

# Investigating the Nonlinear Viscoelastic Behavior of Rubber Materials Through Fourier Transform Rheometry

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Received 16 October 2003; accepted 14 April 2004

DOI 10.1002/app.20798

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Fourier transform rheometry was used to investigate the nonlinear viscoelastic behavior of a series of gum polybutadiene and styrene–butadiene rubbers. A commercial torsional rheometer [the rubber process analyzer (RPA<sup>®</sup>, Alpha Technologies)] was suitably modified for capturing strain and torque signals, using appropriate software developed in Lab View<sup>®</sup> (National Instruments). Proprietary programs, written in MathCad<sup>®</sup> (MathSoft Inc.), were used to perform Fourier transform (FT) calculations and other data treatments. Results showed that FT rheometry provides not only the same information as standard dynamic testing in the linear region, although with a better accuracy, but gives valuable information about the nonlinear behavior of materials. Using a four-parameter equation to model the

variation of the relative 3rd-harmonic component with strain amplitude, it was found that the strain sensitivity of the materials was adequately quantified, with results apparently consistent with their processing shear sensitivity. The only material parameters that were found to significantly affect the strain sensitivity are the chemical nature of the elastomers (i.e., polybutadiene versus styrene–butadiene rubber) and the molecular weight. No clear effect of the microstructure was seen, however, likely because the sampling was not discriminating enough in this respect. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 90–106, 2005

**Key words:** Elastomers; rheology; nonlinear viscoelasticity; Fourier transform rheometry; structure–property relations

## INTRODUCTION

Fourier transform rheometry is a new test technique that allows both the linear and the nonlinear viscoelastic domains of polymer materials' behavior to be accurately investigated. No commercial equipment is readily available, although any instrument can be easily modified to capture the full strain and torque signals generated when submitting samples to harmonic deformations at fixed frequency and temperature. Fourier transform (FT) calculation techniques are applied to captured signals to resolve them in their main component and other harmonics, if any. Contrary to standard dynamic testing methods, whose validity in extracting the elastic and viscous components from the (measured) complex torque is limited to the linear viscoelastic range, Fourier transform rheometry provides valid results, whatever the response of the tested material, even in the far nonlinear range.

Because of their high viscosity and stiffness, rubber materials need special instruments for rheometrical testing. Consequently, a commercial torsional rheometer—the rubber process analyzer (RPA<sup>®</sup>; Alpha Technologies, Swindon, UK)—was suitably modified for capturing strain and torque signals, through appropri-

ate software developed using LabVIEW<sup>®</sup> (National Instruments, Austin, TX). Details of the modification were previously reported,<sup>1</sup> as well as a description of the measuring technique.<sup>2</sup> Proprietary data handling programs, written in MathCad<sup>®</sup> (MathSoft Inc., Cambridge, MA), were used to perform Fourier transform calculations and other data treatments.

The aim of the present study was to further illustrate the capabilities of this new rheometrical technique by presenting experimental data obtained on a series of well-characterized gum elastomers.

## EXPERIMENTAL

### Test materials

Several polybutadiene rubbers (BRs) and styrene–butadiene rubbers (SBRs) with various macromolecular and structural characteristics were selected to consider a broad spectrum of viscoelastic nonlinear behaviors. Description, coding, and characteristics of samples are given in Table I.

### Test protocols for strain sweep experiments

Samples for RPA testing were prepared as follows: out of around 2-cm thick slices, pieces of circular cross section were cut with an 18-mm diameter die. Each sample was weighed and, if necessary, adjusted to maintain its weight within  $3.05 \pm 0.4$  g.

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**TABLE I**  
**Polybutadienes (BR) and Styrene-Butadiene Rubbers (SBR) Samples**

Sample description	Coding	Microstructure			$M_w, \times 1000$ (g/mol)	MWD	Sample origin	Source of data
		<i>cis</i> -1,4 (%)	<i>trans</i> -1,4 (%)	Vinyl-1,2 (%)				
Linear BR (broad MWD)	LBRBR	96	3	1	440	3.5	— <sup>a</sup>	— <sup>a</sup>
Linear BR (narrow MWD)	LBRNA	96	3	1	350	2.3	— <sup>a</sup>	— <sup>a</sup>
Branched BR ( $g = 0.95$ ) <sup>b</sup>	BBR92	92	4	4	350	(2.6)	— <sup>a</sup>	— <sup>a</sup>
Branched BR ( $g = 0.86$ ) <sup>b</sup>	BBR96	96	3	1	340	(2.6)	— <sup>a</sup>	— <sup>a</sup>
High- <i>cis</i> BR (NeoCis BR40)	BRN40	97	3	1	450	3.2	— <sup>c</sup>	— <sup>d</sup>
Linear SBR <sup>e</sup>	LNSBR	18	17	65	520	2	— <sup>a</sup>	— <sup>a</sup>
Branched SBR <sup>e</sup> ( $g = 0.95$ ) <sup>b</sup>	BCSBR	20	18	63	580	(2.5)	— <sup>a</sup>	— <sup>a</sup>
Star SBR <sup>e</sup> ( $g = 0.79-0.91$ ) <sup>b,f</sup>	STSBR	20	15	65	750	1.2	— <sup>a</sup>	— <sup>a</sup>

<sup>a</sup> Polimeri, Italy (received 12/2002); microstructure measured by Infrared spectroscopy.

<sup>b</sup> Branching index, measured by MALLS.

<sup>c</sup> Enichem, France (received 10/2001).

<sup>d</sup> Univ. P. & M. Curie (Paris 6); microstructure measured by <sup>13</sup>C- NMR.

<sup>e</sup> 25% styrene.

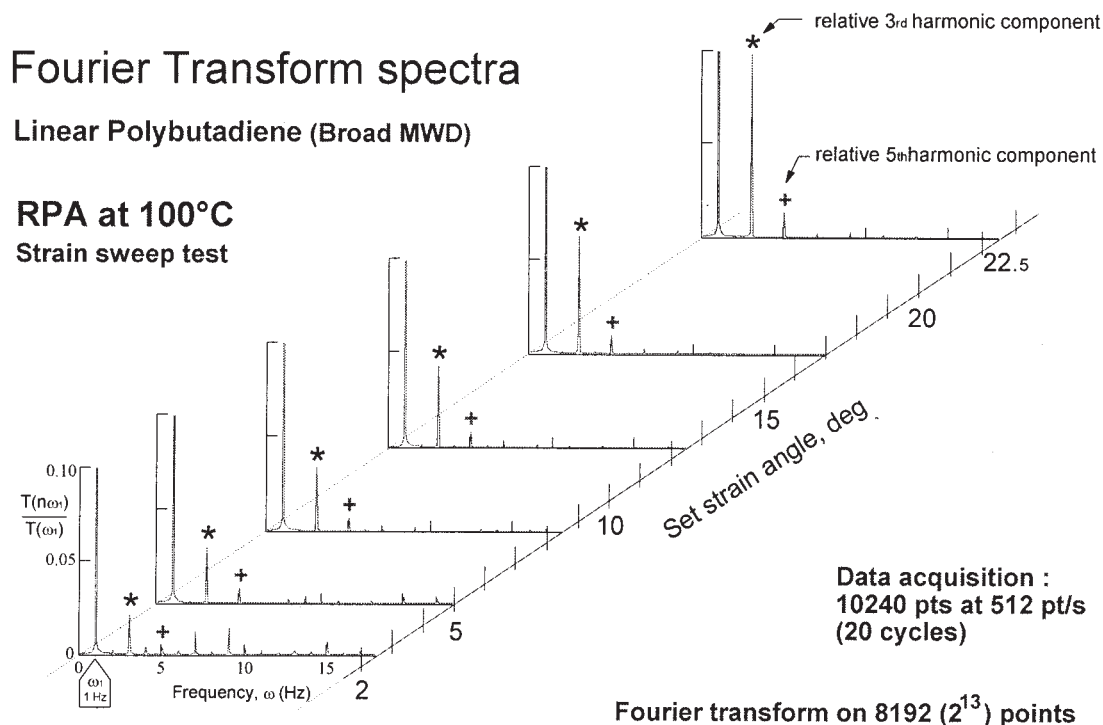
<sup>f</sup> 90% trichain.

Strain sweep tests were performed with the RPA, according to protocols given in Table II. Each protocol describes 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, using protocols named “Ssweep\_1Hz\_A” and “Ssweep\_1Hz\_B” such that, through inversion of the

strain sequences (i.e., run 1 and run 2), sample fatigue effects would be detected, if any. At each strain sweep step, the data acquisition for Fourier transform treatment was made to record 10,240 points at the rate of 512 points/s. Twenty cycles were consequently recorded at each strain step, with the immediate requirement that the RPA was set to apply a sufficient num-

**TABLE II**  
**RPA Strain Sweep Test Protocols**

Test protocol Ssweep_1Hz_A			Test protocol Ssweep_1Hz_B		
RPA test conditions Temp (°C): 100 Freq. (Hz): 1			PA test conditions Temp (°C): 100 Freq. (Hz): 1		
Sample conditioning Preheating: 3 min, at rest Fixing: 30 s; 1 Hz; 0.05 deg			Sample conditioning Preheating: 3 min, at rest Fixing: 30 s; 1 Hz; 0.05 deg		
Strain sweep (run 1)		Strain sweep (run 2)	Strain sweep (run 1)		Strain sweep (run 2)
Strain deg	Dwell time	Strain deg	Strain deg	Dwell time	Strain deg
0.5	2 min, at rest	0.6	0.6	2 min, at rest	0.5
1.0		1.5	1.5		1.0
2.5		3.5	3.5		2.5
5.0		6.7	6.7		5.0
8.5		10.0	10.0		8.5
12.0		14.5	14.5		12.0
17.0		20.0	20.0		17.0
22.5		25.0	25.0		22.5
27.5		30.0	30.0		27.5
31.5		33.0	33.0		31.5



**Figure 1** Typical Fourier transform spectra obtained when testing a linear polybutadiene at 1 Hz. The magnitude of the odd harmonics, relative to the excitation frequency, increases with the strain amplitude.

ber of cycles (i.e., 40 cycles; the so-called stability condition) for the steady harmonic regime to be reached. The data acquisition was activated as soon as the RPA test-monitoring screen had informed the operator that the set strain was reached and apparently stable. With the protocols described in Table II, an experiment lasted some 23 min per sample. Strain and torque signals were analyzed by Fourier transform according to the data treatment technique described below.

#### Fourier transform data treatment

The RPA was modified in such a manner that both the strain and torque signals were readily captured and made available as data files of actual harmonic strain and stress readings versus time. The PC-card used to capture the data had a resolution of 16 bits with a maximum sampling rate of around 205K samples/s. The instrument was handled as follows: first, the actual test conditions in terms of temperature, frequency, and strain angle were selected through built-in capabilities, then a sample was positioned on the lower die and the cavity was closed. The test was started and the data acquisition system was manually activated to record the selected number of data points, with respect to the acquisition parameters used.

