

Nonlinear Viscoelastic Properties of Molten Thermoplastic Vulcanisates: An Insight on Their Morphology

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ABSTRACT: A series of thermoplastic vulcanisates (TPVs) in the molten state were submitted to large amplitude oscillating strain tests at different frequencies, to investigate their nonlinear viscoelastic properties. A purposely modified torsional harmonic tester with a closed cavity was used to run such experiments, whose results were treated with a Fourier transform (FT) algorithm to extract main torque and strain components, and harmonics if any. Quarter cycle integrations of (averaged) torque signal were also performed, to supplement FT analysis, namely to distinguish extrinsic and intrinsic nonlinear viscoelasticity. The nonlinear viscoelastic character of TPVs was found substantially differing from the one of a molten polypropylene (PP) used for comparison. Within the strain window investigated, no linear behavior is observed with TPVs, in contrast with the pure PP. However, extrapolated "linear" complex modulus G^*_0 tends to de-

crease with increasing hardness of TPVs, but subtle differences between the various grades are clearly detected, when using simple models to fit experimental data. While the (room temperature) hardness is somewhat related with the viscoelastic behavior in the molten state, the strain sensitivity of TPVs appears essentially affected by the extractible content (mainly oil). TPVs nonlinear viscoelastic character appears to depend on the strain amplitude: mainly intrinsic, i.e., due to their morphology, at low strain, and essentially extrinsic, i.e., due to the large strain amplitude, at high strain, and in this respect, qualitatively similar to pure PP. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 4193–4205, 2006

Key words: blends; viscoelastic properties; rheology; morphology

INTRODUCTION

So-called thermoplastic vulcanisates (TPVs) are essentially blends of a crystalline thermoplastic polymer (e.g., polypropylene, PP) and a vulcanizable rubber composition, prepared through a special process called dynamic vulcanization,¹ which yields a fine dispersion of micron-size crosslinked rubber particles in a thermoplastic matrix.² By nature, such materials belong to the class of complex polymer systems (like filled rubber compounds, polymer blends and alloys, etc.), i.e., multiphase, heterogeneous, typically disordered materials such that each sample is somewhat a product of its particular history, while its internal local organization (or morphology) is not arbitrary, but conformed to rules, dictated by many factors, including interphase behavior. Structure is then as important as composition and it owes more to engineering practice and artifice than to the laws of thermodynamics and physical chemistry. In this respect, thermoplastic elastomers offer a range of interesting properties,

profitably used in a number of engineering applications, for which pragmatic (and costly) development often overrides basic understanding, particularly in what flow properties are considered.

For the rheologist, TPVs are consequently a very interesting class of polyphasic systems, commercially available from various suppliers, in grades differing essentially with respect to their hardness and other application properties, but with sometimes very large difference in their processing behavior. Like with many complex polymer systems, correctly assessing their rheological properties is a challenging task for several reasons: taking for granted the uniformity of their composition, TPVs are indeed very complicated materials, not only heterogeneous and with an associated morphology related to their composition, but also with the capability to be affected by the flow field used and in the meantime to significantly alter the boundary flow conditions owing to the migration of small labile ingredients (e.g., oil, curative residue, etc.). The aim of the work reported here was to investigate a series of commercial TPVs through the so-called Fourier transform rheometry, a testing technique especially developed to accurately investigate the nonlinear viscoelastic domain. Results will be tentatively interpreted in terms of material structure.

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DYNAMIC VULCANIZATION AND TPVs: A BRIEF OVERVIEW

The key-manufacturing step of TPVs is the dynamic vulcanization, a specific process whose origin can be traced back in the earlier work of Gessler and Haslett³ at Esso. By shear mixing blends of polypropylene and carbon black filled chlorobutyl rubber compounds at high temperature, these authors obtained vulcanization in the rubber phase, yielding thermoplastic materials with some rubbery properties. No product was commercialized but the essential aspects of dynamic vulcanization, as practiced today, were captured in this pioneering work. Fisher⁴ at Uniroyal further developed the technology by shear mixing peroxide-filled ethylene-propylene rubber (EPR or EPDM) with polyolefins; dynamic vulcanization occurred, which yielded 90% gelled rubber phase in a thermoplastic matrix. Uniroyal's TPR®, commercialized in 1972, is based on Fischer's work. About the same period, Hartman⁵ at Allied Chemical Corp. demonstrated that butyl rubber could be grafted onto polyethylene using a resole-type phenolic curing system, while melt blending the rubber and the plastic on open mill. No product was commercialized however. Monsanto entered the field in the 70s with the important contribution of Coran and Patel² and a series of patents^{6,7} where the work of Fischer was extended to dynamic vulcanization of diene rubbers in a polyolefin matrix. Thermoplastic materials with rubbery properties could be obtained even when the rubber was fully vulcanized, and it was realized that then called thermoplastic vulcanisates (TPV) would exhibit superior physical properties when dynamic vulcanization is pursued until a high cure state is achieved while very small rubber particles (less than 1–2 μm in diameter) are obtained. However, either peroxide or sulfur curing of the rubber phase proved to give unstable melt morphology and the final obstacle to commercialization by Monsanto was eventually overcome when Abdou-Sabet and Fath⁸ developed the use of a resole-type phenolic resin as curing system.

Since the market introduction of Santoprene® (PP/EPDM) TPVs in the early 80s, Monsanto patents went public, and nowadays, there are a number of suppliers of thermoplastic elastomers prepared by dynamic vulcanization, namely ExxonMobil (which recently absorbed Advanced Elastomer Systems, A.E.S., the Monsanto-Exxon joint venture set up in the early 90s to exploit Santoprene® and related products), Mitsui (Milastomer®), Sumitomo (Sumitomo TPE®) and DSM (Sarlink® TPV). The worldwide consumption of TPVs is nowadays above 500,000 ton/year with an average annual growth rate of around 9%. Many (rubber/plastic) compositions and grades are commercially available within quite a large hardness range

(from Shore A 35 to Shore D 80), in the 2.47–6.36 Euro/kg price range.⁹

Despite their growing commercial importance, the flow behavior of TPV materials has been poorly studied in literature and processing developments remain essentially pragmatic (trial-and-error). The basic rheology of these materials is however described in a few publications,^{10–13} essentially a stronger dependence to shear than to temperature changes and relatively mild elastic effects, for instance modest extrudate swell. Wall slip in shear flow is suspected but not clearly demonstrated for such materials and extensional flow properties, while essential in many shaping processes (e.g., blow molding) are not well-documented.

