

Modeling the Strain Dependence of Torque Harmonics as Measured Through Large-Amplitude Oscillatory Shear Rheometry

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ABSTRACT: Data describing the stress response to large-amplitude oscillatory shear can be considered as the nonlinear viscoelastic signature of polymer materials. How such data can be fitted with an appropriate equation is a problem of prime importance because (1) it allows results gathered in a large strain window to be summarized in a small number of representative parameters and (2) it permits a physical significance to be sought for equation parameters. This article analyzes and discusses several mathematical relationships that were proposed in the literature to fit harmonics vs. strain data, and probes their relative merits with various sets of experimental results. A simple four-parameter model is shown to encompass all the other approaches and to yield parameters that correctly describe not only material behavior in the linear-to-nonlinear transition region but also in the asymptotic high-strain range. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: polymer rheology; viscoelastic properties; modeling

INTRODUCTION

When submitting to a harmonic (i.e., cyclic) strain $\gamma(t)$ a pure, homogeneous viscoelastic material that is maintained in an appropriate testing gap where homogeneous shear flow develops (i.e., cone-plate geometry), a stress response $\sigma(t)$ is obtained, which is also harmonic. Except in the limit of (infinitesimally) small strain, stress and strain are generally not simply proportional. For experimental purposes, it is customary to apply to materials cyclic strains that correspond to easy and simple mathematical definition, for example $\gamma(t) = \gamma_0 \sin(\omega t)$ where γ_0 is the maximum strain amplitude, ω the frequency (rad/s) and t the time (s). One can thus expect to describe the general stress response with a summation of terms, that is $\sigma(t) = \sum_i \sigma_i \sin(i\omega t - \delta_i)$ where the δ_i terms allow accounting for an out-of-phase retard of the stress component σ_i with respect to the applied strain. In the limit of infinitesimally small strains, such a series is expected to reduce to only the first term when the material is exhibiting a so-called linear viscoelastic response.¹ When higher terms are necessary to (mathematically) describe the actual stress response of the material, the latter is said to be in its nonlinear viscoelastic domain. It has

been claimed,² numerically supported³ and somewhat experimentally proved,⁴ that only odd terms of the summation do contain material's information. Even terms are owing either to imperfect boundary conditions or to secondary flows in the testing gap, or more simply to imperfections in the (mechanically) applied strain.

So-called Fourier Transform (FT) rheometry is a technique of growing importance as it gives access to both the linear and the nonlinear viscoelastic characters of polymer materials. Essentially, FT rheometry consists of resolving captured strain and torque signals into their harmonic components by means of the appropriate calculation algorithms. Suitably modified torsional dynamic rheometers are generally used but the principle of FT rheometry does apply to any other dynamic modes. Dealy⁵ recently commented that *unfortunately, there is no way to interpret specific harmonics in terms of particular features of molecular structure or specific features of a constitutive equation*. Although the author essentially agrees with this statement, numerous experiments on many polymer systems have, however, shown that the manner odd torque (or stress) harmonics significantly increase with higher strain amplitude can be considered as a typical nonlinear viscoelastic "signature" of tested materials. Harmonics vs. strain curves are, therefore, a research theme of interest and the very subject of this article, whose objectives are (i) to review a few mathematical relationships that were proposed to fit harmonics vs. strain data

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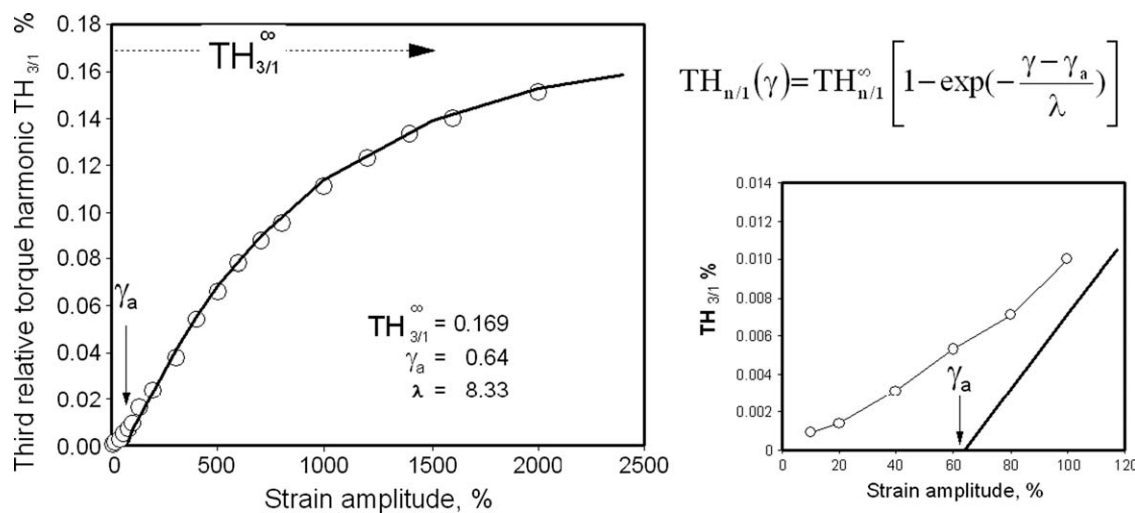


Figure 1 Third relative torque harmonic vs. strain amplitude as measured on 10% solution of PIB in oligoisobutylene by Wilhelm et al.⁷ and fitted curve with eq. (1); PIB: $M_v = 1.11 \times 10^3$ kg/mol, $M_w = 0.89$ Mw, $M_n/M_w = 2$; cone-plate, 50 mm dia., cone angle = 0.02 rad; 0.1 Hz; 298 K.

and (ii) to probe their relative merits with various sets of experimental results.

TORQUE (STRESS) HARMONICS VARIATION WITH STRAIN AMPLITUDE

Earlier approaches

It has long been recognized that the relative intensity of any (torque) harmonics $Th(n\omega)$ normalized to the fundamental frequency torque harmonic $Th(\omega)$ offers an easy manner to quantify the nonlinearity under specific conditions and that, upon increasing strain amplitude, relative harmonics vary according to a sigmoidal trend. Wilhelm et al.^{6,7} used the following exponential equation to describe this behavior, that is (note that all equations in this report have been written using the list of symbols given in appendix, under heading “NOMENCLATURE”):

$$TH_{n/1}(\gamma) = TH_{n/1}^{\infty} \left[1 - \exp\left(-\frac{\gamma - \gamma_a}{\lambda}\right) \right] \quad (1)$$

where $TH_{n/1} = Th(n\omega)/Th(\omega)$ is the relative n th harmonic (corresponding to frequency ω) and γ the set strain amplitude (in fraction of 1). $TH_{n/1}^{\infty}$ is the so-called maximum degree of nonlinearity for each harmonic, expected to be reached at sufficiently large strain amplitude, γ_a is the strain for the apparent onset of nonlinearity, and the parameter λ describes the relative change (or inverse slope) of the n th harmonic as a function of the shear amplitude (quoting Wilhelm,² p 93). Note that if γ and γ_a are expressed in % strain, λ has also to be expressed in %. It is quite obvious that eq. (1) has no capability to meet sigmoidal curves but it allows some features in the small- and medium-amplitude ranges to be adequately cap-

tured. Figure 1 shows the meaning of the parameters of eq. (1), using data published by Wilhelm et al.⁷ (Fig. 4 in their article).

Assuming that separation of time and strain effects could be considered, as in several constitutive equations for nonlinear viscoelasticity, Wilhelm² developed an argument based on a time-dependent damping function $h[\gamma(t)]$ to propose another equation, that is:

$$TH_{n/1}(\gamma) = TH_{n/1}^{\infty} \left[1 - \frac{1}{1 + (P\gamma)^Q} \right] \quad (2)$$

where $TH_{n/1}$, γ , and $TH_{n/1}^{\infty}$ have the same meaning as above. The parameter P expresses the power law dependence for small-strain amplitudes and Q is the prefactor (so-called pivot point in Wilhelm’s article) of this power law dependency. Note that in the quoted publications, the 3rd relative harmonic, that is $TH_{3/1}$, was specifically considered in the proposed equations, but the author sees no reason to restrict the discussion to the most intense harmonic. Equations (1) and (2) were thus rewritten as to suit relative harmonics of any order. Figure 2 shows the meaning of the parameters of eq. (2), using the data published by Wilhelm et al.⁷ (Fig. 4 in their article). As it is clear, eq. (2) corresponds to a sigmoidal curve whose asymptotic limit at infinitely small strain is zero, but the maximum degree of nonlinearity $TH_{n/1}^{\infty}$, as obtained by nonlinear fitting, is a very far extrapolated value.

