

## Fourier Transform rheometry : a new tool to investigate intrinsically non-linear viscoelastic materials

Jean L. Leblanc

University P. & M. Curie (Paris 6)

Polymer Rheology and Processing

60, rue Auber – F-94408 Vitry-sur-Seine cedex, France

### INTRODUCTION

Fourier transform (FT) rheometry is a development of the so-called dynamic (or harmonic) testing to investigate both the linear **and** the non-linear viscoelastic domains of polymer materials. It consists in considering the frequency spectrum of the torque signal obtained when submitting a material to high strains. Standard dynamic testing requires strict proportionality between strain and stress for valid resolution of the (measured) complex modulus into its elastic and viscous components. No such condition is needed for FT rheometry, which finds its roots in large amplitude oscillatory strain (LAOS) experiments<sup>1,2,3</sup>. When implemented on appropriate instruments, this test technique can readily be applied on complex polymer systems, for instance filled rubber compounds. Incompatible polymer blends or thermoplastic vulcanizates, in order to yield significant and reliable information<sup>4</sup>. FT rheometry suits particularly well complex polymer systems whose main characteristic is generally a strong non-linear viscoelastic behavior. Any dynamic rheometer can conveniently be modified for FT testing, in order to capture the full strain and torque signals generated when submitting samples to harmonic deformations at fixed frequency and temperature. Fourier transform calculation techniques are then used to resolve captured signals into their main component and other harmonics, if any.

When submitted to sufficiently large strain, any simple (pure) polymer eventually exhibits non-linear viscoelastic properties; in such case the observed behavior is called **extrinsic** non-linear viscoelasticity, since owing to external factors (i.e. the applied strain). Most complex polymer systems appear to be **intrinsically** non-linear, since their response to applied strain has an internal origin, i.e. their morphology, and superposes to the non-linearity associated with large strain<sup>5</sup>. FT rheometry allows to precisely documenting non-linear viscoelastic behavior, but the distinction between extrinsic and intrinsic non-linear materials requires additional data treatment.

The objectives of this presentation are (i) to briefly describe the FT rheometry technique, as implemented on a commercial torsional harmonic rheometer, with the appropriate test protocols and data treatments that allow a full investigation of the non-linear viscoelastic properties of polymer materials, (ii) to illustrate the capabilities of the technique with data on several intrinsically non-linear materials.

### EXPERIMENTAL

#### A modified torsional dynamic tester for Fourier transform rheometry

Owing to their high viscosity and stiffness, most complex polymer systems need special instruments for rheometrical testing and, even for simple drag flow measurements, it has long been shown that

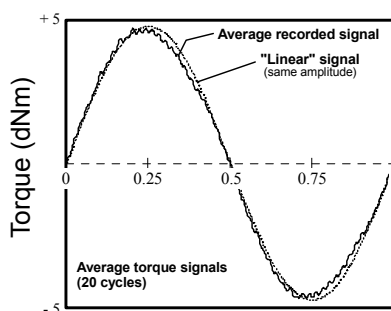
only pressurized conditions allow reproducible data to be obtained<sup>6</sup>. Consequently, appropriate modifications were brought to a commercial torsional rheometer, initially developed for rubber materials, i.e. the Rubber Process Analyzer RPA® (Alpha Technologies), in order to capture strain and torque signals, using suitable codes developed using LabView® software (National Instruments). Details on the modification and the measuring technique were previously reported<sup>2</sup>. Proprietary data handling programs, written in MathCad® (MathSoft

Inc.), are used to perform Fourier transform calculations and other data treatments. Figure 1 shows typical results on a sample of atactic polypropylene<sup>a</sup> at different strain amplitude. Left graphs are average torque signals out of 20 recorded cycles; perfect sinusoids of same amplitude are drawn for comparison. Right graphs are the corresponding FT spectra

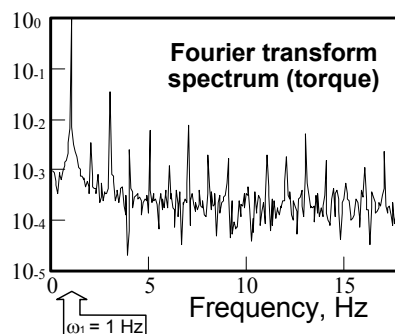
<sup>a</sup> Mn = 55 297 g/mol ; Mw = 124 739 g/mol ; kindly supplied by R. Koopmans (Dow Chemicals, Terneuzen, Netherlands)

### RPA-FT; 100°C; 1 Hz; Atactic Polypropylene

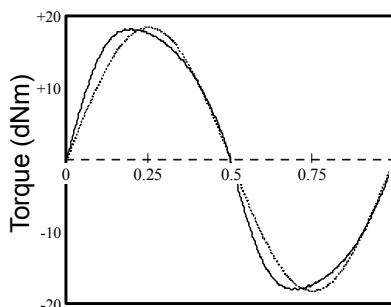
Strain : 3.5 deg (48.9 %)



$$\frac{T(n\omega_1)}{T(\omega_1)}$$



Strain : 33 deg. (461 %)



$$\frac{T(n\omega_1)}{T(\omega_1)}$$

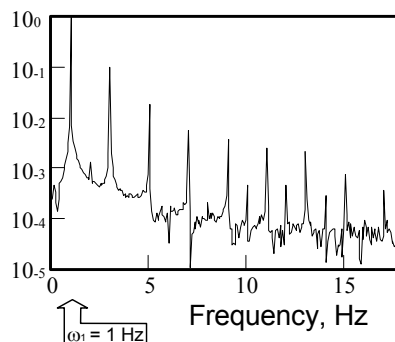


Figure 1 : Typical LAOS and Fourier transform experimental results on a simple (pure) polymer material.

As can be seen, upon a strain amplitude of 33 deg. (i.e. 461 % strain), the torque signal is clearly distorted, which corresponds to a non-linear character well assessed by the FT spectrum with significant odd harmonics. However, at lower strain (3.5 deg.; 48.9%), a slight distortion is nevertheless noted and characterized also by odd harmonics, in agreement with the strain dependence detected on the complex modulus (Figure 2).

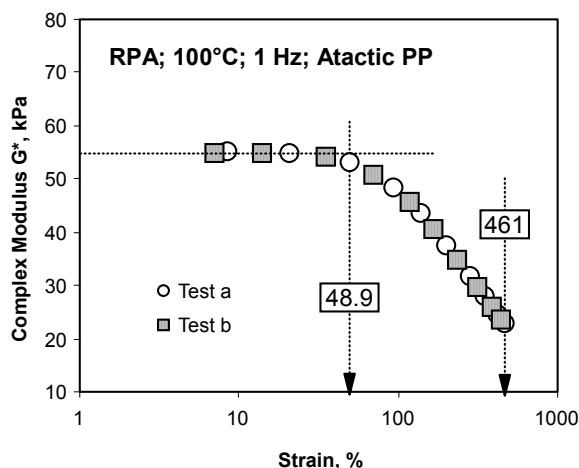


Figure 2 : Typical strain sweep test on a simple (pure) polymer.

With respect to Figure 2, standard harmonic testing would be limited to around 40% strain ( $\approx 3$  deg) for valid splitting of  $G^*$  into elastic  $G'$  and viscous  $G''$  components; otherwise apparent (and meaningless) data would be obtained. Fourier Transform rheometry is thus not limited to the linear response of polymer materials, but allows the overall viscoelastic behavior to be investigated in details.