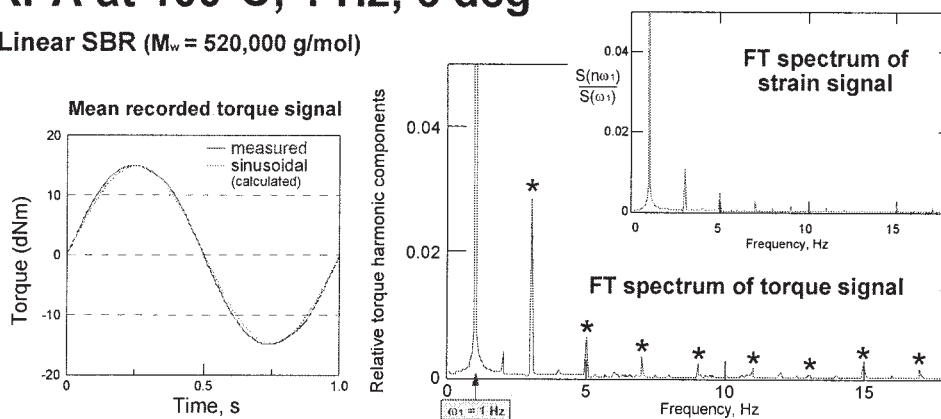
The size of the data file is an obvious aspect in selecting the optimum number of acquired data points

but not the most important one. First, a steady harmonic regime must be reached before a set of data points suitable for FT is obtained. Indeed, because of instrumental limits (i.e., mechanics, electronics, etc.) there are always startup transients in the input strain, which are causing some aperiodicity in the measured stress signal, at the start of any dynamic test. Several cycles are consequently needed before the initial transients become negligible. Second, most common fast Fourier transform algorithms require  $2^n$  data points, and the value of  $n$  is a compromise between the number of necessary acquired data for optimal signal-to-noise (S/N) ratio and the size of the data file (for instance, a 3 columns  $\times$  10,000 rows file corresponds to some 300 kilo-octet). By experience,  $n = 12$  (i.e., 4096 data points) was found to be a satisfactory minimum, providing that such points correspond to the steady harmonic response of the material.<sup>2</sup> However, when testing pure elastomers at 1 Hz, the steady harmonic regime is generally quickly reached, which allows use of the last 8096 points (i.e.,  $n = 13$ ) of the 10,240 set collected during each strain step, thus obtaining an excellent S/N ratio, as illustrated in Figure 1.

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 the test frequency) and the relative magnitudes (in %) of the odd-harmonic components [i.e.,  $I(n \times \omega_1)/I(\omega_1)$ ]. [Note

## RPA at 100°C; 1 Hz; 5 deg

Linear SBR ( $M_w = 520,000$  g/mol)



Fourier transform spectrum; odd harmonic components analysis

Nr pts	Freq. resol	Main freq.	3 <sup>rd</sup> harm.	5 <sup>th</sup> harm.	7 <sup>th</sup> harm.	9 <sup>th</sup> harm.	11 <sup>th</sup> harm.	13 <sup>th</sup> harm.	15 <sup>th</sup> harm.
$t_{tot}$	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) %	S(9/1) %	S(11/1) %	S(13/1) %	S(15/1) %
8192	0.063	1	3	5	7	9	11	13	15
15.0	512	693.03	2.845	0.641	0.344	0.203	0.150	0.024	0.210
		227.55	1.065	0.490	0.246	0.163	0.104	0.023	0.123

**Figure 2** Fourier transform analysis of a 5° dynamic strain experiment at 1 Hz on a linear styrene-butadiene rubber. The mean recorded torque signal (averaged out of 20 cycles) is shown in comparison with a pure sinusoidal signal of equal amplitude. FT spectra of both the strain and torque signal are shown as well as the results of the analysis in terms of harmonic components.

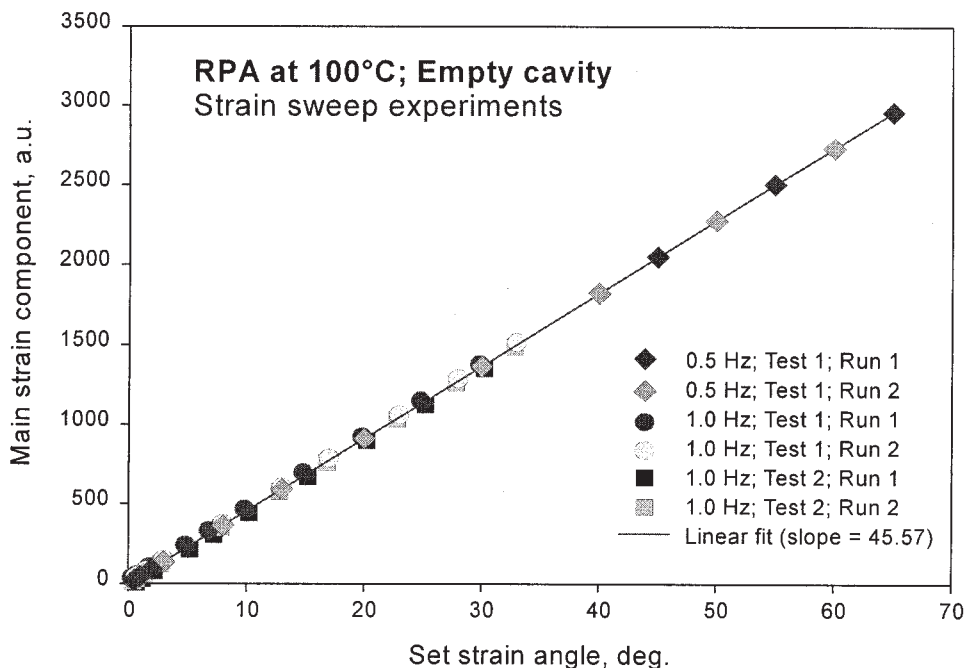
that in this article  $I(n\omega_1)/I(\omega_1)$  or the abridged form  $I(n/I)$ , is used to describe the  $n$ th relative harmonic component of any harmonic signal;  $S(n\omega_1)/S(\omega_1)$  or  $S(n/1)$  specifically means that a strain signal is considered;  $T(n\omega_1)/T(\omega_1)$  or  $T(n/1)$  is used for the torque signal.] The number of data points used, the frequency resolution (Hz), the acquisition time (s) and the sampling rate (point/s) are also provided. Figure 2 shows the single FT spectrum obtained by analyzing the last 8192 points of the signals recorded when submitting a linear SBR sample to 5 deg dynamic strain at 1 Hz. The results of the odd-harmonic components analysis are displayed in the inserted table.

### Documenting harmonic strain quality

Ideal dynamic testing implies that a perfect sinusoidal deformation at controlled frequency and strain is applied on the test material. With viscoelastic fluids, most dynamic methods consist in drag flow experiments, in the sense that the (harmonic) probing of the material occurs by means of a vibrating rigid body, for instance, the cone in a cone-and-plate device, or the lower die in the RPA. Modern instruments make use of high-precision motors, operated and monitored through quite a complex electronic system, generally

patented, with very little, if any, details disclosed by the manufacturer. Whatever the system is, there are always technical limits in accurately producing any harmonic mechanical motion and, with respect to dynamic testing, other difficulties arise depending on the method used to transfer the harmonic mechanical displacement to the material under testing. The accuracy of the harmonic displacement of the vibrating body, of course, depends on system design and manufacturing care, but because no easy facility is provided to check it, the quality of the applied signal is often taken for granted by operators. Fast Fourier transform of the strain (i.e., applied) signal allows this aspect to be easily documented. Would the applied strain be of perfect quality, no (significant) harmonics should be found when performing FT analysis on recorded strain cycles.

A series of strain signals were thus captured by running the empty cavity of the RPA through strain sweep sequences either at 1.0 or at 0.5 Hz frequency. Depending on the frequency, there are limits in maximum strain angle, for instance, up to 33 deg ( $\approx 461\%$ ) at 1.0 Hz and about 65 deg ( $\approx 908\%$ ) at 0.5 Hz. No significant torque signal was obtained, of course. For each test condition, 10,240 points were acquired and the last 8192 points ( $=2^{13}$ ) were used to extract the



**Figure 3** Fourier transform analysis of strain sweep experiments when the test cavity is empty. The main component of the strain signal at the excitation frequency is strictly proportional to the set strain angle. Note that data points at 1.0 Hz have been slightly displaced from their exact position to make them appear below the 0.5 Hz data.

Fourier transform spectra of the harmonic motion of the lower die. As expected, a linear relationship was observed between the set strain angle and the main strain component (in arbitrary units) revealed by FT analysis (Fig. 3), and no influence of the frequency was noted. Linear regression yields a straight line of slope 45.57, which passes through zero.

FT analysis revealed relatively significant (i.e., larger than noise) odd-harmonics components, where the 3rd harmonic is obviously the larger one. However, as shown in Figure 4, the relative 3rd-harmonic component of strain signal decreases as the strain amplitude increases, and is below 1% of the main component when the strain angle is higher than 1.3–1.5 deg. Data obtained at 0.5 or 1.0 Hz superimpose well and a simple three-parameter hyperbolic decay equation was found adequate to model this effect, that is

$$S(3/1) = a + \frac{bc}{c + \gamma} \quad (1)$$

where  $\gamma$  is the strain angle and  $a$ ,  $b$ , and  $c$  are fit parameters. The curve in Figure 4 was drawn with  $a = 0.094$ ,  $b = 9.068$ , and  $c = 0.148$  ( $r^2 = 0.97$ ). The (hypothetical) zero strain component equal to 9.16%, which can be calculated using these parameters, obviously has no physical meaning, but demonstrates only that the lower the strain angle, the poorer the quality of the applied strain signal. Equation (1) allows calcu-

lating that, for the 3rd-relative harmonic strain component to be below 1% of the main signal component, the strain angle has to be higher than 1.33 deg (i.e., >18.5% deformation).

