harm.
t_{acq}	Sampling pt/s	Main torque a.u.	T(3/1) %	T(5/1) %	T(7/1) %	T(9/1) %	T(11/1) %	T(13/1) %	T(15/1) %
		Main strain a.u.	S(3/1) %	S(5/1) %	S(7/1) %	ST(9/1) %	S(11/1) %	S(13/1) %	S(15/1) %
8192	0.063	1	3	5	7	9	11	13	15
16.0	512	1180.0	10.261	1.493	0.245	0.129	0.048	0.041	0.054
		546.8	0.610	0.344	0.156	0.066	0.026	0.012	0.011

Figure 1. Recorded torque signal when submitting a SMR CV 60 gum sample to 12º strain at 1 Hz; Fourier Transform resolution of torque and strain signals into harmonic components; odd harmonic components analysis. Note: Main and strain components are given in arbitrary units, whilst harmonic components are relative.

rubbers and, in addition, has been observed to affect more the right part of the half-signal, when active fillers are used in the formulation. There is thus a substantial difference between the non-linear viscoelastic behaviour of a pure, unfilled polymer and of a filled material. The former essentially exhibits non-linearity through the application of a sufficiently large strain and this behaviour was called extrinsic non-linear viscoelasticity (occurring through *external* causes, i.e. the applied strain), whilst the latter shows intrinsic non-linear viscoelasticity (owing to the *internal* morphology of the material). It is quite obvious that standard strain sweep experiments, whilst possibly detecting the occurrence of the non-linear viscoelastic response, have absolutely no capability to distinguish extrinsic and intrinsic characters.

Up-dating a Torsional Dynamic Tester for Fourier Transform Rheometry

Any commercial torsional dynamic tester can be conveniently up-dated for FT rheometry. However, conventional open gap rheometers, for instance parallel disks and cone-and-plate instruments, have been shown on one hand to be limited to relatively low strain amplitude experiments[14], and on the other hand, to 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. As they were designed for easy handling of very stiff material, such as filled rubber compounds, closed cavity torsional testers are particularly suitable for FT rheometry. Therefore, the appropriate modifications were made to a Rubber Process Analyzer, RPA 2000®(Alpha Technologies Ltd, now a division of Dynisco LLC, Franklin, MA, USA) in order to capture strain and torque signals. Details on the modification and the measuring technique have been previously reported[15]. Essentially, strain and torque signals, as provided by the instrument, are collected by means of an electronic analogic – digital conversion card that reads tensions which are proportional to the applied strain and the transmitted torque. The card has a resolution of 16 bits with a maximum sampling rate of around 205 K sample/second for 2 inputs of ± 10 mV to ± 10 V. Read values are converted into physical quantities (i.e. degree angle and dNm) and recorded with a PC, through the appropriate codes written in the LabView® software (National Instruments). Test results consist thus of data files of actual harmonic strain and stress readings *versus* time. Proprietary data handling programs, written in MathCad® (MathSoft Inc.), are used to perform FT calculations and other data treatments.

Extensive experiments were in fact needed before optimal test and acquisition conditions were eventually set (for details, see Leblanc and de la Chapelle[10]). In any fixed strain and frequency conditions, data acquisition is made in order to record 10 240 points at the rate of 512 pt/s, i.e. 20 cycles at 1.0 Hz or 10 cycles at 0.5 Hz. FT spectra are obtained through calculation on the last 8192 points of the recorded signals. FT analysis yields essentially two types of information: first, the main signal component, i.e. the peak in the FT spectrum that corres-ponds to the applied frequency [hereafter noted either $T(1\omega)$ or $S(1\omega)$ with respect to the torque or strain signals, respectively], second 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.), was used to obtain the amplitude of the main stress and strain components (corresponding to 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 $I(n\omega_1)/I(\omega_1)$ or the abridged form $I(n/1)$, describes the nth 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 Non-linear Viscoelasticity Investigations

When submitting pure polymers to harmonic strain, non-linear viscoelastic behaviour occurs at a high strain amplitude. Consequently a strain sweep test is the method of choice to investigate non-linearity and the appropriate test protocols were developed, which essentially consisted of performing strain sweep experiments through two subsequent runs separated by a resting period of 2 min. At least two samples of the same material were tested (more if results revealed 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 68º (≈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 0.5º (6.98%), below which the harmonic content of the strain signal becomes so high that measured torque is excessively scattered and likely meaningless. Test protocol at 0.5 Hz were designed to probe the material's viscoelastic response within the 0.5º to 68º range, with up to 20 strain angles investigated, whilst at 1.0 Hz, the 0.5º to 33º range was investigated.

Even with quality design and care in manufacturing instruments, there are always technical limits in accurately submitting test material to harmonic strain. FT analysis of the RPA strain (i.e. applied) signal allows its quality to be precisely documented and, if needed, the appropriate correction to be brought on torque harmonics. Indeed extensive experiments have shown that plots of the relative torque harmonics $T(n\omega/1\omega)$ *vs.* the relative strain harmonics $S(n\omega/1\omega)$ pass through a minimum and appear to be bounded by a straight line[16]. A simple correction method was consequently developed for torque harmonics, according to:

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

where $T(n\omega/1\omega)_{TF}$ and $S(n\omega/1\omega)_{TF}$ are the nth relative harmonic components of the torque and strain signals respectively, and CF is the correction factor, as derived from a plot of $T(n\omega/1\omega)$ vs. $S(n\omega/1\omega)$. The correction also applies when considering the so-called 'total torque harmonic content' (TTHC), i.e. the sum $\Sigma T(n\omega/1\omega)$ of all the odd harmonics up to the 15th. At low strain, when the viscoelastic response of the material is expectedly linear, the corrected relative torque harmonics vanish, in agreement with theory[9]. As shown in the right graph of *Figure 2*, $\Sigma T(n\omega/1\omega)$ *vs.* $\Sigma S(n\omega/1\omega)$ decreases, passes through a minimum and appears to be bounded by a straight line whose slope provides the correction factor. The correction method is based on a simple argument that, if the applied strain was perfect, all $\Sigma T(n\omega/1\omega)$ data points would fall on the vertical axis.

Modeling the Effect of Strain Amplitude on FT Rheometry Results

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

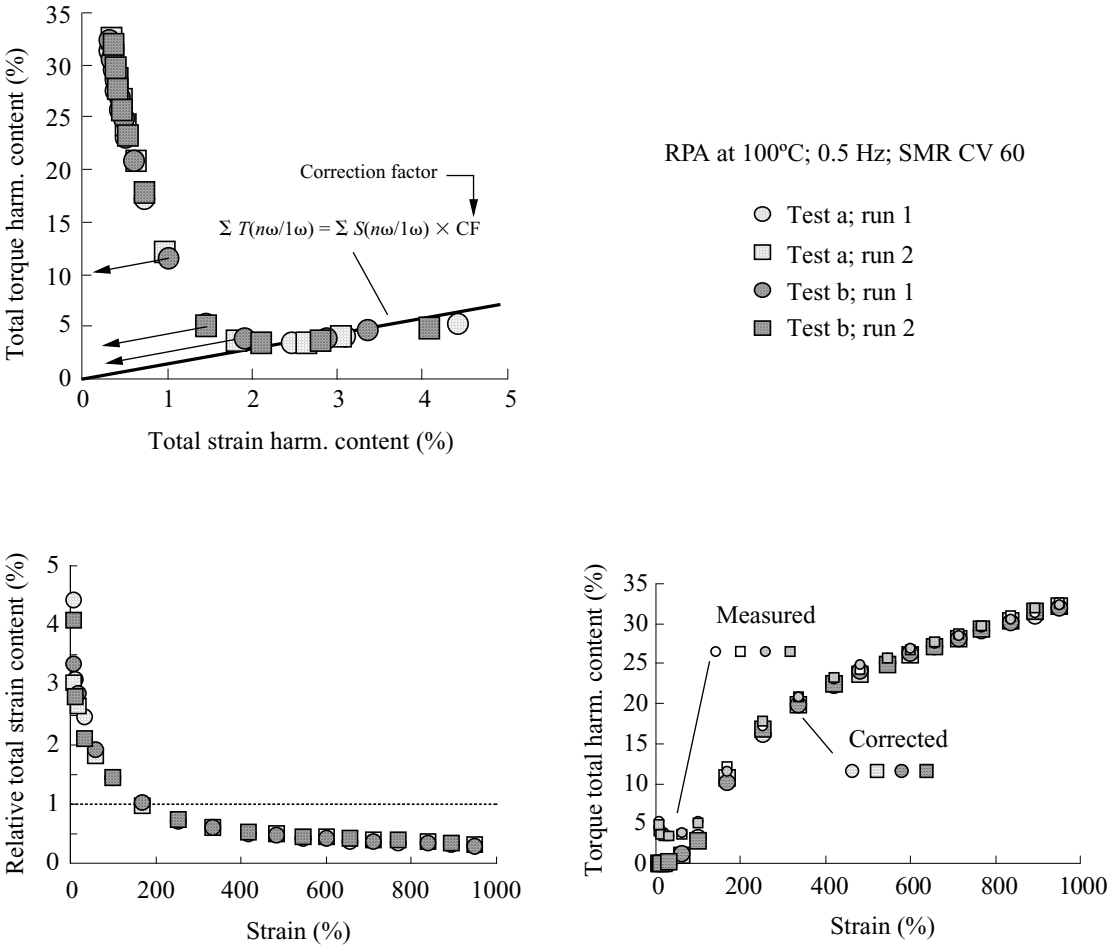


Figure 2. Correction method on total relative torque harmonic content.

