Engineering Performance and Material Viscoelastic Analyses Along a Compounding Line for Silica-based Compounds, Part 2: Nonlinear Viscoelastic Analysis

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ABSTRACT: In the first part of this article, a mixing line for silica-based compounds was thoroughly described and its performance was studied in terms of mixing fingerprints. Along the mixing line, the compound experiences a large spectrum of strain, stress and temperature conditions such that important "cascade" or "stream" effects occur. At a given point of the process, the material has an important strain-stress-temperature history that is obviously affecting its behavior during the subsequent steps, and the situation is further complicated by the *in situ* silanisation, which obviously must be complete for stabilized rheological properties to be obtained at the end of the line. In this second part of the article, results are reported which were obtained with a new and promising rheometrical technique, i.e., the so-called Fourier Transform rheometry, implemented on a commercial torsional dynamic rheometer. As shown, Fourier Transform (FT) rheometry provides a number of information about the complex set of events that occur along the silica-silane mixing line. Odd torque harmonics become significant as strain increases, and therefore the variation of torque harmonics with strain amplitude can be considered as the nonlinear viscoelastic "signature" of tested materials. Silica filled materials exhibit also a typical pattern, with a "bump" appearing in the 500% strain range, essentially on the third relative harmonic versus strain curves and changing as optimal silica dispersion and silinisation are achieved. The appropriate modeling of experimental results provide parameters with typical variations along the mixing line which are interpreted with respect to current views on the *in situ* silanisation process and are found in line with the mixing signatures analysis. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 1128–1141, 2009

Key words: silica; silane; mixing; rubber compounds; LAOS; dynamic modulus

INTRODUCTION

In the first part of this article, a mixing line for silica-based compounds was thoroughly described and its performance studied in terms of mixing fingerprints, i.e., the complex set of curves (power, energy, temperature, etc.) that are routinely recorded during operations in internal mixers. Silica needs silanisation[1] to fully develop its reinforcing capabilities and the current industrial practice consists in achieving it during the mixing operations.[2] It means that a condensation reaction must be activated, controlled, and completed in a highly viscous matrix, while the optimum dispersion of filler particles is achieved. In sharp contrast with carbon black filled compounding, the preparation of silanated-silica-based materials is nowadays made on relatively complex mixing lines, according to specific procedures that were essentially and successfully developed through a pragmatical approach. This leaves however room for improvement, providing the complex set of events that take place during the process is better understood. Exploiting the mixing fingerprints allows rubber engineers to control and somewhat monitor the mixing line with a certain degree of confidence. Further improvement is expected through a better understanding of the variation of certain key properties of the compound along the line.

Along a mixing line, a rubber compound experiences a large spectrum of strain, stress and temperature conditions such that important "cascade" or "stream" effects occur. Indeed, at a given point of the process, the material has an important strain-stress-temperature history that is obviously affecting its behavior during the subsequent steps. When preparing silica filled compound, the situation is further complicated by the *in situ* silanisation, which obviously must be complete for stabilized rheological properties to be obtained at the end of the line. In this second part of the article, a new and promising rheometrical technique is used to study how nonlinear viscoelastic properties of the material evolve along the line.

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FOURIER TRANSFORM RHEOMETRY WITH AN UPDATED CLOSED CAVITY TORSIONAL RHEOMETER

Principle of Fourier transform rheometry

Fourier Transform (FT) rheometry is a dynamic testing technique which essentially consists in performing large amplitude oscillatory strain (LAOS) experiments on polymer melts or solutions.[3,4] When implemented on appropriate instruments, the technique can readily be applied on complex polymer systems, for instance filled rubber compounds, to yield significant and reliable information.[5] Fourier Transform analysis of torque signals yields essentially two types of information: first the main signal component, i.e., the peak in the FT spectrum that corresponds to the applied frequency, second the harmonics, with the third (i.e., the peak at $3 \times$ the applied frequency) the most intense one. The variation of odd torque harmonics is the "nonlinear viscoelastic signature" of the material in the conditions of the experiments. Filled polymer systems exhibit quite typical "nonlinear signatures" which result from the superimposition of strain and morphology induced nonlinear effects.[6] Any simple polymer can exhibit nonlinear viscoelastic properties when submitted to sufficiently large strain; in such case, the observed behavior is **strain-induced nonlinear viscoelasticity** (or so-called **extra** nonlinear viscoelasticity, owing to external factors, i.e., the applied strain). When polymer materials have a sufficient, sizeable level of heterogeneity, they are complex systems and they exhibit morphology-induced effects, which superimpose to strain induced effects. We call this behavior **morphology-induced nonlinear viscoelasticity** (or **intra** nonlinear viscoelasticity, because owing to the internal morphology of the material). Filled rubber compounds are known for long to be nonlinear and FT rheometry allows a very fine characterization of their behavior, which has however to be supplemented by additional data treatment, would one want to distinguished strain-induced and morphology-induced effects, as detailed below.

Essentially, Fourier transform rheometry consists in capturing strain and torque signals during dynamic testing and in using Fourier transform calculation algorithms to resolve it into their harmonic components. In other terms, harmonic signals are mathematically handled to resolve their information, gathered in the time domain, into a representation of the measured material property in the frequency domain, in the form of 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 test frequency.

A nonlinear response is characterized by a number of additional peaks at odd multiples of the applied strain frequency.

Any commercial torsional dynamic tester can be conveniently up-dated for Fourier transform rheometry, but conventional open gap rheometers, for instance parallel disks and cone-and-plate instruments, are limited to relatively low strain amplitude experiments on materials exhibiting a relatively modest elasticity. 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. 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,[7] as well as the experimental procedure and data treatment.[5,6,8]

Strain sweep tests are the method of choice to investigate nonlinear viscoelasticity and the appropriate test protocols were developed, which essentially consist in performing strain sweep experiments through two subsequent runs (i.e., run 1 and run 2) separated by a resting period of 2 min. At least two samples of the same material are tested, 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-plate or parallel disks torsional rheometers. Whatever the frequency, the lower strain angle limit is 0.5° (6.98%) below which the signal-to-noise ratio of the strain signal becomes so high that the corresponding measured torque is excessively scattered and likely meaningless. Test protocols at 0.5 Hz were therefore designed to probe the material's viscoelastic response within the permitted 0.5–68° range, with up to 20 strain angles investigated.

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(1ω) or S(1ω) with respect to the torque or strain signals respectively], (2) the harmonics, with the third (i.e., the peak at three times the applied frequency) the most intense one. A specific calculation program, written using the FT algorithm available in MathCad 8.0® (MathSoft.), is used to obtain the amplitude of the main stress and strain components (corresponding the test frequency) and the relative magnitudes
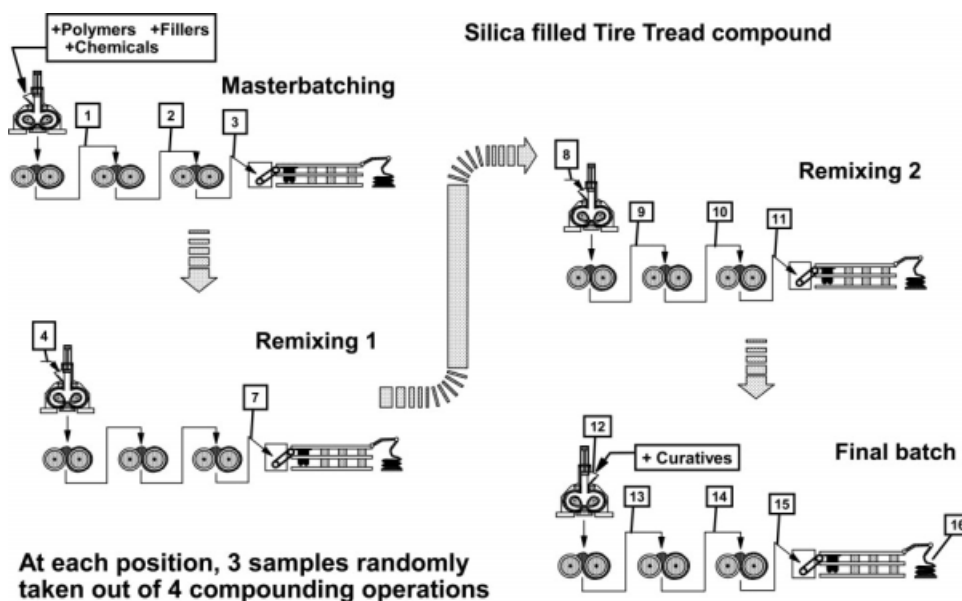
Figure 1 Sampling along a mixing line for a Silica filled compounds.