As it can be seen, only two fit parameters per equation (i.e., γ_a , λ , P , and Q) are within the experimental window, whereas the maximum relative harmonic $TH_{n/1}^{\infty}$ is readily a far extrapolated value. Both γ_a and λ were reported to exhibit strong dependencies on molecular weight. The apparent onset of nonlinearity as expressed by γ_a decreases with increasing

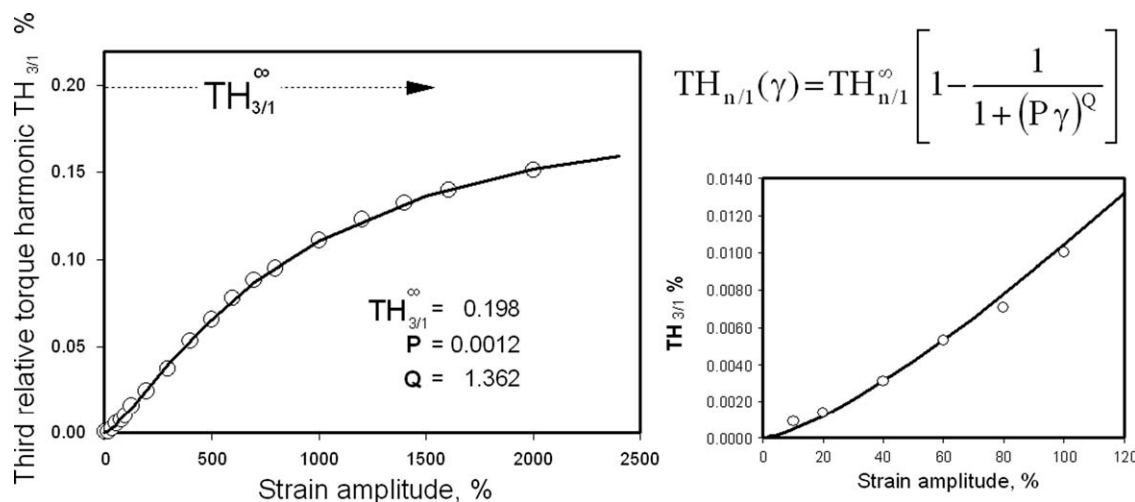


Figure 2 Third relative torque harmonic vs. strain amplitude as measured on 10% solution of PIB in oligoisobutylene by Wilhelm et al.⁷ and fitted curve with eq. (2); PIB: $M_v = 1.11 \times 10^3$ kg/mol, $M_w = 0.89$ Mw, $M_n/M_w = 2$; cone-plate, 50 mm dia., cone angle = 0.02 rad; 0.1 Hz; 298 K.

molecular weight and the contrary is observed for λ .^{2,6,7,8} No similar information was reported for parameters P and Q of eq. (2) but similar dependencies on macromolecular dimensions may be expected.

Hyun et al. equation

In the small- and medium-amplitude oscillating strain (MAOS) ranges, Hyun et al.^{8,9} suggested to fit the 3rd relative torque harmonic $TH_{3/1}$ vs. strain γ (in fraction of 1) data with the following equation:

$$\log[TH_{3/1}(\gamma)] = a + b \times \log[\gamma] \quad (3)$$

where b is the slope of $TH_{3/1}$ vs. γ in double-logarithm plot and the parameter a (unfortunately called “intercept” by these authors) can readily be defined as the $\log(TH_{3/1})$ value at strain amplitude = 1 (or 100% strain).

Several authors used this equation to fit their FT data in a limited strain range, however, which is usually 100–200% strain. Although b has sometimes been experimentally found close or equal to 2, whether a slope of 2 should be a general rule or not for polymers is still a subject to debate. Earlier considerations,^{10,11} based on the Doi–Edwards theory for polymer dynamics, predicted indeed $b = 2$ but it is worth underlining that they were founded on the observation that *the shear stress response is phenomenologically described by a power series in deformation amplitude* (quoting Helfand and Pearson, 1982, p 1252). Such a power series has only odd terms, so that the main (torque) harmonic $T_{1\omega} \propto \gamma^1$ (which is strictly true in the linear viscoelastic region) whilst the 3rd harmonic $T_{3\omega} \propto \gamma^3$, so that this approach is bound to predict that the relative 3rd harmonic is proportional to γ^2 . As this approach consists in injecting a

phenomenologically valid equation into a theoretical model (i.e., Doi–Edwards), the final argument is debatable in the author’s opinion. Through molecular dynamics simulation of electrorheological fluids, Sim et al.¹² came, however, to the same conclusion.

Hyun et al.⁹ performed simulations with three well-known constitutive equations (Giesekus, exponential Phan–Thien Tanner, and Pom–Pom model) and obtained slope b close or equal to 2, generally not affected by models’ parameters that describe molecular behavior. Parameter a was found depending on the shear thinning character, as expressed through the appropriate parameter(s) of the constitutive equation. The same authors have also reported a number of experimental data in the MAOS range for various polymers; some were found to be conformed to the above (simulation) considerations, whereas others were not. Table I is a compilation of published values for the slope of $\log TH_{3/1}$ vs. $\log \gamma$ graphs as experimentally found on a variety of polymers.^{2,9,13–15}

Several authors, whose data are summarized in Table I, reported difficulties in obtaining accurate and reproducible results in the very low strain region, owing to limited sensitivity of torque transducers. Conversely, there are also limitations in the high-strain region. Indeed, when FT rheometry experiments are conducted with open gap rheometers (cone-plate geometry), the high-strain range is frequently out of reach (particularly with high-molecular-weight [MW] molten polymers) either because of edge fracture or because of other instabilities associated with the second normal stresses difference N_2 , or because the torque transducer becomes overloaded at large strain amplitude. It follows that, at best, only the small- and the medium-strain range (up to 200–300%) can be safely investigated with open gap rheometers (for a practical demonstration of the capabilities of open and

TABLE I
Published Values for the Slope b in Hyun *et al.* Equation (eq. (3))

Material	Frequency (rad/s)	Temperature (°C)	Slope " b "	Ref.
Linear PS (various MWs) solutions in iso-dioctyl phthalate (various concentrations)	0.628	21–77	1.37	Neidhöfer <i>et al.</i> ¹³ (from Fig. 5)
			1.54	
PIB (Oppanol [®] B100) solution in isobutylene (10% wt)	0.1	25	1.39	Wilhelm ² (2002) ² (from Fig. 8)
Linear and branched PE	0.193	150	0.959 (long branches)	Fleury <i>et al.</i> ¹⁴ (calculated from Fig. 5)
			1.554 (short branches)	
Linear PP "PPD"	0.5	180	1.821 (linear)	Hyun <i>et al.</i> ⁹
			1.972	
			2.012	
			1.956	
			1.992	
Linear PP "PPE"	0.5	180	1.996	
			2.001	
			1.997	
			1.95	
			2.007	
Linear PP	1	180	2	
Branched PP	1	180	1.6	
HDPE strain hardening	1	180	1.589 ± 0.038	
		220	1.56	
HDPE no strain hardening	1	180	1.998 ± 0.014	
		220	2	
Epoxy-modified PLA; various EPO levels	1	180	1.916 0.004	
			1.737	
			1.712 ± 0.006	
			1.925 ± 0.030	
			1.856 ± 0.008	
			1.733 ± 0.035	
PS various MW	1, 2, 3, 5	170–240	Around 2.01	
Linear and comb PS	0.1–10	160–200	Around 2.0	Hyun and Wilhelm ¹⁵

closed cavity rheometers, see Leblanc¹⁶), and to find a strain region where eq. (3) readily applies is rather a question of (arbitrary) choice. Closed cavity torsional rheometers with biconical dies do not suffer such limitations so that reproducible large-amplitude oscillatory shear (LAOS) experiments can be performed up to 1000% strain (depending on the frequency, however), even on relatively stiff materials such as filled rubber compounds or short-fiber-filled thermoplastics.

Fitting the overall variation of harmonics vs. strain amplitude

Through numerous FT experiments on a variety of polymer systems with a closed cavity torsional rheometer, the author obtained torque harmonic data (3rd and 5th harmonics) up to around 1000% strain (at 0.5 Hz) that generally exhibited a sigmoidal trend, as shown in Figure 3 in the case of a commercial polyethylene. Such data are well fitted with the following equation^{16–18}:

$$TH(\gamma) = (TH_0 + \alpha\gamma) [1 - \exp(-C\gamma)]^D \quad (4)$$

where TH stands for any relative harmonic (i.e., TH_{3/1}, TH_{5/1}, ...) and even for the sum of all the

harmonics (in practice from the 3rd up to the 15th with the experimental setup used by the author), γ is the strain amplitude (usually expressed in % strain) and TH₀, α , C , and D parameters of the model. Data obtained on the same material but with another similar instrument (Alpha Technology Lab., Louvain-la-Neuve, Belgium) are also shown in the graph. Both instruments give reasonably similar data and while eq. (4) was fitted only to author's data, it is quite obvious that data obtained in the other laboratory could be fitted as well with the same equation.

The first right member of equation (4), i.e. (TH₀ + $\alpha\gamma$), obviously governs the asymptotic high-strain behavior of (relative) torque harmonics. TH₀ is the extrapolation toward $\gamma = 0$ of the high-strain linear variation and α is the slope of the asymptotic high-strain behavior. If indeed the occurrence of a plateau is visible in the experimental strain window, parameter α will be found so small that sometimes it can readily be assigned a zero value. In such a case, TH₀ is the plateau value, analog to the maximum degree of nonlinearity for each harmonic $TH_{n/1}^\infty$ in eqs. (1) and (2).