Let us consider the main torque component; the ratio $T(1\omega) / \gamma$ 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 units 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 behaviour is well modeled with the following equation:

$$G^*(\gamma) = G^*_f + \left[\frac{G^*_0 - G^*_f}{1 + (A\gamma)^B} \right] \quad \ldots 3$$

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.

Odd torque harmonics become significant as strain increases and are therefore considered

as the non-linear viscoelastic 'signature' of tested materials, only available through FT rheometry. With respect to strain amplitude, relative torque harmonic components generally vary according to S-shape curves. In previous publications[10,12], such behaviour was modeled with an equation that considers a maximum plateau value at a high (infinite) strain:

$$TH(\gamma) = TH_{max} \times [1-\exp(-C\gamma)]^D \quad \ldots 4$$

where γ is the deformation (%), TH_{max} a maximum plateau value at a high (infinite) strain, C and D fit parameters. TH stands for either the total harmonic content [i.e. TTHC = $\Sigma T(n\omega/1\omega)$] or any relative torque harmonic, for instance $T(3/1)$, $T(5/1)$, etc. In some materials, the (extrapolated) maximum value was found to be larger than the maximum measured data and was therefore considered with care. Experimentally, it was also frequently observed that if the likeliness of a near plateau value at a large strain was supported by test data, one could also consider TH_{max} as a pure mathematical artifact, since it is explicit in the fitting equation. Overall harmonic content curves $TTHC(\gamma)$ are by nature 'envelop' curves of all detected harmonics, and are actually obtained up to the 15th one with the up-dated RPA. It is quite obvious that, for a given set of experimental data, the actual value of $TTHC_{max}$ is dependant on the number of data points used in running the FT algorithm. As previously explained[10], using 8192 (i.e. 2^{13}) points is sufficient to give an acceptable signal/noise ratio and confidence up to the 15th harmonic. However, if the number of data points used is infinite, the total harmonic content (extrapolated) at infinite strain would also be infinite because the number of harmonics is infinite, though they get smaller as their position on the frequency axis increases. It follows that a far more realistic model to consider odd harmonic variation with strain amplitude is provided for by the following equation:

$$TH(\gamma) = (TH_0 + A\gamma) \times [1-\exp(-C\gamma)]^D \quad \ldots 5$$

where the member $TH_0 + A\gamma$ expresses a linear variation of harmonics in the high strain region, while the member $[1-\exp(-C\gamma)]^D$ describes the onset of non-linear viscoelastic response as illustrated in *Figure 3*. The physical meaning of parameters TH_0 and α is obvious and as shown in the lower part of the figure, parameter C somewhat reflects the extent of the linear viscoelastic region (i.e. no harmonics), while parameter D indicates the strain sensitivity of the non-linear character.

It is worth noting that in using *Equation 4* or *Equation 5*, one may express the deformation (or strain) γ either in degree angle or in %. Obviously all parameters remain the same except α and C, whose values depend on the units for γ. Conversion factor is : $\frac{100 \times \pi}{180 \times 0.125}$

In summary, the FT rheometry protocols described above and the associated data treatment yield considerable information about the viscoelastic character of materials. In less than one hour, two samples are tested and the full data treatment is performed (using the present combination of VBA macros and MathCad® routines) in a few seconds.

EXPERIMENTAL

Test Materials

A series of NR grades, as described in *Table 1*, were collected, thanks to the courtesy of the Rubber Research Programme of Thailand. A commercial high *cis*-1,4 polybutadiene was also included in the study.

STR 5L is a technically specified light-coloured rubber grade, obtained by

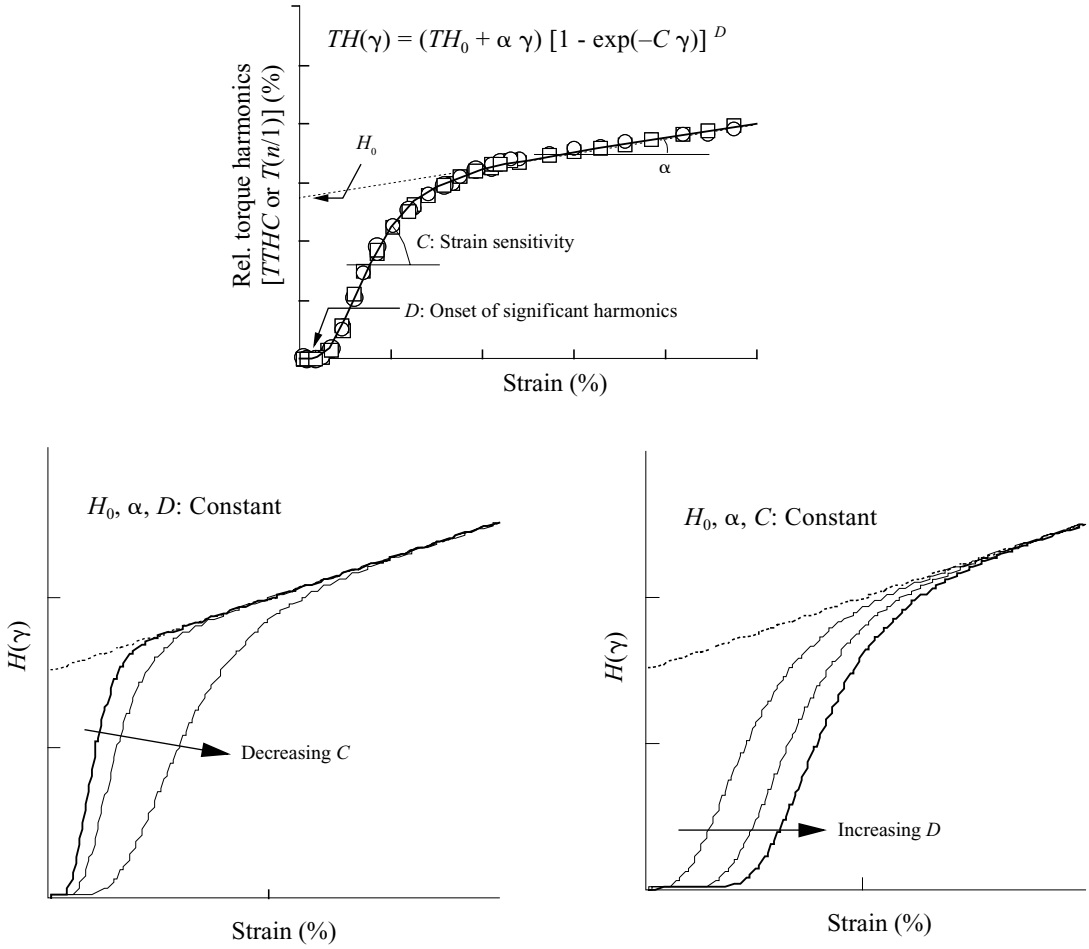


Figure 3. Modeling torque harmonic variation with strain amplitude.

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 110ºC–125ºC, 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, initial Plasticity, P_O = 35 (min.) and a minimum PRI 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 diluted 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 are graded according to their colour, consistency and observed impurities. RSS 3 meets the following specifications: 0.20% dirt content (maximum), 1.00% ash content (maximum); 0.60% nitrogen content (maximum); P_O = 30 (min) and PRI = 50 (min).

TABLE 1. TEST SAMPLES

Sample code	Material description	Origin	Mooney $ML(1+4)_{100°C}$	Mol. weight Mn (g/mol)
STR 5L	NR, Standard Thai Rubber, 5L grade	Thailand	70	n.a.
CV 60	NR, Constant viscosity grade	Thailand (Jana)	63	650 000
RSS 3	NR, RSS 3	Thailand	67	1 000 000
OMNR	NR, Optimized molecular weight	Thailand	60	n.a.
BRN 40	98% *cis*-1,4 polybutadiene, Neo*Cis* BR 40	Polimeri, Italy	43	450 000

TSR CV 60 is a technically specified 'constant viscosity' grade, produced from field latex with its viscosity stabilized to a specified Mooney viscosity [i.e. ML(1+4)100ºC = 60 ± 5], through the addition of a suitable chemical. Dirt, ash and N_2 contents are maximum 0.05%, 0.6% and 0.6%, respectively. PRI is a minimum of 60. On storage, this grade of rubber is expected to remain within eight hardness units.