#### Test protocols for non-linear viscoelastic investigation; FT data treatment

Test protocols were developed for non-linear viscoelastic investigation, which essentially consist in performing strain sweep experiments through two subsequent runs separated by a resting period of 2 min. At least two samples of the same material are tested (more if results reveal test material heterogeneity), in such a manner that, through inversion of the strain

sequences (i.e. run 1 and run 2), sample fatigue effects are detected, if any. At each strain sweep step, data acquisition is made in order to record 10240 points at the rate of 512 pt/s; twenty cycles are consequently recorded at each strain step. Differences are expected between runs 1 and 2 for materials sensitive to strain amplitude. Out of Fourier Transform treatment of torque signal, one extracts essentially two types of information: first the main torque component, i.e. the peak in the FT spectrum that corresponds to the applied frequency [hereafter noted  $T(\omega)$ ], second the harmonics, with the third (i.e. the peak at 3 x the applied frequency) the most intense one. FT treatment of the strain signal provides information about the quality of the applied deformation and, as explained below, allows correcting data for technical limits of the instrument.

Figure 3 compares data obtained from strain sweep experiments on a simple (pure) polymer using either standard harmonic testers or Fourier Transform rheometers<sup>b</sup>. Complex modulus data obtained with the RPA correspond to ARES plate-plate results only when the gap with the latter is 8 mm. Main torque component from the RPA-FT tester shows the expected linear variation at low strain, then a typical non-linear deviation. Close cavity rheometers, such as the RPA, allows accurate and reproducible results to be obtained up to the largest strain permitted by the instrument, whilst open cavity testers are limited to relatively modest strain for adequate boundary conditions to be maintained, as recently documented by Friedrich *et al.*<sup>7</sup> The non-linear response of the material is documented by odd harmonics detected in the torque signal, with the 3<sup>rd</sup> the most intense one. As shown in the upper right graph of Figure 3, the (relative) 3<sup>rd</sup> torque harmonic as measured with the up-dated RPA, does not correspond to theoretical

<sup>b</sup> plate-plate data (at two different gaps) were kindly obtained by M. Wilhelm, Max Planck Institute, using his purposely modified Rheometrics ARES tester.

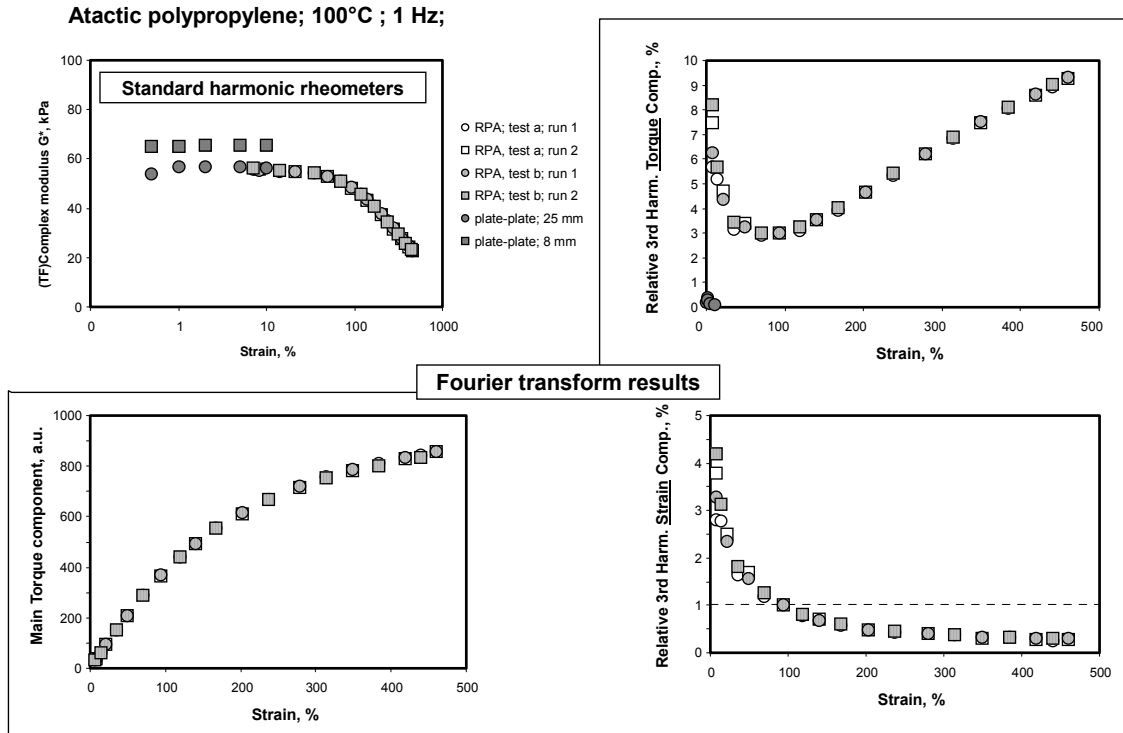


Figure 3 : Harmonic strain sweep experiments; standard testing vs. Fourier transform rheometry on a simple (pure) polymer

expectation since an up-turn is noted as low strain. Third torque harmonics measured with the open cavity rheometer (i.e. Rheometrics ARES) are close to zero at low strain amplitude.

Ideal dynamic testing requires that a perfect sinusoidal deformation at controlled frequency and strain be applied on the test material. This aspect is rarely considered in literature and the quality of the applied signal is generally taken for granted. Whatever are the quality design and the care in manufacturing instruments, there are always technical limits in accurately submitting test material to harmonic strain. Fast Fourier transform of the strain (i.e. applied) signal allows this aspect to be documented. As detailed elsewhere<sup>4</sup>, FT analysis reveals relatively significant (i.e. larger than noise) odd harmonics components in RPA strain signal, with obviously the 3<sup>rd</sup> the larger one, particularly at low strain amplitude. The relative 3<sup>rd</sup> were perfect, all T(3/1) data points would fall on the vertical axis. Consequently T(3/1) data are corrected according to :

harmonic strain component, i.e. S(3/1), decreases as strain amplitude increases, whatever the test conditions, and generally passes below 1% of the main component when the strain angle is higher than 1.3 – 1.5 deg. (18-20%). In other terms, high strain tests are performed in better-applied signal conditions than low strain ones.

As shown in Figure 4 (right upper graph), a plot of T(3/1) vs. S(3/1) suggests however an adequate method to correct 3<sup>rd</sup> torque harmonic component for deficiencies in applied strain. Indeed, T(3/1) vs. S(3/1) decreases, passes through a minimum and appears to be bounded by a straight line whose slope is a multiple of  $\frac{1}{3}$ . If an ideal elastic material, for instance the calibration spring, is tested then the slope is  $\frac{2}{3}$ . The correction method is based on the simple argument that, if the applied strain perfect

$$T(3/1)_{corr} = T(3/1)_{TF} - S(3/1)_{TF} \times \frac{CF}{3} \quad (\text{Eq. 1})$$

where  $T(3/1)_{TF}$  and  $S(3/1)_{TF}$  are the 3<sup>rd</sup> relative harmonic components of the torque and strain signals respectively, and CF the correction factor, as derived from the  $T(3/1)$  vs.  $S(3/1)$  plot. The lower right graph in Figure 4 shows how this correction method

works, with the immediate result that at low strain, when the viscoelastic response of the material is expected to be linear, the correct 3<sup>rd</sup> relative torque harmonic component vanishes, in agreement with theory<sup>1</sup>.