The second right member $[1 - \exp(-C\gamma)]^D$ describes the torque harmonic variation in the

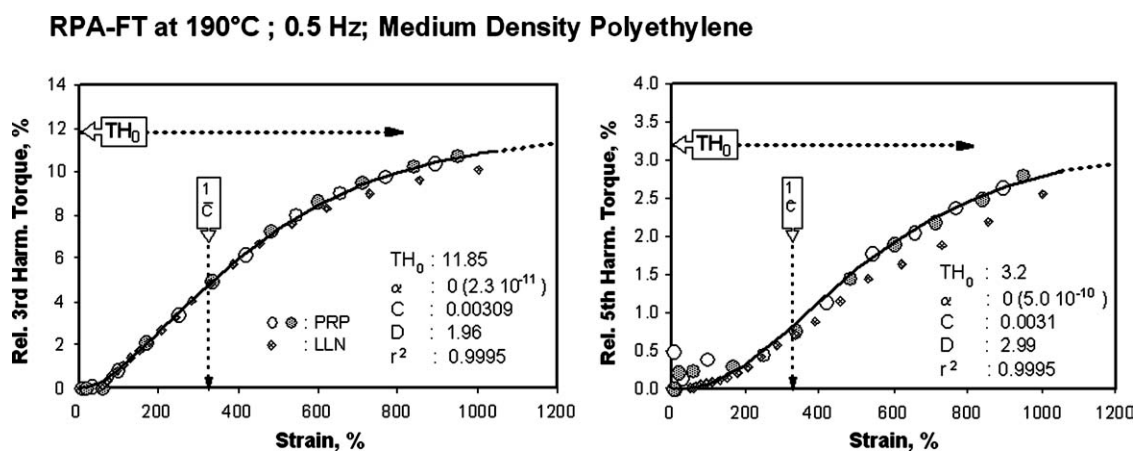


Figure 3 Third and fifth relative torque harmonics vs. strain amplitude as measured on molten polyethylene (medium density) at 190°C, 0.5 Hz frequency, using closed cavity dynamic rheometers; fit parameters of eq. (4) are given in the inset. Data were obtained either by the author (: PRP) or in Alpha Technology laboratory (: LLN).

linear-to-nonlinear region. As such, this part of the equation corresponds to a sigmoidal curve that goes asymptotically to 1, whatever the values for C and D , but D is clearly associated with the extent of the linear region (where torque harmonics must asymptotically go to zero), whereas C is associated with the strain sensitivity, in other words with the manner the material goes from the linear to the nonlinear region. The inverse of C corresponds thus to a critical strain of the material and in fact is to the position of the maximum of the 1st derivative of the equation, as will be discussed in the **EXPERIMENTAL** section. Equation (4) is thus highly flexible, with the capability to meet nearly all experimental data, providing, however, that there is no singularity associated with some strain sensible substructures of the material. This is the case with certain highly filled polymer systems, in which case

additional terms must be added to eq. (4), as previously reported.¹⁸

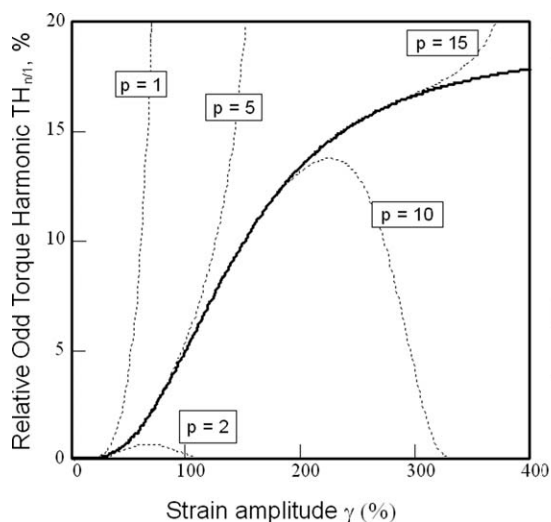
Hyun's eq. (2) is conveniently rewritten as:

$$\log [TH_{3/1}(\gamma)] = \log(A) + b \times \log[\gamma] \quad (5)$$

so that the following explicit power law form is directly obtained:

$$TH_{3/1}(\gamma) = A\gamma^b \quad (6)$$

Doing so, A is clearly the value of the torque harmonic when $\gamma = 1$ (or 100% strain), the unfortunate wording "intercept a " as used by several authors is avoided and a straight comparison can be developed with eq. (4). Note, however, that to comply with eq. (3) where the strain is in %, a comparison between eqs. (4)–(6) is feasible if A is considered as the torque harmonic at $\gamma = 100\%$. The exponential term in eq. (4) can be expanded, that is $\exp(-C\gamma) = \sum_n \frac{(-1)^n}{n!} C^n \gamma^n$, and



Full model :

$$TH(\gamma) = (TH_0 + \alpha \gamma) [1 - \exp(-C\gamma)]^D$$

Model parameters : $TH_0 = 15.89$
(used in calculating curves) $a = 0.0054$
 $C = 0.015$
 $D = 4.6$

Expanded equation :

$$TH(\gamma) = (TH_0 + \alpha \gamma) (C\gamma)^D \left(\sum_{n=0}^{p-1} \frac{(-1)^n \cdot (C\gamma)^n}{(n+1)!} \right)^D$$

Figure 4 Comparing the full model (eq. (4)) and the expanded equation (eq. (8)) through calculation with typical model parameters.

RPA-FT; 100°C; Natural Rubber (gum samples)

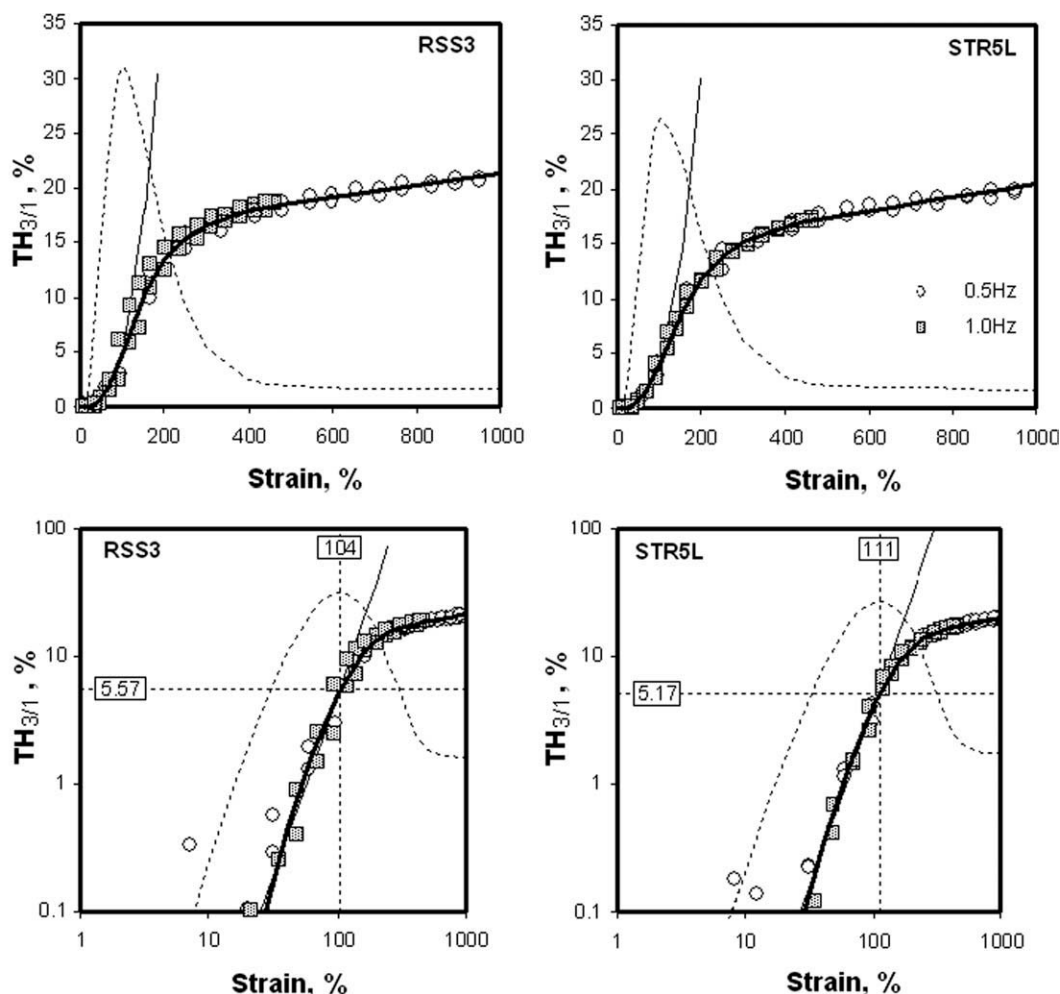


Figure 5 Variation of the 3rd relative torque harmonic with strain amplitude as measured in the author's laboratory at either 0.5 or 1.0 Hz on gum natural samples; bottom graphs are the same results as in the upper graphs but drawn with logarithmic scales; the bold curves correspond to eq. (4) and the dashed lines to its first derivatives; the fine curves correspond to eq. (3). The positions and values of the maximum of the first derivative are indicated in the bottom graphs. Note that first derivative data have been multiplied by 300.