(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 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. 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 %]. When linear viscoelasticity is observed, G^* data from FT analysis are identical to G^* from the RPA built-in data treatment. When large strain effects are observed, limited confidence can be given to data provided by the software of the commercial instrument.

Fourier Transform analysis of torque signal allows clearly quantifying the nonlinear response of viscoelastic materials, but experiments with complex polymer systems have revealed that, when submitted to high strain, whether the torque signal is distorted "on the left" or "on the right," with respect to a vertical axis drawn at the first quarter of the cycle, does not reflect in the FT spectrum.[9,10] It was observed, however, that most complex polymer systems, e.g., filled rubber compounds, exhibit severer distortions, which sometimes affect more the right part of the half signal, when strong interactions can be suspected between components (i.e., phases) of materials. As previously mentioned, we expressed this difference between the nonlinear viscoelastic behavior of a pure, unfilled polymer and of a complex polymer material through the terms **extra** (strain induced) and **intra (morphology induced)** nonlinear viscoelasticity. To supplement FT analysis,

quarter cycle integration was developed as an easy data treatment technique to distinguish extrinsic and intrinsic nonlinear viscoelasticity. The ratio of the first to second quarters torque signal integration, i.e., Q1/Q2 allows clearly distinguishing between the strain amplitude effect on a pure (or homogeneous) and a complex polymer materials. With the former, Q1/Q2 ratio is generally 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). Complex polymer materials generally exhibit Q1/Q2 ratio lower than one, which furthermore varies with strain amplitude. This likely reflects changes in interactions between phases that, sometimes, vanish at high strain, thus indicating a profound modification of the compound morphology.

SAMPLING ALONG THE SILICA COMPOUNDING LINE

Preparing silica filled compounds is by far the most complex mixing operation in tire technology and practical observations are really challenging,[11] essentially because the silanisation process is performed in internal mixer, concomitantly with the dispersion of filler particles and other compounding ingredients. The order of addition of formulation ingredients and the control of mix temperature variation through shear warming-up, are important aspects of the process, likely typical of the mixing line considered and an essential know-how of tire manufacturers. In quite a practical manner, rubber engineers have set up relatively complicated compounding operations for silica-silane filled formulations,
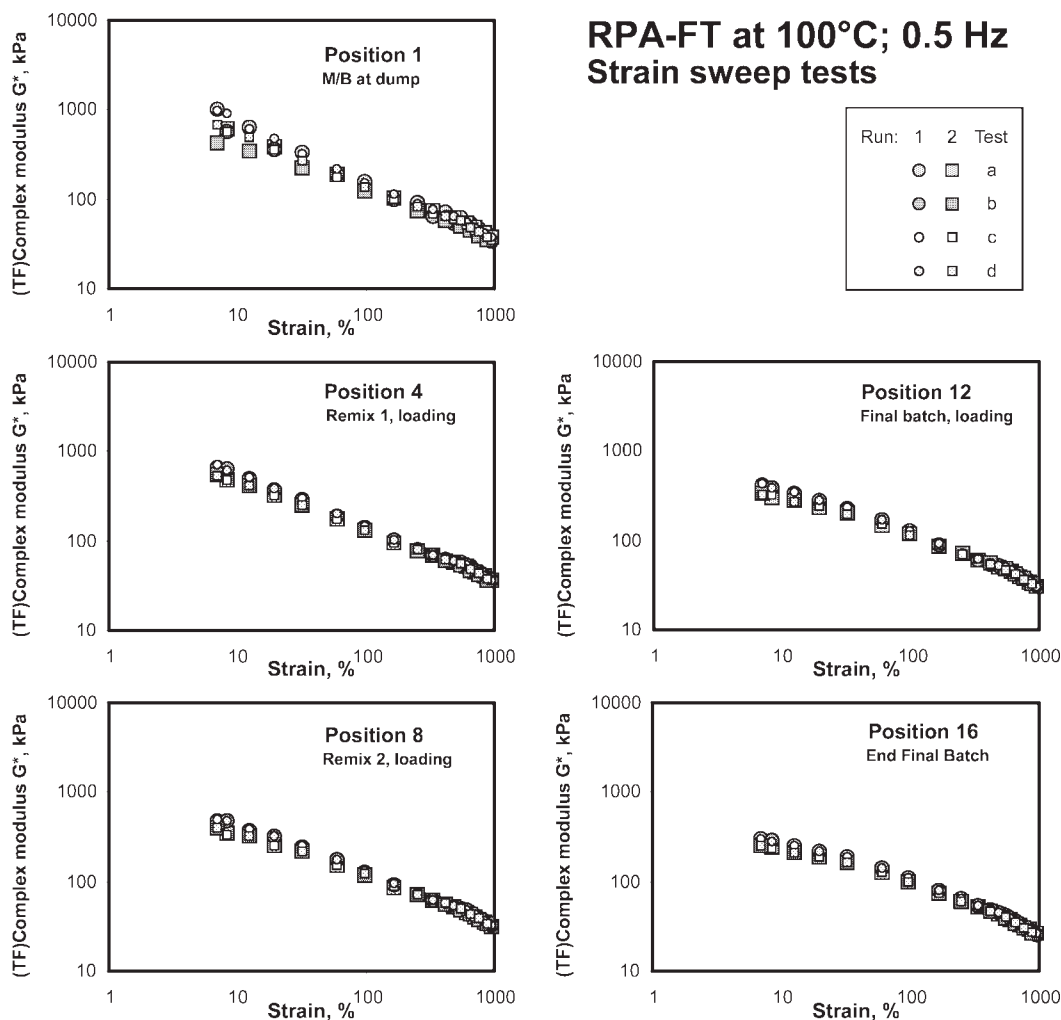
Figure 2 Mixing silica filled compound: complex modulus strain dependence at selected position along the mixing line; four samples tested (a, b, c, and d); two successive strain sweep tests (runs 1 and 2).

involving several dumping, cooling and "remixing" steps, to eventually obtain quality final batches (Fig. 1). Samples were taken along the mixing line, as indicated in the figure. See part I of the article for details on the formulation and the mixing procedure.

At each position, three samples were taken at random during the preparation of four different batches. Samples were received within one week of the operations as rough plaques of up to 2-cm thickness. To eliminate any sample size/geometry effect on RPA-FT tests, cylindrical pieces were die cut out of the plaques, and their weight adjusted before compression molding for 5 min at 60°C in a mold mimicking the RPA test cavity geometry and volume + 5%. RPA-FT strain sweep tests (2 tests: a and b) were performed at 100°C, 0.5 Hz on all samples. All tests were repeated three weeks later (2 tests: c and d), after storage in darkness at room temperature. No significant ageing effects were seen and only results of the second series of tests will be reported

in detail below, in terms of complex modulus G*, torque harmonics and the Q1/Q2 ratio.

