

Observing Changes in Nonlinear Viscoelastic Properties Occurring Throughout the Vulcanization Process

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ABSTRACT: Using a purposely modified Rubber Process Analyzer, a technique has been developed to record the complete torque signal during a vulcanization test, and to split it into a sequence of single oscillations, which are treated through Fourier transform calculations. Various EPDM-based compounds were tested to investigate the capabilities of the technique. It was found that the progressive variation of the harmonic torque signal when vulcanization occurs reflects in singularities in the manner that all harmonic components vary during cure. Contrary to the main torque component (i.e., the torque amplitude) that exhibits a smooth variation as vulcanization proceeds, harmonic components exhibit sharp up and down changes at precise times that seem to be related to critical steps in the curing process. For instance, pair harmonic components passes through ex-

tremes (maximum or minimum) when scorch time is reached. Odd harmonic components show a singularity that is likely associated with the precise moment when the vulcanizing material passes from a still “liquid” state to an essentially “solid” one. This event does not coincide with the time for the maximum cure rate to be reached but occurs either before or after it, depending on the compound or the curing parameters. Such results support the view that rubber vulcanization presents some analogy with a nucleation process and underline the promising capabilities of the test technique. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1140–1150, 2006

Key words: rubber; elastomers; crosslinking; vulcanization

INTRODUCTION

During a vulcameter test, a rubber sample, maintained within the appropriate testing gap, is submitted to a harmonic strain at fixed amplitude, frequency, and temperature. The resulting harmonic stress within the sample is measured, generally through the torque in the so-called torsional vulcameters, either the resistive torque when the measurement is made on the shaft of an exciting body (disc) embedded in the material,¹ or transmitted when made on a wall opposite to the exciting one.^{2–5} Either oscillating disk⁶ or moving die vulcameters⁷ are used in such cases. Whatever be the test technique, only the magnitude of the harmonic torque is considered in standard instruments, which essentially record the envelop curve of the (harmonic) torque signal as vulcanization proceeds, i.e. the typical S-shaped cure curve. So-called curing parameters are read on such curves, i.e., scorch time, induction period, rate of cure, optimum cure, etc., as defined in standard testing methods.

Till today, commercially available curemeters reflect the technology available two decades ago for torque measurement and signal processing. In such instru-

ments, the straining signal is sinusoidal (or assumed so) and its amplitude and frequency remain constant during the whole test. The measured torque signal is harmonic with the same frequency but its amplitude varies as vulcanization proceeds, and therefore it is expected to differ from a simple sinusoid, at least for the very simple reason that the amplitude increases as the test material becomes stiffer through networking. It follows that strain and torque signals are surely no longer proportional when vulcanization occurs. In other terms, if the torque-to-strain ratio is reflecting the viscoelastic response of the tested material, this response is expectedly nonlinear during curing. As long as the torque envelop curve is the only information gathered during the cure test, this is of no (or at least minor) consequence with respect to standard curing parameters. However, while using standard curemeter readings for modeling the vulcanization process with respect to the likely associated sequence of chemical reactions, several authors have faced difficulties in obtaining accurate data.^{8,9} For instance, it is fairly obvious that when the “degree of cure” is defined with respect to minimum and maximum values of the torque curve, the accuracy of such reading is questionable; all the more for the “delay time” (i.e., the “scorch time”), which is practically taken at the intersection between an horizontal line passing through the minimum torque and line whose slope should in principle correspond to the (average) cure rate.

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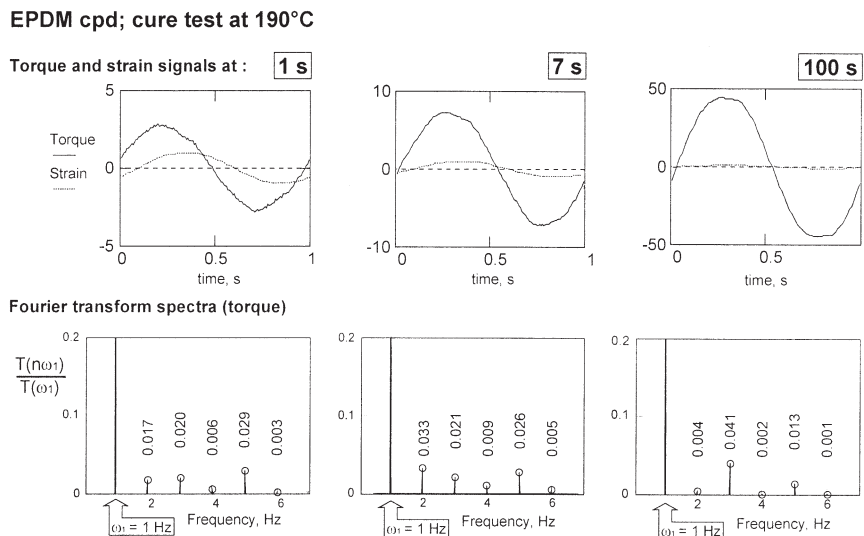


Figure 1 Fourier transform analysis of torque signal as recorded during a vulcanization test.