substituted so that, after simplification and rearrangement, one obtains:

$$TH(\gamma) = (TH_0 + \alpha\gamma)(C\gamma)^D \left(1 - \frac{1}{2}C\gamma + \frac{1}{6}C^2\gamma^2 - \frac{1}{24}C^3\gamma^3 + \frac{1}{120}C^4\gamma^4 - \dots \right)^D \quad (7)$$

or

$$TH(\gamma) = (TH_0 + \alpha\gamma)(C\gamma)^D \left(\sum_{n=0}^{p-1} \frac{(-1)^n \cdot (C\gamma)^n}{(n+1)!} \right)^D \quad (8)$$

Expanding the exponential term remains, in principle, valid so long as γ remains below 1 but using typical experimentally found values for the parameters, it is observed that quite a large number of expansion terms is necessary to obtain a curve similar to eq. (4). Reduced to $TH(\gamma) = (TH_0 + \alpha\gamma)(C\gamma)^D$ (i.e., $p = 1$ in eq. (8)), the equation yields, however, nearly the same curve as eq. (4) up to $\gamma = 2\%$ only. When higher terms of the expansion are used, the point of divergence between the full model, that is eq. (4) and its expanded version, moves to higher strain values. Beyond the point of divergence, the error is positive when the expansion term is odd and negative when the expansion term is even, as shown in Figure 4.

In the (very) low strain region, eqs. (7) and (8) reduce to:

$$TH(\gamma) = (TH_0)(C\gamma)^D \quad (9)$$

when the insignificant term $\alpha\gamma$ is neglected. It follows that the combination TH_0C^D of eq. (4) parameters, that is eq. (9) when $\gamma = 1\%$, might be considered as a typical quantity for a given polymer material in the conditions of the LAOS experiment. With respect to the mathematical forms of eqs. (6) and (9), it comes immediately that the log relationship of Hyun et al. (eq. (3)) is indeed nothing else than a local variation of the full model as expressed with eq. (4). As the Hyun et al. equation was introduced to fit the torque harmonics in the small- and medium-strain amplitude regions, one may expect that in the very low strain region, torque harmonics calculated with eq. (3) exhibit some proportionality with the quantity TH_0C^D , as will indeed be demonstrated below, after the **EXPERIMENTAL** section.

Such considerations explain obviously that reason why, when found applicable, eq. (3) is observed valid only within a limited strain range with (carefully) selected data. Moreover parameter A (or $\log a$) is related with the linear–nonlinear transition region, as well as parameters C and D of eq. (4). Parameter D is associated with the extent of the linear region, which is known to depend on the polymer considered; it follows that D cannot be identical for all polymers, as indeed experimentally observed. The mathematical similarity between eqs. (6) and (9) suggests also that the value $b = 2$ predicted by numerical simulations might thus only reflect inherent limitations of the constitutive equations used in such simulations.

The above considerations lead to at least four remarks:

1. The general model, that is eq. (4), is always valid, suffers no restriction regarding the strain range, but its use implies obviously that reproducible experimental data are obtained in a sufficiently large strain range, so that the asymptotic high-strain behavior is conveniently documented.
2. Over a limited span in the low- and the early-medium strain range, a power law is sufficient to correctly fit relative torque harmonic data (whatever they are, $TH_{3/1}$, $TH_{5/1}$... and even the overall (odd) harmonic content $\sum_n TH_{n/1}$)
3. The various values experimentally found for the slope b in eq. (3) essentially reflect the inherent difficulties in finding the exact strain range where the torque harmonics vs. strain behavior can be safely approximated with the power law.
4. In the small- and medium-strain range, a simple power law holds, either $TH_{n/1}(\gamma) = (TH_0)(C\gamma)^D$ or $TH_{n/1}(\gamma) = A\gamma^b$. If, as suggested by certain authors,¹⁵ D (or b) is a constant for most polymers and equals to 2, one has:

$$Q = \frac{TH_{n/1}(\gamma)}{\gamma^2} = TH_0 C^2$$
 where $TH_{n/1}$ is for instance $TH_{3/1} = I_3/I_1$ with respect to the formalism used by those authors. At given frequency and temperature, for a given polymer, TH_0 and C are constants, not depending on strain, so that defining a parameter Q_0 such that: $Q_0 = \lim_{\gamma \rightarrow 0} Q$, has no real meaning, because Q is anyway constant for a given polymer.

The author sees no physical reasons for the exponent D (or b) to be a constant (equals to 2) whatever is the polymer (system) and, in agreement with most experimental evidences so far gathered, it is quite plausible that D (or b), as well as the other parameters of eqs. (3) and (4) are polymer dependent, and also somewhat affected by testing conditions. In the asymptotic low-strain region, eq. (4) readily reduces to TH_0C^D , a quantity that can indeed be considered as a true material characteristic, obviously related to both the linear and the nonlinear behaviors.

EXPERIMENTAL

Experimental approach

A fast and convenient technique to investigate the nonlinear viscoelastic response of polymer materials consists in performing strain sweep tests from the lowest up to the highest strain amplitude either permitted by the instrument or before boundary conditions between the sample and the test gap walls cease to be optimal. With high-molecular-weight polymers or with highly stiff (molten) polymer systems, only torsional dynamic rheometers, with a reciprocal cones test chamber whose upper and lower dies are maintained with a sufficient closing force, proved to provide very reproducible and meaningful results under LAOS conditions. These instruments are conveniently referred to as “closed cavity” torsional rheometers, are essentially rotorless instruments, and are commercially available, for example the “Rubber Process Analyzer,” RPA 2000[®], the “Production Process Analyzer,” PPA[®] (Alpha Technologies, now a division of Dynisco LLC, Franklin, MA), the “Moving Die processability tester,” MDpt[®] (TechPro, now a division of Dynisco LLC), the MonTech D-RPA 3000 (MonTech Werkstoffprüfmaschinen GmbH, Buchen, Germany), and so on. All such instruments meet the requirements for standard

TABLE II
Parameters of eqs. (3) and (4) Corresponding To Experimental Results shown in Figures 5–11

Test material	Figure	Equation (4) $TH(\gamma) = (TH_0 + \alpha\gamma)[1 - \exp(-C\gamma)]^D$					Equation (3) $\log[TH(\gamma)] = a + b \times \log[\gamma]$		
		TH_0	α	C	D	r^2	a	b	$10^a = TH_{100\%}$
RSS3; TH _{3/1}	5	15.89	0.0054	0.01499	4.600	0.9919	0.711	2.87	5.140
STR5L; TH _{3/1}	5	14.50	0.0059	0.01383	4.450	0.9973	0.621	2.85	4.178
SMR10CV; TH _{3/1}	6	15.04	0.0037	0.00800	3.210	0.9959	0.356	2.53	2.270
ENR05; TH _{3/1}	7	14.03	0.0031	0.00768	2.630	0.994	0.444	2.15	2.780
ENR25; TH _{3/1}	7	12.99	0.0042	0.00638	2.770	0.9981	0.223	2.28	1.671
ENR50; TH _{3/1}	7	13.66	0.0043	0.00403	2.120	0.9988	0.133	1.85	1.358
SBR1500; TH _{3/1}	8	16.17	0.0000	0.00390	2.530	0.9975	-0.033	2.20	0.927
SBR1500; TTHC	8	23.96	0.0000	0.00303	2.190	0.9977	0.103	1.95	1.268
SBR cpd; TH _{3/1}	9	14.69	0.0000	0.00741	2.270	0.9976	0.529	1.85	3.381
SBR cpd, TTHC	9	16.13	0.0079	0.00763	2.350	0.9978	0.587	1.96	3.864
MDPE; TH _{3/1}	10	10.46	0.0010	0.00357	2.000	0.9973	-0.021	1.75	0.953
PIB solut.; TH _{3/1}	11	0.141	0.00001	0.00165	1.384	0.9994	-1.98	1.34	0.010

measurements of rheological properties of unvulcanized rubber,¹⁹ and their measuring principle has been fully validated,^{20,21} but they need to be suitably modified for FT rheometry experiments. It is quite clear that, owing to the relatively complicated shape of the test cavity only an average strain situation is achieved but similar comments can be made for most rheometrical techniques. Numerical simulation revealed that the peripheral higher stress region imparted by the closed edge of the cavity has no significant effect on the actually measured dynamic modulus, as experimentally demonstrated.²² To fully exploit LAOS experiments, suitable modifications of commercial “closed cavity” torsional instruments are, however, required. The experimental results hereafter reported were obtained either in the author’s laboratory with a purposely modified RPA or in the Alpha Technology laboratory in Louvain-la-Neuve, Belgium (by courtesy of H. Burhin), with a similar instruments but using the oversampling technology.²³