RESULTS AND DISCUSSION

FT Complex modulus versus strain

Figure 2 shows complex modulus G* versus strain curves, as measured on samples taken at expected key positions in the process: at dump of the masterbatch (position 1), when loading for the first remixing (position 4), when loading for the second remixing (position 8, when loading for curatives addition (position 12), at the end of the line (position 16). Results for 2×2 tests are shown and as can be seen a large scatter is observed at dump of the masterbatch, likely reflecting a poor homogeneity, which is immediately improved by passing on the three subsequent open mills. Indeed, at position 4, results appear well reproducible with a small but significant strain history effect (i.e., run 1 and run 2 data do not

TABLE I
Mixing Silica Filled Compound; RPA-FT Results at 0.5 Hz, 100°C; Complex
Modulus Dependence on Strain; Fit Parameters of eq. 1

Sample identification							
Location	Position	Run (a and b)	G_0^* (kPa)	G_f^* (kPa)	1/A (%)	B	r^2
M/B at dump	1	1	8602.0	23.3	0.53	0.8015	0.9992
		2	3526.0	15.5	0.83	0.6990	0.9985
	2	1	2925.0	7.9	1.15	0.6721	0.9997
		2	1313.0	15.7	4.32	0.7325	0.9999
	3	1	2272.0	19.0	2.65	0.7838	0.9989
		2	2217.0	6.6	1.16	0.6290	0.9980
Remix 1 loading	4	1	3421.0	9.9	0.96	0.6847	0.9996
		2	1259.0	13.8	4.16	0.7084	0.9999
	7	1	1095.0	8.4	5.36	0.7096	0.9998
		2	723.9	4.1	7.78	0.6477	0.9999
Remix 2 loading	8	1	1068.0	8.0	5.68	0.7084	0.9998
		2	908.9	(−4.0)	4.07	0.5744	0.9983
	9	1	890.5	3.8	7.34	0.6900	0.9992
		2	661.1	(−6.0)	8.24	0.5888	0.9994
	10	1	972.8	0.4	5.81	0.6601	0.9999
		2	533.7	0.6	14.28	0.6538	0.9994
	11	1	922.1	(−0.8)	6.08	0.6495	0.9996
		2	550.2	(−2.0)	12.85	0.6394	0.9998
Final batch loading	12	1	882.4	(−3.0)	6.08	0.6277	0.9994
		2	549.7	0.0	13.02	0.6411	0.9996
	13	1	498.1	(−7.0)	14.91	0.6310	0.9998
		2	368.7	(−7.1)	22.89	0.6213	0.9999
	14	1	467.6	(−5.4)	16.31	0.6425	0.9998
		2	381.0	(−6.7)	21.13	0.6218	0.9993
	15	1	443.5	(−5.0)	18.88	0.6564	0.9998
		2	361.8	(−6.1)	24.09	0.6353	0.9999
End batch	16	1	468.7	(−6.4)	16.91	0.6394	0.9997
		2	356.7	(−5.1)	25.11	0.6422	0.9999

Modeling summary report: G* vs. Strain%.
Test: S_Sweep_05 Hz_2 Runs_100; Temp. (°C): 100; Freq. (Hz): 0.5.

superimpose). At all positions, strong strain dependence is observed, with the limit of the linear region barely visible at the end of the process (position 16). Within the experimental strain window, the compound maintains a strong nonlinear viscoelastic character along the full mixing line.

For a material exhibiting both linear and nonlinear viscoelasticity within the experimental window, a plot of G* versus 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:

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

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. It is only at the end of the compounding process that silica filled compounds tend to show the occurrence of a linear plateau at low strain amplitude, but this

observation justifies the modeling of all the results with eq. (1).

Fitting data with eq. (1) is excellent as reflected by correlation coefficients given in Table I with all fit parameters, and as illustrated by the curves drawn in Figure 3. The fitting somewhat compensates for experimental scatter and clearly shows that the nonlinear character significantly changes along the compounding line (compare graphs in Fig. 3). One notes in Table I that negative values for G_f^* are sometimes obtained, which of course must be kept as such for data fitting purposes, but must be discarded from discussion as they have no physical meaning.

Parameters in Table I allow to describe how nonlinear viscoelasticity changes along the compounding line by simply considering G_0^*, the (extrapolated) zero strain modulus, B the strain sensitivity parameter and the critical strain 1/A. The variation of viscoelastic parameters during mixing operations reveals key steps of the process. For instance, recalculated complex modulus at 10% strain show that, as expected, intensive shearing steps in internal mixer readily improve the processing behavior (i.e.,
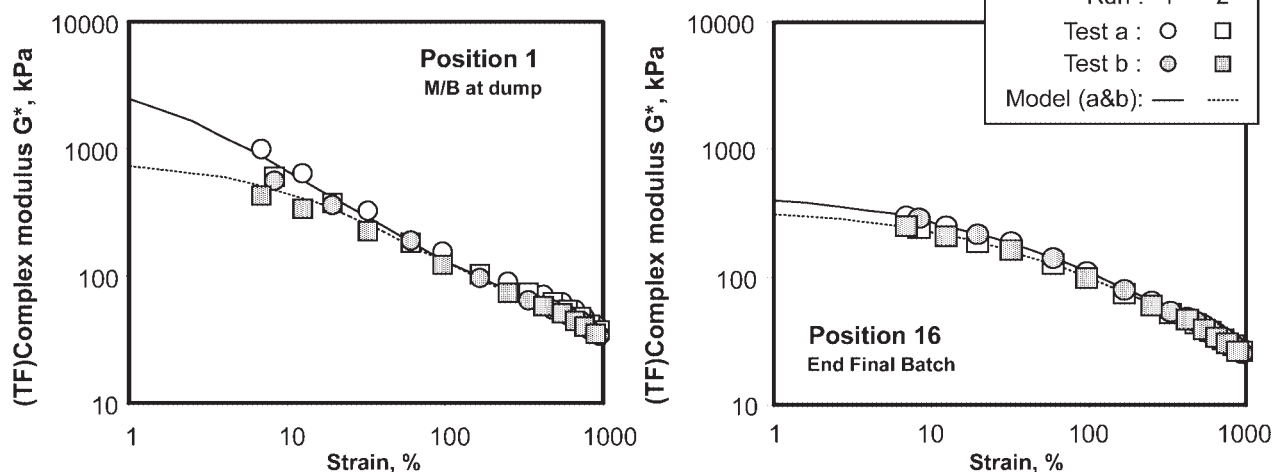
Figure 3 Mixing silica filled compounds: overall changes in nonlinear viscoelastic character along the mixing line; two samples tested (a and b); two subsequent strain sweep tests (runs 1 and 2); curves drawn according to eq. (1).

through a decrease of the complex modulus, and therefore of the viscosity), likely by contributing to the completion of the silica-silane reactions and by further homogenizing the compound. This is clearly seen in the upper graph of Figure 4. Another interesting observation is the strong effect of curatives addition; not only the modulus drops by around 100 kPa, which reflects a kind of plasticizing effect of such chemicals, but also the mid modulus critical strain 1/A increases by 6–7% (lower graph in Fig. 4). With respect to the mathematical form of equation 1, the parameter 1/A is somewhat related with the extend of the linear viscoelastic region and, therefore, adding curatives appears as an essential step in ultimately smoothing the processability character of the compound.

FT torque harmonics versus strain

Figure 5 shows the torque harmonics versus strain at position 1 (MB at dump); results from two test campaigns within the three week interval after the sampling are plotted; no ageing effects are observed. The third T(3/1) and the fifth T(5/1) relative harmonics are displayed, as well as the "total torque harmonic content" TTHC, in fact the sum of all odd harmonics up to the fifteenth. Of course the TTHC curve envelops the other ones. Again a large scatter is observed on results obtained with samples taken at M/B dump and there are some differences between run 1 and run 2 data, indicating thus significant test strain history effects. One notes also that the scatter is reduced on run 2 data. Figure 6 shows the corresponding results as obtained on samples taken at the end of the line. As expected the scatter reduces as sampling progresses along the line and is thus marginal for the last sample. One notes again
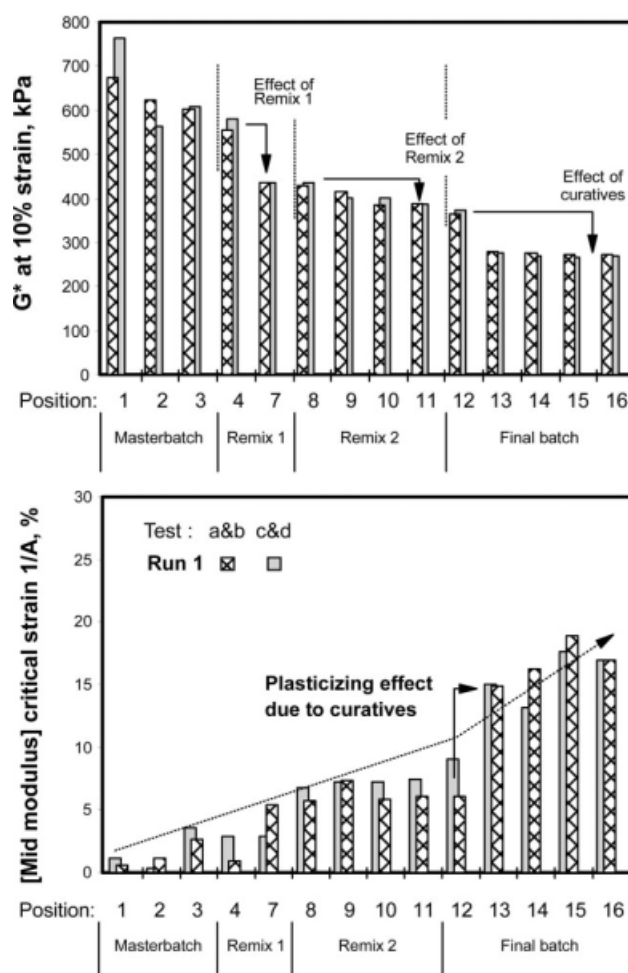