EXPERIMENTAL

Test materials

A series of commercial (PP/EPDM) TPVs and the corresponding polypropylene, as described in Table I, was obtained thanks to the courtesy of suppliers. Shore hardness, generally the first material property used to compare thermoplastic elastomers, was considered in selecting test materials, to cover a broad range. As it is well-known that TPVs formulations include significant amounts of oil, which could potentially affect their flow properties through changes either in their actual morphology or in boundary conditions, xylene extraction experiments were performed at room temperature. Available information about PP content is also included. To allow comparison materials with respect to a common hardness scale, the following empirical relationships have been used to derive IRHD values from Shore A and D data:

$$\text{IRHD} = 0.9995 \times \text{ShoreA}$$

$$\text{IRHD} = -0.0275 \times \text{ShoreD}^2 + 3.0203 \times \text{ShoreD} + 16.22$$

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.¹⁷ Appropriate modifications were therefore brought to a commercial torsional rheometer, initially developed for rubber materials, i.e., the Rubber Process Analyzer, RPA® (Alpha Technologies), to capture strain and torque signals, using suitable codes developed with LabView® software (National Instruments). Details on the modification and the measuring technique were previously reported.¹⁸ Proprietary

TABLE I
Test Materials

Sample code name	Hardness Shore ^a	Hardness IRHD	Spec. Grav. ^b (g/cm ³)	Trade names (supplier)	Color	Extractible ^c	PP ^{d,e} (% weight)
STP55A	55,A	54.97	0.97	Santoprene 201-55 (A.E.S.)	Natural	43.9 ± 0.4	11 (12)
STP64A	64,A	63.97	0.97	Santoprene 201-64 (A.E.S.)	Natural	40.9 ± 0.8	(15)
STP80A	80,A	79.96	0.97	Santoprene 201-80 (A.E.S.)	Natural	32.5 ± 1.1	31
STP40D	40,D	92.87	0.94	Santoprene 203-40 (A.E.S.)	Natural	23.1 ± 2.4	45 (70)
HFX10A	30,D	82.11	0.88	Hifax PP CA 10A (Basell)	White	3.5 ± 0.6	100

^a ASTM D2240.

^b ISO 1183.

^c 480 h xylene extraction at room temperature; 2 tests.

^d Boiling xylene extraction technique.

^e Values in parentheses are from literature; DSC-based technique.

data handling programs, written in MathCad® (Math-Soft Inc., Cambridge, Mass.), are used to perform Fourier transform calculations and other data treatments. Figure 1 shows typical results on a sample of atactic polypropylene [$M_n = 55,297$ g/mol; $M_w = 124,739$ g/mol; kindly supplied by R. Koopmans (Dow Benelux N.V., Terneuzen, Netherlands)] at 1 Hz frequency and different strain amplitudes. 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.

As can be seen, upon a strain amplitude of 33° (i.e., 461% strain), the torque signal is clearly distorted, which corresponds to a nonlinear character well-as-

sessed by the FT spectrum, which exhibits significant odd harmonics. However, at lower strain (3.5°; 48.9%), a slight distortion is nevertheless noted and characterized also by odd harmonics. Torque signal distortion and the associated harmonics obtained through FT analysis provide a clear, nonambiguous characterization of the nonlinear viscoelastic response of materials.

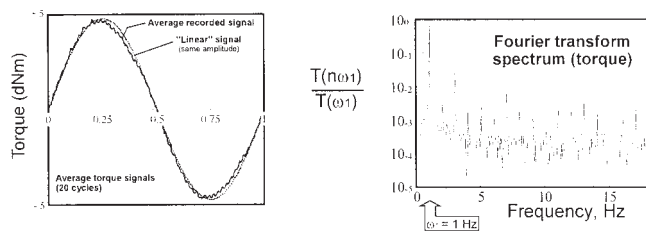
Test protocols for nonlinear viscoelastic investigation: FT data treatment

Test protocols were developed for nonlinear viscoelastic investigation, which essentially consist in performing strain sweep experiments, at constant temperature and frequency, through two subsequent runs separated by a resting period. 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., runs 1 and 2), sample fatigue effects are detected, if any. Differences are expected between runs 1 and 2 for materials sensitive to strain amplitude. Using the RPA built-in testing software, each strain step is set to apply a sufficient number of strain cycles for a stable torque response to be obtained, for instance 40 cycles at 1 Hz, and 20 cycles at 0.5 Hz. At each strain sweep step, data acquisition is made to record 10,240 points at the rate of 512 pt/s; when the testing frequency is 1 Hz, twenty cycles are consequently recorded at each strain step, and 10 cycles at 0.5 Hz. Within the limit permitted by the frequency used, 10 strain steps are applied during each run, so that by combining results gathered on two samples, results over 20 strain steps are obtained, from (0.5 to 33)° (7 to 461%) at 1 Hz, and from (0.5 to 68)° (7 to 950%) at 0.5 Hz, from either first or second run.

Through FT treatment of *torque signal*, two types of information are obtained: first, the main torque com-

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

Strain : 3.5 deg (48.9 %)



Strain : 33 deg. (461 %)

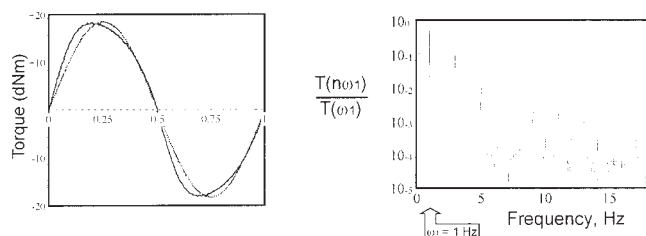


Figure 1 Typical LAOS and Fourier transform experimental results on a simple (pure) polymer material.

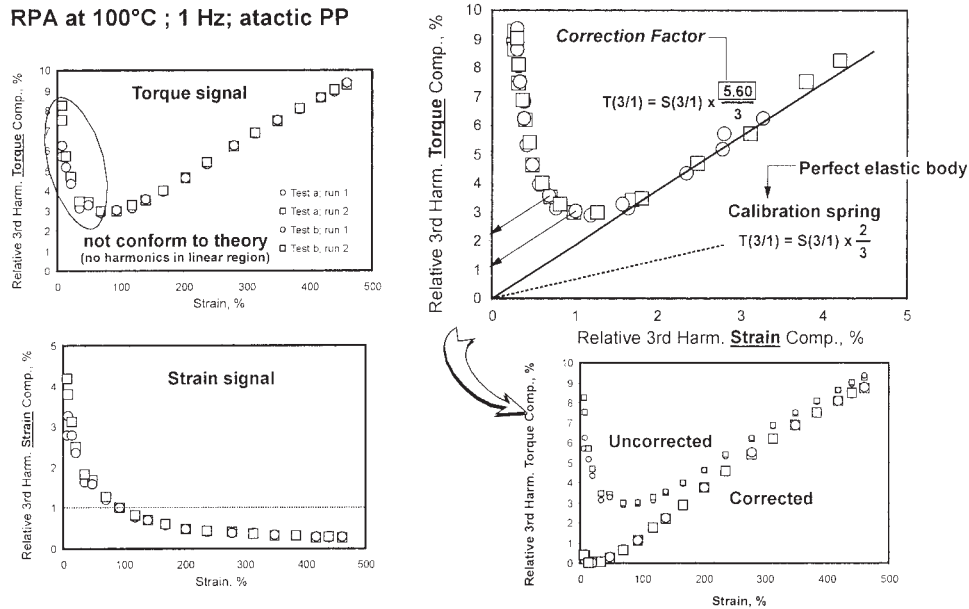


Figure 2 Correction method on 3rd relative torque component data.

ponent, 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 $3 \times$ the applied frequency) the most intense one. In addition, FT treatment of the *strain signal* provides information about the quality of the applied deformation and, as detailed elsewhere,¹⁹ allows correcting data for technical limits of the instrument.