To experimentally compare the relative merits of eqs. (3) and (4) in suiting torque (stress) harmonic variation with strain amplitude, a number of FT rheometry tests were performed with a variety of different polymer systems. Test protocols consisted in performing two subsequent strain sweep experiments (at fixed frequency and temperature) separated by a resting period of 2 min (note: 2 min is an arbitrary choice, but generally found largely sufficient for viscoelastic recovery with most polymer systems tested so far when no permanent structural damage has occurred during the first run). At least two samples of the same material were 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 indeed expected between runs 1 and 2 for materials exhibiting strain memory effects, either permanent or at least not

RPA-FT; 100°C; SMR10CV gum

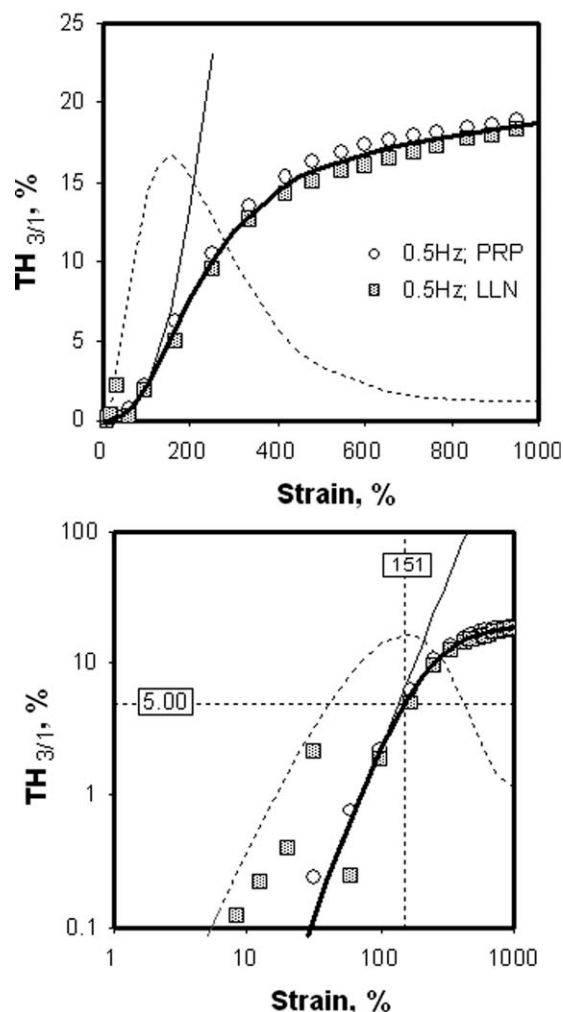


Figure 6 Variation of the 3rd relative torque harmonic with strain amplitude as measured at 0.5 Hz on a constant viscosity natural rubber sample in the author’s laboratory (data quoted PRP) and in Alpha Technology laboratory (data quoted LLN); see the caption of Figure 5 for curve identification.

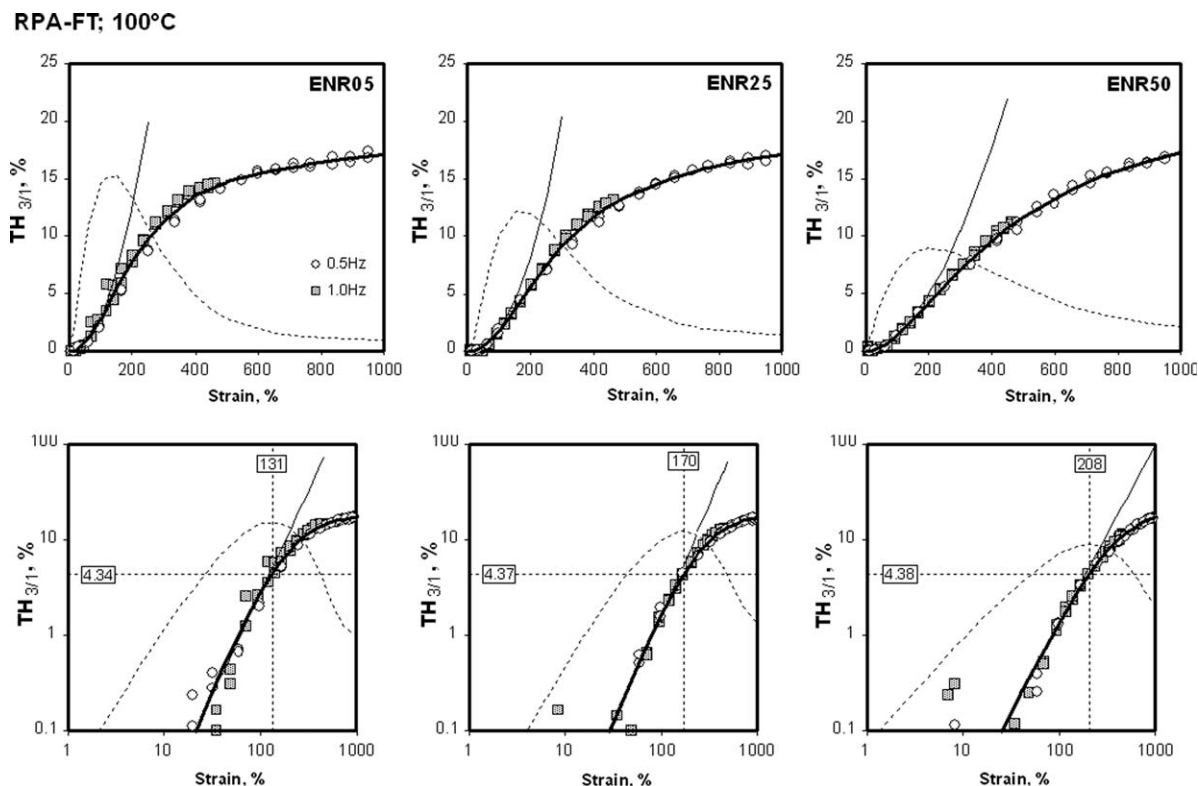


Figure 7 Variation of the 3rd relative torque harmonic with strain amplitude as measured at either 0.5 or 1.0 Hz on a series of ENR 05, 25, and 50 stand, respectively, for 5, 25, and 50 mol % epoxidation; see the caption of Figure 5 for curve identification.

fully dampened after the resting period. Strain memory effects are practically never observed with pure, unfilled polymers, and standard carbon black filled rubber compounds but are quite common with certain complex polymer systems, namely highly loaded systems and compounds with short fibers. With the author's equipment, in any fixed strain and frequency conditions, data acquisition was made to record 10,240 points at the rate of 512 pt/s, that is 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. Similar testing protocols were used with the Alpha Technology instrument, but the oversampling technique was used so that the FT was immediately performed in real time, without keeping records of the torque and strain signals.

Results on gum natural rubber samples

Figure 4 shows the results obtained in the author's laboratory on two gum natural rubber samples. RSS3 is a so-called Ribbed Smoked Sheet grade produced in Thailand from whole field latex. The sample tested has a $ML(1 + 4)_{100^\circ C} = 70$ and the following macromolecular characteristics (SEC-MALS): $M_n = 1143 \pm 27$ kg/mol, $M_w = 1685 \pm 29$ kg/mol, and $M_z = 2597 \pm 84$ kg/mol. STR 5L is a technically specified light color rubber grade, produced in Thai-

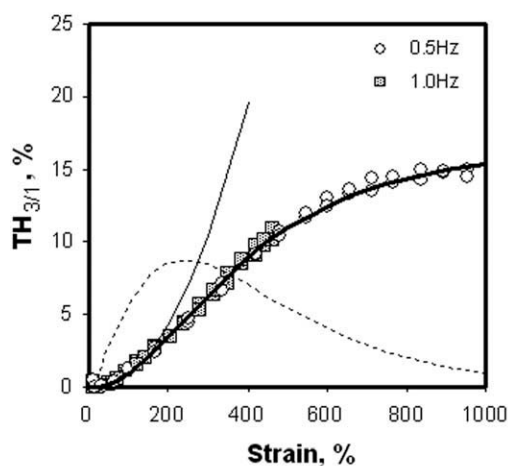
land by coagulating freshly collected high quality latex. The sample tested meets the Technical Standard Rubber L specifications and has a Mooney viscosity $ML(1 + 4)_{100^\circ C} = 70$. Its macromolecular characteristics were measured by SEC-MALS: $M_n = 679 \pm 31$ kg/mol, $M_w = 1278 \pm 11$ kg/mol, and $M_z = 2375 \pm 21$ kg/mol.