In developing an experimental setup for FT rheometry, with a commercial cone-and-plate rheometer (ARES®; Rheometric Scientific, Piscataway, NJ), Wilhelm<sup>3</sup> found a slight nonlinear contribution from the instrument in the  $10^{-3}$  to  $10^{-4}$  range, relative to the response at the excitation frequency. In another publication,<sup>4</sup> he also reported that the shear geometry, either cone-and-plate or parallel plates, affects the degree of nonlinear behavior as characterized by the  $T(3\omega_1)/T(\omega_1)$  ratio. Similar geometrical effects are expected with the RPA, likely enhanced because measurements are made in a closed cavity in which the material is maintained under pressure. Because our approach consists in simultaneously analyzing the strain (input) and the torque (output) signals by Fourier transform, we have the capability of probing the quality of the strain signal when the test cavity is fully loaded. Figure 5 shows, for instance, how the  $S(3\omega_1)/S(\omega_1)$  ratio varies with strain angle when performing strain sweep tests on several polybutadiene and SBR samples. Although the chemical nature of the tested gum seems to have a slight effect (i.e., at equal strain angle, the strain harmonics'/amplitude is slightly higher with polybutadiene), the essential results are (1) that the quality of the strain signal improves as the applied deformation increases and (2) that the strain

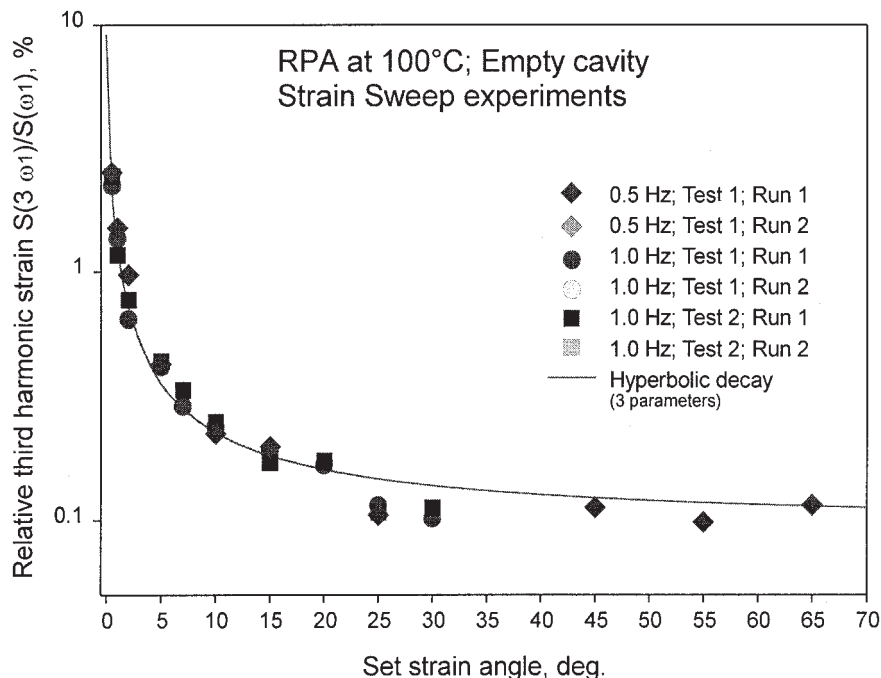


Figure 4 Relative third-harmonic component of the strain signal when the test cavity is empty as obtained through FT analysis: the larger the strain amplitude, the purer the strain signal. A hyperbolic decay model provides a good fit to the experimental data.

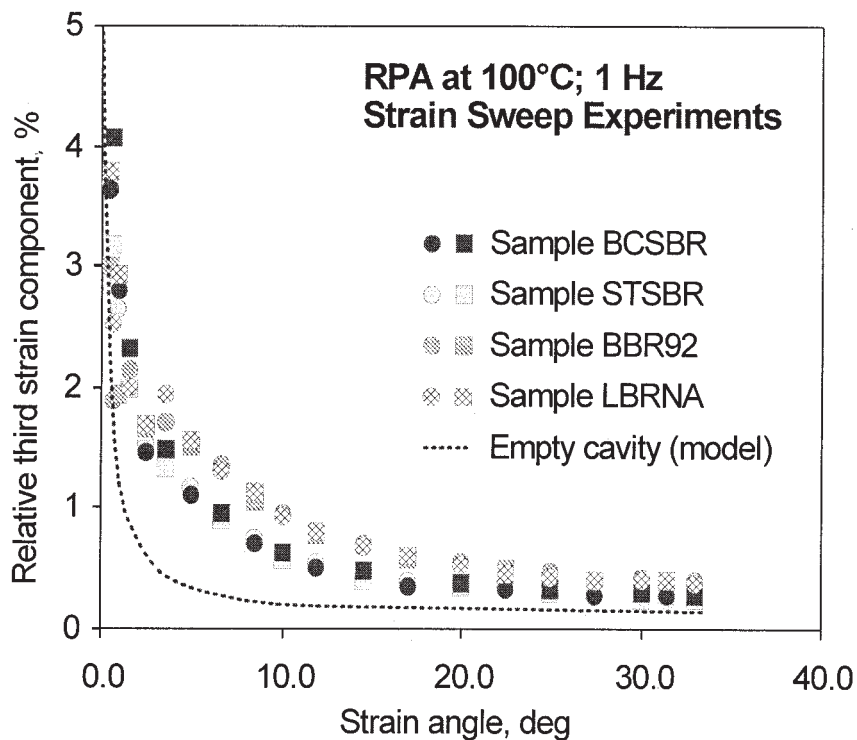


Figure 5 Relative third-harmonic component of the strain signal with material in the test cavity as obtained through FT analysis: the larger the strain amplitude, the purer the strain signal. BCSBR is a branched SBR; STSBR is a star SBR, BBR92 is a 92% *cis*-1,4 branched polybutadiene; LBRNA is a 96% *cis*-1,4 linear polybutadiene with a narrow molecular weight distribution. The (modeled) data measured when the cavity is empty are shown for comparison.

signal quality is somewhat deteriorating when the test cavity is full. This latter aspect is clearly seen with respect to the decaying curve drawn from tests made with the cavity empty and eq. (1) described above. Data in Figure 5 show that, for the 3rd-relative harmonic strain component to be below 1% of the excitation signal component, the strain angle must be higher than 5 deg ( $\approx 70\%$  deformation) with gum SBRs and 10 deg ( $\approx 140\%$  deformation) with gum polybutadienes.

## RESULTS AND DISCUSSION

### Results on polybutadiene samples

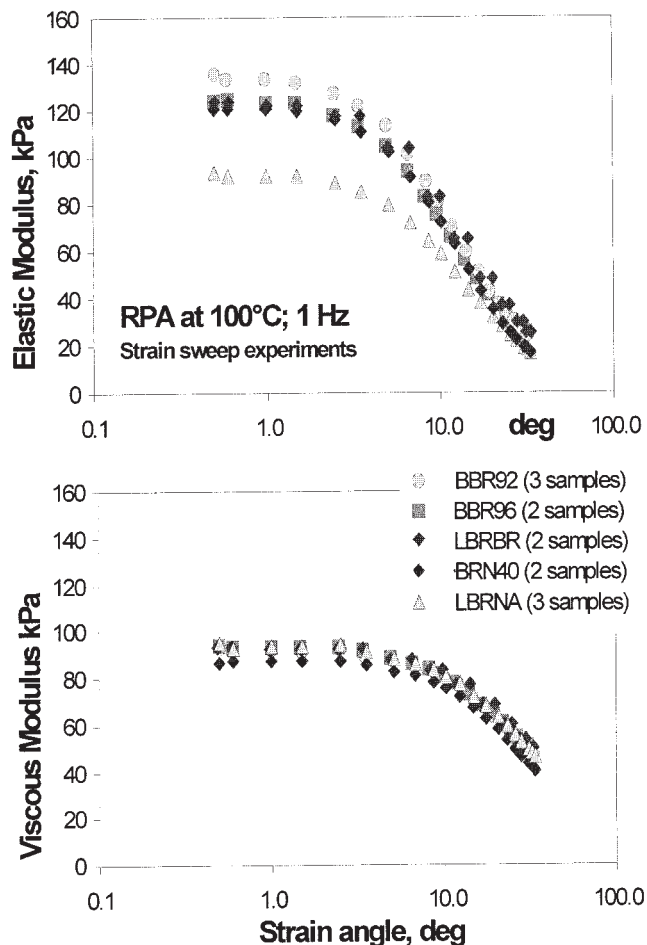
Standard RPA data treatment of strain sweep test results

Built-in capabilities of the RPA yield the elastic and viscous moduli according to a so-called standard data treatment, which is strictly valid only when both the strain and torque signals are perfectly sinusoidal, in principle when a material is tested in its linear viscoelastic domain. A traditional method to assess the extent of the linear region consists in performing strain sweep experiments; so long as dynamic moduli remain independent of the strain amplitude, the material is said to exhibit linear viscoelastic behavior. Figure 6 shows elastic and viscous moduli variations with strain angle, as measured on polybutadiene samples. As can be seen, the linear viscoelastic domain appears limited to around 2 deg ( $\approx 28\%$ ) with respect to  $G'$  and around 3 deg ( $\approx 42\%$ ) with respect to  $G''$ . Averaged  $G'$  and  $G''$  moduli were calculated from the respective linear regions (Table III).

No significant difference can be detected in terms of viscous modulus between the five polybutadiene samples. The highest elastic modulus is exhibited by the 92% *cis*-1,4 branched polybutadiene (BBR92) and the lowest  $G'$  by the linear material with a narrow molecular weight distribution (LBRNA). No significant difference in  $G'$  is seen between the three other samples (BBR96, LBRBR, and BRN40).

### Fourier transform results

According to the calculation technique described earlier, Fourier transform was performed on all signals recorded during strain sweep tests with the data acquisition system. FT spectra were obtained from which the magnitude (in arbitrary units) of the main torque component (i.e., at 1 Hz), the test frequency, and the relative odd-harmonic components [i.e., the ratio  $T(n\omega_1)/T(\omega_1)$ , in %, where  $n = 3, 5, 7 \dots$ ] were extracted. Tests were at least repeated, and even performed three times (three samples) with two materials (BBR92 and LBRNA).



**Figure 6** Dynamic moduli as obtained from RPA built-in capabilities on various polybutadiene samples; BBR92 is a 92% *cis*-1,4 branched polybutadiene; BBR96 is a 96% *cis*-1,4 branched polybutadiene; LBRBR is a 96% *cis*-1,4 linear polybutadiene with a broad MWD; BRN40 is the commercial NeoCis BR 40 polybutadiene (EniChem); LBRNA is a 96% *cis*-1,4 linear polybutadiene with a narrow molecular weight distribution.

Main torque components from FT treatment of strain sweep test results on the five polybutadiene samples are given in Table IV. Calculated standard deviations shows that fairly reproducible results are obtained, which underlines the accuracy of the testing technique, the quality (homogeneity) of the materials, and the absence of significant strain memory effects (i.e., the strain history associated with run 1 does not affect the results of run 2). Figure 7 shows how  $T(\omega_1)$  varies with the deformation. In the low-strain region, a linear variation is observed, as reflected by the linear fit of the first six data points (up to 3.5 deg,  $\approx 49\%$  deformation). Fit straight lines passed through zero and the slope depends on the elastomer, as shown in Table V.