Ideal dynamic testing requires that a perfect sinusoidal deformation at controlled frequency and strain be applied on the test material, but whatever are the manufacturing design and quality, 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. Indeed, FT analysis reveals relatively significant (i.e., larger than noise) odd harmonics components in RPA strain signal, with obviously the 3rd the larger one, particularly at low strain amplitude.²⁰ The relative 3rd harmonic strain component, i.e., $S(3\omega)/S(\omega)$ or $S(3/1)$, 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 $(1.3\text{--}1.5)^\circ$ (18–20%). In other terms, high-strain tests are performed in better-applied signal conditions than low-strain ones.

The correction method for $T(3\omega)/T(\omega)$ [or $T(3/1)$] data is illustrated in Figure 2. As shown in the upper right graph, $T(3/1)$ versus $S(3/1)$ decreases, passes through a minimum and appears to be bounded by a straight line whose slope is a multiple of $1/3$. If an ideal elastic material, for instance the calibration spring, is tested then the slope is $2/3$. The correction method is based on the simple argument that, if the

applied strain perfect were perfect, all $T(3/1)$ data points would fall on the vertical axis. Consequently $T(3/1)$ data are corrected according to:

$$cT(3/1) = T(3/1)_{TF} - S(3/1)_{TF} \times \frac{CF}{3} \quad (1)$$

where $T(3/1)_{TF}$ and $S(3/1)_{TF}$ are the 3rd relative harmonic components of the torque and strain signals respectively, and CF the correction factor, as derived from the $T(3/1)$ versus $S(3/1)$ plot. The lower right graph in Figure 2 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 3rd relative torque harmonic component vanishes, in agreement with theory.²¹

RPA-FT results, according to test protocols described earlier, yield essentially two types of information, which reflects how the main torque, i.e., $T(\omega)$, and the (corrected) 3rd relative torque harmonic component, i.e., $cT(3/1)$, vary with the strain amplitude. 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, one gets the most familiar picture of a plateau region at low strain, then a typical strain dependence. FT 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 γ in %).

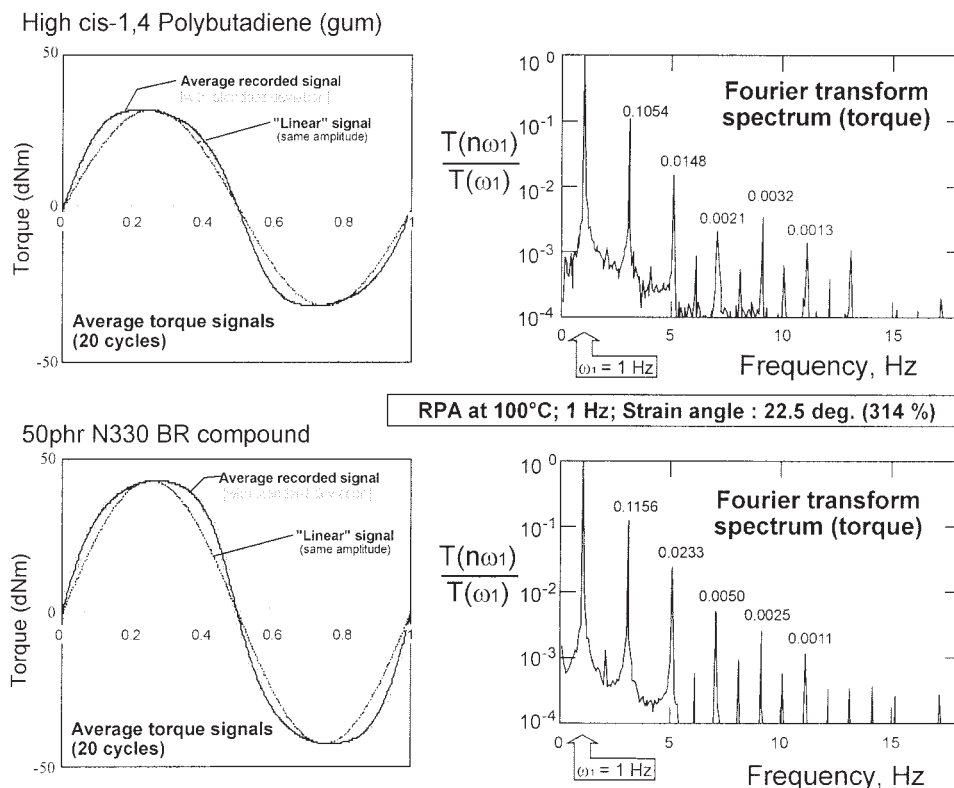


Figure 3 Recorded torque signals during RPA tests at high strain on a gum and a 50 phr carbon black filled polybutadiene compound; Fourier transform torque spectra.

Quarter cycle integration technique: Extrinsic versus intrinsic nonlinear viscoelasticity

Experiments with complex polymer systems, for instance carbon black filled rubber compounds have revealed a limit of FT data treatment. For instance, Figure 3 shows average torque signals (out of 20 recorded cycles) as recorded when submitting either a high *cis*-1,4 polybutadiene sample (gum cut from the bale) or a 50 phr N330 filled compound (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 $\approx 1500 \text{ MJ/m}^3$) to a large strain amplitude (22.5°; 314%) torsional harmonic test at 1 Hz (left graphs). For the sake of comparison, perfect sinusoidal traces of same amplitude are drawn. Torque signals are clearly distorted, which reflects in harmonics rich FT spectra, but the filled material exhibits a severer distortion, which in addition affects more the right part of the half signal.

This effect is obviously due 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 nonlinear viscoelastic behavior of a pure, unfilled polymer and of a filled material. The former essentially exhibits nonlin-

earity through the application of a sufficiently large strain and we called this behavior extrinsic nonlinear viscoelasticity (because occurring through *external* causes, i.e., the applied strain), while the latter shows intrinsic nonlinear viscoelasticity (because owing to the *internal* morphology of the material). It is quite obvious that FT analysis of torque signal, while offering an attractive quantification of the nonlinear viscoelastic response, has limited capabilities to distinguish extrinsic and intrinsic characters.