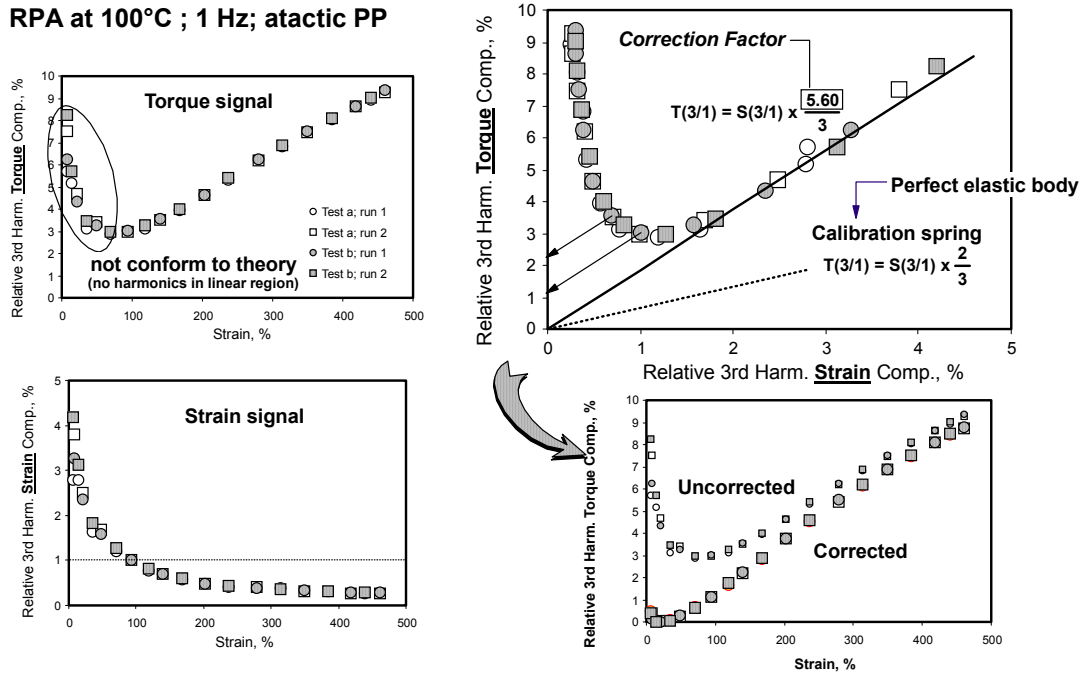


Figure 4 : Correction method on 3<sup>rd</sup> relative torque component data

RPA-FT results, according to test protocols described above, yield essentially two types of information, which reflects how the main torque, i.e.  $T(\omega)$ , and the (corrected) 3<sup>rd</sup> relative torque harmonic component, i.e.  $T(3\omega)/T(\omega)$  or  $T(3/1)$ , vary with the strain amplitude. At low strain (and providing that the test material exhibits a linear response within the experimental strain window; i.e. between 0.5 and 33.0 degree at 1 Hz with the RPA),  $T(\omega)$  shows a linear variation with the set strain  $\gamma$ , and then deviates from linearity as non-linearity develops. The ratio  $T(\omega)/\gamma$  has obviously the meaning of a modulus and, for a material exhibiting linear viscoelasticity within the considered strain amplitude range (not the case for the filled rubber compound used in the Figure), one gets the most familiar picture of a plateau region at low strain, then a typical strain dependence. Fourier Transform yields the main torque component in arbitrary units, but with respect to the data acquisition conditions used for Fourier transform calculation, the following equality holds:

$$G^*(\text{kPa}) = 12.335 \times \frac{T(\omega)}{\gamma}$$

(with  $T(\omega)$  in arbitrary unit and  $\gamma$  in %).

Quarter cycle integration technique:  
extrinsic vs. intrinsic non-linear  
viscoelasticity

Fourier transform analysis of torque signal allows the non-linear response of viscoelastic materials to be clearly quantified, but experiments with complex polymer systems reveal a limit of this data treatment. Figure 5 shows, for instance, average torque signals as recorded when submitting either a high cis-1,4 polybutadiene sample (gum cut from the bale) or a 50phr N330 filled compound<sup>c</sup> to a large strain amplitude (22.5 deg; 314 %)

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<sup>c</sup> NeoCis BR 40 : 100 ; N330 carbon black : 50; Zinc oxide : 5; Stearic Acid : 3; Process Oil : 5; Tri-methyl quinoline, polymerized : 2; Iso-propyl-paraphenylenediamine : 1; compound prepared in Banbury mixer with a mixing energy of  $\approx 1500 \text{ MJ/m}^3$

torsional harmonic test at 1 Hz (left graphs). Torque signals were averaged out of 20 recorded cycles and were very stable, as demonstrated by the standard deviation gray zone, hardly visible behind the mean traces. For the sake of comparison, perfect sinusoidal traces of same amplitude are drawn. One clearly sees that torque signals are distorted, which reflects in harmonics rich FT spectra.

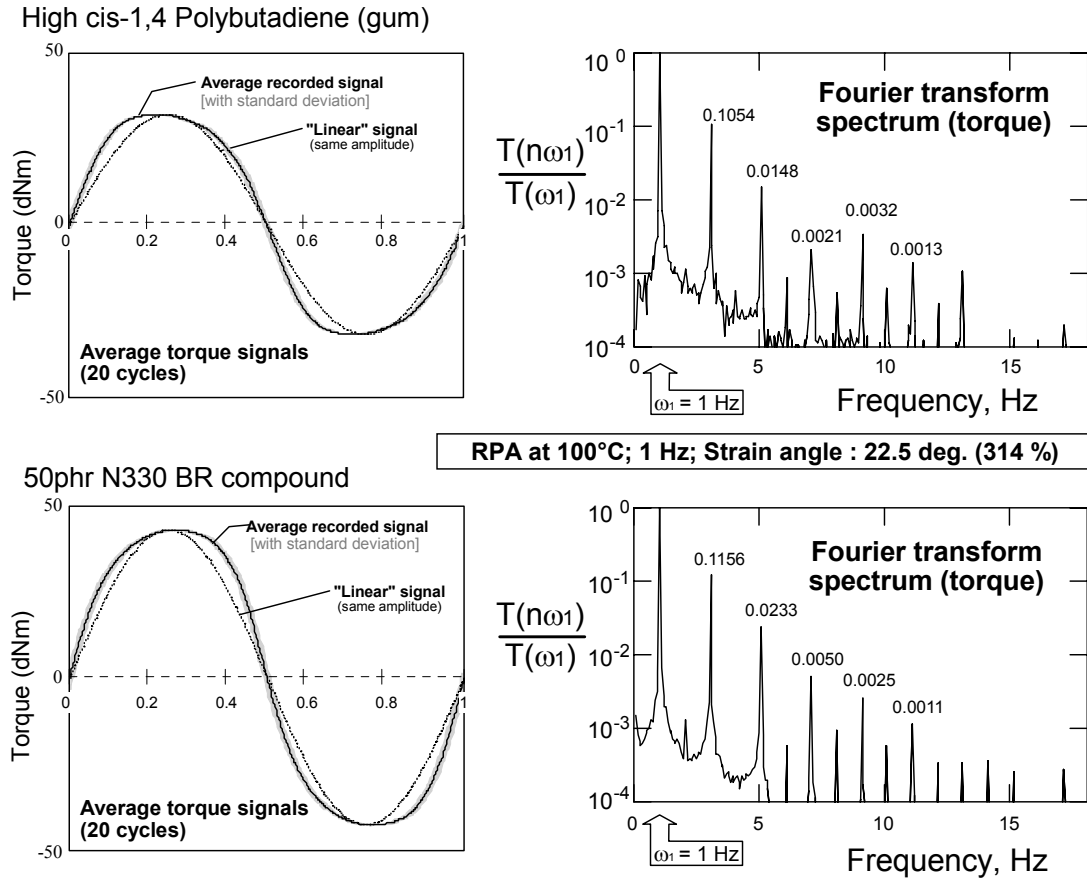


Figure 5 : Recorded torque signals during RPA tests at high strain on a gum and a 50 phr polybutadiene compound; Fourier transform torque spectra.