Figure 4 Mixing silica filled compounds: complex modulus versus strain amplitude as modeled with eq. (1); typical changes in nonlinear viscoelastic features along the mixing line; four samples tested (a, b, c, and d); results from first strain sweep test (run 1).

RPA-FT at 100°C; 0.5 Hz - Strain sweep tests
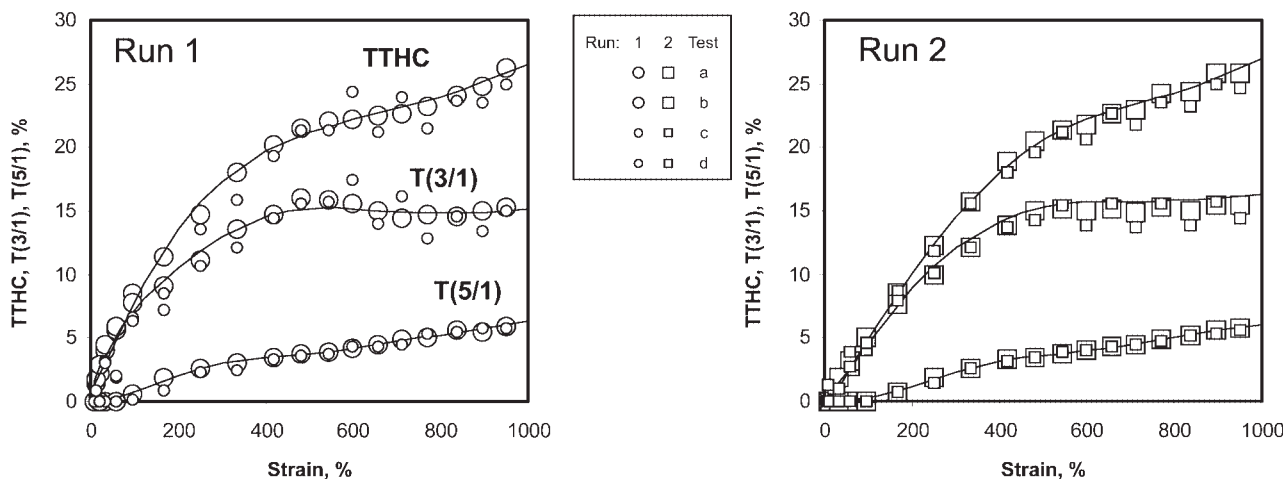**Samples at position 1**

Figure 5 Mixing silica filled compounds: relative harmonics versus strain amplitude; samples at position 1 (M/B at dump); four samples tested (a, b, c, and d); two successive strain sweep tests (runs 1 and 2).

substantial differences between the two runs: certain features of run 1 curves seem to be dampened in run 2.

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. When compared with similar data on pure, unfilled rubbers,[8] the curves in Figures 5 and 6 display a singularity at around 500% strain, which prompted the recent development of an appropriate model for highly filled systems.[6] It was considered that the "bump," clearly observed in the intermediate strain region of either TTHC or T(3/1) versus strain curves, reflects in fact an additional response of the filler, superimposed on the nonlinear signature of the polymer matrix. The latter, common to most "pure" (or virgin, unfilled) polymers, corresponds to a "sigma" trace that becomes asymptotic to a straight line in the high strain region. The filler response would correspond to a curve passing through a maximum at a typical strain value.

A model was consequently expected developed with respect to the following views. Because of strong interactions between the viscoelastic matrix and the discrete phase, a kind of soft composite network is embedded in the (free) rubber phase. This gives initially additional harmonics in the medium strain range, which enhance the nonlinear response of the material. Then, as strain further increases,

RPA-FT at 100°C; 0.5 Hz - Strain sweep tests
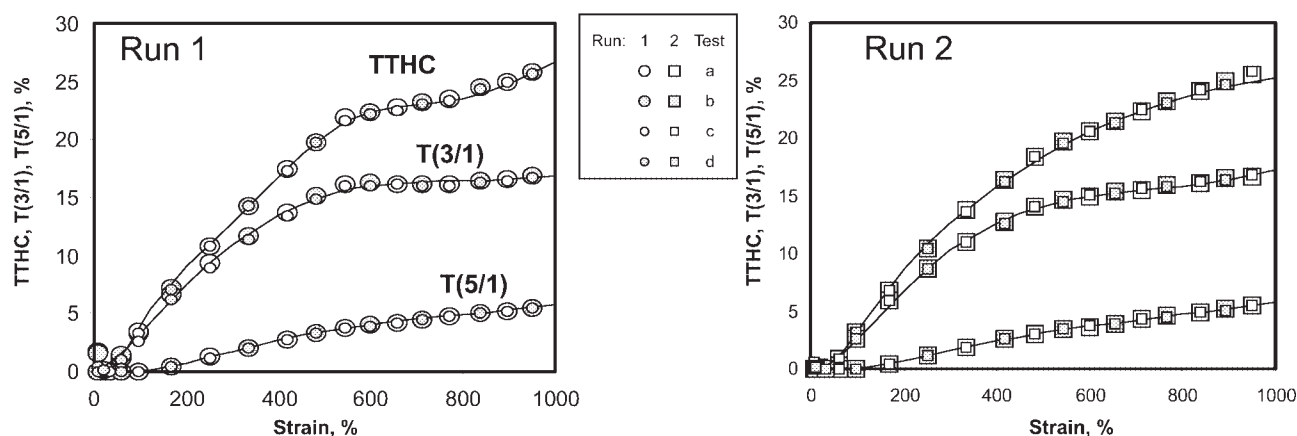**Samples at position 16**

Figure 6 Mixing silica filled compounds: relative harmonics versus strain amplitude; samples at final position 16 (finished compound); four samples tested (a, b, c, and d); two successive strain sweep tests (runs 1 and 2).
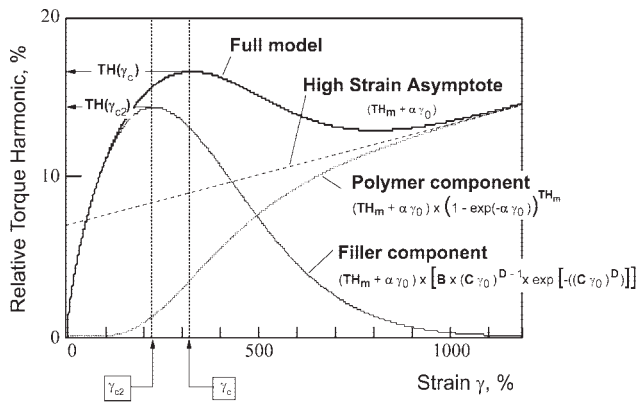
Figure 7 Modeling the relative torque harmonics variation with strain amplitude of filled materials.

filler-polymer interactions decrease and/or eventually vanish in such a manner that, for a sufficiently high strain amplitude, essentially the high strain response of the polymer matrix plays yet a role. The following five parameters equation corresponds to such a behavior:

$$TH(\gamma_0) = (TH_m + \alpha\gamma_0) \times \left\{ [1 - \exp(-\alpha\gamma_0)]^{TH_m} \right.$$
$$\left. + B(C\gamma_0)^{D-1} \exp\left[-(C\gamma_0)^D\right] \right\} \quad (2)$$

where $TH(\gamma_0)$ stands for any relative torque harmonic, i.e., $T(n\omega/1\omega)$, and also for the so-called total torque harmonic content TTHC [i.e., $\sum T(n\omega/1\omega)$].