Would one have a suitable technique to consider it? The evolution of viscoelastic properties during curing is a priori interesting, since one may expect to observe a linear viscoelastic response (i.e. torque to strain ratio remaining constant) as long as the scorch period is not exhausted, a nonlinear behavior during curing, and again a linear response when the material is fully cured (again a constant torque to strain ratio but higher than earlier vulcanization). There are likely more information to be gained from such an approach of the cure test because there is no reason for the viscoelastic properties of a “liquid” rubber system (i.e. before curing) to retain the same features when the material has reached a “solid” state (i.e. through networking).

The aim of this article is to report an investigation of the capabilities of a Fourier transform-based treatment of harmonic stress signals recorded during vulcanization tests.

EXPERIMENTAL

Data capture and treatment

A Rubber Process Analyzer RPA®2000 (Alpha Technologies), suitably modified to allow capturing of full torque and strain signals, was used in gathering results presented in this report. Details of the RPA modification,¹⁰ as well as its use in investigating the nonlinear viscoelastic behavior of various rubber materials,¹¹ have been previously reported. In the experiments reported here, the RPA was essentially used as a simple vulcameter, i.e. by running the so-called cure tests, while the full acquisition of strain and torque signals was made, at a given acquisition rate (points per second) and during a fixed time. Then through the appropriate subsequent treatment of recorded data,

additional information was obtained. The acquisition rate was selected as an entire power of 2, with 128 = 2⁷ points/s found sufficient for both a good definition of harmonic signals and an acceptable calculation time in subsequent data treatment.

The acquisition duration depends on the range of information sought, either over the whole cure curve or over a part of it. Recorded data consist of three columns files, i.e., time scale, strain, and torque, whose size depends on the acquisition rate and duration selected. Data files are processed in the following manner. At selected times, single oscillations are extracted from both the strain and torque signals, and analyzed with a fast Fourier transform algorithm to yield the main component and the harmonics, both pair and odd ones, which are sorted out and stored as FT results files. In the meantime, the crest torque signal is extracted from recorded data to generate the standard cure curve. All such calculations are made with programs written in MatCad®8.0 (MathSoft, Cambridge, MA). The full data treatment lasts for less than 2 min when compared with typical cure test duration of 10 min. Results files are subsequently loaded in Excel worksheets for archiving and analysis (using VBA macros).

Figure 1 illustrates the FT analysis on three single oscillations extracted at various periods of the vulcanization process. As can be seen, torque oscillations are far to be perfect sinusoids and therefore harmonics are detected whose relative magnitudes depend on the extent of the vulcanization process.

Out of FT analysis of single oscillations as recorded during the vulcanization test, one obtains the main component and harmonics that proved to be significant (i.e., larger than the noise) up to the sixth one, for both the strain and torque signals. The FT analysis of the strain gives essentially the magnitude of the de-

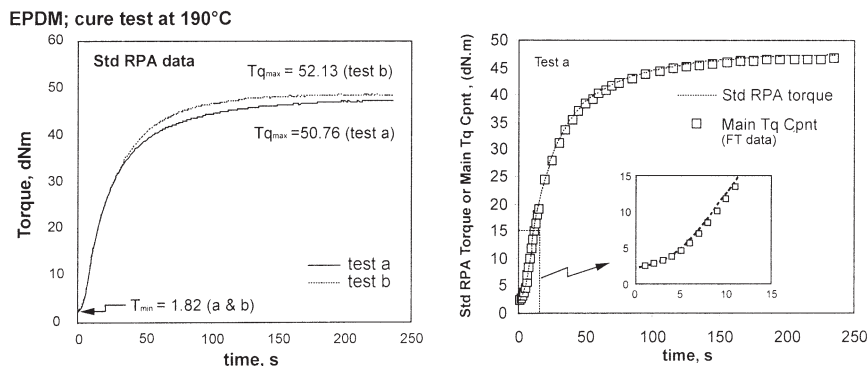


Figure 2 Standard RPA cure curves as compared with FT main torque component.

formation through the main component, and harmonics that document the quality of the applied strain. It was demonstrated elsewhere¹⁰ that, with the RPA, the quality of the strain (signal) decreases at lower strain angle, as reflected by the occurrence of harmonics. Vulcanization tests were performed at 1° strain angle, i.e., 14.98% deformation. In what way the applied strain is concerned? Nearly constant 3rd relative harmonics in the $2.5\% \pm 0.2\%$ range are detected during a whole cure test, as well as 5th relative harmonics in the $1.4\% \pm 0.1\%$ range, corresponding to the expected strain signal quality at this strain amplitude. Pair harmonics are not significant ($<0.5\%$).