To supplement FT analysis, quarter cycle integration of (averaged) torque signal was therefore considered as an easy data treatment technique to distinguish extrinsic and intrinsic nonlinear viscoelasticity. So far, the ratio of the first to second quarters torque signal integration, i.e., $Q1/Q2$, has permitted to clearly distinguishing between the strain amplitude effect on an unfilled and a filled materials, when there are strong interactions occurring between the rubber matrix and the discrete phase. 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., $Q1 > Q2$). More complex variations of $Q1/Q2$ have so far been observed with a number of complex polymer systems, for instance extrinsic-to-intrinsic transitions occurring as applied strain or as discrete particles content vary.

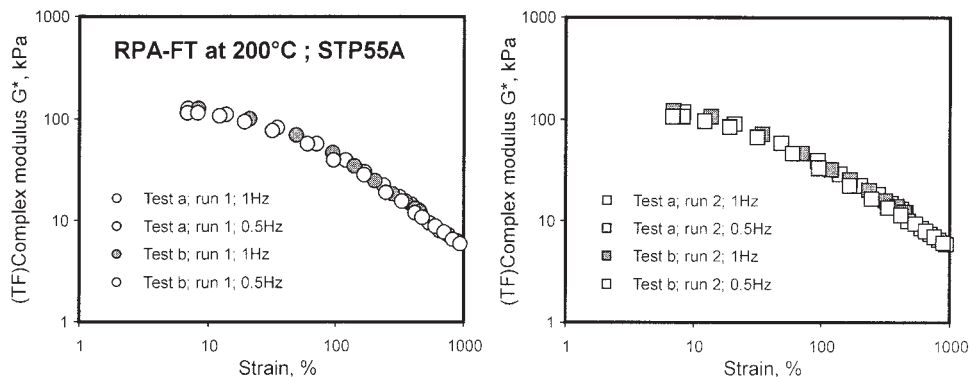


Figure 4 RPA-FT strain sweep tests on 55 Shore A TPV samples; complex modulus variation G^* versus g .

FT RHEOMETRY ON TPVS: EXPERIMENTAL RESULTS

Strain sensitivity of complex modulus G^*

TPVs samples were therefore submitted to strain sweep experiments at 0.5 and 1.0 Hz, according to test protocols described above. Since materials were obtained as pellets, it was necessary to prepared test specimens by compression molding at 200°C. A mold with the same reciprocal cone geometry but a 5% excess volume as the RPA test cavity (0.125 radian cone-cone angle; volume: 3 cm³) was used. Practical experience demonstrates that highly reproducible results are obtained when sample preparation is correctly made.

Figure 4 shows how the dynamic modulus G^* of the 55 Shore A TPV varies with strain amplitude; run 1 results at both 0.5 and 1 Hz are given in the left graph, run 2 results in the right graph. No linear region is observed with the experimental strain window and, as expected (frequency dependence effect), 0.5 Hz data are (slightly) below 1 Hz ones. Very small, if any, differences are seen between run 1 and run 2 data, which indicates that the material morphology is either not significantly affected when large strain amplitude is applied or that all strain effects are immediately

recovered during the 2 min resting period between runs. It is worth underlining here that G^* data are derived from the main component of the torque signal, as obtained through FT analysis. Would one want to consider G^* data as given by the built-in data treatment of the RPA, a qualitatively similar figure would be obtained, with however an error by default, as previously demonstrated.¹⁸

Similar data on pure polypropylene are shown in Figure 5. A linear region [i.e. $G^* \neq f(\gamma)$] is observed up to 60% strain, with larger frequency dependence. No strain history effects occur, runs 1 and 2 giving identical results.

Significant differences are seen with respect to TPV grades (Fig. 6). The higher the hardness, the lower the complex modulus, which became even lower than the ones of PP for the 40 D Shore A grade. The nonlinear character of TPVs is kept whatever the hardness, and hence the PP content.

Strain amplitude sensitivity (at constant frequency and temperature) is considered as a typical nonlinear viscoelastic response. In the case of filled (rubber) materials, the significant reduction of elastic modulus with increasing strain amplitude of filled (vulcanized) elastomers is usually termed "Payne effect," but de-

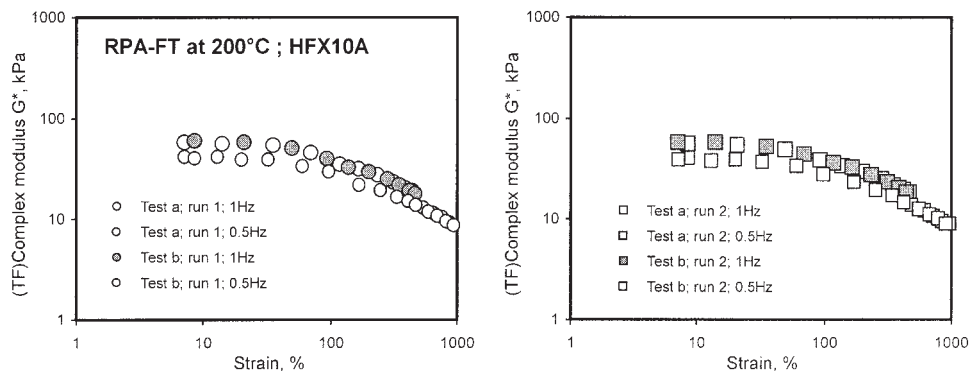


Figure 5 RPA-FT strain sweep tests on pure polypropylene; complex modulus variation G^* versus g .

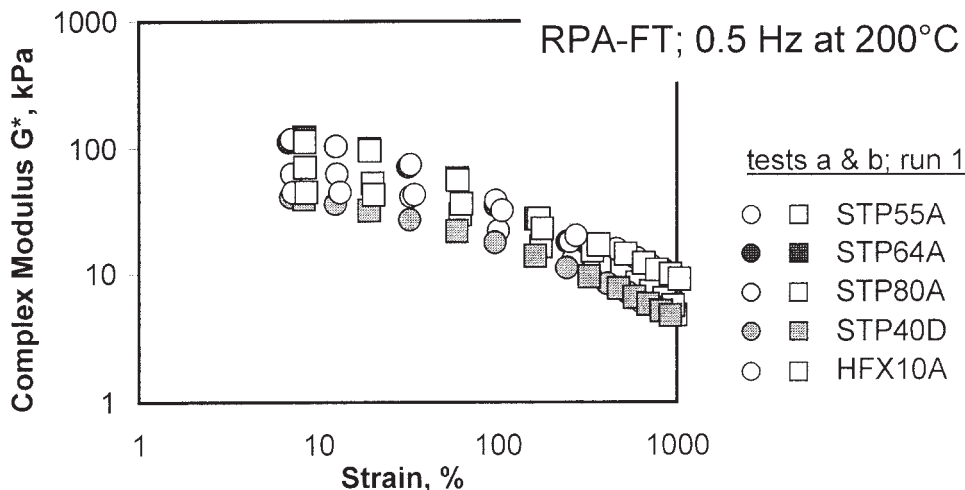


Figure 6 RPA-FT strain sweep tests on TPVs and PP samples; complex modulus variation G^* versus γ at 0.5 Hz.

spite numerous investigations,²²⁻²⁶ the interpretation of results in terms of both reinforcement and nonlinearity remains a controversial issue in the author's opinion. Indeed, strain amplitude sensitivity is observed with unfilled polymers, but becomes larger either when discrete particles are incorporated or when the material is such that it has a heterogeneous morphology, e.g., blends of incompatible polymers, thermoplastic elastomers, and TPVs of course. Results presented earlier do conform to such observations: TPVs exhibit larger strain sensitivity than pure PP, with however a clear difference, which can be assigned to their particular morphology.