The physical meaning of the parameters of eq. (2) is easily understood when one considers that it consists of three members, as illustrated in Figure 7:

– one describing the asymptotic high strain behavior:

$$(TH_m + \alpha\gamma_0) \quad (2a)$$

– one describing the polymer response, the so-called polymer component:

$$(TH_m + \alpha\gamma_0) \times (1 - \exp(-\alpha\gamma_0))^{TH_m} \quad (2b)$$

– one describing the filler response, the so-called filler component:

TABLE II
Mixing Silica Filled Compounds; RPA-FT Results at 100°C; third-relative torque harmonic vs. strain; fit parameters of eq. 2

Sample identification			Model parameters					
Location	Position	Run (a and b)	TH_m	α	B	C	D	r^2
M/B at dump	1	1	8.18	0.0053	2.49	0.0021	1.92	0.9870
		2	1.43	0.0110	3.09	0.0022	1.52	0.9940
	2	1	5.38	0.0047	3.72	0.0018	1.75	0.9920
		2	1.45	0.0120	2.86	0.0023	1.68	0.9980
	3	1	7.20	0.0047	3.08	0.0019	1.92	0.9951
		2	1.58	0.0128	2.54	0.0022	1.71	0.9985
Remix 1 loading	4	1	7.30	0.0045	3.28	0.0019	2.04	0.9956
		2	1.53	0.0120	2.92	0.0022	1.74	0.9986
	7	1	2.39	0.0117	2.52	0.0019	2.32	0.9971
		2	3.36	0.0121	1.53	0.0021	2.16	0.9994
Remix 2 loading	8	1	2.24	0.0120	2.62	0.0019	2.20	0.9980
		2	3.05	0.0130	1.62	0.0021	2.09	0.9990
	9	1	2.67	0.0130	2.00	0.0019	2.29	0.9980
		2	3.41	0.0130	1.29	0.0020	2.12	0.9990
	10	1	2.71	0.0127	1.93	0.0019	2.25	0.9984
		2	3.51	0.0129	1.31	0.0020	2.15	0.9991
	11	1	2.57	0.0125	2.06	0.0019	2.23	0.9985
		2	3.61	0.0127	1.29	0.0021	2.19	0.9992
Final batch loading	12	1	2.18	0.0124	2.37	0.0019	2.08	0.9985
		2	3.42	0.0130	1.33	0.0020	2.14	0.9989
	13	1	3.30	0.0133	1.41	0.0019	2.33	0.9991
		2	3.61	0.0132	1.04	0.0020	2.16	0.9995
	14	1	3.27	0.0136	1.36	0.0019	2.35	0.9990
		2	3.55	0.0131	1.07	0.0020	2.14	0.9992
	15	1	3.08	0.0110	1.89	0.0018	1.83	0.9960
		2	3.67	0.0130	1.00	0.0020	2.20	0.9990
End batch	16	1	3.21	0.0134	1.39	0.0019	2.28	0.9992
		2	3.53	0.0133	1.04	0.0020	2.15	0.9995

Modeling summary report: T(3/1) vs. Strain%.
Test: RPA-FT, two samples; two runs; Temp. (°C): 100; Freq. (Hz): 0.5.

$$(TH_m + \alpha\gamma_0) \times B(C\gamma_0)^{D-1} \exp\left(-\lfloor (C\gamma_0)^D \rfloor\right) \qquad (2c)$$

As can be seen, at low strain, the nonlinear character is essentially controlled by the filler component, i.e., the $(TH_m + \alpha\gamma_0) \times B(C\gamma_0)^{D-1} \exp(-[(C\gamma_0)^D])$ term. At higher strain, the influence of the filler vanishes and harmonics variation is essentially controlled by the polymer component. The maximum of the filler component curve corresponds to a critical strain, i.e., γ_{c_2}, at which decreasing polymer-filler interaction would start to override the nonlinear character enhancement due to the dispersed phase. The actual maximum in the measured torque harmonics corresponds to the critical strain γ_c, obviously higher than γ_{c_2} owing to the high strain asymptote member. At sufficiently high strain, the effect of the filler is likely reduced to mere hydrodynamic influences. Using fit parameters of eq. (2),

easy mathematical handling yields the critical strains, and any remarkable features such as the maximum of the "bump."

The model expressed by eq. (2) applies to all harmonic versus strain curves, including the total torque harmonic content, but the third harmonic T(3/1) is the most intense one and consequently highlights the additional response of the filler. Therefore, only fit parameters for T(3/1) data will be discussed hereafter. Model parameters as obtained from results of the first test campaign (tests a and b) are given in Table II; similar values are obtained from results of the second test campaign (c and d).

Correlation coefficient are excellent, which means that the model fits well experimental data and that model parameters are offering a fine analysis of the nonlinear viscoelastic signature of the silica filled compound as it evolves along the mixing line. First we consider the low and middle strain behavior, indeed reflected by parameters of the filler
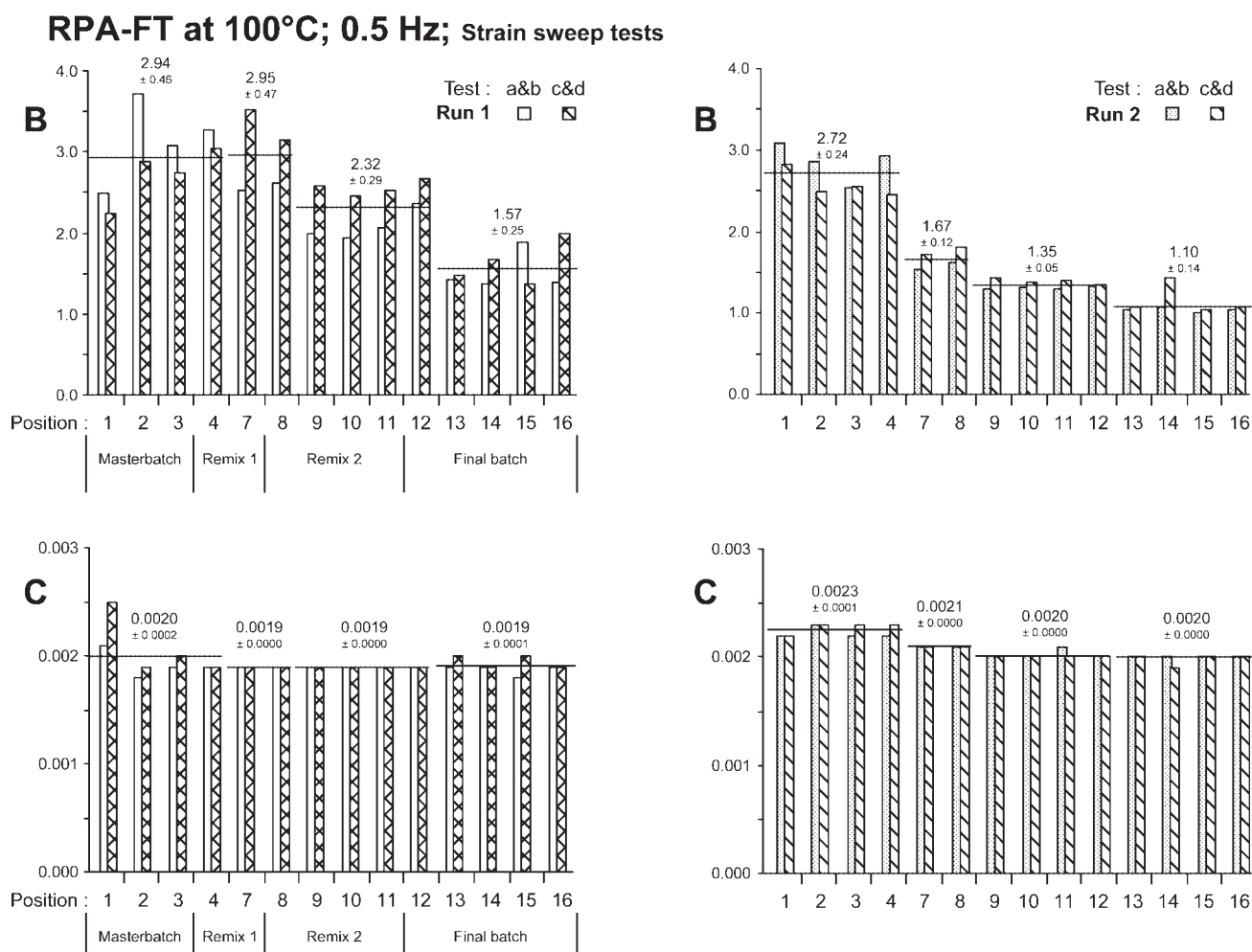