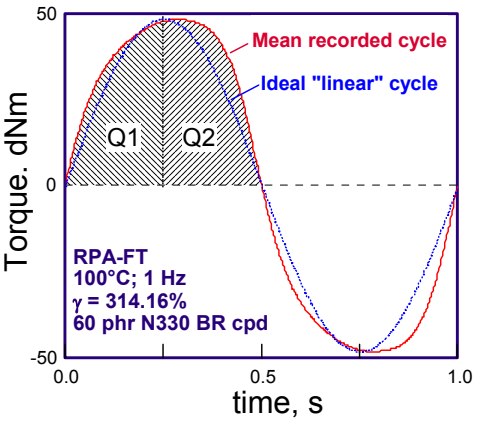
The filled material exhibits however a severer distortion, which in addition affects more the right part of the half signal. This effect is attributed to the presence of carbon particles but hardly corresponds to differences in the FT torque spectrum. In other terms, there is a substantial difference between the non-linear viscoelastic behavior of a pure, unfilled polymer and of a filled material. The former essentially exhibits non-linearity through the application of a sufficiently large strain and we called this behavior **extrinsic non-linear viscoelasticity** (because occurring through *external* causes, i.e. the applied strain), whilst the latter shows **intrinsic non-linear viscoelasticity** (because owing to the *internal* morphology of the material). It is quite obvious that Fourier Transform analysis of torque signal, whilst offering an attractive quantification of the non-linear viscoelastic response, has limited

capabilities to distinguish extrinsic and intrinsic characters.

In order to supplement FT analysis, we therefore considered quarter cycle integration as an easy data treatment technique to distinguish extrinsic and intrinsic non-linear viscoelasticity (Figure 6). The ratio of the first to second quarters torque signal integration, i.e. Q1/Q2 allows to clearly distinguishing between the strain amplitude effect on an unfilled and a filled materials (right graphs in Figure 6). In the case of the former, Q1/Q2 ratio is always higher than one and increases with strain amplitude; in such a case the torque signal is always distorted “on the left” (i.e. Q1 > Q2). With the filled compound, Q1/Q2 is first higher than one a low strain, then quickly passes below one as  $\gamma$  increases, which correspond to a distortion “on the right”, as shown in the upper left graph. If one considers the Q1/Q2 ratio at high strain for a

series of compound with increasing carbon black content (lower left graph), then one sees that, as filler level increases, the non-linear character changes from extrinsic to

intrinsic. Expectedly the transition extrinsic-to-intrinsic occurs at a carbon black content that corresponds to the so-called percolation level (around 12-13% in volume fraction).



Effect of strain amplitude on Q1/Q2 ratio

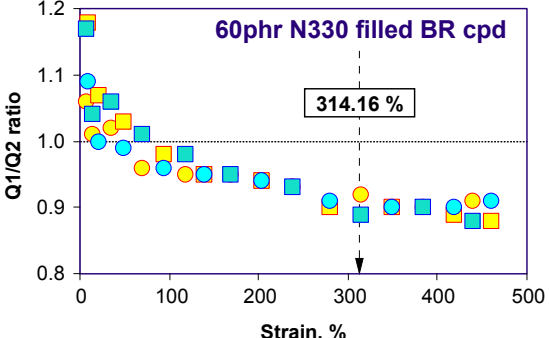
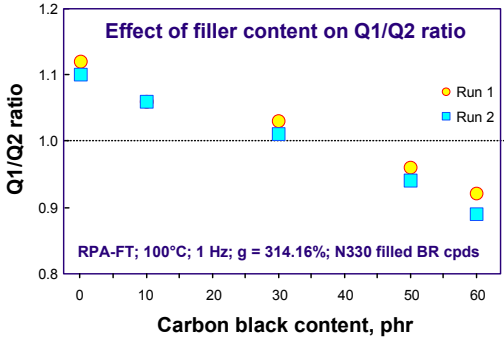
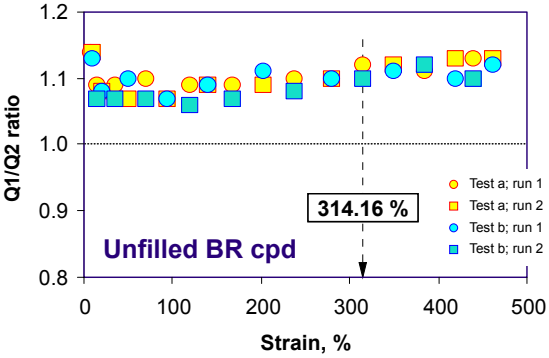


Figure 6 : Documenting extrinsic and intrinsic non-linear viscoelastic character through quarter cycle integration of averaged torque signal

In summary, the Fourier Transform rheometry protocols described above and the associated data treatments yield considerable information about the viscoelastic character of materials. Within one hour, two samples are tested (for documenting material's quality) and the full data treatment is performed in around 3 minutes (using the present combination of VBA macros, MathCad® routines and SigmaPlot® worksheets).

#### CAPABILITIES OF FT RHEOMETRY IN CHARACTERIZING INTRINSICALLY NON-LINEAR MATERIALS

##### Carbon black filled rubber compounds

Whatever their chemical nature, nearly all heterogeneous materials exhibit complicated responses when submitted to strain or to flow. In the case of filled (rubber) materials, it is known whilst not fully understood, that strong interactions between filler particles and polymer matrix play an important role in the flow properties of such materials. Following the pioneering work by Payne nearly 40 years ago, the significant reduction of elastic modulus with increasing strain amplitude of filled (vulcanized) elastomers, usually termed "Payne effect", has been investigated by a number of authors<sup>8,9</sup>, but the very mechanism for both reinforcement and non-linearity remains a controversial issue. In contrast with the classical view that the Payne effect is due to the breakdown upon increasing strain of a secondary carbon black structure (the so-called carbon black network), assumed to exist in the compound in addition to the vulcanized rubber network, there are recent contributions that consider either stress-induced debonding of polymer chains from the filler surface<sup>10</sup>, or release of trapped entanglements, i.e. temporary bonding of chains, from the filler surface<sup>11,12</sup>. Dynamic modulus decrease upon increasing strain amplitude has also been observed in unvulcanized systems<sup>12,13</sup>, but the associated loss of stress – strain proportionality (i.e. the basic condition for

dynamic testing in linear viscoelastic condition) and the corresponding distortion of the harmonic signals were not directly considered, owing to instrument limitations. Carbon filled polybutadiene compounds (see Table 1) were therefore submitted to Fourier Transform rheometry, using test protocols described above, in order to observe how extrinsic non-linear viscoelasticity (as arising for large strain) combines with the intrinsic non-linear character (i.e. due to the structure of the material) of complex polymer systems.