The initial linear strain dependency of  $T(\omega_1)$  obviously reflects the linear viscoelastic behavior of the materials up to around 49% deformation and the

**TABLE III**  
**Linear Elastic and Viscous Moduli of Polybutadiene Samples (Strain Sweep Tests at 100°C and 1 Hz)**

Sample	Linear elastic modulus $G'$		Linear viscous modulus $G''$	
	Averaged <sup>a</sup> (kPa)	SD (kPa)	Averaged <sup>b</sup> (kPa)	SD (kPa)
Polybutadiene				
BBR92	133.67	1.73	92.30	0.75
BBR96	123.58	0.97	92.68	0.41
LBRBR	123.36	0.79	92.87	0.49
BRN40	120.94	0.33	87.04	0.12
LBRNA	93.00	0.75	93.70	0.85
Styrene-butadiene rubber				
LNSBR	137.90	0.84	49.71	0.66
BCSBR	127.23	0.70	48.20	1.14
STSBR	135.14	1.03	51.36	0.58

<sup>a</sup> Linear  $G''$  up to  $\gamma = 2$  deg for polybutadienes; up to  $\gamma = 1$  deg for SBR samples.

<sup>b</sup> Linear  $G''$  up to  $\gamma = 2.5$  deg for polybutadienes; up to  $\gamma = 12$  deg for SBR samples.

slopes obtained by linear regression are, as expected, commensurate with the dynamic data, as provided by the built-in capabilities of the instrument. However, as shown in Figure 8,  $T(\omega_1)$  versus deformation is likely to be a more pertinent linear datum than the standard  $G'$  or  $G''$ . Indeed there is no reason for the linear BR with a broad MWD (sample LBRBR) not to follow the linear relationship between the standard  $G''$  (or  $G'$ ) and the initial  $T(\omega_1)$  versus deformation slope, as exhibited by the other samples. The standard data treatment likely provides excessive dynamic moduli for LBRBR.

The Fourier transform approach allows an unambiguous limit of the linear viscoelastic behavior to be

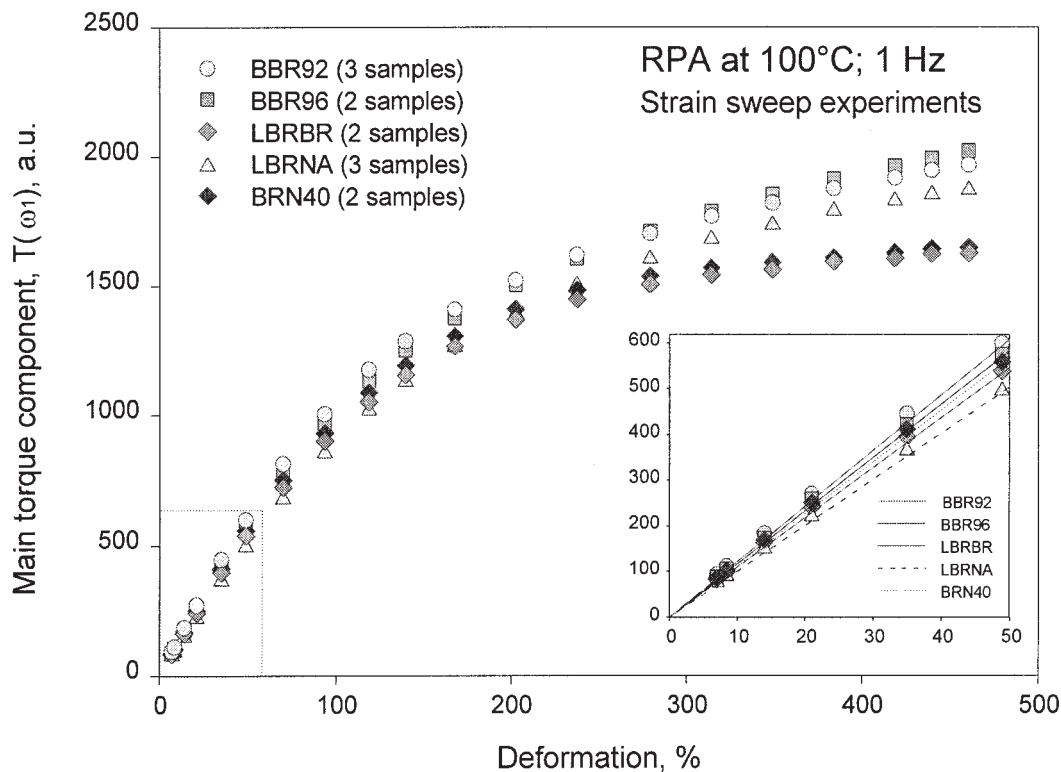
determined, by noting when the linear dependency of  $T(\omega_1)$  on the deformation ceases to be obtained. In addition, significant differences between materials are observed in the large-deformation region, which indicates that fine information must be sought in the analysis of the odd-harmonic components.

Through Fourier transform on 8192 ( $2^{13}$ ) data points, harmonics up to  $T(15\omega_1)$  or higher are detected but, above the 5th harmonic, they become too small to be unambiguously distinguished from the noise. The limit of the relative torque harmonic  $T(n\omega_1)/T(\omega_1)$  is expected to be equal to  $1/n$ , and  $T(3\omega_1)/T(\omega_1)$  is consequently the most intense contribution compared to that of all other harmonics. As shown in Figure 9 for

**TABLE IV**  
**Main Torque Components from Fourier Transform Analysis of Strain Sweep Experiments (100°C; 1 Hz) on Polybutadiene Elastomers**

Strain (deg)	Strain (%)	Mean $T(\omega_1)$ (a.u.)				
		BBR92	BBR96	LBRBR	LBRNA	BRN40
0.50	6.98	93.6 ± 1.6	88.5 ± 1.0	82.3 ± 2.2	75.9 ± 1.5	85.1 ± 2.2
0.60	8.38	110.8 ± 1.0	106.2 ± 0.9	98.3 ± 1.4	90.1 ± 0.4	102.0 ± 1.7
1.00	13.96	184.1 ± 2.2	174.0 ± 1.6	162.4 ± 3.1	149.5 ± 2.2	168.9 ± 3.3
1.50	20.94	270.4 ± 2.0	259.5 ± 2.5	241.1 ± 3.8	220.4 ± 0.8	250.4 ± 3.4
2.50	34.91	445.3 ± 3.7	421.5 ± 3.6	395.3 ± 5.3	364.6 ± 4.0	410.7 ± 7.3
3.50	48.87	600.2 ± 4.7	575.7 ± 6.9	537.9 ± 8.3	495.4 ± 2.5	558.0 ± 5.2
5.00	69.81	813.3 ± 4.0	774.2 ± 2.6	724.2 ± 5.6	679.3 ± 6.4	751.3 ± 10.8
6.70	93.55	1005.7 ± 5.0	968.9 ± 6.7	901.4 ± 12.0	855.0 ± 1.9	931.1 ± 6.2
8.50	118.68	1176.7 ± 3.5	1133.0 ± 0.0	1052.5 ± 6.4	1019.3 ± 9.1	1087.5 ± 12.0
10.00	139.63	1286.3 ± 4.0	1251.0 ± 8.5	1156.5 ± 7.8	1130.7 ± 0.6	1192.5 ± 4.9
12.00	167.55	1409.3 ± 3.5	1375.0 ± 2.8	1266.5 ± 3.5	1264.0 ± 9.6	1305.5 ± 7.8
14.50	202.46	1523.0 ± 4.6	1504.5 ± 13.4	1370.5 ± 3.5	1393.0 ± 1.0	1411.0 ± 1.4
17.00	237.36	1620.3 ± 5.7	1608.0 ± 1.4	1448.5 ± 3.5	1505.0 ± 10.6	1483.0 ± 2.8
20.00	279.25	1704.7 ± 6.7	1712.5 ± 19.1	1507.0 ± 7.1	1605.7 ± 1.5	1539.0 ± 2.8
22.50	314.16	1771.7 ± 4.5	1789.5 ± 2.1	1543.0 ± 15.6	1682.3 ± 9.3	1570.5 ± 10.6
25.00	349.07	1821.7 ± 6.0	1855.5 ± 19.1	1563.5 ± 6.4	1737.7 ± 2.1	1592.5 ± 3.5
27.50	383.97	1877.7 ± 4.5	1914.0 ± 1.4	1595.0 ± 19.8	1791.0 ± 5.2	1610.5 ± 0.7
30.00	418.88	1918.0 ± 6.0	1964.0 ± 14.1	1607.5 ± 9.2	1830.7 ± 1.2	1629.5 ± 4.9
31.50	439.82	1948.0 ± 5.3	1994.5 ± 3.5	1624.5 ± 13.4	1854.7 ± 4.5	1644.5 ± 2.1
33.00	460.77	1968.3 ± 3.5	2022.5 ± 12.0	1627.5 ± 10.6	1871.3 ± 1.2	1650.0 ± 5.7





**Figure 7** Main torque signal component from Fourier transform analysis on various polybutadienes. The insert is an enlargement of the linear region, which shows the perfect linear fit of experimental data; the slope of the strain line is commensurate with the linear elastic modulus. See legend of Figure 6 for sample coding.

the 92% *cis*-1,4 branched polybutadiene (sample BBR92), this is indeed the case, and similar figures are obtained with the other materials. The 3rd and the 5th relative harmonic components are clearly detected and, as expected, their intensity increases with the strain angle. At low strain angle, there is some scatter that is likely to reflect the deteriorating quality of strain signal as the deformation angle decreases, as previously discussed.

Relative 3rd-harmonic components at all strain angles tested are given in Table VI; mean values with their respective standard deviations show that the higher the strain angle, the better the reproducibility.