Figure 8 Modeling the variation of the relative third torque harmonic with strain amplitude; filler component of eq. (2); parameters B and C; note that results from the two test campaigns are given, i.e., four samples tested (a, b, c, and d); two successive strain sweep tests (runs 1 and 2).
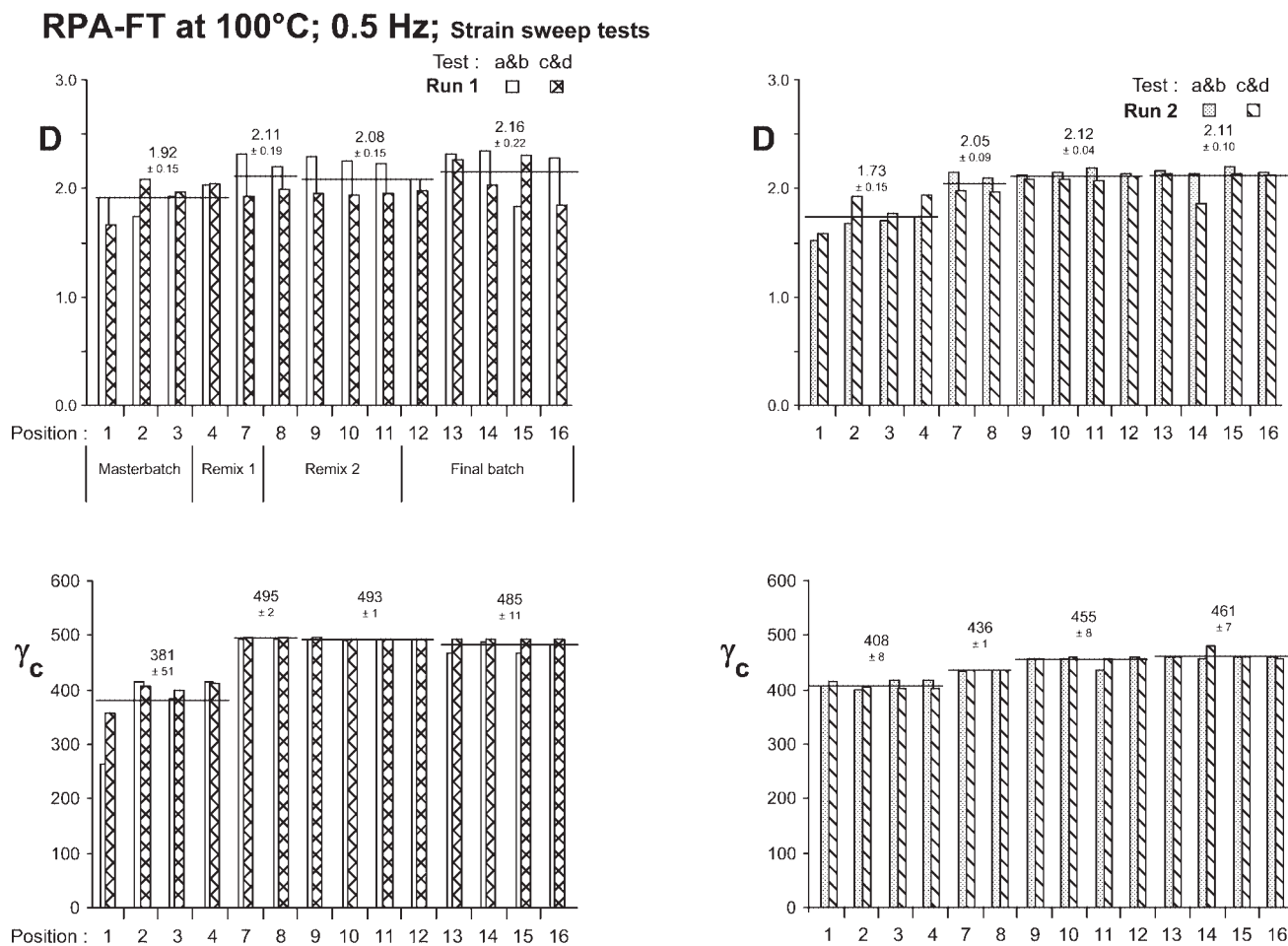
Figure 9 Modeling the variation of the relative third torque harmonic with strain amplitude; filler component of eq. (2); parameter D and critical strain γ_C; note that results from the two test campaigns are given, i.e., four samples tested (a, b, c, and d); two successive strain sweep tests (runs 1 and 2).

component [eq. 2(c)], i.e., B, C and D. Figure 8 shows how B and C vary along the mixing line; Figure 9 gives the variation of D, and the critical strain γ_C which is the position of the "bump."

As seen in Figure 8, parameter B exhibits significant sharp decreases that essentially correspond to intensive mixing steps. Scatter is large on run 1 data but relatively marginal on run 2 data. Sheeting-out and cooling on open mills have marginal effects and this observation suggests to average B values in four groups, as indicated in the figure. Parameter C tends also to decrease along the line but the variations are marginal.

In a previous study on various carbon black compounds,[6] parameter B was found to increase with higher filler level up to values of the order of 7–8 for excessive carbon black contents. Expectedly B tended to vanish for low filled or unfilled compounds, in agreement with model development. The level of carbon black rather than its structure was found to be the influential factor on B. Parameter C was also found to increase with carbon black level, from 0.001

for unfilled compounds up to 0.004 for highly loaded materials. Although the effects of carbon black and silica on rheological properties can hardly be compared, the values obtained along the silica mixing lines are fairly coherent with our previous findings. Indeed C can be considered as fixed when the masterbatch is dumped from the first mixer and remains in fact nearly constant along the line, in the 0.002 range. C value is thus likely directly related to the silica level and consequently expected to be relatively constant for a given compound, as indeed observed. One does expect B to be also related to filler level, but the previous study on carbon black filled materials was made with optimally dispersed compounds. In the study here, silica dispersion is of course improving along the line and is depending on the achievement of the silanisation process. In this respect parameter B is likely giving a direct insight on the efficiency of the silica compounding line.