G^* versus strain curves are adequately modeled with the following equation:

$$G^*(\gamma) = G_f^* + \frac{[G_0^* - G_f^*]}{1 + (A\gamma)^B} \tag{2}$$

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

TABLE II
Fit Parameters of Eq. (2) for All Compounds Tested

Sample	Test freq. (Hz)	Run	G_0^* (kPa)	G_f^* (kPa)	1/A (%)	B	r^2
STP55A	0.5	1	133.2	0.8	43.4	1.041	0.9998
		2	131.9	2.7	31.9	1.045	0.9999
	1	1	147.2	(-0.4)	43.6	1.013	0.9996
		2	148.0	5.2	30.8	1.077	0.9999
STP64A	0.5	1	137.9	2.6	37.8	1.079	0.9964
		2	143.7	2.7	25.5	0.975	0.9998
	1	1	148.4	5.9	40.3	1.187	0.9955
		2	155.9	5.5	27.1	1.021	0.9991
STP80A	0.5	1	74.9	3.0	36.7	1.035	0.9974
		2	105.8	0.0	10.6	0.665	0.9997
	1	1	107.9	3.8	27.9	0.975	0.9998
		2	105.1	3.5	18.6	0.818	0.9994
STP40D	0.5	1	55.0	(-2.5)	32.6	0.578	1.0000
		2	41.9	(-2.3)	55.2	0.588	0.9999
	1	1	48.9	(-0.2)	81.8	0.803	0.9996
		2	62.8	(-3.4)	42.7	0.590	0.9998
HFX10A	0.5	1	43.6	4.9	163.5	1.160	0.9986
		2	41.3	3.9	192.8	1.143	0.9991
	1	1	60.0	13.0	122.0	1.415	0.9967
		2	58.9	7.1	155.0	1.153	0.9983

Values in parentheses indicate parameter values without physical meaning.

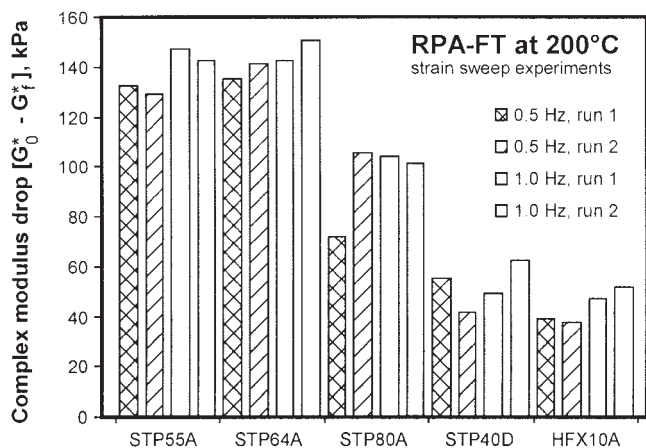


Figure 7 Net complex modulus drop upon increasing strain amplitude.

initial slope of the $T(\omega)$ versus γ graph. 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. Table II gives fit parameters of eq. (2) for all the compounds tested. The fit is excellent, as shown by the values of r^2 .

The (extrapolated) "linear" modulus G^*_0 tends to decrease with increasing hardness of tested samples, and differences between data gathered during runs 1 and 2 of the test procedure are generally marginal, except for STP80A at 0.5 Hz and STP40D at 1.0 Hz. In terms of modulus, the net effect of the strain sweep is best illustrated by considering differences $G^*_0 - G^*_f$, which were calculated by considering that the modulus at infinite strain was zero when the fit G^*_f had negative value. As shown in Figure 7, the two softest grades are very close but different and the hardest grade (STP40D) is close to pure PP.

Both the critical strain $1/A$ and the strain sensitivity parameter B are typical nonlinear viscoelastic parameters, which allow an easy comparison of tested materials. The critical strain is somewhat related with the extent of the linear viscoelastic region and, in agree-

ment with Figures 4–6, significant differences are seen between TPVs and pure PP (Fig. 8). A careful examination of Figure 8 yields interesting observation. At 0.5 Hz, $1/A$ decreases with increasing hardness for the Shore A samples, with a clear strain history effect: run 2 gives systematically lower values. The same observation is made with results at 1.0 Hz. At 0.5 Hz, the hardest TPV grade (STP40D) shows the same strain history effect as pure PP, i.e., run 2 is higher than run 1. At 1.0 Hz, STP40D exhibits the same strain history effect than the softer TPV grades.

TPVs have lower strain sensitivity parameter B than the pure PP, with a tendency to decrease as hardness increases, while the effect is only clear when run 2 data are considered, whatever the test frequency. However the strain sensitivity of TPVs is not related to the PP content, but rather to the extractible content (mainly oil), as shown in Figure 9. The higher the oil content, the larger is the strain sensitivity of TPVs. The significant difference between TPVs and pure PP in terms of parameter B , as well as the oil content dependence (for TPVs) suggest that the nonlinear viscoelastic properties of the former are strongly depending on their morphology, at the temperature of the test. In deed, by nature PP is the matrix in (PP-EPDM) thermoplastic vulcanisates, whatever their hardness. Therefore, one would expect the strain sensitivity of molten TPVs to be first related to the ones of the molten matrix PP. If one considers the values of parameter B in Table II, this curiously is not observed for the hardest TPV grade, but seems to be the case for the softest one (STP55A). Commercial TPVs are however not simply blends of a rubber and a thermoplastic; there are other formulation ingredients (a proprietary information of the manufacturer) with a processing oil that plays a critical role, as recently recognized.^{27–29} Indeed, when performing xylene extraction experiments at room temperature, only the oil and other labile ingredients are removed from materials, and it is observed that dried extracted samples are very hard, harder than pure PP, without any thermoplastic elastomer character. This observation, in relation with the oil effect on strain sensitivity parameter (Fig. 9),

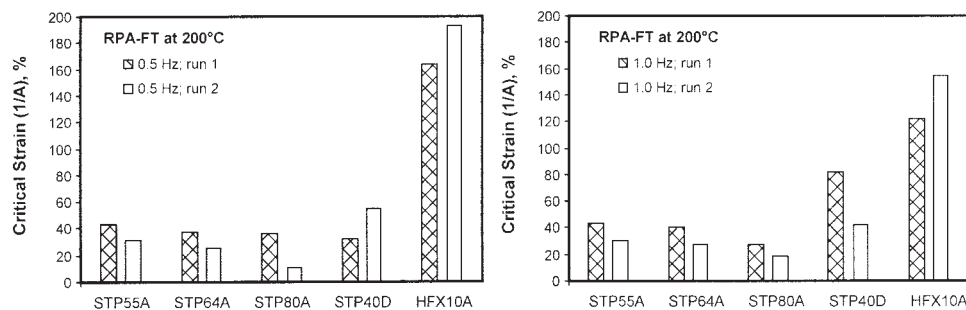


Figure 8 Strain sweep effect on complex modulus; critical strain parameter.