Optimized molecular weight NR (OMNR) is a new grade currently being developed in Thailand. Selected field latex is coagulated, its viscosity is reduced and stabilized through a chemical treatment (undisclosed). No stabilizer or oil is added. OMNR is relatively similar to TSR CV 60 but is expected to show no variation on ageing.

Europrene NeoCis BR 40 is a 98% *cis*-1,4 polybutadiene from a Ziegler-Natta process with a neodynium salt as catalyst, commercially available from Polimeri Europa (Italy).

Experiments with the RPA

With respect to its testing principle, the RPA must be loaded with an excess volume 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 100ºC in a 3 cm^3 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 revealed anomalies). As described above, strain sweep test protocols at 0.5 Hz and 1.0 Hz were used.

Frequency (0.1 Hz to 17 Hz) – temperature (60ºC to 160ºC) sweep experiments within the linear region of tested materials (i.e. at 1 degree, 13.96%) were also performed in order to build G'(ω) and G"(ω) mastercurves at 100ºC, through application of the time-temperature superposition principle.

Experiments with an Open Testing Gap Rheometer

A Bohlin C-VOR rheometer with 25 mm diameter parallel disks was used to perform strain sweep experiments at 0.5 Hz. Frequency sweep tests (10^{-2} Hz to 10^2 Hz; $\gamma = 0.005$) were

also performed at 100ºC on all samples, for comparison with data gathered from the RPA. For strain sweep tests, three subsequent sub-tests (0.001% to 100%) were performed at 0.5 Hz by applying 20 cycles at each set strain, in order to check for any thermal degradation. It must however be noted that the lower strain limit of 0.001% is quite theoretical; the lowest strain for reproducible measurements is actually 0.006%–0.007% as below 0.0064% results were erratic and therefore discarded. For frequency sweep tests, three subsequent cycles (up and down in the tested frequency range) were performed for the same reason. Generally, no significant differences were seen.

Gum (unmasticated) NR is a highly elastic material and a number of difficulties were met before an acceptable test protocol for the C-VOR was in hand. After many unsuccessful attempts, the following approach was eventually used: a sample of the test material was first compression moulded (200 kPa) at 100ºC between polyester sheets into a 1.0 – 1.1 mm thick foil and allowed to cool down to room temperature under a 5 kPa load. A disk, 27 mm in diameter was then die cut out and disposed on the plate of the rheometer. The oven was closed and after the temperature was back to the set level (i.e. 100ºC), the upper disk was moved down towards the set gap, i.e. 1 mm. With some samples, reaching the set gap was a matter of a few minutes under the available compression force of the rheometer (i.e. around 2.0 kgf). With others, namely RSS 3, radial flow under axial compression was found to be practically null, presumably due to excessive elastic behaviour that exceeds the capabilities of the rheometer. In such cases, the actual gap reached after a 10 min dwell time was used as the testing gap. It was also found that leaving excess material at the periphery of the gap was a better approach than attempting to remove it, because in such cases, tearing occurred, thus giving the gap an incomplete filling and hence incorrect torque readings. In the course of such experiments, the experimental limits of open cavity rheometers in testing highly elastic materials were clearly seen, namely in terms of poor reproducibility with certain NR grades.

RESULTS AND DISCUSSION

(RPA-FT) Complex Modulus *vs.* Strain

Complex modulus G^* *versus* strain curves are shown in *Figure 4*. In all cases, the two tested samples (a and b) gave identical results thus demonstrating the excellent homogeneity of tested materials as well as the reproducibility of the testing method. For all NR samples, the frequency effect is hardly visible, thus indicating very small frequency dependence in the range considered. The polybutadiene sample exhibited the expected frequency dependence. For all materials, very small, if any, differences were seen between run 1 and run 2 data, which indicates that either there were 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 were derived from the main component of the torque signal, as obtained through FT analysis. Qualitatively, similar graphs were obtained when G^* values from the standard RPA (built in capabilities) were used but with an error by excess, particularly in the non-linear region.

Figure 4 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 effects up to around 50% strain. *Figure 5* compares some strain sweep test results from the RPA and the Bohlin V-COR. Similar figures were obtained with the other samples. As can be seen, the low strain C-VOR data match well with RPA results, however, there is a significantly better

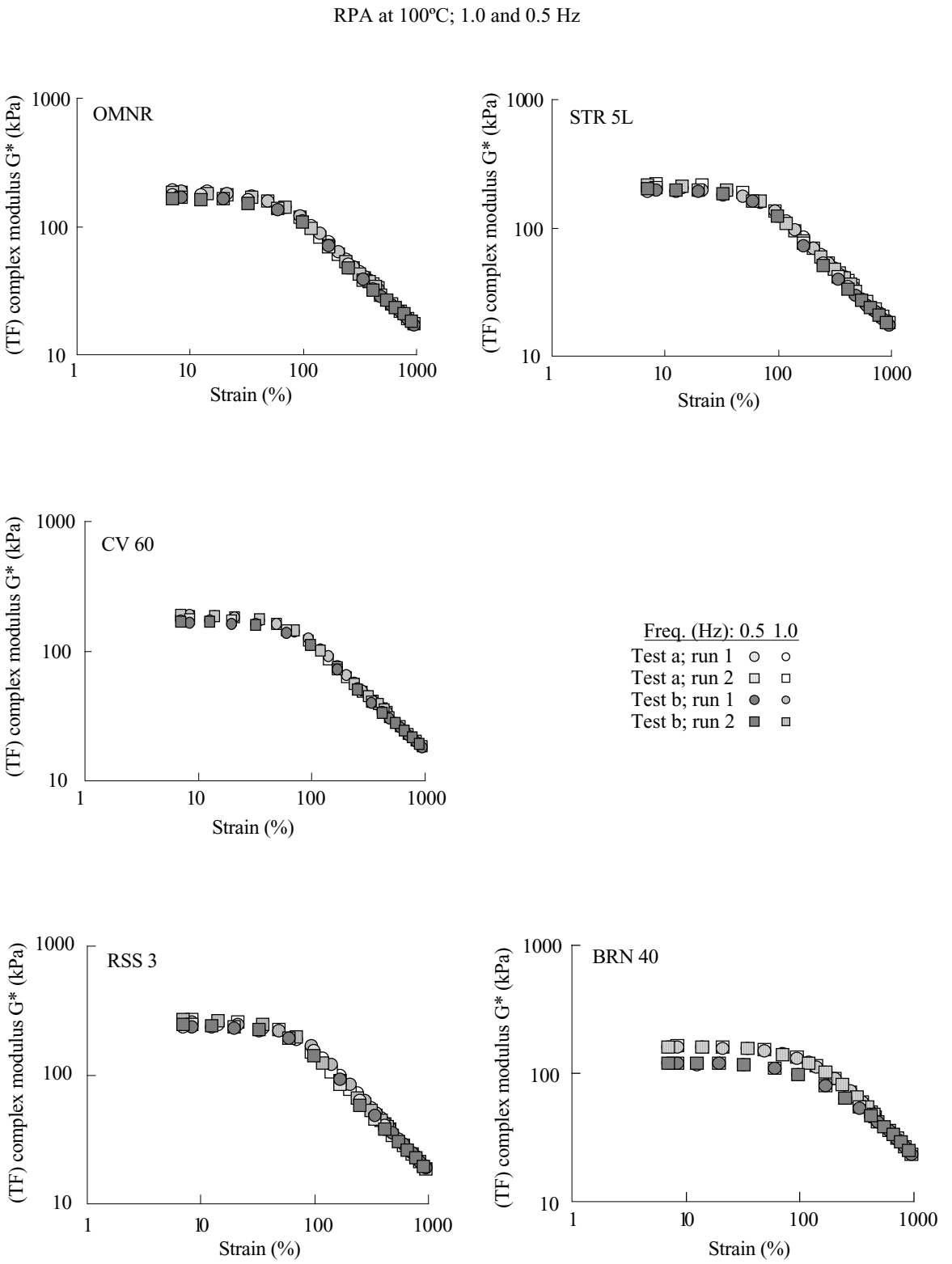


Figure 4. RPA-FT at 100ºC on Natural rubber gum samples; complex modulus G* vs. *strain; strain sweep tests at 0.5 Hz and 1.0 Hz.*