Table 1 : Carbon black filled polybutadiene compounds

Compound coding :	BRC00	BRC10	BRC30	BRC50	BRC60
High cis-1,4 BR <sup>a</sup>	100	100	100	100	100
N330 carbon black	-	10	30	50	60
Zinc oxide	5	5	5	5	5
Oil	5	5	5	5	5
Stearic acid	3	3	3	3	3
TMQ <sup>b</sup>	2	2	2	2	2
IPPD <sup>c</sup>	1	1	1	1	1
$\Phi_{\text{black}}$ <sup>d, f</sup>	0	0.043	0.119	0.184	0.213
$\Phi_{\text{fillers}}$ <sup>e, f</sup>	0.007	0.050	0.126	0.190	0.219
<sup>a</sup> NeoCis BR40 (Polimeri); 98% cis-1,4; $M_w = 450.000$ g/mol; MWD = 3.2 <sup>b</sup> Tri-methyl quinoline, polymerized <sup>c</sup> Iso-propyl-paraphenylenediamine <sup>d</sup> carbon black volume fraction <sup>e</sup> (carbon black + zinc oxide) volume fraction <sup>f</sup> specific gravity data used in calculation (g/cm <sup>3</sup> ): BR 0.90; N330 1.80; ZnO 5.57; Oil 0.92; Stearic Acid 0.98; TMQ 1.08; IPPD 1.17					

Figure 7 shows the main torque component variation upon strain and its corresponding (FT) complex modulus curve for the gum elastomer. Reproducibility is excellent and there is no strain history effect (runs 1 and 2 superimpose). The  $G^*$  curve is adequately modeled with the following equation:

$$G^*(\gamma) = G_f^* + \left[ \frac{G_0^* - G_f^*}{1 + (A\gamma)^B} \right] \quad (\text{Eq. 2})$$

where  $G_0^*$  is the modulus in the linear region,  $G_f^*$  the modulus for an infinite strain, A the reverse of a critical strain (which corresponds to  $\frac{G_0^* + G_f^*}{2}$ ), and B a parameter describing the strain sensitivity of the material. The so-derived linear modulus is obviously the initial slope of the  $T(\omega)$  vs.  $\gamma$  graph. No difference is seen between data gathered through runs 1 and 2, thus demonstrating that the unfilled compound is not sensitive to strain history or that any memory effect is conveniently damped down during the two minutes dwell time.

Figure 8 shows the corresponding data for the 60 phr carbon black filled compound.

Here the picture is notably different, as no linear behavior is observed within the experimental window (i.e. 6.98 to 461 %; 0.5 to 33 deg.). In addition runs 1 and 2 are significantly different, which suggests that the (rubber – filler) morphology has somewhat been altered when straining the material up to 31 – 33 deg., and that no sufficient recovery, if any, occurs during the two minutes resting period

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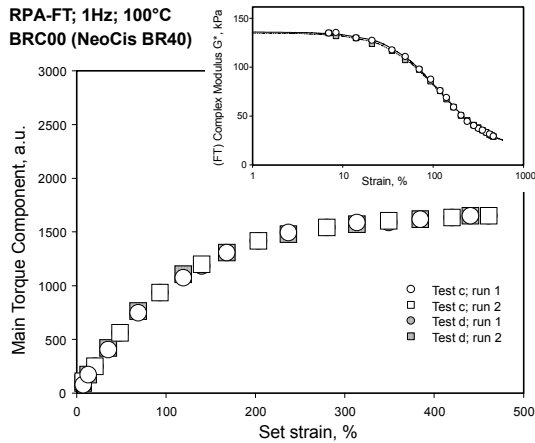
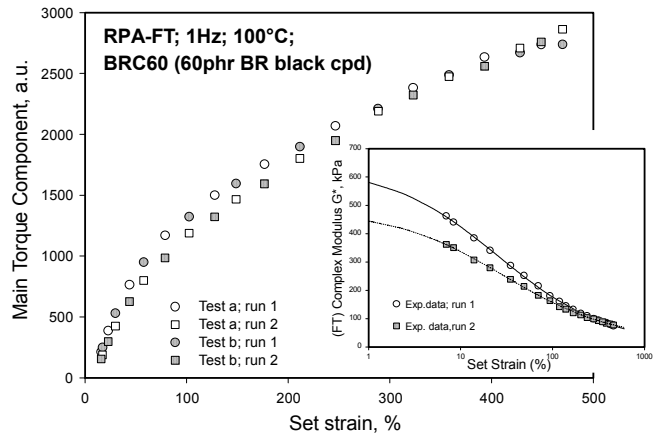


Figure 7 : RPA-FT on gum polybutadiene; main torque component and complex modulus variation on strain.

Table 2 gives fit parameters of Eq. 2 for all the compounds tested. It must be noted that both  $G^*_0$  and  $G^*_f$  are extrapolated values, and therefore of limited meaning, if any, when their numerical value is too far from measured data. For instance, negative  $G^*_f$  values have no physical meaning and must therefore be discarded. The compounding variable in the work reported here is the filler level that can be expressed in term of volume fraction  $\Phi_{black}$ . The linear modulus  $G^*_0$  increases strongly with the carbon black content, in a manner markedly differing from the Guth-Gold-Simha model<sup>14,15</sup>, i.e.  $G_{cpd} = G_0(1 + 2.5 \times \Phi_{black} + 14.1 \times \Phi_{black}^2)$ .

For instance using  $G^*_0 = 114$  kPa, one calculates that with 60 phr ( $\Phi_{black} = 0.213$ ),  $G^*_0$  should be equal to 247.6 kPa, whilst the experimental results is twice this value. The Guth-Gold-Simha equation is however based on mere hydrodynamic considerations and neither the complex structure of the filler, nor the rubber-filler interactions are taken into consideration. Another interesting aspect is the growing difference between runs 1 and 2, as carbon black content increases. The first strain sequence softens the material and the higher the filler level the larger the strain softening effect. The parameter A in Eq. 2 is the reverse of a



critical strain, and the higher the filler level, the lower 1/A with yet a significant strain

Figure 8 : RPA-FT on 60phr filled BR cpd; main torque component and complex modulus variation on strain.

history effect. The strain sensitivity parameter B steadily decreases with  $\Phi_{black}$  and that mixing and compounding significantly modify it (compare the gum BRN40 with the no black compound BRC00).

Table 2 : Filled polybutadiene compounds; fit parameters of Eq. 2

Sample	Run	$\Phi_{\text{black}}$	$G^*_{0}$ , kPa	$G^*_{f}$ , kPa	1/A	B	$r^2$
BRC00	1	0.000	114.1	(-138.1)	204.80	0.58	0.9894
	2	0.000	113.3	17.5	204.08	1.45	0.9999
BRC10	1	0.043	129.1	(-15.4)	268.10	0.81	0.9867
	2	0.043	128.2	15.0	184.84	1.27	0.9996
BRC30	1	0.119	221.0	(-19.3)	103.41	0.60	0.9979
	2	0.119	192.5	6.9	122.70	0.89	0.9997
BRC50	1	0.184	447.2	3.9	16.92	0.57	0.9857
	2	0.184	301.1	27.3	50.58	0.83	0.9992
BRC60	1	0.213	637.9	27.1	10.72	0.67	0.9948
	2	0.213	404.2	45.0	29.82	0.85	0.9994
BRN40	1	0.000	135.9	15.9	116.45	1.52	0.9993
	2	0.000	135.0	14.2	117.80	1.44	0.9994