As it can be seen, the variation of the 3rd torque harmonic with strain amplitude appears sigmoidal in the linear–nonlinear transition region and converges toward a linear variation at high strain, without significant effect of the test frequency. Equation (3) is perfectly fitting experimental results (see fit parameters in Table II). It has been reported in the literature²⁴ that, for Newtonian fluids, high dynamic shear under specific constraints should be limited by a maximum intensity of $Th(n\omega_1)/Th(\omega_1) = 1/n$ for the normalized contribution at $n\omega_1$. Consequently, the limiting 3rd harmonic component at high strain should never exceed 33.33% for Newtonian fluids. Polymer materials are not Newtonian fluids but results in Figure 3 do indeed conform to this rule but also do not suggest the occurrence of a plateau value as the data do correspond well to an asymptotically linear variation at high strain, with a slope (α) small but larger than zero.

Expectedly, eq. (3) has only the capability to meet the initial part of the torque harmonic variation

RPA-FT; 100°C; SBR 1500 Gum

3rd relative torque harmonic



Total torque harmonics content

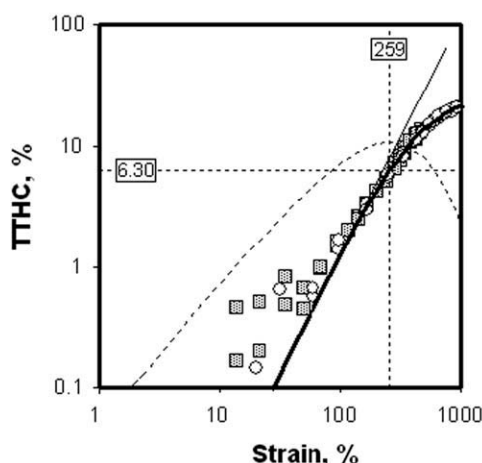
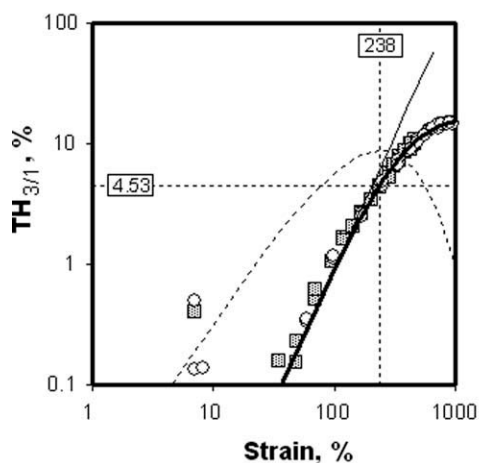
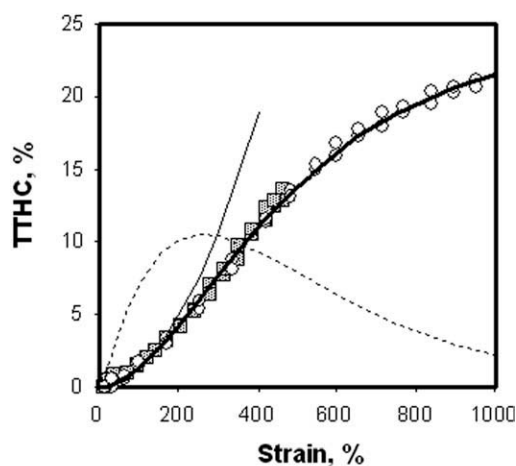


Figure 8 Variation of the 3rd relative torque harmonic with strain amplitude as measured at either 0.5 or 1.0 Hz on a SBR 1500 sample; see the caption of Figure 5 for curve identification.

providing the adequate parameters are used. Parameter a is directly extracted from experimental results as the logarithm of the relative torque harmonic at 100% strain, so that only parameter b has to be adjusted to give the best fit of data. As shown in Figure 4 (bottom graph), eq. (3) corresponds to the low-strain behavior as modeled by eq. (4), but the values found for b (Table II) are significantly differing from 2.

Figure 6 shows the results obtained on a constant viscosity natural rubber grade through experiments performed by the author's and in Alpha Technologies laboratory (Louvain-la-Neuve, Belgium). SMR10CV is a technically specified "constant viscosity" grade, produced from field latex in Malaysia and commercially available in France, whose Mooney viscosity was measured as $ML(1+4)_{100^\circ C} = 71$ (vs. 60 ± 5 , according to technical certification). The viscosity is stabilized by the addition of a suitable

chemical, generally a hydroxylamine salt, so that on storage this grade of rubber is expected to remain within eight hardness units. Dirt, ash, and N₂ contents are maximum 0.05, 0.6, and 0.6, respectively.

As it can be seen, the two instruments used yield essentially the same results that are well fitted with eq. (4). Equation (3) was adjusted to the low- and medium-strain regions data as explained above. Equations parameters are listed in Table II, calling for the same comments as above.

Results on epoxidized natural rubber samples

Epoxidation is a well-known chemical modification of unsaturated polymers that, among other modification of properties, allows changing the chain flexibility without much alteration of the macromolecular dimensions. Well-controlled conditions are, however, needed to obtain specific levels of epoxidized

RPA-FT; 100°C; SBR 1500 / 50phr N330 cpd

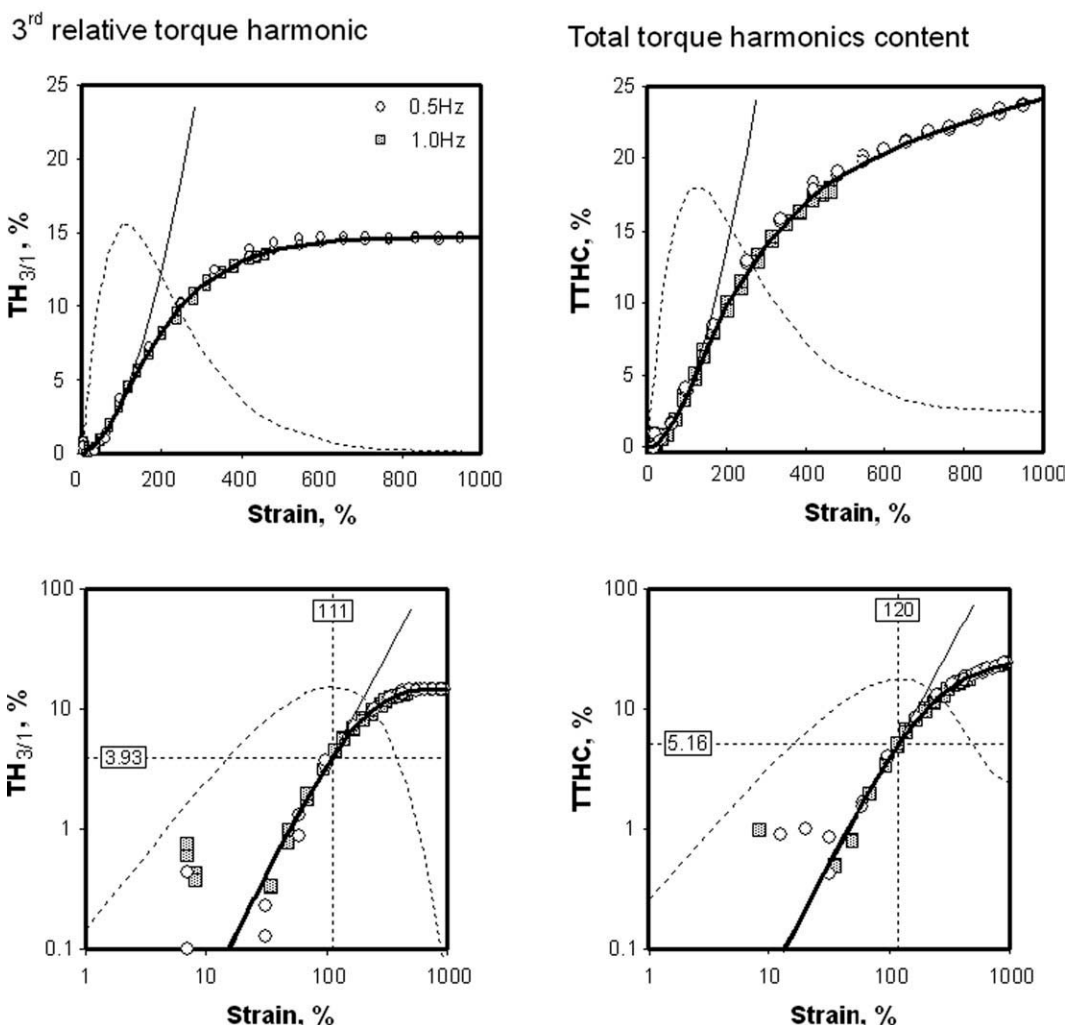


Figure 9 Variation of the 3rd relative torque harmonic with strain amplitude as measured at either 0.5 or 1.0 Hz on SBR 1500 compounded with 50 phr N330 carbon black; see the caption of Figure 5 for curve identification.

natural rubber (ENR) with a random distribution of oxiran groups.²⁵ A series of three commercially available ENR samples with various epoxidation levels, that is 5, 25, and 50 mol % were kindly supplied by the Malaysian Rubber Board and submitted to LAOS tests in the author's laboratory.