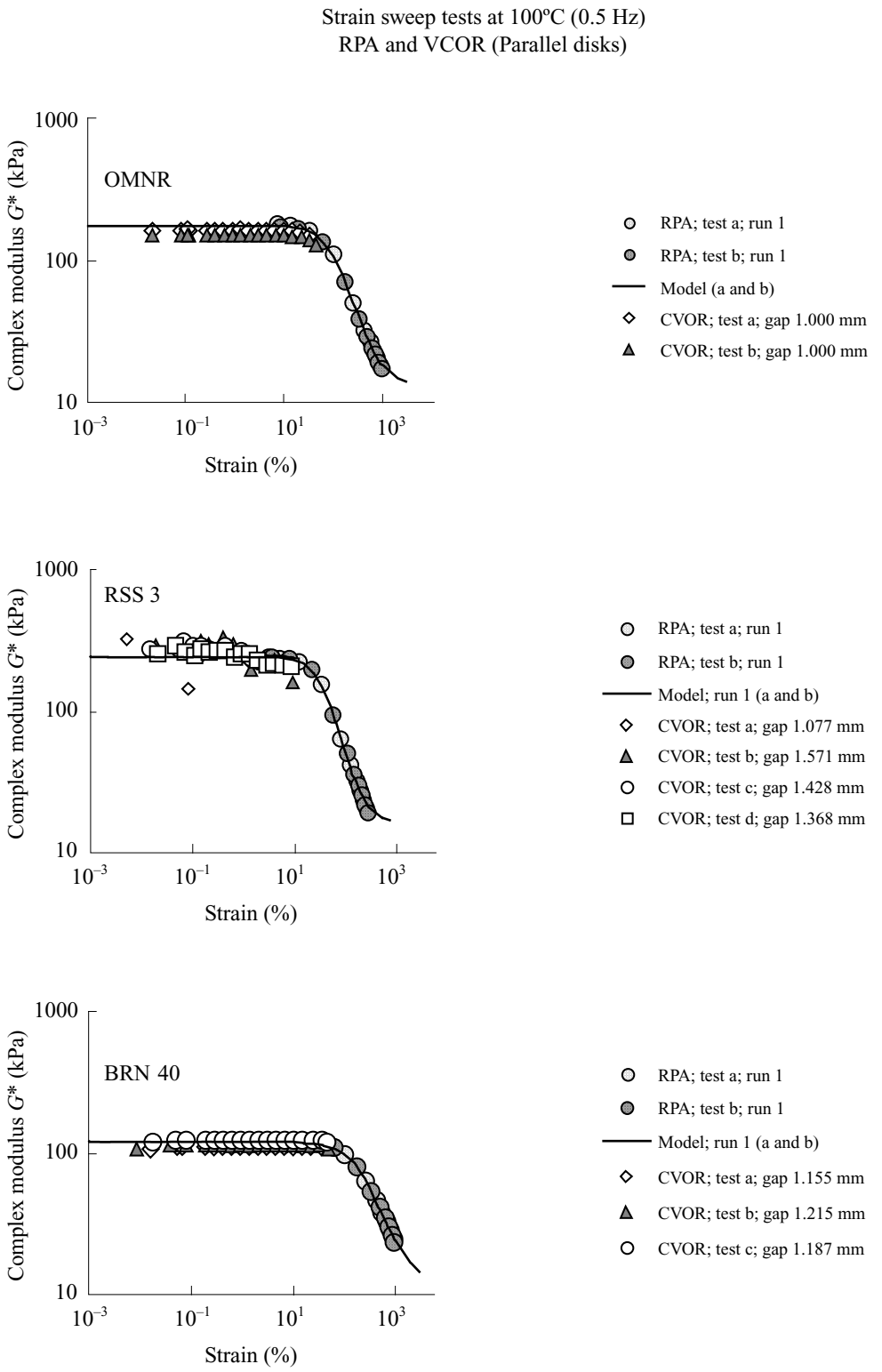


Figure 5. Comparing strain sweep test results at 100ºC from the RPA and the CVOR; strain sweep tests at 0.5 Hz.

reproducibility in the case of the latter. C-VOR results on polybutadiene suffer very little scatter and likely correspond to what can be obtained with easy positioning of the material in the parallel disks gap. Conversely, RSS 3 results are typical of experimental difficulties met with highly elastic materials. In all cases, C-VOR test results do confirm the validity of RPA data at low strain and particularly, the extrapolated 'linear' complex modulus obtained when fitting data with *Equation 3*. Open gap rheometers, such as the C-VOR, are limited to relatively low strain amplitude experiments, around 40%–45% with high molecular weight polymers, essentially because wall slippage and other boundary defects occur. In the RPA, the test material is held in a sealed cavity, with grooved dies, maintained closed under a pressure of 4 MPa. Such testing conditions prevent any slippage and therefore the measured smooth fall in torque (modulus) at high shear strains is a real material response, quite reproducible, and not at all an experimental artifact.

Fit parameters of *Equation 3* are given in *Tables 2* and *3*, from RPA-FT results at respectively, 0.5 Hz and 1.0 Hz. As can be seen, the r^2 values reveal that the fitting is excellent in all cases. Modeling G^* *vs*. strain experiments with *Equation 3* yields three parameters, whose physical meaning is immediate, and which allow a direct comparison between test materials (*Figure 5*).

G^*_0 is the (extrapolated) 'linear modulus', whose values in *Tables 3* and *4* are confirmed by C-VOR data. OMNR and CV 60 exhibit similar values, significantly higher than for polybutadiene BR 40. RSS 3 has the highest complex modulus and STR 5L is slightly stiffer than OMNR and CV 60. One would expect the (number averaged) molecular weight to be the prime macromolecular character affecting the complex modulus of polymer on the rubbery and in the terminal flow region. With respect to the (limited) characterizing information available, it seems that it is indeed the case. The mid-modulus 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 6*, all NR samples are similar, and very different from polybutadiene. The parameter B is quite an original information, revealing however little, if any, differences between the NR grades tested, but a larger strain sensitivity than polybutadiene.

(RPA-FT) Torque Harmonics *vs.* Strain

Figure 7 shows how the overall torque harmonic content, *TTHC* (i.e. the sum of the odd harmonics up to the 15th) varies with increasing strain amplitude for all the samples tested, at 0.5 Hz and 1.0 Hz frequency. Data are well reproducible with no difference between tests a and b, and no difference between runs 1 and 2. Torque signal harmonics appear insensitive to strain history. There is a marked difference between NR samples and synthetic polybutadiene as the latter exhibits a *TTHC* which varies differently with strain amplitude, depending on frequency, at least above 200% strain. With NR grades, data at 1 Hz perfectly superimposes 0.5 Hz data. In principle, BR data can be treated with *Equation 4* or *5* (or any other mathematical relationship that would meet the observed variation) but fit parameters would obviously make little sense since maximum strain observations do not allow us to oversee the occurrence of any limiting value. Conversely, NR samples typically exhibit S-shape curves which, at large strains, appear indeed to be converging towards a linear variation with strains, thus clearly validating *Equation 5*. In terms of chain structure, high *cis*-1,4 polybutadiene differs from NR only by the absence of the pending methyl group, notwithstanding differences in molecular weight. As CV 60 and BRN 40 are very close in this respect, as such it is rather

TABLE 2. RPA-FT STRAIN SWEEP EXPERIMENTS AT 100ºC AND 0.5 Hz; FIT PARAMETERS OF *EQUATION 3*

Freq. (Hz) : 0.5 Sample	Run (a and b)	G^*_0 kPa	G^*_f kPa	1/A %	B	r^2
OMNR	1	175.8	13.2	120.6	1.654	0.9996
	2	166.5	15.5	124.8	1.812	0.9996
STR 5L	1	196.1	16.2	118.3	1.854	0.9996
	2	203.3	16.6	114.1	1.848	0.9997
CV 60	1	172.0	15.0	127.0	1.737	0.9996
	2	173.3	16.5	126.0	1.819	0.9995
RSS 3	1	236.3	15.9	125.0	1.820	0.9998
	2	246.4	17.4	108.0	1.827	0.9997
BR 40	1	120.2	12.0	248.3	1.499	0.9997
	2	120.9	10.7	250.4	1.447	0.9998

TABLE 3. RPA-FT STRAIN SWEEP EXPERIMENTS AT 100ºC AND 1.0 Hz; FIT PARAMETERS OF *EQUATION 3*

Freq. (Hz) : 1.0 Sample	Run (a and b)	G^*_0 kPa	G^*_f kPa	1/A %	B	r^2
OMNR	1	192.0	19.4	112.0	1.749	0.9998
	2	184.5	25.7	107.6	2.012	0.9998
STR 5L	1	206.0	24.6	116.7	1.960	0.9996
	2	216.8	29.2	105.2	2.087	0.9995
CV 60	1	189.3	23.2	115.2	1.901	0.9998
	2	188.9	26.7	109.6	2.032	0.9998
RSS 3	1	254.5	25.0	117.1	1.937	0.9995
	2	269.1	32.1	97.5	2.088	0.9996
BR 40	1	161.4	9.1	224.5	1.607	0.9997
	2	162.5	12.4	216.3	1.636	0.9998

structural aspects rather than chain size that are likely associated with such differences in non-linear behaviour. The marked difference in the total harmonic content between the two types of rubber, as well as the frequency effect in the case of BR, is therefore worth noting and this calls for further work.