Figure 9 shows that parameter D tends to increase along the mixing line towards a plateau value in the 2.1–2.2 range, again an observation fairly coherent
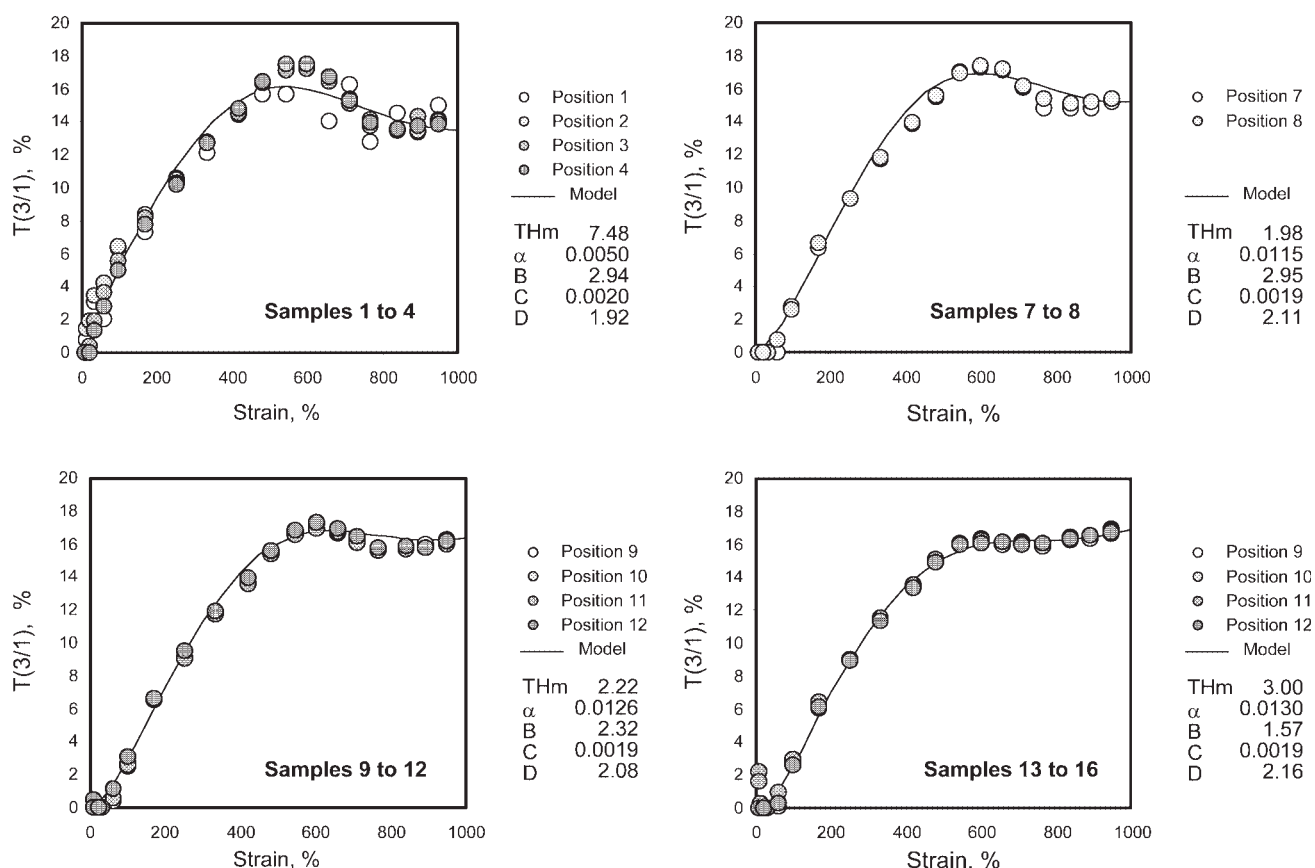
RPA at 100°C; 0.5 Hz; Run 1

Figure 10 Assembling nonlinear experimental signatures in four groups, with respect to the main steps of the mixing line; run 1 data from first test campaign; given model parameters are averaged values from the two test campaign results.

with reported results on carbon black filled compounds, for which D was found to decrease from a value approximately equal to 2.5 at zero or low filler level. The critical strain γ_c marks the position of the bump and is clearly evolving towards a constant value of around 460–480% strain amplitude at the end of the line, when the complex rubber-filler morphology is expectedly fully developed.

With respect to the process line described in Figure 1, it is fairly obvious that the material receives the largest levels of mixing energy when passing in the internal mixers. Sheeting-out and cooling on open mills concern relatively lower levels of energy, not measurable anyway. Consequently, one does expect significant changes in nonlinear viscoelastic properties to be noted only when comparing data gathered before and after internal (re)mixing. As shown by Figures 7 and 8, model parameters values can therefore be assembled in four groups, with respect to the four major steps of the process: masterbatching (samples 1 to 3), remix 1 (samples 4 and 7), remix 2 (samples 8–11) and final batch, involving curatives addition (samples 12–16). This grouping of parameter values is further validated by Figures 10 and 11 where experimental data from runs 1 and 2

respectively, are plotted in four groups, with "mean" model curves drawn by using average model parameters (as given in the Figures).

Figures 10 and 11 clearly show that the "bump," i.e., the singularity in the harmonic versus strain curve tends to smoothen along the mixing line. A possible interpretation of this observation would be that some physicochemical events, for instance the silica silanisation and dispersion, initiated in the earlier stages of the compounding process, need quite an extended time (and energy) to be completed. Indeed, if the silanisation is not complete, the rubber-filler interphase is not stabilized and, for instance, some silanol groups might remain available that would hinder the full dispersion of silica particles. The nonlinear viscoelastic response to increasing (dynamic) strain of a bulk compound with incomplete silanisation would therefore have two contributions, one from the rubber matrix plus one from the rubber-filler interphase region, until strain is large enough to dislocate the latter, thus leaving only the rubber matrix viscoelastic response. The fact that, at position 16, the singularity is still visible on run 1 data, but not on run 2 ones, supports this explanation.

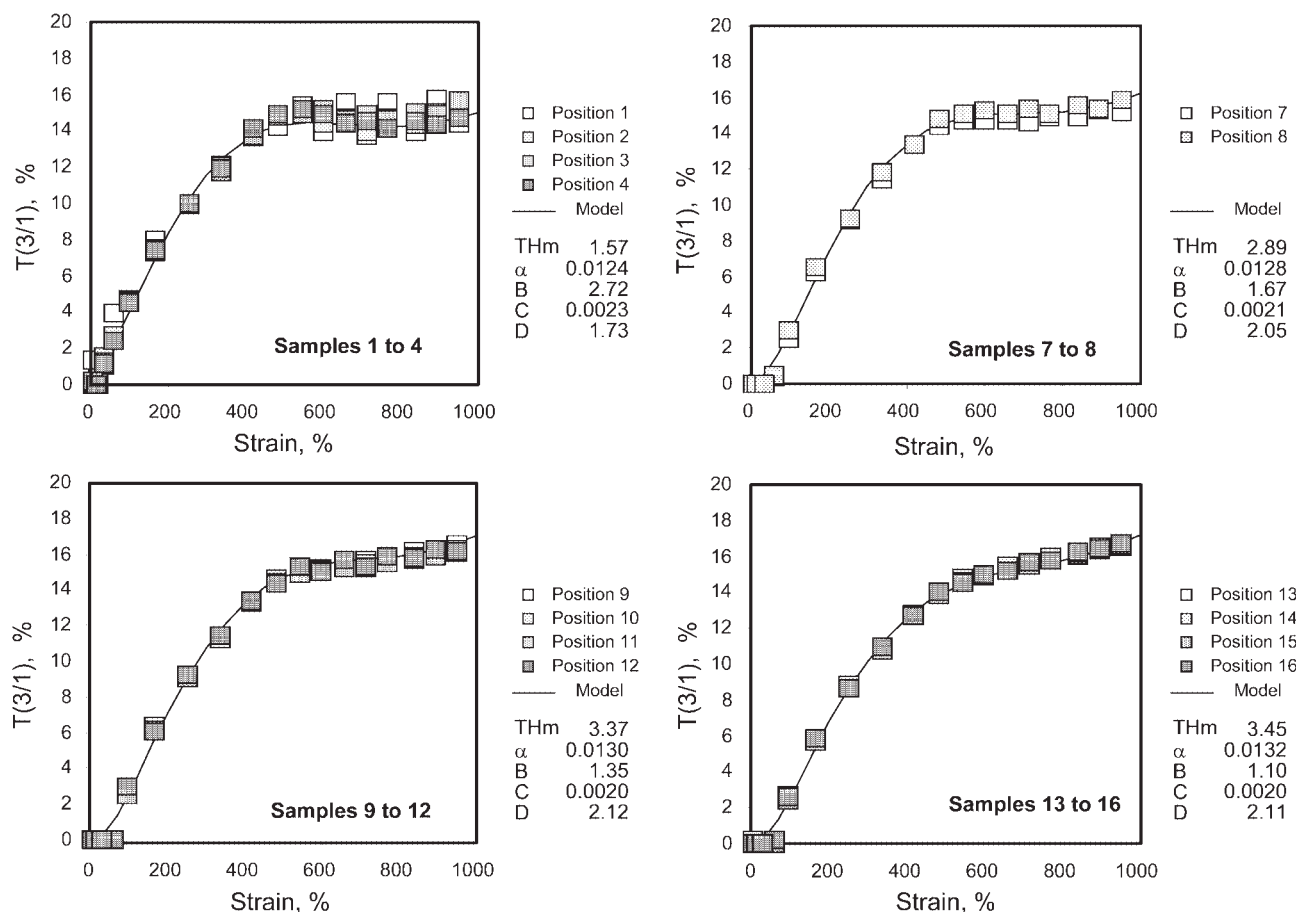**RPA at 100°C; 0.5 Hz; Run 2**

Figure 11 Assembling nonlinear experimental signatures in four groups, with respect to the main steps of the mixing line; run 2 data from first test campaign; given model parameters are averaged values from the two test campaign results.