Figure 9 shows how the relative 3<sup>rd</sup> torque harmonic varies with increasing strain amplitude for all the compounds tested. Data are well reproducible with no difference between tests a and b, and no difference between runs 1 and 2. Torque signal harmonics appear thus insensitive to strain history (contrary to the main component). We would interpret this information as an indication that rubber – filler interactions resist large strain amplitude (i.e. up to 500% at 1 Hz). Mixing and compounding however markedly affect the non-linear character as shown by the two upper graphs (gum vs. unfilled cpd). As observed in previously reported works<sup>2,4</sup>, the variation of the relative 3<sup>rd</sup> torque harmonic component with the strain amplitude appears such that an S-shape curve is generally observed, from zero at low strain up to a maximum at high strain. According to theoretical considerations by Wilhelm *et al.*<sup>16</sup>, the upper limit of the relative torque harmonic  $T(n\omega)/T(\omega)$  [or  $T(n/1)$ ] should be expected to be equal to  $1/n$ . Accordingly, with all the various materials we have tested so far, we never measured  $T(3/1)$  higher than 33% but, when the occurrence of a plateau  $T(3/1)_{\text{max}}$  could be foreseen without doubt, the value was significantly lower than 33%. Figure 9 shows that the filler content must be higher than 30 phr ( $\Phi_{\text{black}} > 0.12$ ) for an S shape of  $T(3.1)$  vs. strain to be clearly observed, and at the highest filler

fraction considered, the  $T(3/1)_{\text{max}}$  plateau value is within the experimental strain window. Such data suggest the following model for conveniently fitting  $T(3/1)$  vs.  $\gamma$  curves :

$$T(3/1)_{\gamma} = T(3/1)_{\text{max}} \times [1 - \exp(-C\gamma)]^D \quad (\text{Eq. 3})$$

where  $\gamma$  is the deformation (%), C and D fit parameters<sup>d</sup>. With respect to non-linear viscoelastic behavior, the most significant information is provided by the two parameters C and D of Eq.2 that “quantify” the strain sensitivity of materials. The first derivative of Eq. 3 allows calculating the slope of  $T(3/1)$  vs.  $\gamma$  curves at any strain, an easier manner to quantify strain effect than simultaneously considering C and D.

<sup>d</sup> In using Eq. 3 to model  $T(3/1)$  variation with strain, one may express the deformation (or strain)  $\gamma$  either in degree angle or in %. Obviously all parameters remain the same except C, whose value depends on the unit for  $\gamma$ . The following equality applies for the conversion :  $C(\gamma, \text{deg}) = \frac{180}{100} \frac{\alpha}{\pi} \times C(\gamma, \%)$ , where

$\alpha = 0.125 \text{ rad}$ .

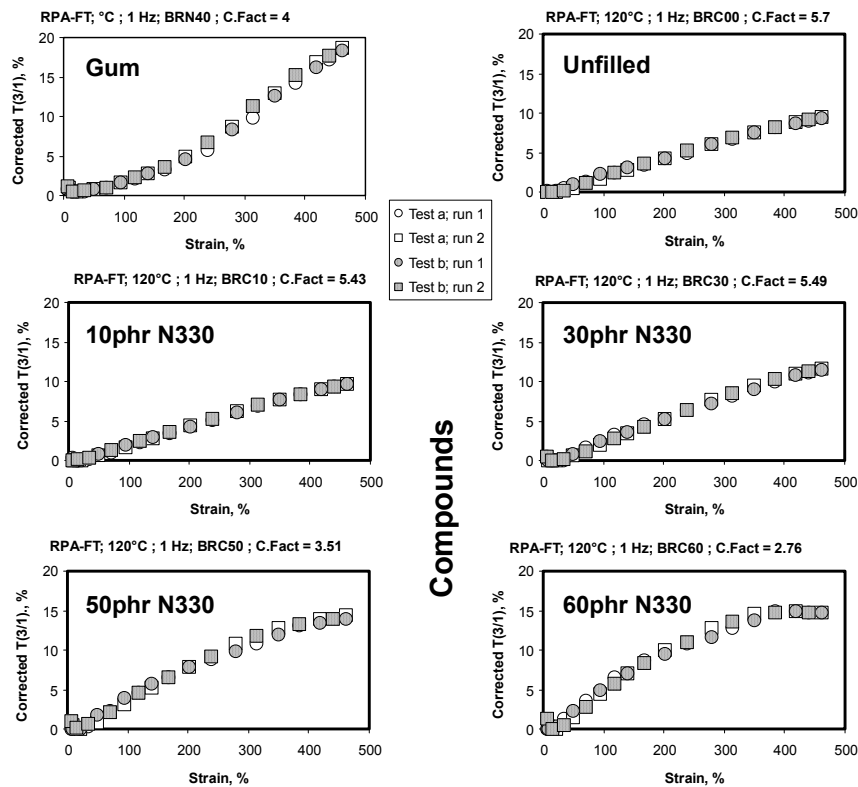


Figure 9 : RPA-FT on filled polybutadiene compounds; relative 3<sup>rd</sup> torque harmonic component variation with strain.

Table 3 gives fit parameters of Eq. 3 and the slope of T(3/1) vs.  $\gamma$  at 200% strain for all the compounds tested. Again it must be stressed here that since  $T(3/1)_{max}$  is an extrapolated value (at “infinite” strain), confidence in the fit data depends on the difference between this parameter and the experimental value at the highest strain tested. Conversely, the slope at 200% reflects precisely the strain sensitivity of the non-linear response, since obtained within the experimental strain range. As seen in Figure 10, the slope at 200% strain is systematically higher for run 2, and the difference tends to increase with the filler fraction. Mixing and compounding significantly affect the non-linear character of materials.

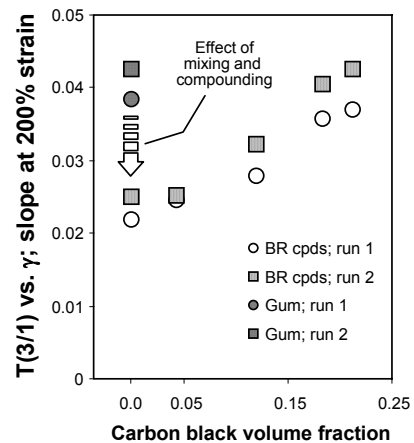


Figure 10 : Effect of mixing and compounding on non-linear response of filled BR compounds

Table 3 : Filled polybutadiene compounds; fit parameters of Eq. 3

Sample	Run	$\Phi_{\text{black}}$	$T(3/1)_{\text{max}}$	C	D	$r^2$	Slope 200%
BRC00	1	0.000	21.44	0.0015	1.19	0.9985	0.0219
	2	0.000	13.97	0.0034	1.67	0.9991	0.0250
BRC10	1	0.043	17.00	0.0025	1.46	0.9984	0.0245
	2	0.043	14.92	0.0031	1.56	0.9995	0.0252
BRC30	1	0.119	20.25	0.0023	1.36	0.9973	0.0279
	2	0.119	16.08	0.0040	1.84	0.9989	0.0322
BRC50	1	0.184	17.98	0.0040	1.41	0.9966	0.0357
	2	0.184	16.76	0.0056	1.86	0.9973	0.0406
BRC60	1	0.213	16.74	0.0058	1.43	0.9969	0.0370
	2	0.213	15.96	0.0082	2.15	0.9959	0.0426
BRN40	1	0.000	187.06	0.0007	1.83	0.9957	0.0385
	2	0.000	72.76	0.0015	1.98	0.9948	0.0426

### Green coconut fiber filled PVC composites

To further illustrate the capabilities of Fourier transform rheometry in obtaining reliable data on complex systems, selected results obtained on composites made of polyvinyl chloride and Green Coconut fibers (GCF) are presented hereafter<sup>17</sup>. Test materials, as described in Table 4, were prepared by dry blending ingredients then melt mixing in a Haake Rheocord 900, using a 85 cm<sup>3</sup> mixing chamber with cam rotors. Immediately after melt mixing, around 2 mm thick plaques were prepared by compression molding at 160°C.