TTHC vs. strain curves envelop single harmonic ones, as illustrated in *Figure 8*. Whatever the harmonic considered, there is transient behaviour after the onset of the non-linear response, an asymptotic linear variation at high strain. As can be seen, *Equation 5* allows us to perfectly model experimental data, thus offering an easy comparison between materials through its fit parameters. Fit parameters for *TTHC*, *T*(3/1) and *T*(5/1) *vs*. strain are given in *Table 4* and compared in *Figure 9*.

TABLE 4. RPA-FT AT 100ºC; 0.5 AND 1.0 HZ ON NR SAMPLES; MODELING RELATIVE HARMONICS *VS*. STRAIN WITH *EQUATION 5*

Sample		*TTHC*	*T*(3/1)	*T*(5/1)
OMNR	TH_0	14.66	13.89	1.579
	α	0.01833	0.00621	0.00604
	C	0.01403	0.01464	0.01741
	D	5.22	5.59	12.78
	r^2	0.9998	0.9996	0.9991
STR 5L	TH_0	15.00	14.30	1.747
	α	0.01942	0.00610	0.00615
	C	0.01380	0.01436	0.01385
	D	4.78	4.82	7.95
	r^2	0.9991	0.9991	0.9979
CV 60	TH_0	15.24	14.76	1.451
	α	0.01795	0.00548	0.00632
	C	0.01337	0.01377	0.01763
	D	4.88	5.01	18.74
	r^2	0.9998	0.9996	0.9991
RSS 3	TH_0	18.70	15.65	3.157
	α	0.01905	0.00569	0.00556
	C	0.01422	0.01609	0.01548
	D	4.92	5.38	9.63
	r^2	0.9988	0.9986	0.9986

Torque harmonics quantify the non-linear viscoelastic behaviour and how they vary with increasing strain amplitude will likely reflect on how structural characteristics of polymers monitor the strain response. Torque harmonic variations with strain amplitude are adequately expressed through the two groups of parameters in *Equation 5*. The low and middle strain behaviour is quantified by parameters *C* and *D*, the high strain behaviour with parameters TH_0 and α. *Figure 9* consequently reflects subtle macromolecular differences between the NR samples considered. RSS 3 is clearly different, as expected with respect to its highest molecular weight, and likely to its high gel content. OMNR and CV 60 are close but not identical. Such results obviously call for further investigations, namely fine structural characterization of NR grades.

Quarter Torque Signal Integration

As shown above, FT analysis of strain signal allows clear qualification of the non-linear response of viscoelastic materials submitted to high strain, but experiments with complex 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, in order 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 quarter torque signal integration, i.e. Q1/Q2 offers a clear distinction of the non-linear response of polymer materials. With

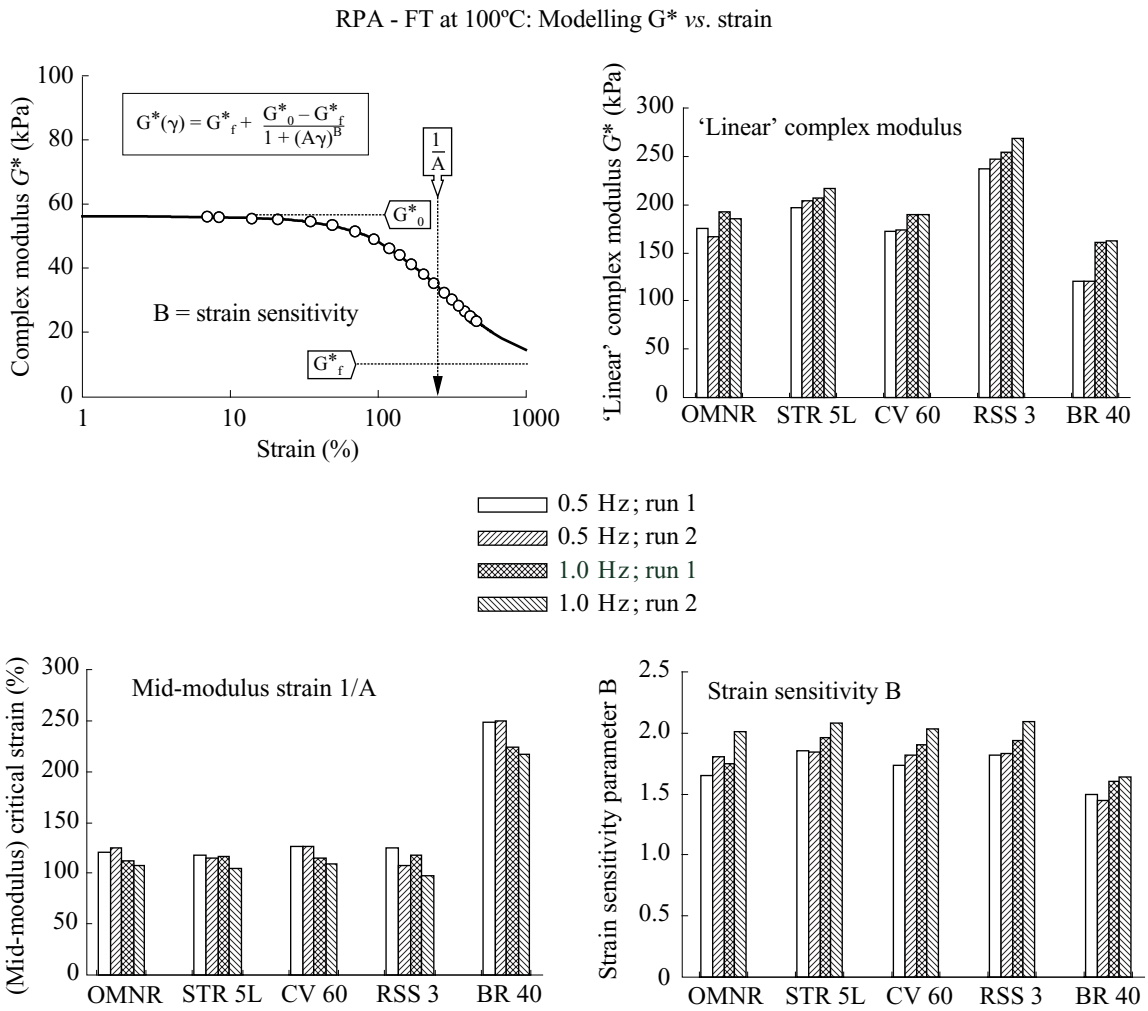


Figure 6. Comparing test materials through parameters of Equation 3.

most pure polymers, 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 reflects some structural character of the material, which enhances their non-linearity.

Figure 10 shows the Q1/Q2 ratio *vs*. strain amplitude for all samples. Only two tests results from run 1 are shown. Run 2 exhibits qualitatively similar features. Only OMNR and polybutadiene, and in a lower extent CV 60, do conform to the expected behaviour for pure polymers, i.e. Q1/Q2 is always higher than one, thus reflecting essentially a distortion 'on the left'. Such materials are said to be 'extrinsically non-linear' because they exhibit non-linearity through the application of a sufficiently large