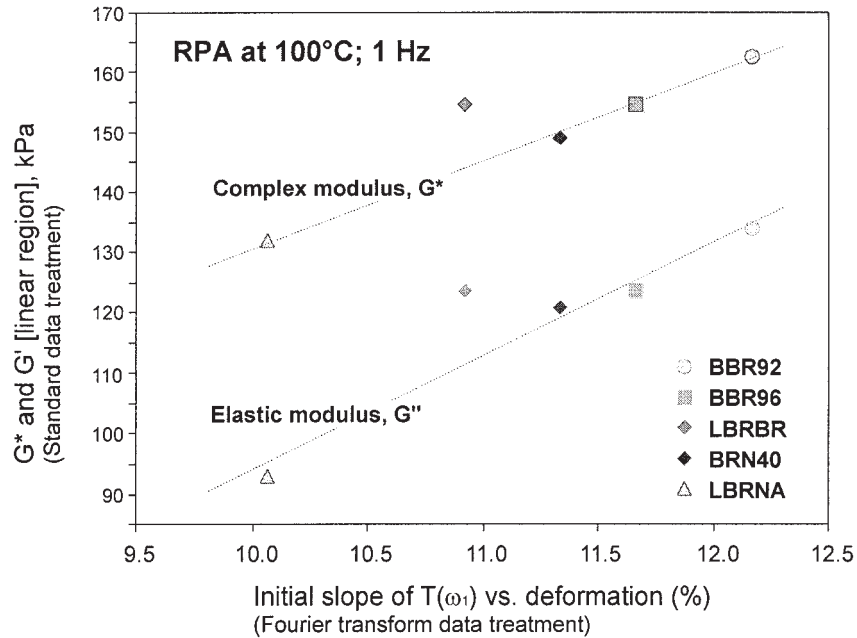
**TABLE V**  
**Mean Linear Dynamic Moduli (Standard Test Technique) Versus Main Torque Component (FT Rheometry) of Polybutadiene Samples**

Sample	Mean $G'$ (kPa)	Mean $G''$ (kPa)	$T(\omega_1)$ versus % deformation	
			Slope	$r^2$
BBR92	$133.7 \pm 1.7$	$92.3 \pm 0.8$	12.17	0.995
BBR96	$123.6 \pm 1.0$	$92.7 \pm 0.4$	11.66	0.996
LBRBR	$123.4 \pm 0.8$	$92.9 \pm 0.5$	10.92	0.997
LBRNA	$93.0 \pm 0.7$	$93.7 \pm 0.8$	10.07	0.997
BRN40	$120.9 \pm 0.3$	$87.0 \pm 0.1$	11.34	0.997

Figure 10 shows test results obtained on three samples of the 92% *cis*-1,4 polybutadiene (BBR92). Material homogeneity is excellent and no significant strain history effect is observed. As outlined in a previous publication,<sup>2</sup> the variation of the relative 3rd-harmonic component with the strain amplitude appears such, that an S-shape curve is generally observed, from a (scattered) plateau value at low strain up to a maximum at high strain. The insert is a magnification of the low strain data by using a logarithmic scale for the strain angle; there is a large scatter when the set deformation is lower than 14% ( $\approx 1$  deg). Providing low strain (scattered) data are discarded, a sigmoidal type of equation is appropriate to meet experimental observations; that is

$$T(3/1)_\gamma = T(3/1)_{\min} + [T(3/1)_{\max} - T(3/1)_{\min}] \times [1 - \exp(-b\gamma)]^c \quad (2)$$

where  $T(3/1)_{\min}$  and  $T(3/1)_{\max}$  are the limiting 3rd-harmonic components at very low and very high (infinite) strain, respectively;  $\gamma$  is the deformation (%);  $b$  and  $c$  are fit parameters. In using eq. (2) to model  $T(3/1)$  variation with strain, one may express the deformation (or strain)  $\gamma$  either in degree angle



**Figure 8** Comparison of dynamic data in the linear viscoelastic region, as provided either by the standard approach ( $G'$  and  $G^*$ ) or by Fourier transform rheometry. See legend of Figure 6 for sample coding.

or in %. Obviously all parameters remain the same except  $b$ , whose value depends on the unit for  $\gamma$ . The following equality applies for the conversion:

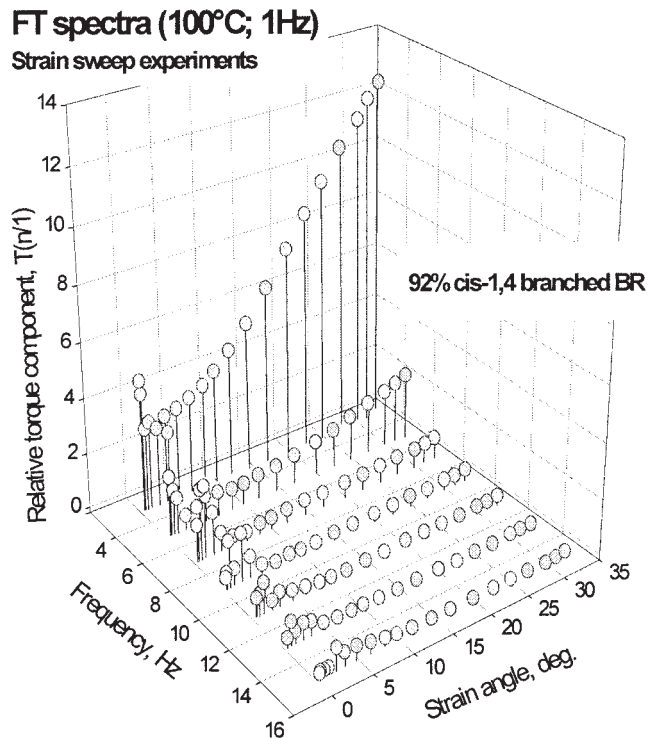
$$b(\gamma, \text{deg}) = \frac{180\alpha}{100\pi} \times b(\gamma, \%)$$

where  $\alpha = 0.125$  rad.

The line in Figure 10, calculated with  $T(3/1)_{\min} = 2.89$ ,  $T(3/1)_{\max} = 20.10$ ,  $b = 0.00384$ , and  $c = 3.13$ , fits the data perfectly ( $r^2 = 0.998$ ). Similar graphs were obtained with other test materials (Fig. 11) and the corresponding fit parameters are given in Table VII.

Two samples (BRN40 and LBRBR) are clearly more sensitive to strain amplitude than the other materials. NeoCis BR40 is a commercial material (EniChem, Novara, Italy) and Fourier transform data thus show this polymer is very similar to the linear BR with a broad MWD, as indeed suggested by molecular characteristics given in Table I. When compared with the other materials, these two samples have in common the broad molecular weight distribution (i.e.,  $>3.2$ ), although their microstructure and their  $M_w$  are similar. Strain amplitude sensitivity, as revealed by nonlinear dynamic testing and Fourier transform, is likely to be connected to shear sensitivity and it is well known that shear thinning (and processability) is affected by the molecular weight distribution. In this respect, the three other polybutadiene samples would be expected to be more difficult to process, with respect to their curves in Figure 11, where again the MWD is the most influential macromolecular characteristic.

The two parameters,  $b$  and  $c$ , in eq.(2) determine how the relative 3rd-harmonic component varies with the strain amplitude, but both  $b$  and  $c$  affect the shape on the curve in quite a complex manner. At constant  $b$ , the lower  $c$ , the smoother the transition from  $T(3/1)_{\min}$



**Figure 9** Fourier transform spectra of BBR92 polybutadiene, in terms of relative torque component  $T(n\omega_1)/T(\omega_1)$  versus frequency and strain angle. Significant variations of the relative third and fifth-harmonic components are observed as the deformation increases.

**TABLE VI**  
**Relative 3rd-Harmonic Components from Fourier Transform Analysis of Strain Sweep Experiments (100°C; 1 Hz) on Polybutadiene Elastomers**

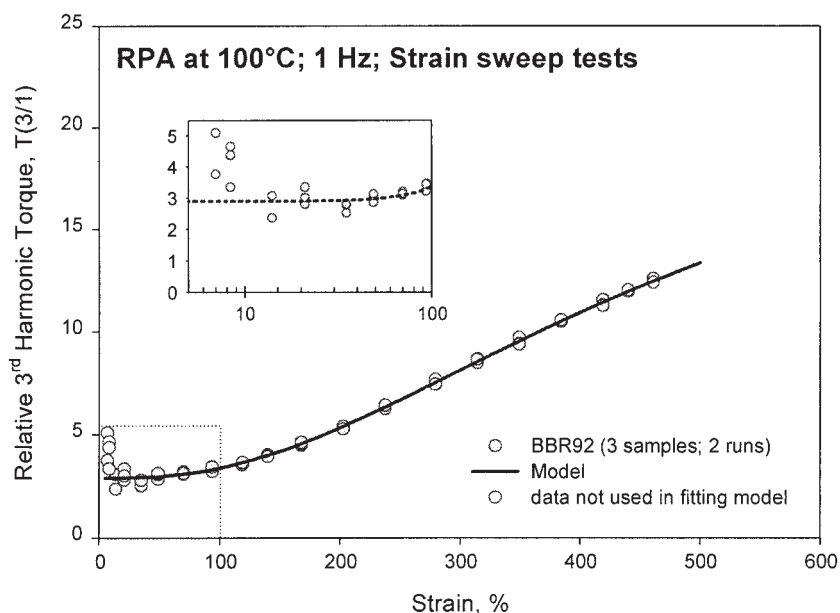
Strain (deg)	Strain (%)	Mean $T(3\omega_1)/T(\omega_1)$				
		BBR92	BBR96	LBRBR	LBRNA	BRN40
0.50	6.98	4.6 ± 0.8	3.7 ± 2.1	5.7 ± 2.6	6.0 ± 1.7	4.6 ± 1.2
0.60	8.38	4.1 ± 0.7	4.5 ± 2.5	4.2 ± 0.1	4.4 ± 0.3	3.7 ± 0.7
1.00	13.96	2.8 ± 0.4	3.0 ± 1.9	3.1 ± 1.2	4.2 ± 0.9	2.6 ± 0.4
1.50	20.94	3.0 ± 0.3	1.7 ± 1.0	2.1 ± 0.7	3.1 ± 0.3	2.1 ± 0.8
2.50	34.91	2.7 ± 0.2	3.0 ± 1.8	2.5 ± 0.5	2.7 ± 0.3	2.4 ± 0.4
3.50	48.87	3.0 ± 0.1	2.6 ± 1.4	2.9 ± 0.5	3.3 ± 0.3	2.6 ± 0.1
5.00	69.81	3.1 ± 0.1	3.1 ± 1.4	3.1 ± 0.1	3.1 ± 0.2	2.9 ± 0.1
6.70	93.55	3.4 ± 0.1	3.2 ± 1.2	3.1 ± 0.0	3.3 ± 0.1	3.2 ± 0.0
8.50	118.68	3.6 ± 0.1	3.5 ± 1.1	3.5 ± 0.1	3.4 ± 0.1	3.5 ± 0.1
10.00	139.63	4.0 ± 0.0	3.8 ± 0.9	3.9 ± 0.0	3.8 ± 0.0	4.0 ± 0.1
12.00	167.55	4.6 ± 0.1	4.3 ± 0.8	4.5 ± 0.2	4.2 ± 0.0	4.5 ± 0.3
14.50	202.46	5.3 ± 0.1	5.0 ± 0.7	5.4 ± 0.2	4.9 ± 0.0	5.6 ± 0.2
17.00	237.36	6.4 ± 0.1	5.7 ± 0.6	6.8 ± 0.7	5.7 ± 0.1	7.1 ± 0.8
20.00	279.25	7.5 ± 0.1	7.0 ± 0.6	8.7 ± 0.2	6.7 ± 0.1	9.3 ± 0.1
22.50	314.16	8.6 ± 0.1	7.7 ± 0.5	10.8 ± 1.3	7.7 ± 0.1	11.3 ± 1.1
25.00	349.07	9.5 ± 0.2	8.9 ± 0.5	12.8 ± 0.2	8.6 ± 0.0	13.4 ± 0.3
27.50	383.97	10.6 ± 0.0	9.6 ± 0.5	14.5 ± 1.3	9.6 ± 0.2	15.4 ± 0.7
30.00	418.88	11.4 ± 0.2	10.7 ± 0.5	16.3 ± 0.2	10.6 ± 0.1	17.1 ± 0.4
31.50	439.82	12.0 ± 0.0	11.0 ± 0.4	17.2 ± 0.7	11.3 ± 0.3	18.0 ± 0.4
33.00	460.77	12.5 ± 0.1	11.6 ± 0.4	18.3 ± 0.2	11.8 ± 0.2	19.1 ± 0.2

to  $T(3/1)_{\max}$ ; at constant  $c$ , the lower  $b$ , the longer the delay before  $T(3/1)$  starts to significantly increases with strain. In a sense, the parameter  $b$  could be viewed as describing the transition toward a strong nonlinear behavior, but no clear dependency of  $b$  (or  $c$ ) on microstructural features (e.g., *cis*-1,4 content) arises from the results reported here.