Table 4 : PVC-Green Coconut fibers composites

Sample codes	VC00m	VCF80	VCF70
:	i	mi	mi
PVC (% w)	87.72	71.94	63.75
GCF (% w)	-	17.99	27.32
DOP <sup>a</sup> (% w)	8.77	7.19	3.68
UBZ <sup>b</sup> (% w)	3.51	2.88	2.55
Preparation	dry blend + laboratory mixer		
Conditions	Starting temperature : 130°C Fill factor : 0.70 Cam rotors speed : 50 RPM Final torque : 17 – 19 Nm.min Dump temperature : 158 – 160°C		
<sup>a</sup> di-octyl phtalate			
<sup>b</sup> UBZ-790; antidegradant			

Samples for RPA testing were prepared by die cutting disks of appropriate diameter out of the molded plaques. If necessary, samples were adjusted in order to maintain their size within the cavity volume + 5%. To ensure an easy filling of the RPA cavity, samples were disposed for 2-3 minutes on the lower die at the test temperature (160°C) before closing the test chamber. Strain sweep tests were performed with the RPA, according to protocols previously described (section 2.2).

Figure 11 shows that, within the experimental strain window permitted by the RPA, PVC-GCF composites do exhibit a strong non-linear behavior. However, by resolving the measured torque signal into its main component, one has access to a complex modulus which is adequately fitted with a modified version of Eq.2, i.e.

$$G^*(\gamma) = \frac{G_0^*}{1 + (A\gamma)^B} \quad (\text{Eq. 4}), \text{ to yield a so-called}$$

“linear”  $G_0^*$ , a critical strain  $1/A$  and a strain sensitivity parameter  $B$ . When derived from run 1 measurements,  $G_0^*$  accounts for the net effect of filler loading, independently of the structural damages due to the amplitude of the applied strain. The same quantity, obtained from run 2 data, provides a quantitative assessment of morphology changes imparted by the first strain sweep.

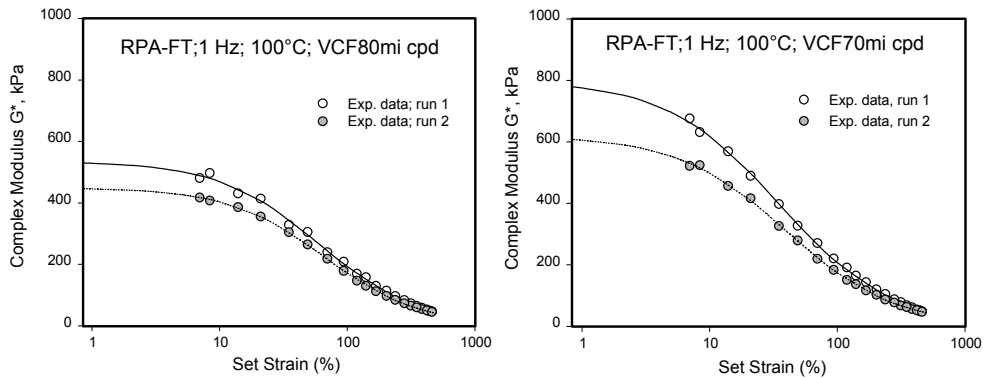


Figure 11 : PVC-GCF composites; variation of dynamic modulus with strain amplitude; effect of fiber content and shear damages (i.e. run 1 vs. run 2)

The slight reinforcing effect of green coconut fibers is clearly detected when plotting the linear modulus versus the fiber volume fraction (Figure 12). However, as GCF level effect remains below what would be predicted using the Guth-Gold-Simha model, such a modulus increase at best reflects a mere hydrodynamic effect of fibers, without evidence of interactions with the PVC matrix, except maybe good wetting.

the shorter the linear viscoelastic region, since  $1/A$  corresponds to a strain magnitude at which half the linear modulus is measured. The parameter  $B$  expresses the sensitivity of the material to strain amplitude; the smaller  $B$ , the severer the modulus drop. The variation of both  $1/A$  and  $B$  with fiber volume fraction is essentially linear, with no significant effect of strain history (i.e. runs 1 and 2 give the same results).

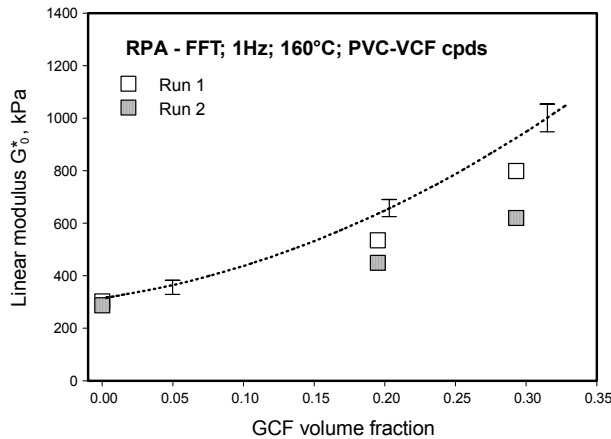


Figure 12 : RPA-FT on PVC-GCF composites; effect of fibers loading

The non-linear character of PVC-GCF composites strongly depends on fiber content, as clearly reflected by fit parameters of Eq. 4 (Table 5). Parameters  $A$  (or  $1/A$ ) and  $B$  concern the strain sensitivity of materials. The higher the fiber content,

Table 5 : Complex modulus  $G^*$  vs. strain  $\gamma$  ; fitting parameters for Equation 4.

Sample	Run	$G^*_0$ , kPa	$1/A$ , %	$B$	$r^2$
VCF00mi	run 1	302.0	140.6	1.48	0.9975
VCF00mi	run 2	287.5	136.1	1.44	0.9978
VCF80mi	run 1	534.9	59.5	1.10	0.9976
VCF80mi	run 2	449.2	65.8	1.15	0.9997
VCF70mi	run 1	798.6	34.7	0.99	0.9991
VCF70mi	run 2	619.6	39.9	1.02	0.9994

Relative 3<sup>rd</sup> torque harmonics were corrected as described in section 2.2 and fit using Eq. 3. As illustrated in Figure 13 for the unfilled PVC and the 27%w GCF composite, the S shape is observed with the experimental strain window, with no significant differences between runs 1 and 2, as clearly seen through fit parameters of Eq.3 (Table 6).

RPA-FT; 1 Hz; 160°C; VCF00mi

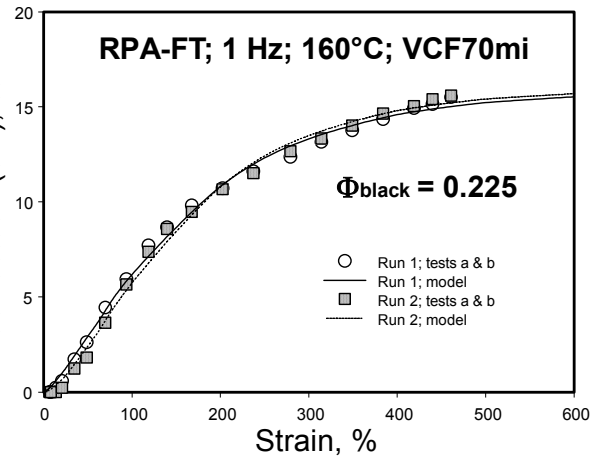
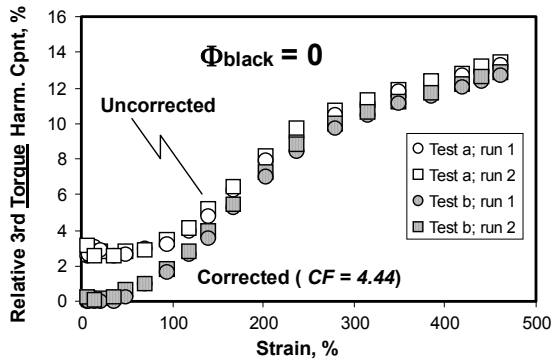


Figure 13 : PVC-GCF composites; RPA-FT; relative 3<sup>rd</sup> torque harmonic component.