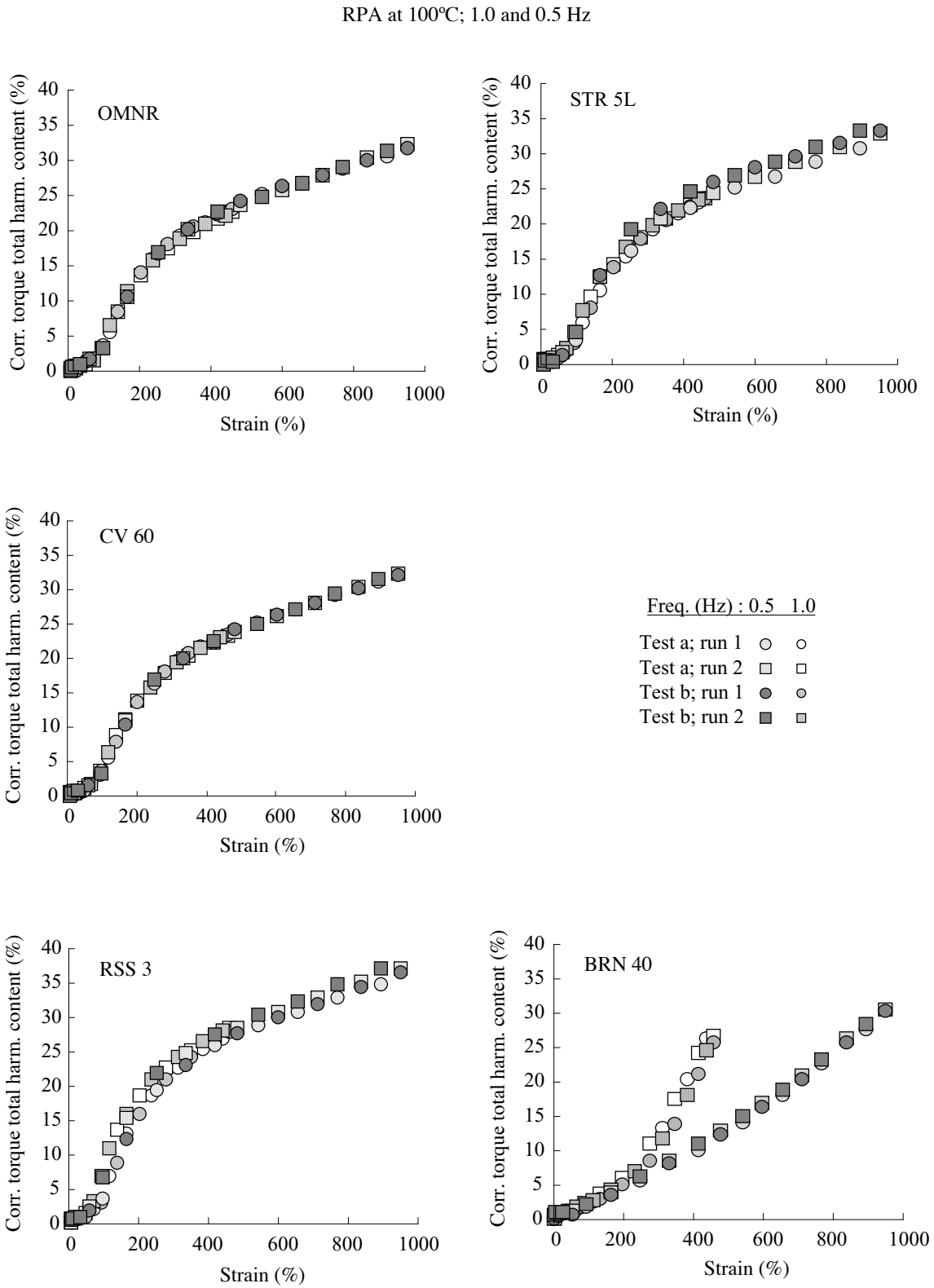


Figure 7. RPA-FT; total harmonic content vs. strain.

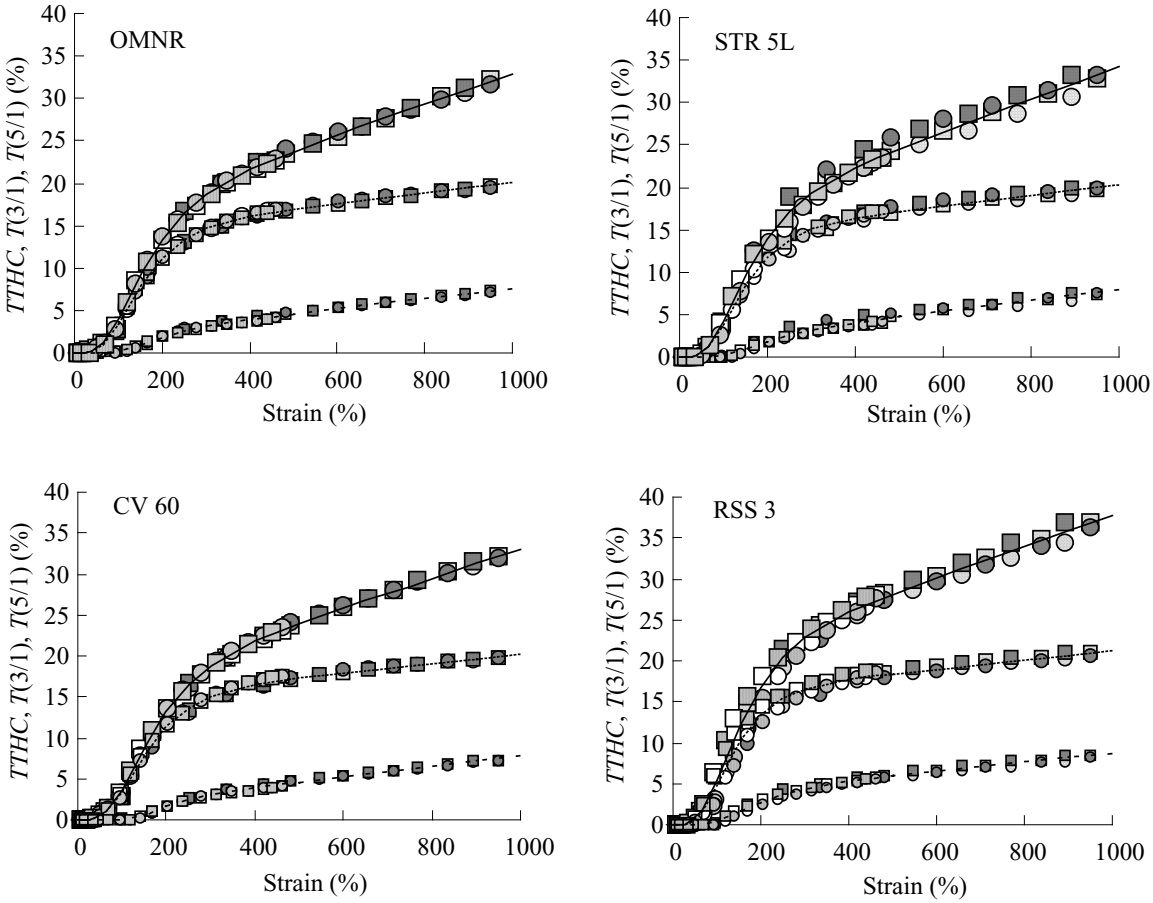


Figure 8. RPA-FT; torque harmonics vs. strain; 5th relative torque harmonic T*(5/1); 3rd relative torque harmonic* T*(3/1); total torque harmonic content* TTHC.

strain. It is quite interesting to observe that RSS 3 and partially STR 5L, tend to show 'intrinsic non-linearity', which would result from a heterogeneous structure, possibly due to semi-permanent aggregates of many molecules. Such a view was expressed by Melvin Mooney half a century ago[17], in a theory for the viscosity of raw rubbers. Briefly, Mooney postulated that microscopic rheological units, like small, tacky and elastic solid particles are controlling the macro-scopic flow of the rubber, through their rela-tive 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. It is worth noting that contemporary views about the likely structure of NR[18–22] supports the existence of such rheological units in grades that have a significant amount of gel. Indeed, chain terminal groups, appear to play a key role in the so-called 'green strength' of the material, as well as in other bulk viscosity dependent properties. It is nowadays considered that

through such terminal groups, rubber chains may assemble and form pseudo-crosslinked structures. Dispersed in the gel-free matrix, such units would give the bulk rubber certain characteristics of 'complex polymer systems', namely the capability to exhibit an intrinsic viscoelastic non-linearity, i.e. Q1/Q2 <1 in dynamic strain sweep experiments as indeed observed with STR 5L and RSS 3. Conversely, OMNR and CV 60 (as well as BRN 40), which are reported 'gel free', show essentially extrinsic non-linearity.

Mastercurves at 100ºC

G' and *G*" mastercurves at 100ºC, as derived from measurements with the RPA, are compared in *Figures 11* and *12*, respectively, with results from two V-COR frequency sweep tests at the same temperature. Results gathered with both instruments are generally very close if not identical, but experimental difficulties met when using an open gap rheometer with highly elastic materials, e.g.. RSS 3, directly reflect in such data. When considering *G*' and *G*" curves of RSS 3, it is clear that one can be more confident in RPA results than of VCOR ones. The advantages in using closed cavity rheometers to assess the dynamic properties of highly elastic materials are clearly under-lined here. Through the application of the time – temperature superposition principle, the frequency range is enlarged and covers nearly two decades, in such a manner that materials' dynamic behaviour is well documented in the terminal zone. Such results are typically linear viscoelastic data (since experiments had been made at a sufficiently low strain amplitude to be far from the strain dependent region) and NR grades exhibit nearly similar behaviour, but of course very different from polybutadiene. With the exception of RSS 3, all materials exhibit a $G'(\omega)$ behaviour that seems to correspond to the generalized Maxwell model, i.e. $G' \alpha\ \omega^2$ but this comment does not apply to $G''(\omega)$.

Frequency sweep tests data are typical linear viscoelasticity results which are clearly less discriminating than non-linear data when comparing different NR grades.