As shown in Figure 7, the epoxidation level has a significant effect on the 3rd torque harmonic vs. strain amplitude curves. Fitting with eq. (4) is excellent (see correlation coefficient in Table II) so that fit parameters perfectly reflect the variation in the nonlinear signatures of the materials as the oxiran content increases. First derivative curves are also shown in Figure 7, using parameters listed in Table II. The position and value of the maximum of the derivative are easily obtained and are shown in the bottom graphs. The maximum of the first derivative is a critical point in the linear-to-nonlinear region that corresponds to the maximum strain sen-

sitivity of the material, and is expectedly related to structural aspects. This maximum of the first derivative is clearly decreasing with the epoxidation level and the strain for this maximum strain sensitivity is also moved to higher strain as the epoxy content increases. A direct explanation can be offered by considering that as epoxidation level increases, some higher rigidity or stiffness is imparted to the *cis*-1,4 polyisoprene chains, either because epoxy groups are stiffer than double bonds or because oxiran groups have a higher steric hindrance, or through a combination of both effects. Equation (3) gives curves that meet the experimental data in the low- and medium-strain regions, with the adequate choice for the value of a , however. Table II summarizes that if a (or $TH_{100\%}$) is clearly decreasing with higher epoxidation level, parameter b does not follow a clear trend and is anyway not equal to 2.

RPA-FT; 190°C; Polyethylene

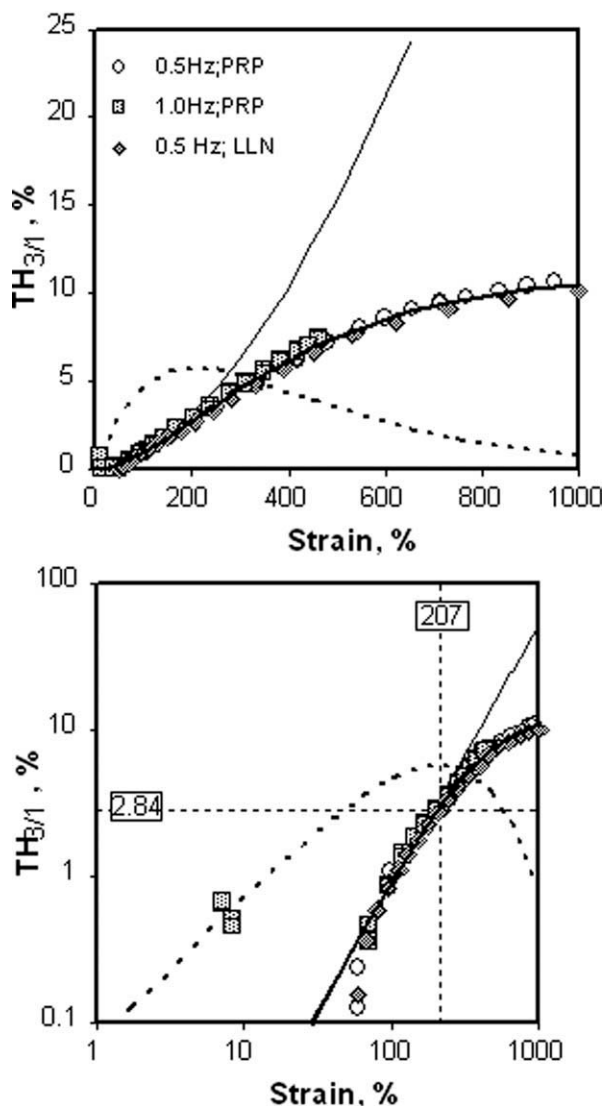


Figure 10 Variation of the 3rd relative torque harmonic with strain amplitude as measured at either 0.5 or 1.0 Hz on MDPE at 190°C; tests were performed in the author's laboratory (data quoted as PRP) and in Alpha Technology laboratory in Louvain-la-Neuve, Belgium (data quoted as LLN); see the caption of Figure 5 for curve identification.

Results on styrene-butadiene rubber systems

Emulsion Styrene-Butadiene Rubber SBR 1500 is quite a common synthetic rubber grade whose most properties are designed to match Natural Rubber as closely as possible. There are many suppliers of SBR 1500, so that the material is currently sold as a commodity that meets the demand by different tire makers. The SBR 1500 samples used for the hereafter reported experiments have the following characteristics: styrene content: $23.4 \pm 0.5\%$; $M_n = 78 \pm 2$ kg/mol; $M_w = 405 \pm 19$ kg/mol; Mooney viscosity, $ML(1 + 4)_{100^\circ\text{C}} = 49$. Figure 7 shows the variation on strain amplitude of the 3rd torque harmonic $T(3/1)$

and also of the so-called total torque harmonics content, TTHC, in fact the sum of all the odd harmonics up to the 15th. As it can be seen, sigmoidal curves, well fitted through eq. (4), are obtained. Fit parameters are listed in Table II, as well as parameters of eq. (2). In contrast with the results reported so far, the 3rd torque harmonic of SBR 1500 appears to plateau out at high strain toward a limiting value equal to 16.17, nearly appearing in the experimental strain window. Correspondingly, the nonlinear fitting algorithm (i.e., Levenberg–Marquardt) used to treat experimental data yields zero for parameter α (in fact values below 10^{-18} were obtained that were conveniently rounded to zero). One sees obviously that the TTHC curve envelops the $TH_{3/1}$ one but is also well fitted with eq. (4).

Either with $TH_{3/1}$ or TTHC data, eq. (3) does correspond to the low-strain behavior and meets eq. (4), providing the appropriate parameters are used (Table II), with again slope b differing from 2.

It is well known that adding reinforcing filler to a rubber brings important modification in the viscoelastic character with, among other changes, a quasi-disappearance of the linear viscoelastic response from the available experimental strain window in dynamic testing. To compare the merits of eqs. (3) and (4) in the particular case of filled systems, a standard carbon black filled compound was prepared in a Banbury mixer using 50 phr (part per hundred rubber) of N330 carbon black and the usual ingredients (Naphthenic oil: 5; zinc oxide: 5; Stearic acid: 3; Trimethylquinoline, polymerized: 2; *N*-isopropyl-*N'*-phenyl-*p*-phenylene diamine: 1). LAOS experiments were performed in the author's laboratory using test protocols described above. Figure 8 shows the variation on strain amplitude of the 3rd relative torque harmonic $TH_{3/1}$ and the so-called TTHC and the curves obtained through the application of eqs. (3) and (4). Corresponding parameters are listed in Table II.

Curves in Figure 9 must be examined in comparison with their counterparts in Figure 8. As it can be seen clearly, the filled SBR does show a plateau behavior for the 3rd torque harmonic within the experimental strain windows. Correspondingly, the value of the parameter α is zero. One sees also (Table II) that the limiting $TH_{3/1}$ at high (infinite) strain is also significantly lower for the filled than the pure SBR sample. Corresponding changes are noted on the TTHC, so that how the reinforcing filler affects the viscoelastic properties is conformed with a strong enhancement of the nonlinear behavior up to the quasi-disappearance of any linear response, whatever low is the strain amplitude in the experimental window. Fitted to $TH_{3/1}$ or TTHC data at low strain, eq. (3) yields slope b values that are clearly below 2.

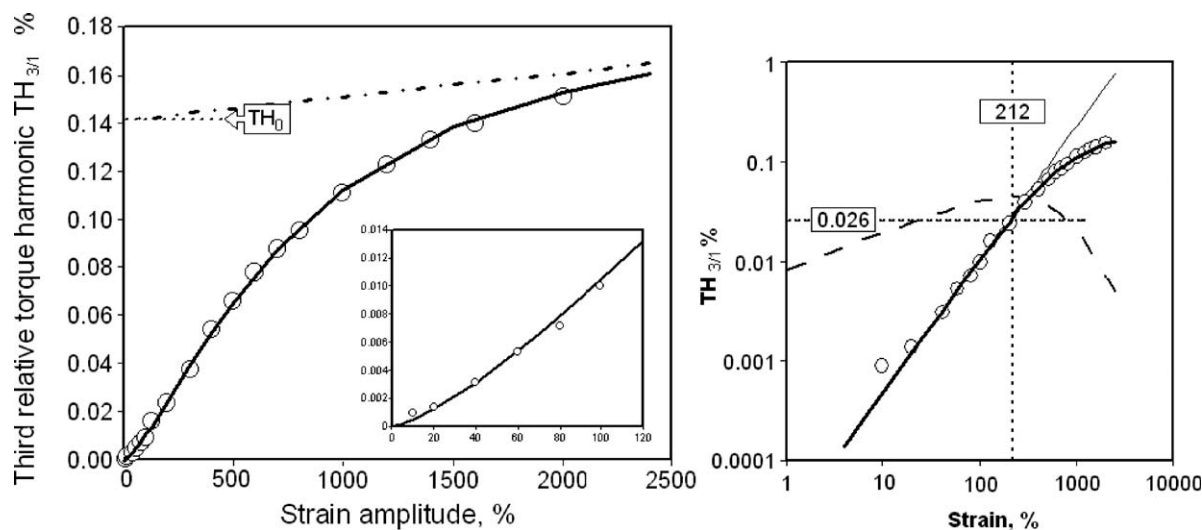


Figure 11 Third relative torque harmonic vs. strain amplitude as measured on 10% solution of PIB in oligoisobutylene by Wilhelm et al.⁷ and fitted curve with eq. (4); PIB: $M_v = 1.11 \times 10^3$ kg/mol, $M_w = 0.89$ Mw, $M_n/M_w = 2$; cone-plate, 50 mm dia., cone angle = 0.02 rad; 0.1 Hz; 298 K. The right graph compares fitting with eqs. (3) and (4) (bold line); the dashed line is the first derivative (300 \times) of eq. (4), whose maximum position is indicated.