Quarter cycle integrations

Figure 12 shows quarter cycle integration results at five key positions of the compounding line, in terms of Q1/Q2 ratio. As can be seen, Q1/Q2 ratio is always lower than 1, and exhibits large variations with increasing strain amplitude. Such a behavior is the "signature" of morphology-induced (intra) nonlinear viscoelasticity. The morphology that results from rubber–silica interactions is the controlling factor in the harmonic response of the compound. Consequently, a large scatter is observed at position 1 because the dumped masterbatch is still far from being well dispersed and, as previously shown, the silanisation process is also not yet completed. Passage on three open mills is however sufficient to improve the dispersion, as reflected by the considerably reduced scatter on data at position 4, but physicochemical events still occur in subsequent stages. How Q1/Q2 versus strain curves evolve along the line is quite interesting, because it further supports some of our arguments above regarding the still on-

going silanisation reactions up to the very end of the compounding process. Figure 12 shows indeed that Q1/Q2 versus γ curves pass through a minimum at around 600%, but the extent of this minimum decreases towards the end of the compounding line. At high (dynamic) strain amplitude, the final batch has a Q1/Q2 ratio which tends to go back to zero; in other terms, the torque signal is then nearly symmetrical, whereas not sinusoidal, as reflected by the important harmonic content. In (silane treated) silica filled systems, the widely accepted chemical scheme for the silanisation is a two-step process, with the second one, i.e., the strong interactions with the rubber network, occurring only during the vulcanization process, when sulfane groups are broken to form covalent bonds with rubber chains.[12,13] The first step concerns condensation reactions between silane's ethoxy functions and silanol groups present on the silica surface, with an alcohol as side product. It is obvious that optimal dispersion of silica particles is achieved when this primary reaction is complete and it is known that, providing mixing
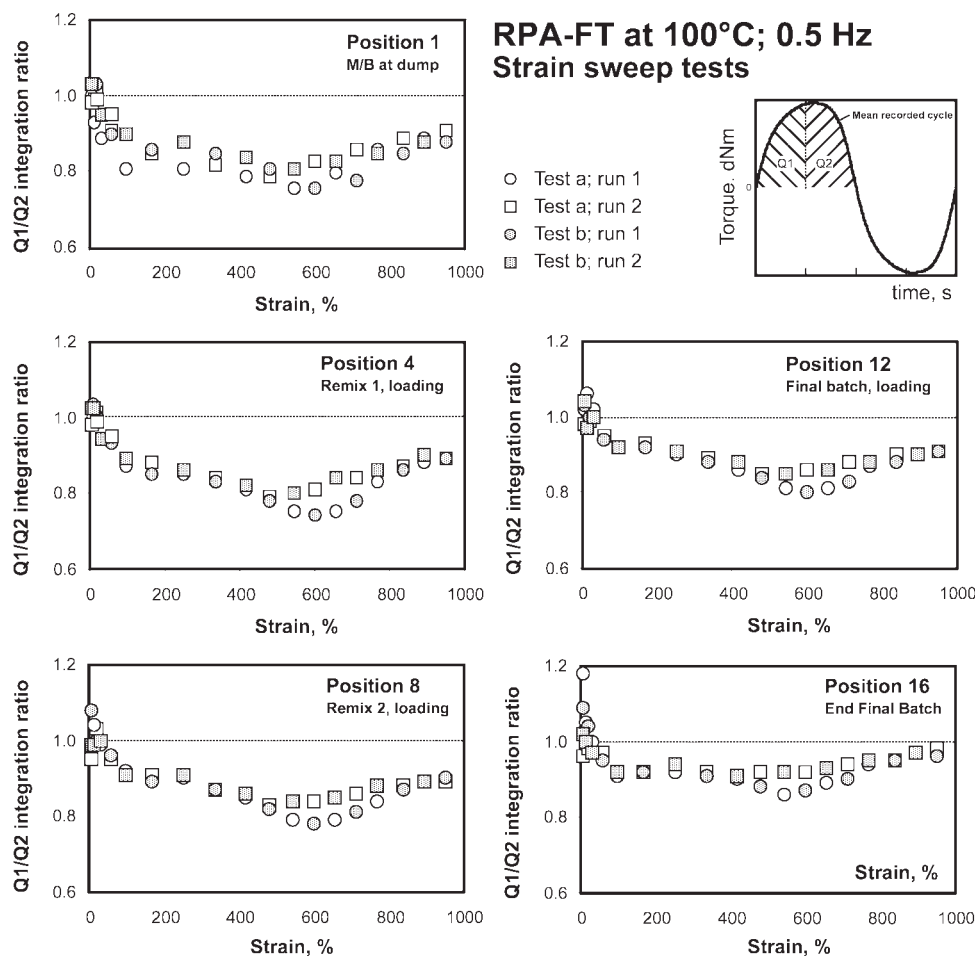
Figure 12 Mixing silica filled compound; quarter cycle integrations of (average) torque signal; variation of Q1/Q2 ratio along the compounding line; four samples tested at each position (a, b, c, and d); two successive strain sweep tests (runs 1 and 2).

temperature is kept below the activation level of crosslinking reaction, the second step does not occur during compounding operations. This suggests that the lower right graph in Figure 11 describes the nonlinear viscoelastic behavior of a heterogeneous system consisting of fully silanated silica particles, well dispersed in a rubber matrix but not forming a strong soft network, in sharp contrast with carbon black filled compounds.

CONCLUSIONS

Fourier Transform rheometry with closed cavity torsional dynamic rheometers is a powerful method to study the complex set of events that occur along mixing lines. Appropriate sample preparation and testing procedures are however needed for reproducible results. FT spectra contain all the information available through harmonic testing and a deep nonlinear viscoelastic analysis can made by considering the main torque component $T(\omega_1)$ and the relative harmonic torque components versus the strain amplitude. The main torque component gives access

to the complex modulus, whose variation with strain amplitude is adequately modeled with a simple four parameters equation. Fit model parameters provide quite relevant information on the variation of the viscoelastic character of silanated-silica rubber compounds.

Odd torque harmonics become significant as strain increases and therefore the variation of torque harmonics with strain amplitude can be considered as the nonlinear viscoelastic "signature" of tested materials, only available through Fourier Transform rheometry. In agreement with results on carbon black filled compounds, silica filled materials exhibit also a typical pattern, with a "bump" appearing in the 500% strain range, essentially on the third relative harmonic versus strain curves. An appropriate model equation, based on the hypothesis that such typical nonlinear viscoelastic signatures reflect the superimposition of two responses, one from the rubber matrix and one expressing the filler contribution, was used to fit experimental data. Fit parameters exhibit variation along the mixing line which are interpreted on one hand with respect to similar data on

carbon black filled materials and on the other hand with respect to current views on the *in situ* silanisation process.

Quarter cycle integration of (average) torque signal provides additional information to FT analysis, with namely results suggesting that the silanisation process is not finished when dumping the masterbatch but needs most of the compounding line to be completed.

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