CONCLUSION

NR Gum is easily and conveniently charac-terized with advanced harmonic testing methods. Closed cavity rheometers are needed however with such materials; indeed, due to their high elasticity in the molten state, radial flow is hardly obtained under the axial compressive force available with open cavity instruments, when loading the testing gap. Using a purposely-modified closed cavity rheometer, strain sweep test protocols give reproducible results, particularly in the high strain region. Minor instrumental deficiencies are easily compensated for with the appropriate data treatment, in order to yield meaningful results, suitable for a very fine characterization of materials. As non-linear viscoelastic responses are obtained at large strain amplitudes, results must be analyzed through special techniques, using for instance FT. FT spectra contain all the information available through harmonic testing and a basic analysis on non-linear viscoelastic behaviour is made by considering the main torque component $T(\omega 1)$ and the relative harmonic torque components *versus* the strain amplitude. Easy modeling methods give access to various parameters, thus providing a clear quantification of the non-linear viscoelastic character.

FT rheometry (and the appropriate data treatment for G^* *vs.* strain and for torque harmonics *vs*. strain) provides results that belong to both the linear and non-linear domains. Linear viscoelastic results appear far less discriminating than non-linear ones when comparing different NR grades. Two aspects of FT rheometry are worth underlining in this respect: firstly, torque harmonics variation

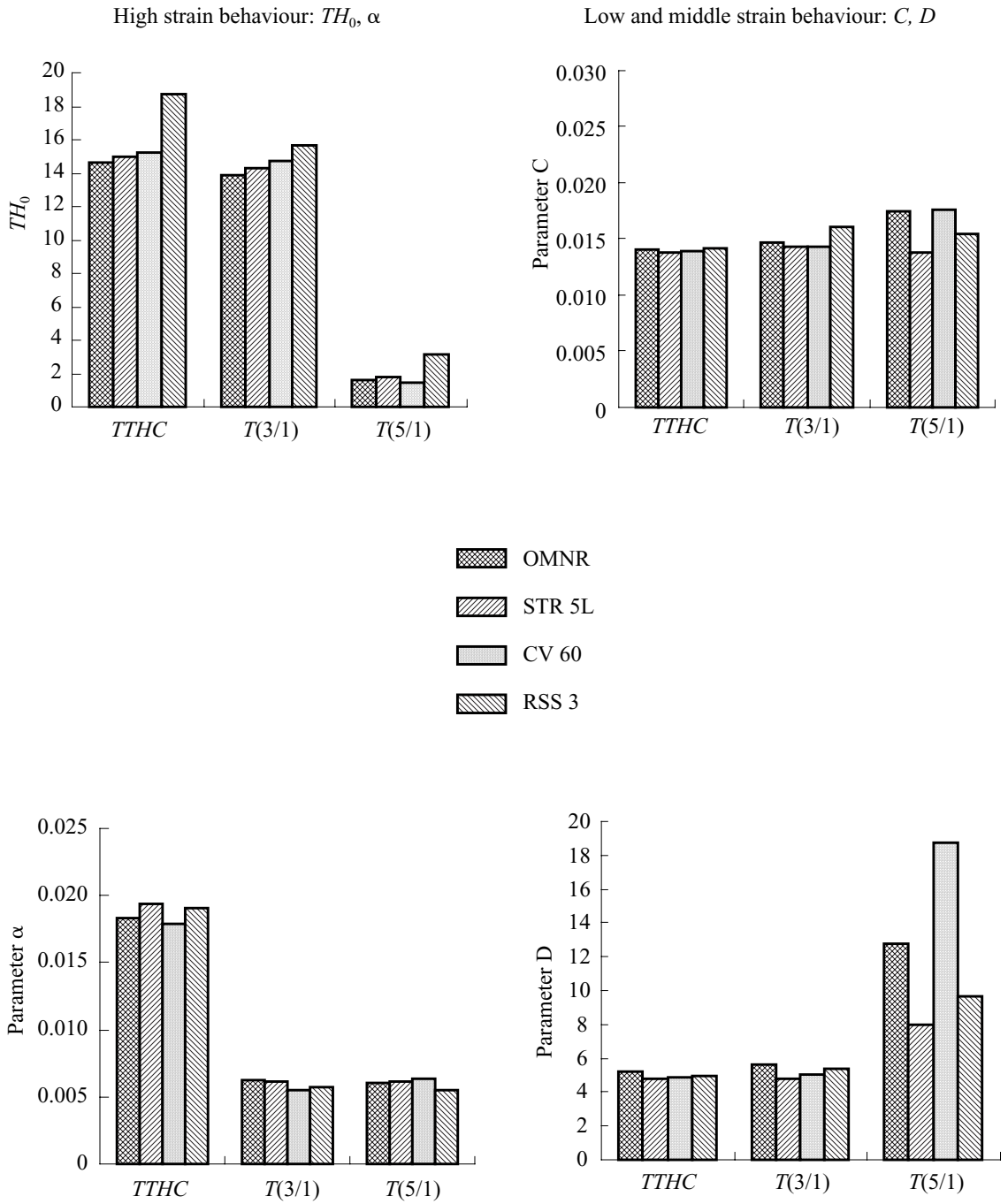


Figure 9. RPA-FT on NR samples; variation of torque harmonics with strain amplitude; comparing parameters given in Table 4.

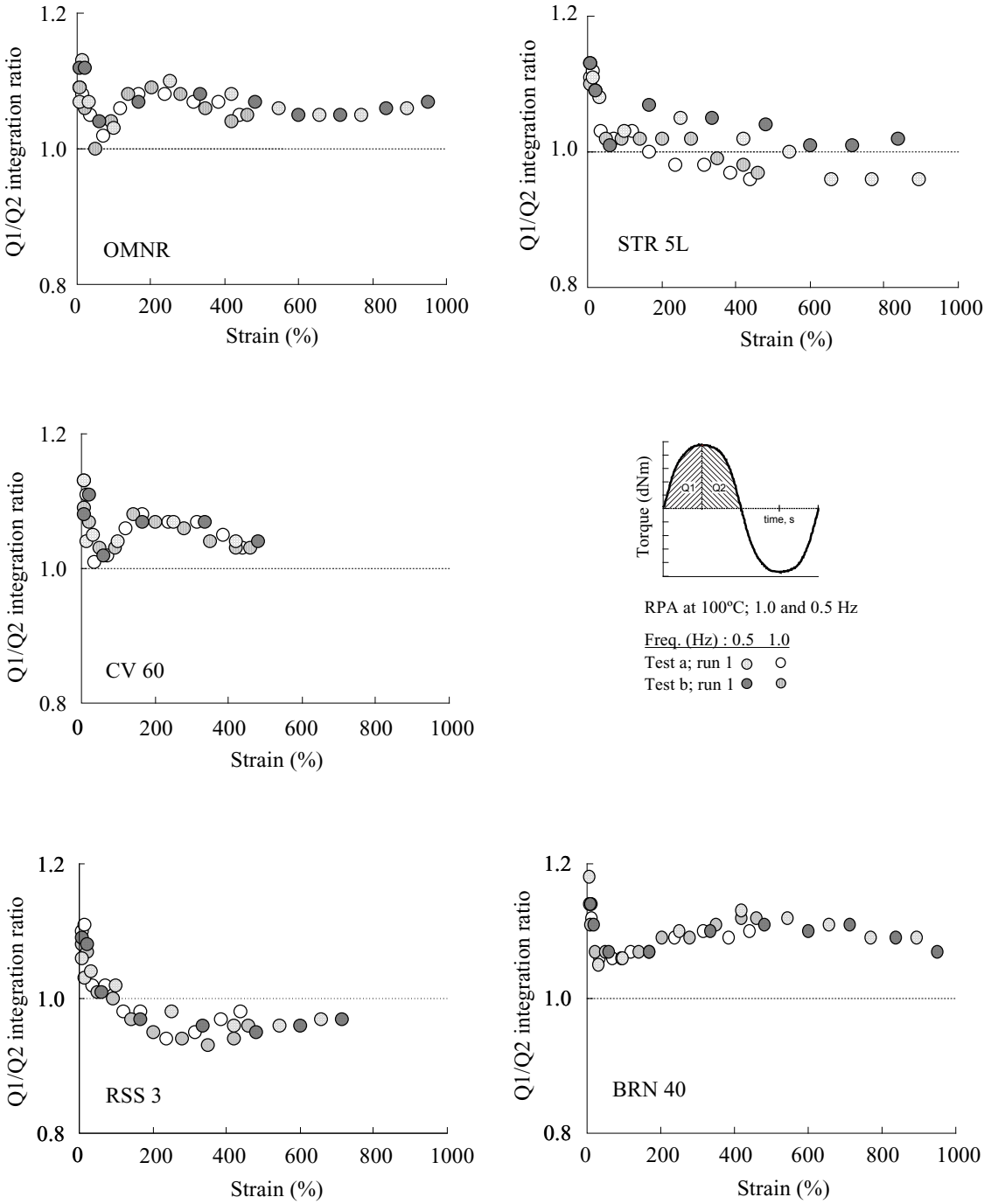


Figure 10. Assessing extrinsic/intrinsic non-linear viscoelastic character through quarter cycle torque integration.