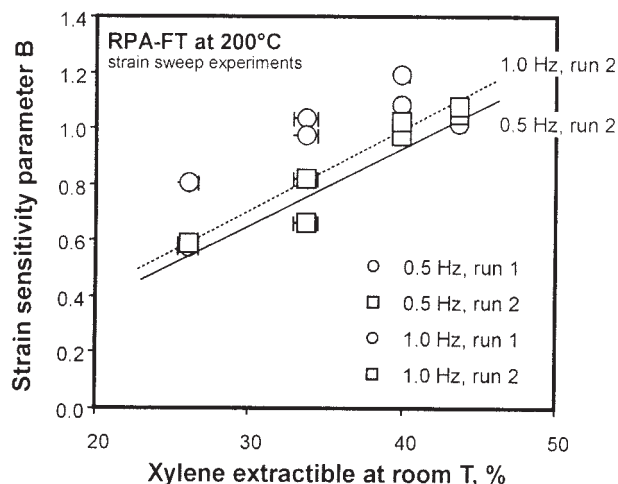


Figure 9 Modeling G^* versus γ of TPVs; strain sensitivity parameter B.

suggests first that the nonlinear viscoelasticity of TPVs has its roots in their morphology and second that extractibles (mainly oil) are distributed between the (vulcanized) rubber phase and the polypropylene matrix. At room temperature, the actual oil content in the thermoplastic matrix is somewhat limited by its crystallinity, roughly 45–50% of the PP.²⁸ In the melt state, however, the oil must be distributed between the PP and the EPDM, in such a manner that it is indeed a “plasticized” thermoplastic phase with a dispersion of soft particles that controls the flow behavior. Comparing the flow properties of TPVs with the ones of pure PP has to be made with respect to this remark.

Third relative harmonic component of torque signal

At high strain amplitude, torque signal remains harmonic but become clearly distorted. FT is nothing else that a mathematical technique that resolve harmonic signals in their components. Odd harmonics become

significant as strain increases and are therefore considered as the nonlinear viscoelastic “signature” of tested material. Figure 10 shows the typical S-shape pattern of corrected $T(3/1)$ versus strain γ , as exhibited by the softest TPV grade. Corresponding data for pure PP are given in Figure 11.

Whatever the test frequency, data fall on typical sigmoid curves, with no significant difference between runs 1 and 2, which means that materials are either not affected by the large strain during the first run or that the 2 min resting time between runs 1 and 2 is sufficient to dampen any strain history effects on torque harmonic components. Similar plots are obtained with the other samples. One notes also that the $cT(3/1)$ versus γ curves at 0.5 and 1.0 Hz superpose well; in other terms, frequency does not affect the nonlinearity. Insensitivity to strain history would be interpreted as an indication that the morphology of TPVs resists to large strain amplitude (i.e., up to 1000% at 0.5 Hz).

In agreement with our previous reports,^{18,20} the observed behavior is modeled by a very simple equation, i.e.:

$$cT(3/1)_\gamma = cT(3/1)_{\max} \times [1 - \exp(-C_\gamma)]^D \quad (3)$$

where γ is the deformation (%), $cT(3/1)$, a maximum plateau value at high (infinite) strain, C and D fit parameters. Note that in using eq. (3) (and subsequent ones) to model $cT(3/1)$ variation with strain, one may express the deformation (or strain) γ either in degree angle or in %. Obviously all parameters remain the same, except C , whose value depends on the unit for γ . The following equality applies for the conversion:

$$C(\gamma, \text{deg}) = \frac{180 \alpha}{100 \pi} \times C(\gamma, \%), \text{ where } \alpha = 0.125 \text{ rad.}$$

Figure 12 illustrates how the model fits measured data.

Parameters C and D in eq. (3) reflect precisely the strain sensitivity of tested materials, but appear quite complicated when comparing the responses of differ-

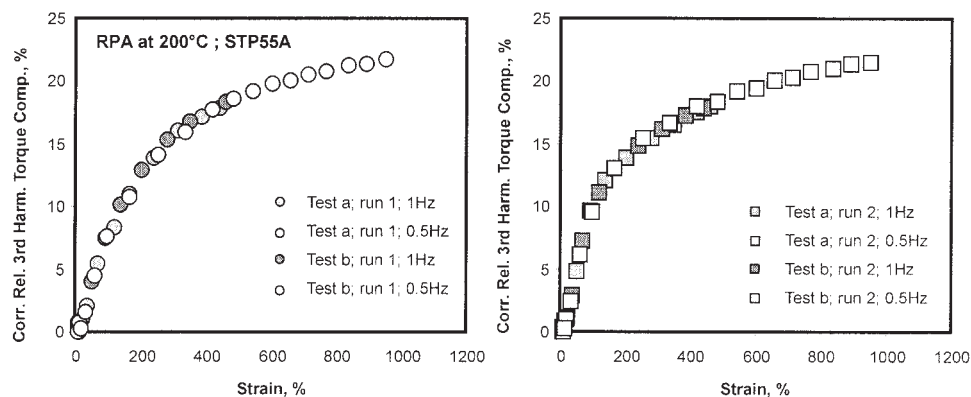


Figure 10 Corrected relative 3rd torque harmonic component versus strain; samples STP55A.