Results on polyethylene

Figure 10 shows the results obtained on a sample of commercial medium-density polyethylene [MDPE 3802 YCF, Total Petrochemicals, Spec. Gravity (23 $^{\circ}$ C) = 0.94 g/cm 3 , MFI (MI-2) = 0.2 g/10 min, MFI (MI-5) = 0.92 g/10 min] using two similar closed cavity torsional rheometers (i.e., RPA), updated for FT experiments. Exactly, the same strain sweep test pro-

cedure was used on both instruments but, as mentioned before (**Experimental approach** section), the manner the torque and strain signals are captured and the torque and strain harmonics are extracted is somewhat different. As shown in Figure 10, results from both instruments perfectly superimpose, so that parameters corresponding to eqs. (2) and (4) were obtained by fitting all data. Parameters are listed in Table II. Slope b is equals to 1.75.

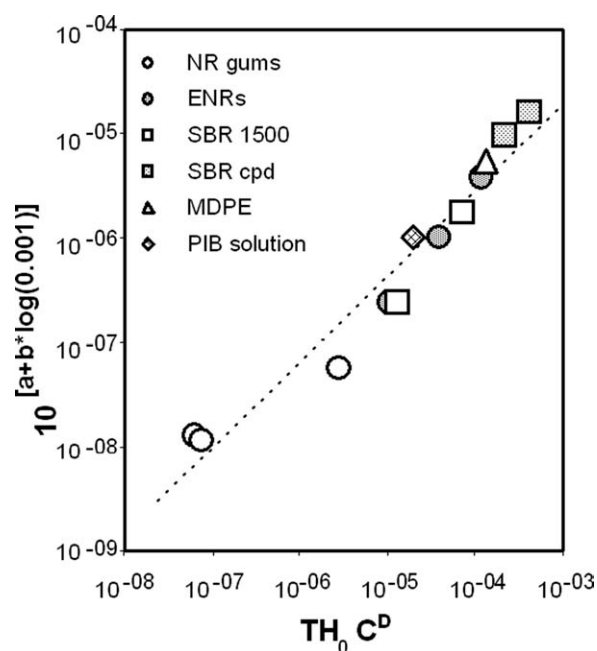


Figure 12 Comparing the material characteristic with the Hyun et al. equation at very low strain amplitude, (i.e.) using data obtained on various polymer systems (Table 2). The dashed line is drawn to underline the proportionality between the two quantities and corresponds to the following equation: $y = 0.0059 \cdot x^{0.8273}$.

Data on PIB solution

As one might question the capabilities of eqs. (3) and (4), respectively, in fitting experimental results on other polymer systems as the ones evaluated with closed-cavity torsional rheometers, Figure 11 shows literature data on a 10% solution of polyisobutylene (PIB) in oligoisobutylene as obtained at 0.1 Hz, 298 K with an open-gap rheometer by Wilhelm et al.⁷ (for experimental details, see the caption of Fig. 1). Corresponding fit parameters for eq. (4) are listed in Table II, as well as the parameters of eq. (3). As it can be seen, eq. (4) fits very well experimental data in the whole experimental window, whereas the asymptotic high-strain behavior is not yet reached by data at the highest investigated strain amplitude. The inset in the left graph shows that eq. (4) also gives an excellent fit in the lowest investigated strain region. The right graph compares eqs. (3) and (4), using logarithmic scales, and shows again that, providing the correct value for b is used (i.e., $b = 1.34$ in the case considered), the Hyun et al. equation is valid in the small- and medium-strain amplitude regions only, and appears as a local version of the full model as expressed by eq. (4).

DISCUSSION

In the infinitesimally low-strain region, no (odd) torque harmonics are expected to be observed, in agreement with theory. As demonstrated above, the proposed four parameters model (eq. (4)) reduces asymptotically in the very low strain region to a combination of only three parameters, that is TH_0C^D . This quantity does not depend on strain amplitude and can be considered as a true material characteristic, obviously related to both the linear and the nonlinear behaviors. Among the experimental data reported above, the series on epoxidized natural rubber (**Results on epoxidized natural rubber samples** section) is very illustrative in this respect because, as the epoxidation level and hence the chain rigidity increases, the quantity TH_0C^D significantly decreases, that is 3.85×10^{-5} , 1.085×10^{-5} , and 1.14×10^{-4} for, respectively, 5, 25, and 50% epoxidation.

The equation proposed by Hyun et al. (eq. (3)) fits well torque harmonics in the small- and medium-strain amplitude regions only, but the parameter b is experimentally found quite differing from 2. As mentioned above, mathematical similarities with the expanded version of eqs. (4) and (3) suitably rewritten as a power law suggest that in the very low strain region, a kind of proportionality can be expected between the quantity TH_0C^D , and a corresponding data calculated with eq. (3), at a sufficiently low and well-selected strain amplitude. Data in Table II were, therefore, used to calculate TH_0C^D and $10^{a + b \log(0.001)}$ for all the systems considered in this article. As shown in Figure 12, torque harmonics calculated with the Hyun et al. equation show the expected proportionality with the quantity TH_0C^D , providing, however, that the strain amplitude is carefully selected. Using a strain amplitude either smaller or larger than 0.001 yields results that are less comparable with TH_0C^D . This comparison further demonstrates that the Hyun et al. equation is a local version of the full model as expressed by eq. (4).

CONCLUSIONS

Closed cavity torsional rheometers allow to submit molten high-molecular-weight polymers and other stiff polymer systems to LAOS experiments whose results are conveniently analyzed through FT of both strain and torque signals. Doing so, torque harmonic variation with strain amplitude can be considered up to relatively high levels, in the 1000% strain range. How odd torque (or stress) harmonics increase with strain amplitude can be considered as a typical nonlinear viscoelastic "signature" of tested materials. Out of the various equations that were proposed to fit harmonics vs. strain curves, a simple four-parameter model (i.e., eq. (4)) was demon-

strated, either through an analysis of its mathematical virtues or through application to a wide selection of experimental results, to offer a highly flexible approach that readily encompasses all the other proposed ones. Although the experimental demonstration was provided with the third and the fifth relative torque harmonics, and the sum of all odd harmonics up to the 15th, this equation is expected to fit any relative torque harmonics, providing, however, that the experimental strain windows is wide enough to encompass both the linear and the nonlinear region. When using logarithmic scales for both the harmonics and the strain amplitude, the model yields a straight line in the low- and medium-amplitude range where the linear-to-linear transition is observed. By treating experimental LAOS data on various systems, it is clearly seen that the slope of this line is a characteristic of the tested material, generally significantly different from 2, in sharp contrast with certain proposals in the literature. It is also demonstrated that a quantity calculated with three parameters of the full model is a true material characteristic (in the frequency and temperature condition of the experiment).

NOMENCLATURE

$\gamma, \gamma_0, \gamma(t)$	respectively strain, maximum strain amplitude, strain as function of time
Fraction of 1 or %	
$\sigma, \sigma_i, \sigma(t)$, Pa	respectively stress, stress component, stress as function of time
ω rad/s	frequency
t, s	time
$Th(\omega)$	fundamental frequency torque
$Th(n\omega)$	n th torque harmonic
$TH_{n/1} = Th(n\omega) / Th(\omega)$, %	relative n th harmonic (corresponding to frequency ω)
$TH_{n/1}^\infty$, %	maximum degree of nonlinearity for each harmonic or relative torque harmonic for an infinite strain amplitude
γ_a , Fraction of 1	strain for the apparent onset of nonlinearity
λ , Fraction of 1	relative change (or inverse slope) of the n th harmonic as a function of the shear amplitude
$h[\gamma(t)]$	time-dependent damping function
P , Fraction of 1	parameter expressing the power law dependency of (relative) torque harmonics for small-strain amplitudes
Q	Q is the prefactor (so-called pivot point) of the power law

	dependency of (relative) torque harmonics
b	slope of $TH_{3/1}$ vs. γ in double-logarithm plot
a	$a = \log[TH_{3/1}(100\%)]$
$TH_0, \%$	extrapolation toward $\gamma = 0$ of the high-strain linear variation of (relative) torque harmonic with strain amplitude
$\alpha, \%^{-1}$	slope of the asymptotic high-strain behavior of (relative) torque harmonic vs. strain amplitude
$C, \%^{-1}$	parameter associated with the strain sensitivity in the linear-to-nonlinear region
D	parameter associated with the extent of the linear region

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