Table 6 : PVC-GCF composites; modeling the variation of the 3<sup>rd</sup> relative torque harmonic with strain; fit parameters of Eq. 3

Test	$\Phi_{GCF}$	$T(3/1)_{max}$	C	D	$r^2$	Slope at $\gamma = 200\%$
VCF00mi, run 1	0.0	13.21	0.0091	3.81	0.9994	0.0452
VCF00mi, run 2		13.45	0.0088	3.45	0.9988	0.0442
VCF80mi, run 1	0.162	15.58	0.0058	1.41	0.9971	0.0342
VCF80mi, run 2		14.95	0.0083	2.18	0.9974	0.0401
VCF70mi, run 1	0.225	15.83	0.0072	1.41	0.9966	0.0341
VCF70mi, run 2		15.93	0.0079	1.69	0.9967	0.0374

The main effect arises from fiber loading and the most obvious one is the quasi disappearance of any linear response in the low strain region. The unfilled PVC compound (VCF00mi) still exhibits near zero  $T(3/1)$  values until 70-80% strain is reached, in contrast with the fiber loaded composites whose torque response has significant 3<sup>rd</sup> (and higher) harmonic components at the lowest strain investigated.

The extrinsic/intrinsic character of PVC-GCF composites is well described by the quarter cycles integration method. Figure 14 shows average measured torque signals at 139.6% strain (10 deg) for the unfilled and the 27%w GCF composite (left graphs) and their corresponding FT torque spectra (middle graphs). In the case of the unfilled compound, torque signal distortion is barely visible but a 5% relative 3<sup>rd</sup> torque harmonic is detected through Fourier transform. At the same strain amplitude, the filled composite shows clearly a distorted torque signal, with a larger distortion “on the right”. This would assign an intrinsic non-linear viscoelastic

character to PVC-GCF composites. Quarter cycles integrations reveal more however, as shown in the right graphs. The unfilled PVC compound is essentially extrinsic non-linear at low and high strain (Q1/Q2 ratio higher than 1) but exhibit an intrinsic character at intermediate strain amplitude, as if under a sufficient strain some structures were formed then destroyed as strain increases. GCF filled composites show an intrinsic non-linear behavior between 50 and 250% strain, which is clearly due to fibers presence (since fiber loading has an effect), then return to extrinsic non-linearity at higher strain. In contrast with similar data on carbon black filled compounds (see Figure 6), Q1/Q2 data on filled composites reinforce the conclusion that there are no interactions between PVC and Green Coconut fiber, except a good wetting.

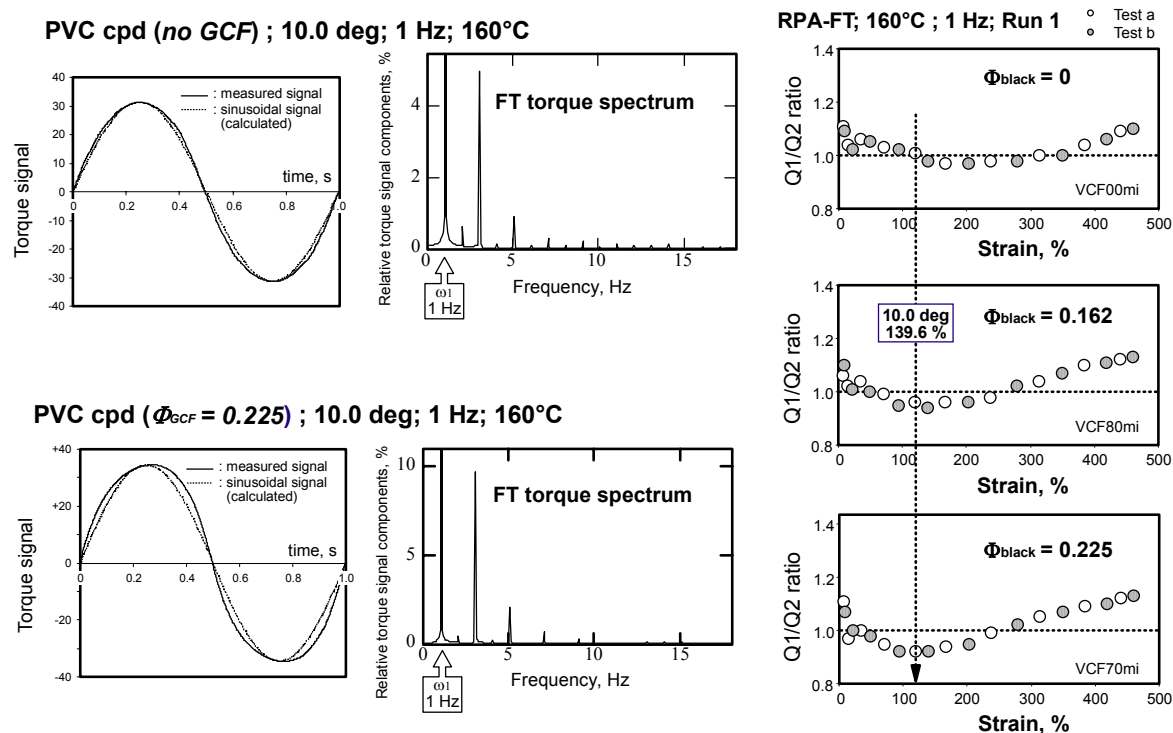


Figure 14 : Quarter cycles integration method to assess the extrinsic/intrinsic non-linear viscoelastic character; PVC-GCF composites

## CONCLUSIONS

Fourier transform rheometry with closed cavity testers is a very fast and accurate technique to investigate the non-linear viscoelastic behavior of polymer materials, particularly complex polymer systems, whose intrinsic non-linear character severely limits the capabilities of standard harmonic instruments. Adequate strain sweep test protocols lead to reproducible results, particularly in the high strain region, thanks to the closed test cavity design of RPA, purposely modified for FT experiments. Appropriate data treatment allows minor instruments deficiencies to be compensated for, in order to yield meaningful results, in line with theoretical expectations.

As such, Fourier transform spectra contain all the information available through harmonic testing, without any condition, as it is the case with linear dynamic testing which requires insensitivity of the modulus on strain amplitude. A basic analysis on the non-linear viscoelastic behavior of polymer systems is made by considering the main torque component  $T(\omega_1)$  and the 3<sup>rd</sup> relative

harmonic torque component  $T(3/1)$ , versus the strain amplitude.

Easy modeling methods give access to various parameters, which clearly reflect the many facets of non-linear viscoelasticity. For instance, “linear complex modulus” data are obtained, even when no linear behavior is seen within the strain window of the instrument, quite a typical observation with many complex systems, for instance filled polymers. In addition, differences in non-linear behavior, due to increasing mineral filler or fiber level are easily and clearly detected and the dependence upon strain of the relative 3<sup>rd</sup> harmonic component is adequately modeled with a simple three parameters model. This model allows single numbers to be extracted from experimental data, which express in a very convenient manner the effect of filler/fiber loading. Quarter cycles integration of mean torque signals reveals an interesting complementary data treatment to Fourier Transform, with the capability to provide additional information about the non-linear viscoelastic behavior of materials. The

distinction between extrinsic and intrinsic non-linear characters is easily made when considering Q1/Q2 ratios.

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