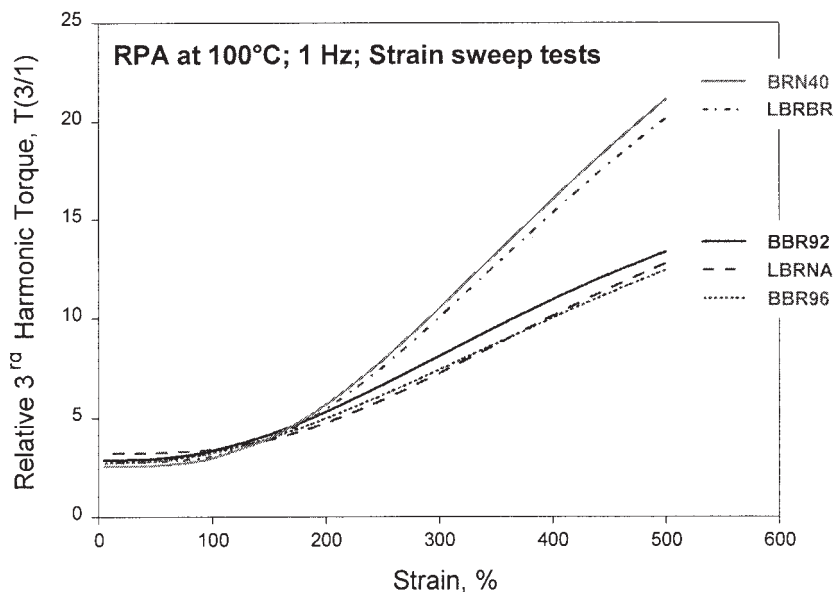
#### Results on styrene–butadiene rubber samples

Standard RPA data treatment of strain sweep test results

Figure 12 shows strain sweep experiments results on SBR samples, in terms of elastic and viscous moduli versus strain angle. As can be seen, the linear vis-



**Figure 10** Modeling the variation of  $T(3\omega_1)/T(\omega_1)$  with strain amplitude (here expressed in percentage deformation) of a 92% *cis*-1,4 polybutadiene. The insert is a magnification of the low strain region (by using a logarithmic scale), which shows that data obtained below 15% deformation ( $\approx 1^\circ$ ) are so scattered that they must be discarded in fitting the model.



**Figure 11** Variation of  $T(3\omega_1)/T(\omega_1)$  with deformation of polybutadiene samples, as modeled with eq. (1); two samples (BRN40 and LBRBR) are clearly exhibiting a stronger strain sensitivity. See legend of Figure 6 for sample coding.

coelastic domain appears limited to around 1 deg ( $\approx 14\%$ ) with respect to  $G'$ , and around 10 deg ( $\approx 140\%$ ) with respect to  $G''$ . Averaged  $G'$  and  $G''$  moduli, calculated from the respective linear regions (insert in Fig. 12 and Table VIII) show marginal differences between the three materials.

The linear viscoelastic behavior of the materials is best characterized by the initial linear strain dependency of  $T(\omega_1)$  on deformation, as derived from FT treatment of torque signal (Fig. 13). Slopes of  $T(\omega_1)$  versus  $\gamma$ , given in Table VIII, are proportional with the complex modulus, as provided by the built-in capabilities of the instrument. As expected, data for SBR materials fall exactly on the same line as that for polybutadiene samples (except LBRBR), as shown in Figure 14. A straight line, forced to pass through zero, provides good fit to such data ( $r^2 = 0.986$ ), to yield the following equality:  $G^* = 13.164 \times [T(\omega_1)/\gamma]$ . Figure 14 reinforces our previous comment that FT rheometry is

likely to give a more accurate assessment of linear dynamic moduli than the standard data treatment.

#### Fourier transform results

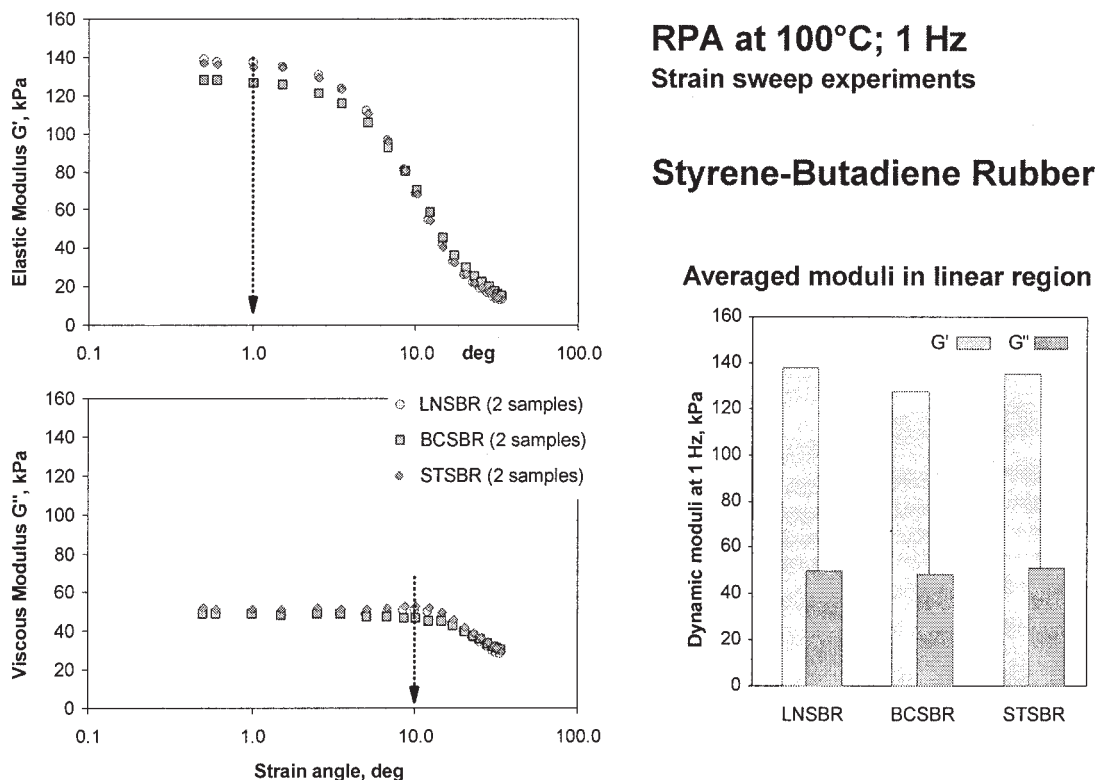
Essentially, the main signal components, as derived by Fourier transform, are very close in the linear region [i.e.,  $<50\%$  deformation (Fig. 13)]. However the slopes of fitted straight lines reveal that the branched SBR has a somewhat different behavior in the linear region (slopes are 11.13, 10.40, and 11.02 for LNSBR, BRSBR, and STSBR, respectively). Again, the main component appears more discriminating than the standard dynamic moduli (see Table IX).

Figure 15 shows typical Fourier transform spectra obtained on SBR materials (here, the linear polymer; other samples give qualitatively similar figures). Significant variations of the 3rd, the 5th, and the 7th relative harmonic components are seen, and the oc-

**TABLE VII**  
Effect of Strain Amplitude on 3rd-Harmonic Component; Fit Parameters Obtained by Nonlinear Regression of Eq. (2); Polybutadiene Tested at 100°C, 1 Hz

Parameter	Material				
	BBR92	BBR96	LBRBR	LBRNA	BRN40
$T(3/1)_{\min}$	2.89	2.75	2.78	3.24	2.57
$T(3/1)_{\max}$	20.10	22.10	33.65	20.49	36.92
$b^a$	$3.84 \times 10^{-3}$	$2.95 \times 10^{-3}$	$4.14 \times 10^{-3}$	$3.98 \times 10^{-3}$	$3.81 \times 10^{-3}$
$c$	3.13	2.66	4.24	4.03	3.81
$r^2$	0.998	0.994	0.993	0.987	0.996

<sup>a</sup> These values of  $b$  apply when the deformation  $\gamma$  is expressed in %; if  $\gamma$  is expressed in degree angle, all fit parameters are unchanged except  $b$ , for which the following conversion applies:  $b(\gamma, \text{deg}) \approx 0.07162 \times b(\gamma, \%)$ .



**Figure 12** Dynamic moduli as obtained from RPA built-in capabilities on three styrene-butadiene rubber samples (25% styrene); LNSBR is a linear polymer ( $M_w = 520,000$  g/mol); BCSBR is a branched polymer ( $M_w = 580,000$  g/mol); STSBR is a star-shaped polymer ( $M_w = 750,000$  g/mol).

currence of a plateau at high strain angle is clearly detected. When comparing Figures 9 and 14, one notes the substantial differences between polybutadienes and styrene-butadiene rubbers with respect to their nonlinear viscoelastic behavior. It is clear that SBRs are more sensitive to strain variation than polybutadienes, which would correspond well with its well-known easier processing. As a matter of fact, the latter is rarely used alone in rubber formulations, but blended with other elastomers (natural rubber or SBR essentially). Such observations obviously suggest that a relationship should exist between the shear thinning behavior (as considered, for instance, in the shear viscosity function) and the

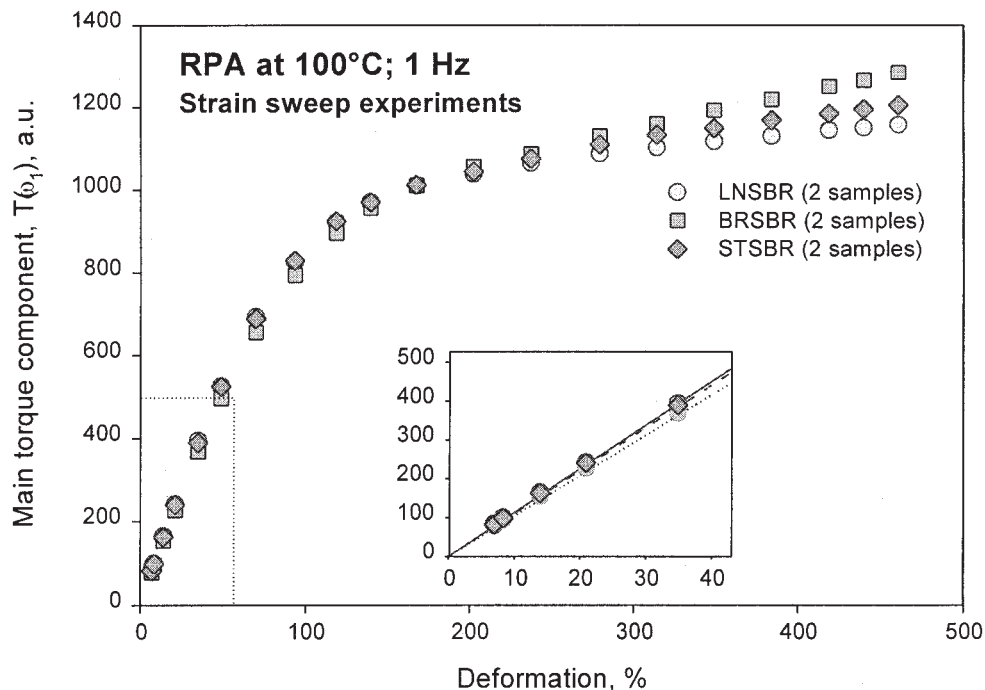
strain sensitivity, as quantified by Fourier transform rheometry.