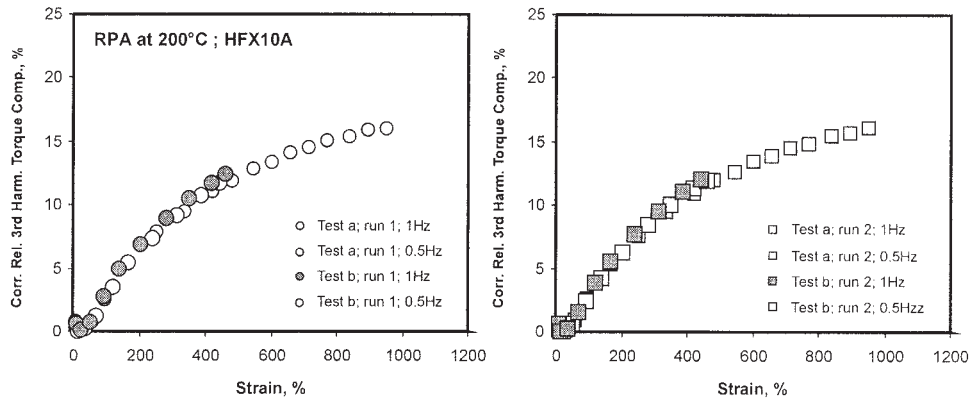


Figure 11 Corrected relative 3rd torque harmonic component versus strain; pure PP.

ent samples. It is therefore useful to consider the first derivative of the above equation, to calculate the slope of $cT(3/1)$ versus γ curves at any strain, for instance at 300% as in Table III.

Parameter $cT(3/1)_{\max}$ is an extrapolated value at infinite strain. Even if eq. (3) is far from perfectly fitting experimental data at the largest strain amplitude investigated, Figures 11 and 12 show that data given in Table III can be considered with confidence. As can be seen, $cT(3/1)_{\max}$ is clearly depending on material hardness for the three softer TPV grades but the extractable content seems the dominant parameter, as shown in the upper inset of Figure 13. The strain sensitivity however, as expressed by the slope at 300% strain [of $cT(3/1)$ versus strain curves], offers quite a complex picture. The softest TPV grade appears comparable in this respect with pure PP, but for the three TPV Shore A grades, the slope at 300% strain decreases with increasing hardness, but is higher for the hardest grade, STP40D. Such results suggest again that, in the molten state, the actual morphology of TPVs is likely to be more influential on their nonlinear viscoelastic properties than the overall composition.

Quarter cycle torque signal integration

The extrinsic/intrinsic character of materials is well-described by the quarter cycle integration method.

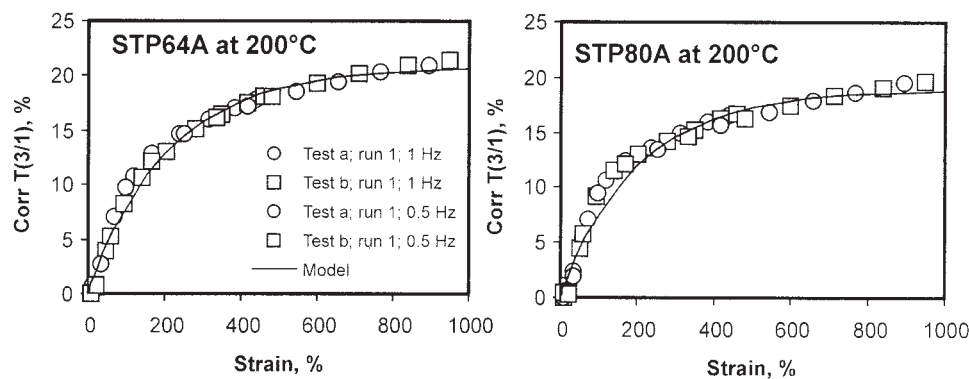


Figure 12 Corrected relative 3rd torque harmonic component versus strain; fitting results with eq. (3).

Figure 14 shows how the $Q1/Q2$ ratio evolves with increasing strain amplitude for all the samples tested, at 0.5 and 1.0 Hz. Run 1 data from two tests are shown, and essentially the same figures are drawn with run 2 data, which further supports the absence of significant strain history effects. A coherent picture emerges from those results: at low strain, all tested samples exhibit a somewhat intrinsic viscoelastic nonlinearity (i.e., $Q2 > Q1$), and then evolve toward a stable extrinsic nonlinearity. For the softest TPV grades, no significant effect is due to frequency, but the hardest grades exhibit $Q1/Q2$ ratio higher at 1 Hz, like pure PP. The final $Q1/Q2$ ratio seems to be related with the oil content (i.e., the higher the oil level, the lower $Q1/Q2$).

Quarter cycle integration is a new approach of the nonlinear viscoelastic character of complex polymer systems, which supplement the information given by FT analysis of strain sweep experiments. Only a limited variety of complex materials were so far analyzed through this approach, but all results obtained¹⁹ suggests that intrinsic nonlinearity is related to the existence of particular structures. When submitted to sufficiently large strains under dynamic conditions, all polymer materials exhibit extrinsic nonlinearity, i.e., $Q1/Q2 > 1$. Intrinsic nonlinearity is possible only if the material is heterophasic with sufficient interactions between phases. In this respect, carbon black

TABLE III
Fit Parameters of Eq. (3) for All Compounds Tested

Sample	Test freq. (Hz)	Run	$cT(3/1)_{\max}$ (%)	C	D	Slope at 300 %	r^2
STP55A	0.5and1.0	1and2	20.94	0.00497	1.04	0.0241	0.9894
STP64A	0.5and1.0	1and2	20.19	0.00545	0.97	0.0209	0.9868
STP80A	0.5and1.0	1and2	18.24	0.00615	1.04	0.0183	0.9837
STP40D	0.5and1.0	1and2	18.14	0.00378	1.13	0.0237	0.9939
HFX10A	0.5and1.0	1and2	16.55	0.00362	1.48	0.0246	0.9961

filled rubber compounds are essentially intrinsically nonlinear and one understands that, with certain systems, interactions between phases might be destroyed or at least modified, upon increasing strain.

Data in Figure 14 show that TPVs have a structure such that the higher their rubbery character, the larger the strain amplitude at which $Q1/Q2$ remains below 1. For instance, $Q1/Q2$ passes above 1 at around 200% strain for STP55 and STP64, at around 50% for STP80A and STP40D. Surprisingly, the pure PP exhibits some intrinsic nonlinearity up to 40–50% strain (at least at 0.5 Hz); nevertheless it shows the largest final $Q1/Q2$ ratio.

DISCUSSION

Within the strain window of the RPA, i.e., 7–950% at 0.5 Hz, no linear behavior is observed with TPVs, in contrast with a pure polypropylene sample which, expectedly, exhibits linear viscoelasticity up to 20% strain. However, extrapolated “linear” complex modulus G^*_0 tends to decrease with increasing hardness of TPVs. In addition, subtle differences in nonlinear behavior are easily and clearly detected, when fitting with a simple three parameters model the dependence upon strain of the relative 3rd harmonic component. The strain sensitivity of TPVs appears for instance essentially affected by the extractable content (mainly

oil). With respect to quarter cycles integrations of mean torque signals, TPVs nonlinear viscoelastic character appears to depend on the strain amplitude: mainly intrinsic, i.e., due to their morphology, at low strain, and essentially extrinsic, i.e., due to the large strain amplitude, at high strain, and, in this respect, qualitatively similar to pure PP.