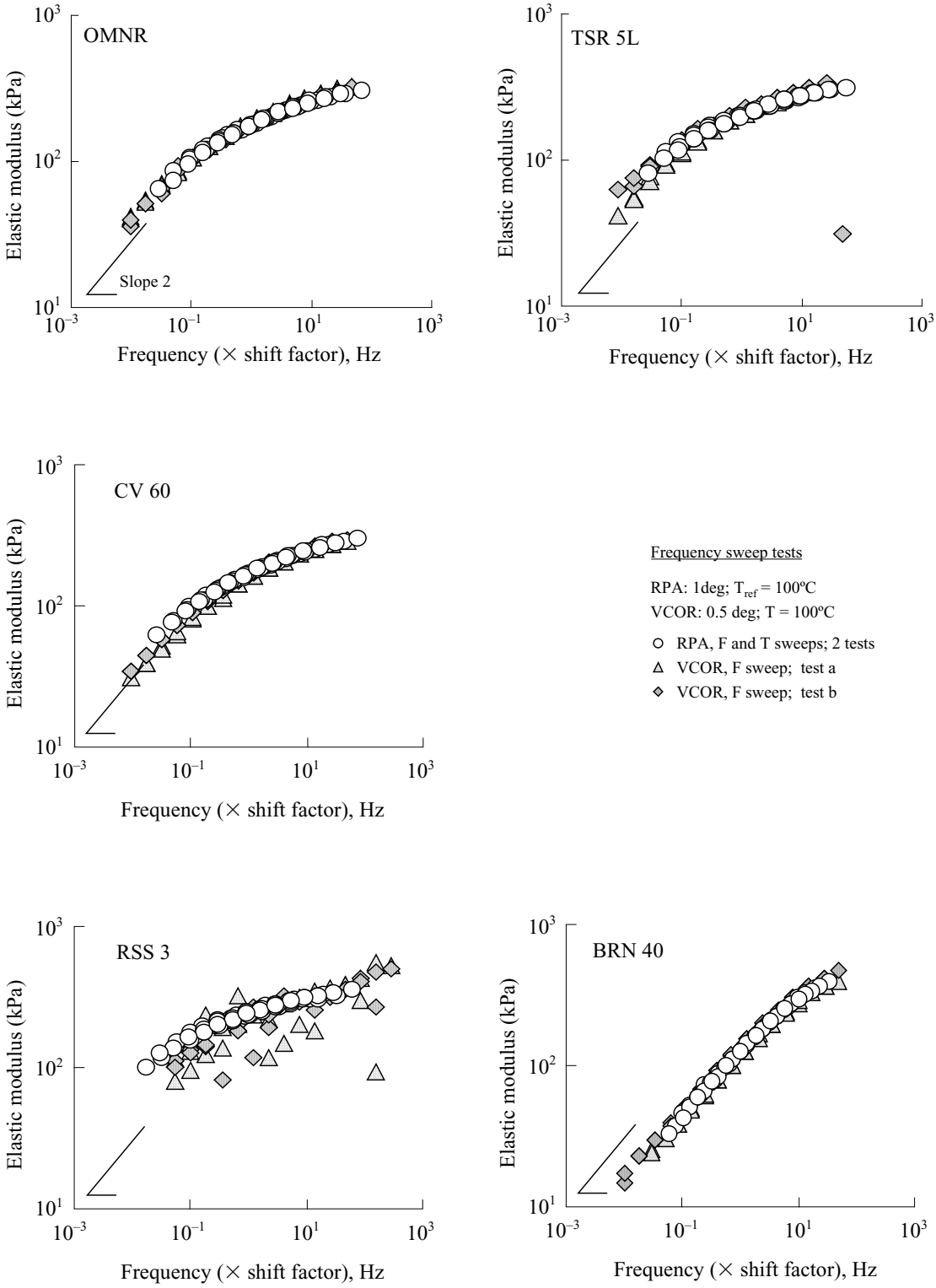


Figure 11. Elastic modulus G' *mastercurves at 100ºC.*

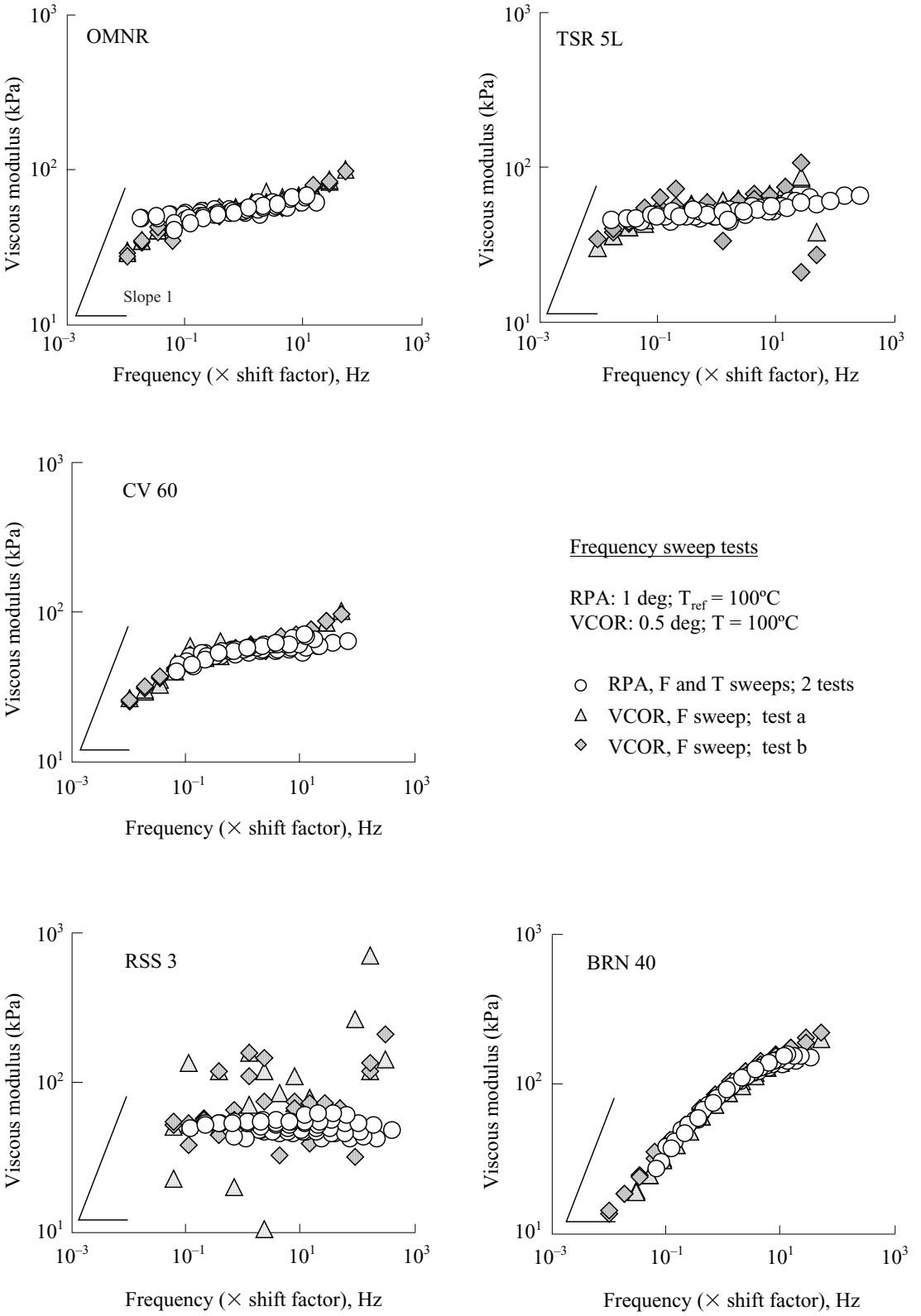


Figure 12. Viscous modulus G" *mastercurves at 100ºC.*

with strain amplitude which reveal structural rather than chain size effects on the non-linear response of gum NR; secondly, quarter signal integrations which show that certain NR grades, likely because of their high gel content, exhibit a rather intrinsic non-linear behaviour, similar to the one exhibited by complex polymer systems. Starting from the same raw material (i.e. *Hevea* latex), the manner in which dry NR is obtained clearly conditions the viscoelastic character of the rubber.

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