Modeling the variation of the 3rd relative harmonic components of the torque signal is made with eq. (2). A comparison between experimental data and the fit curve is shown in Figure 16 in the case of the linear SBR; as can be seen, the fit is excellent. Fit parameters of the corresponding curves for the three SBR samples are given in Table X and Figure 17, respectively.

The net occurrence of a plateau at high deformation with SBR materials clearly supports our choice of eq. (2) to model  $T(3/1)$  variations, and confirm similar observations on a series of SBR 1500.<sup>2</sup> It has been reported in the literature<sup>3,4</sup> that high dynamic shear under specific constraints should be limited by a maximum intensity of  $T(n\omega_1)/T(\omega_1) = 1/n$  for the normalized contribution at  $n\omega_1$ . Consequently, the limiting 3rd-harmonic component  $T(3/1)_{\max}$  should never exceed 33.33%. Table X shows that SBR materials do indeed conform to this rule. As previously reported (Fourier transform results Table VII) two polybutadiene samples give higher maximum  $T(3/1)$  values [i.e., LBRBR with  $T(3/1)_{\max} = 33.65$  and BRN40 with  $T(3/1)_{\max} = 36.92$ ]. However, within the strain capabilities of the RPA at 1

**TABLE VIII**  
Mean Linear Dynamic Moduli (Standard Test Technique) Versus Main Torque Component (FT Rheometry); SBR Samples

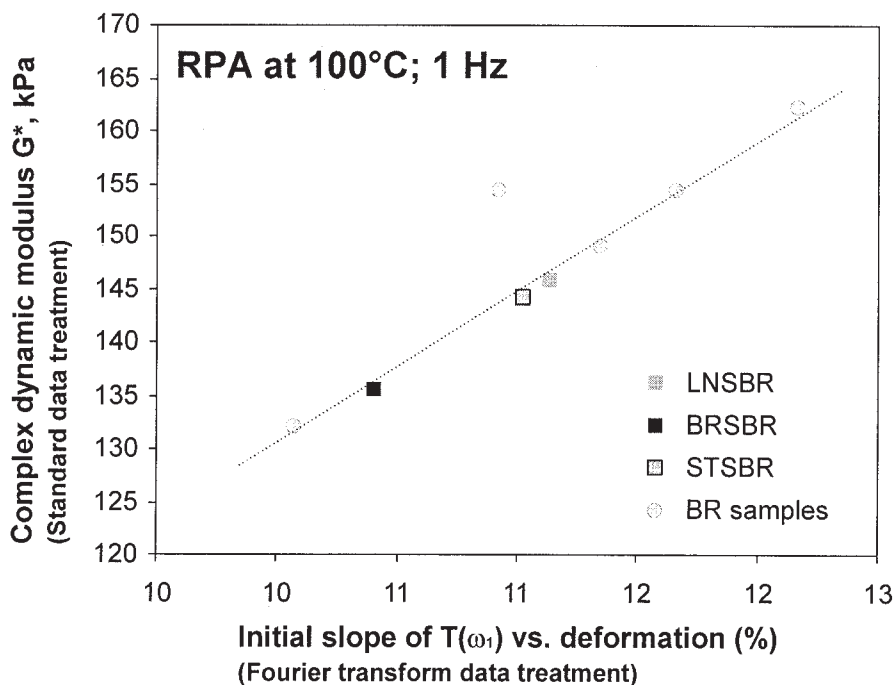
Sample	Mean $G'$ (kPa)	Mean $G''$ kPa	$T(\omega_1)$ % deformation	
			Slope	$r^2$
LNSBR	$137.2 \pm 1.6$	$49.7 \pm 0.7$	11.13	0.984
BCSBR	$126.7 \pm 1.2$	$48.2 \pm 1.1$	10.40	0.986
STSBR	$134.7 \pm 1.2$	$51.4 \pm 0.6$	11.02	0.987



**Figure 13** Main torque signal component from Fourier transform analysis on various SBR samples. The insert is an enlargement of the linear region, which shows the perfect linear fit of experimental data; the slope of the strain line is commensurate with the linear elastic modulus. See legend of Figure 12 for sample coding.

Hz, the (likely) maximum  $T(3/1)$  component is largely outside the experimental window with polybutadiene materials (compare Fig. 11 and 17), and

the fact that LBRBR and BRN40 are two high  $M_w$  materials with broad molecular weight distribution is probably important.



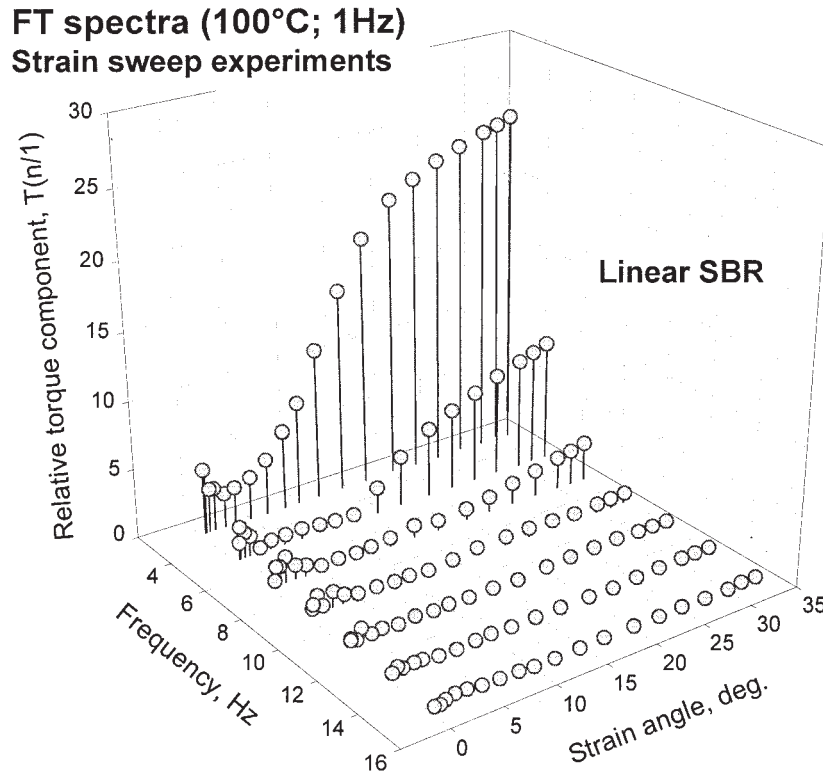
**Figure 14** Comparison of complex modulus data in the linear viscoelastic region, as provided by the standard approach with data from Fourier transform rheometry. See legend of Figure 12 for sample coding; similar data on BR samples are given for comparison.