TPVs formulations are complicated and essentially undisclosed by manufacturers, but laboratory extraction techniques allow considering three major components¹⁴: the xylene extractibles (at room temperature, because boiling xylene dissolved PP), the discrete vulcanized rubber (EPDM) particles, and the polypropylene matrix. TPVs are heterophasic materials, as clearly seen on published microphotographs,²⁷ but nonlinear viscoelastic results reported here suggest that the distribution of oil between the (vulcanized) rubber phase and the PP matrix plays a major role. For instance, one could consider that, for the softest grades, the oil is evenly distributed, simply because the overall content is so high that one has near saturation in both phases. The morphology, imparted by the discrete rubber particles dispersed in a softened PP, is the dominating parameter for such grades, until strain is large enough to produce dislocation. Because the PP matrix is saturated with oil, full recovery of strained (molten) material is possible, as indeed demonstrated by the absence of strain history effects in

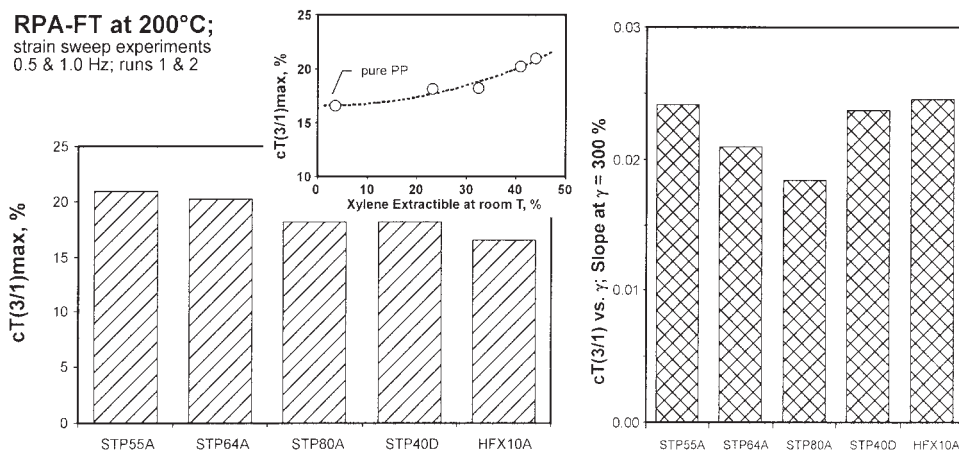


Figure 13 Strain sweep experiments: nonlinear viscoelastic parameters.

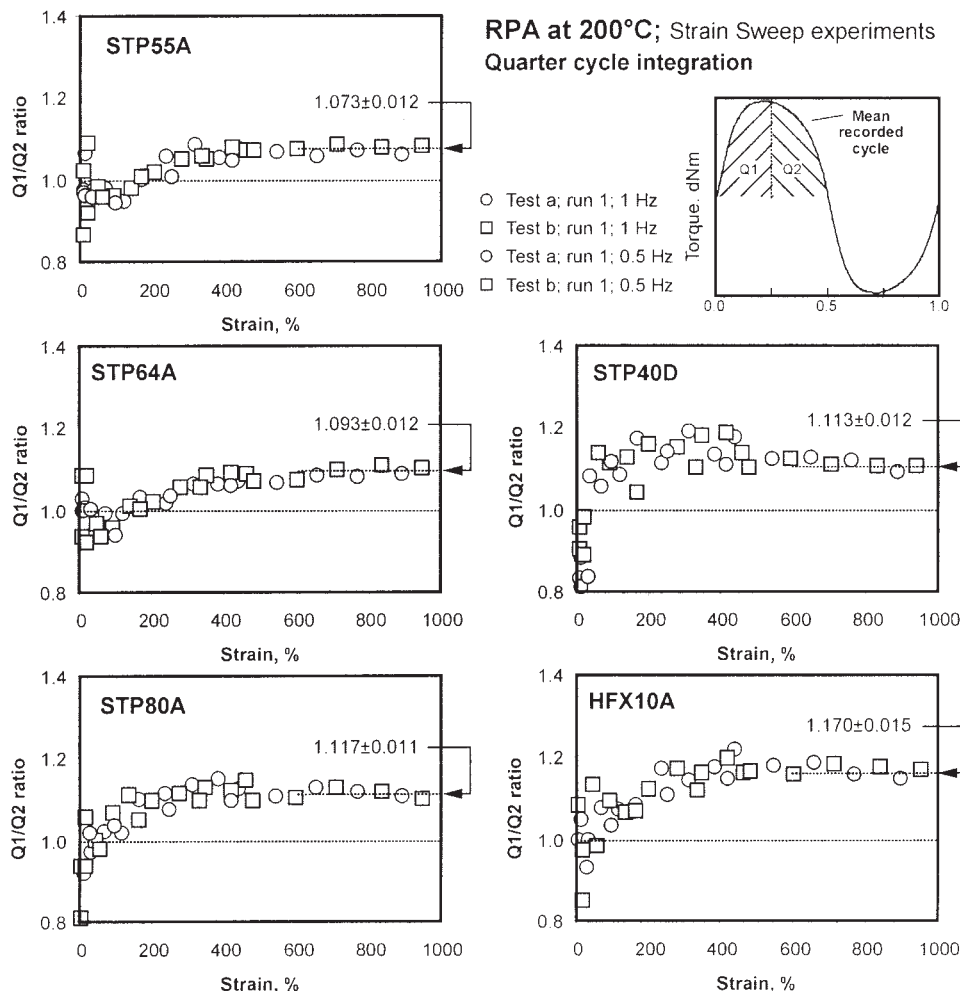


Figure 14 Assessing extrinsic/intrinsic nonlinear viscoelastic character of TPVs through quarter cycle torque integration.

subsequent strain sweep experiments. As the hardness increases, so does the PP content of TPVs, with a concomitant decrease of oil level. Oil free PP regions become then possible in the hardest TPVs grades and consequently their viscoelastic behavior reflects the role of the thermoplastic phase, with namely some strain history effects.

CONCLUSIONS

TPVs are complex polymer systems, which can conveniently be characterized with advanced dynamic testing methods. Using a purposely-modified closed cavity rheometer, strain sweep test protocols performed on a series of TPVs gave reproducible results, particularly in the high strain region. An appropriate data treatment allowed minor instrumental deficiencies to be compensated for, to yield meaningful results, in line with theoretical expectations. Because nonlinear viscoelastic responses were obtained at large strain amplitude, results had to be analyzed through special techniques, for instance the well-

known Fourier transform. Fourier transform spectra contain all the information available through harmonic testing and a basic analysis on the nonlinear viscoelastic behavior of TPVs was made by considering the main torque component $T(\omega_1)$ and the 3rd relative harmonic torque component $T(3/1)$, versus the strain amplitude. Easy modeling methods gave access to various parameters, which clearly reflect the many facets of nonlinear viscoelasticity, and revealed the subtle role played by the extractible content (mainly oil) of such materials.

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