**TABLE IX**  
**Fourier Transform Results on SBR Samples (Strain Sweep Tests at 100°C, 1 Hz)**

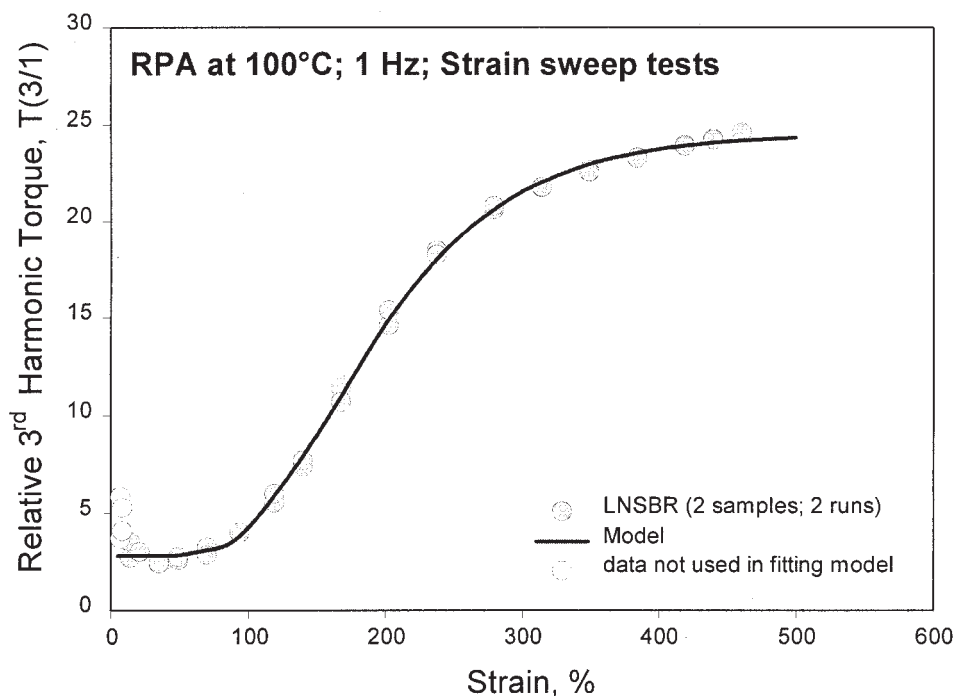
Strain (deg)	Strain (%)	Averaged main torque component, $T(\omega_1)$ (a.u.)			Average 3rd relative harmonic, $T(3\omega_1)/T(\omega_1)$		
		LNSBR	BRSBR	STSBR	LNSBR	BRSBR	STSBR
0.50	6.98	84.2 ± 0.0	78.0 ± 2.5	82.4 ± 0.7	4.8 ± 1.5	5.3 ± 0.6	5.5 ± 0.7
0.60	8.38	99.9 ± 0.4	93.5 ± 2.7	98.7 ± 0.1	4.7 ± 0.9	4.9 ± 0.7	4.4 ± 0.1
1.00	13.96	166.0 ± 0.4	154.1 ± 4.6	163.0 ± 1.0	3.1 ± 0.6	3.9 ± 0.4	3.3 ± 0.2
1.50	20.94	242.7 ± 0.5	227.3 ± 5.9	241.0 ± 0.4	3.0 ± 0.0	2.9 ± 0.3	2.7 ± 0.1
2.50	34.91	395.3 ± 1.5	368.6 ± 9.2	390.2 ± 1.7	2.4 ± 0.0	2.5 ± 0.3	2.3 ± 0.1
3.50	48.87	526.6 ± 0.8	496.3 ± 12.1	525.5 ± 0.5	2.7 ± 0.1	2.5 ± 0.1	2.6 ± 0.2
5.00	69.81	693.5 ± 1.8	655.8 ± 15.3	689.2 ± 1.6	3.1 ± 0.3	2.8 ± 0.1	3.0 ± 0.1
6.70	93.55	826.8 ± 1.6	794.1 ± 14.9	829.9 ± 4.9	4.0 ± 0.0	3.4 ± 0.2	3.7 ± 0.1
8.50	118.68	923.4 ± 8.5	895.9 ± 15.5	925.7 ± 5.5	5.8 ± 0.3	4.3 ± 0.3	4.9 ± 0.1
10.00	139.63	971.9 ± 2.5	956.5 ± 15.5	971.6 ± 8.2	7.5 ± 0.2	5.3 ± 0.3	6.5 ± 0.1
12.00	167.55	1012.0 ± 1.4	1011.6 ± 17.6	1013.0 ± 11.3	11.1 ± 0.5	7.0 ± 0.5	8.9 ± 0.2
14.50	202.46	1039.0 ± 5.7	1056.0 ± 8.5	1045.0 ± 5.7	15.0 ± 0.5	10.3 ± 1.8	12.7 ± 0.4
17.00	237.36	1065.0 ± 5.7	1087.0 ± 12.7	1076.0 ± 11.3	18.4 ± 0.2	14.1 ± 1.5	15.2 ± 0.2
20.00	279.25	1087.5 ± 2.1	1130.5 ± 9.2	1110.0 ± 4.2	20.7 ± 0.1	16.7 ± 0.4	16.7 ± 0.2
22.50	314.16	1102.5 ± 2.1	1159.5 ± 10.6	1135.5 ± 9.2	21.8 ± 0.0	17.5 ± 0.3	17.7 ± 0.0
25.00	349.07	1117.5 ± 4.9	1192.0 ± 7.1	1150.0 ± 1.4	22.6 ± 0.1	18.4 ± 0.1	18.6 ± 0.2
27.50	383.97	1130.5 ± 2.1	1218.5 ± 9.2	1168.5 ± 6.4	23.3 ± 0.0	19.1 ± 0.2	19.5 ± 0.1
30.00	418.88	1144.5 ± 2.1	1250.0 ± 4.2	1185.0 ± 1.4	23.9 ± 0.0	19.8 ± 0.0	20.2 ± 0.1
31.50	439.82	1151.0 ± 5.7	1265.0 ± 5.7	1195.5 ± 4.9	24.3 ± 0.0	20.2 ± 0.1	20.6 ± 0.1
33.00	460.77	1157.5 ± 2.1	1283.5 ± 6.4	1205.0 ± 2.8	24.6 ± 0.0	20.7 ± 0.0	20.9 ± 0.1

In modeling  $T(3/1)$  versus  $\gamma$  variations, we would give more significance to parameters  $b$  and  $c$  than to the limiting harmonic components  $T(3/1)_{\min}$  and

$T(3/1)_{\max}$  for the following reasons. First,  $T(3/1)_{\min}$  corresponds to the strain region where the applied strain has the poorest quality, as revealed by the FT



**Figure 15** Fourier transform spectra of a linear SBR (LNSBR), in terms of relative torque component  $T(n\omega_1)/T(\omega_1)$  versus frequency and strain angle. Significant variations of the relative third-, fifth-, and seventh-harmonic components are observed as the deformation increases.



**Figure 16** Modeling the variation of  $T(3\omega_1)/T(\omega_1)$  with strain amplitude (here expressed in percentage deformation) of a linear SBR. The limiting plateau at high deformation is clearly seen.

analysis of the input signal. As discussed in a previous report,<sup>2</sup> it is not clear whether  $T(3/1)_{\min}$  is material or instrument dependent, or both. Whatever the material tested, the fit values for  $T(3/1)_{\min}$  are generally within the 2.5–3.0 region when test results  $< 1$  deg (i.e.,  $\approx 14\%$ ) are discarded. With respect to  $T(3/1)_{\max}$ , theoretical considerations by Wilhelm et al.<sup>3,4</sup> assign a maximum value of 33.33%, whereas our results on SBR samples are still far from this limit, when plateau values are nevertheless experimentally obtained with confidence.

Parameters  $b$  and  $c$  describe the strain sensitivity of the material. The absolute value of the former depends on the units (degree or percent) used to express the strain  $\gamma$ ; the latter is  $\gamma$  unit insensitive. When consid-

ering results so far obtained on various gum elastomers (i.e., BR and SBR in this article, EPDM and SBR 1500 in a previous report<sup>2</sup>, it is observed that the higher strain sensitivity of a given material compared to that of another, is generally associated with both higher  $b$  and  $c$ , and that the molecular weight is the prime determining factor. This observation corresponds well with practical rubber technology experience and meets the comments made by Neidhöfer et al.<sup>5</sup> when performing FT rheometry tests on polystyrene melts: “small differences in the molecular weight, entanglements or ultimately the topology (of the polymer) should show up in significant differences with respect to the relative intensities of the different harmonics.” Our data confirm this expectation and using eq. (2) to model  $T(3/1)$  variations with  $\gamma$  is just a convenient and simple manner to quantify the nonlinear behavior of materials through dynamic testing and Fourier transform.

**TABLE X**

**Effect of Strain Amplitude on 3rd-Harmonic Component; Fit Parameters Obtained by Nonlinear Regression of Eq. (2) SBR Tested at 100°C, 1 Hz**

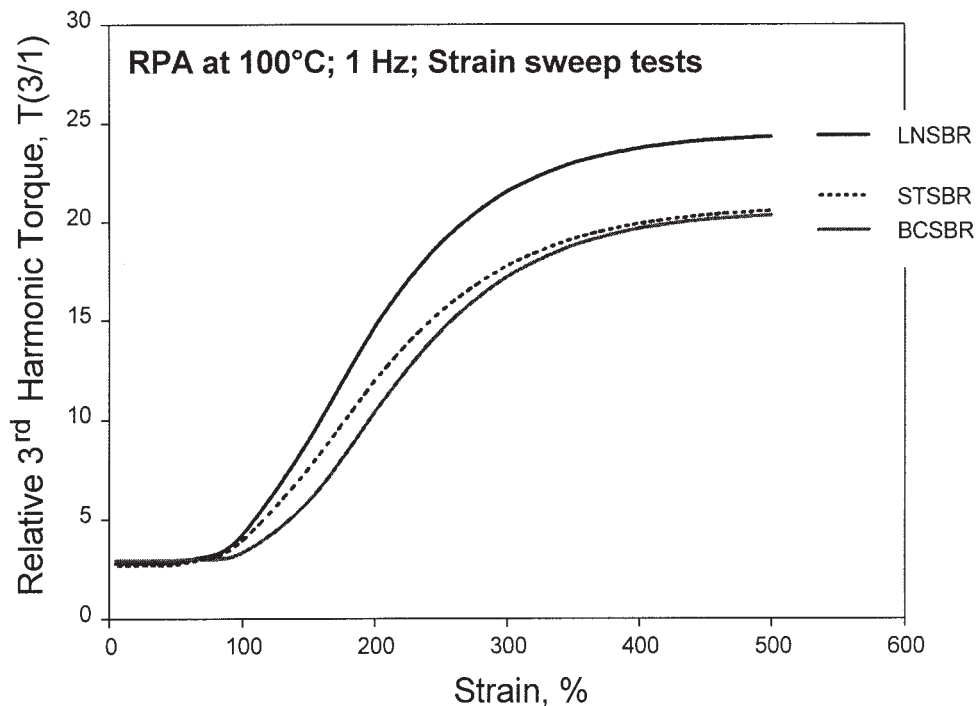
Parameter	Material		
	LNSBR	BCSBR	STSBR
$T(3/1)_{\min}$	2.81	2.96	2.70
$T(3/1)_{\max}$	24.54	20.59	20.86
$b^a$	$1.39 \times 10^{-3}$	$1.38 \times 10^{-3}$	$1.25 \times 10^{-3}$
$c$	9.43	13.10	7.91
$r^2$	0.999	0.993	0.997

<sup>a</sup> These values of  $b$  apply when the deformation  $\gamma$  is in %; the following conversion applies if  $\gamma$  is in degree angle:  $b(\gamma, \text{deg}) \approx 0.07162 \times b(\gamma, \%)$ .

## CONCLUSIONS

The nonlinear viscoelastic behavior of polymers is conveniently investigated through Fourier transform rheometry, a new and a powerful technique easily implemented on torsional dynamic rheometers. The particular design of the rubber process analyzer is obviously an advantage when testing stiff rubber materials, particularly in the high-strain region where reproducible results are obtained thanks to the closed





**Figure 17** Variation of  $T(3\omega_1)/T(\omega_1)$  with deformation of SBR samples, as modeled with eq. (1); the linear SBR (LNSBR) exhibits a stronger strain sensitivity. See legend of Figure 12 for sample coding.

test cavity. Like any other method, FT rheometry requires a careful selection of test conditions, with the right protocol for data acquisition and the appropriate calculation techniques.

Fourier transform spectra contain obviously the same information as provided by standard  $G'$  and  $G''$  data from linear dynamic testing, but likely in a more accurate manner, because one can easily distinguish the main torque component (i.e., the first harmonic at the test frequency) from other harmonics whose relative intensities significantly increase with strain amplitude.

Differences in nonlinear behavior, as exhibited by different polymers, are easily and clearly detected and the dependency on strain of the relative 3rd-harmonic component is adequately modeled with a simple four-parameter model. Although we have considered in the present work a number of gum elastomers with different macromolecular characteristics, the only parameters found to significantly affect the strain sensitivity

are the chemical nature of the elastomers (i.e., polybutadiene versus styrene-butadiene rubber) and the molecular weight. No clear effect of the microstructure was seen, likely because the sampling range was not broad enough in this respect. Further investigation is needed to fully appreciate the capabilities of Fourier transform rheometry.

The elastomer materials used in this study were kindly supplied by either Polimeri, Italy or Enichem, France.

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