Torque's main component evolves as vulcanization proceeds. Torque versus time curve was plotted, and a curve similar to the standard one (i.e., the crest signal) is obviously obtained. With respect to the conditions used for both the tests, the data acquisition and the FT treatment, the following equality holds between the torque (crest signal) and the main torque component:

$$\text{Torque (dN m)} = \frac{T(\omega_1)}{48.217}$$

Figure 2 shows that, as expected, the main torque component provides essentially the same information as the torque recorded with a standard RPA. Sample heterogeneity, if any, reflects in the maximum torque when vulcanization is complete. The main torque component curve tends to be slightly below the standard RPA torque curve, which strongly supports our view that the standard cure curve is an "all inclusive" data, likely hiding information about the vulcanization process.

Besides the usual information, for instance minimum and maximum torque (or modulus), scorch time t_2 and time for 90% cure (t_{90}), splitting the harmonic torque signal in a set of single oscillations, each analyzed through Fourier transform calculation allows a number of pertinent data analyses to be made. Figure 3 shows, for instance, the main torque component and

the cure rate curves (the latter in fact is the first derivative of the former). A maximum in the cure rate curve is clearly detected, far before the t_{90} (i.e., ≈ 75 s in this case). It is worth underlining here that, with respect to the time parameter, the precision of cure test data cannot be better than the duration of one strain oscillation, i.e., 1 s when the strain frequency is set at 1 Hz. The position of the maximum cure rate is thus the value reported ± 0.5 s. If one wants to increase the precision, it is obvious that higher test frequency has to be used. Standard cure tests are made with a frequency of 1.67 Hz (i.e., 100 CPM, cycles per minute); all the experiments reported hereafter were made at 1 Hz, essentially for convenience, i.e., one cycle per second. Of course, no basic difference in the observation reported are expected if another test frequency is used because the variation in the viscoelastic character essentially results from a sequence of chemical reactions. A practical proof of this expectation is brought in appendix where acquisitions at 1 and 2 Hz are shown to provide identical results in terms of torque harmonics.

As shown in the subsequent experimental sections, a number of significant and original information can

EPDM cpd; cure test at 190°C

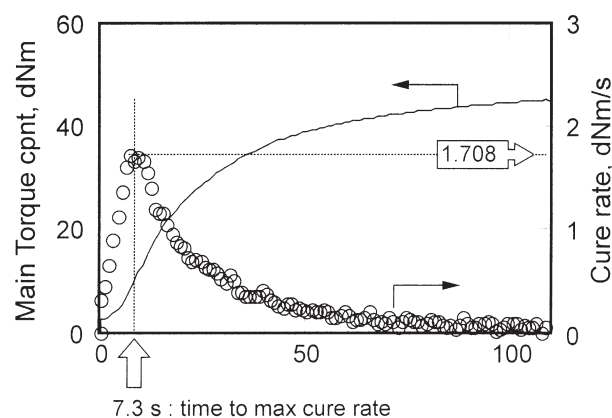


Figure 3 Cure curve from Fourier transform analysis.

TABLE I
Sample Series 1: EPDM Compounds with Gum of Different Origins

Sample code	EPDM A	EPDM B	EPDM C
Vistalon 2504 N	100	—	—
Buna EPG 62470	—	100	—
Keltan 314	—	—	100
N550 carbon black	70	70	70
Plasticizer	20	20	20
ZnO	5	5	5
Stearic acid	0.5	0.5	0.5
Sulfur	2	2	2
Activators (4)	3.5	3.5	3.5
Gum characteristics (supplier's data sheet)			
Ethylene (%)	55.5	69	52
ENB (%)	3.8	4	8
MWD	Broad	Narrow	Broad
ML (1 + 4) at 125°C	25	24	33

be gained from Fourier transform treatment of torque signal.

RESULTS AND DISCUSSION

EPDM compounds and effect of gum origin

Various rubber formulations were used to assess the interest of the test technique described earlier, without seeking for systematic changes in compounding. All samples were obtained from rubber manufacturers, and therefore, not all compounding details were available. Table I provides a basic description of a first series of test samples, which essentially differ by the origin of the gum EPDM used.

Cure tests at 190°C were performed on two samples of each compound; strain frequency and amplitude were 1 Hz and 1° (13.96% strain), respectively. Two

samples were tested for each compound. Data acquisition was made for 10 min at the rate of 128 points/s (i.e., 76,800 data points were recorded). FT analysis was performed as described earlier.

Let us first consider in detail the information obtained through FT treatment of EPDM A data. Figure 4 shows how the main torque component, i.e. $T(\omega_1)$, evolves during vulcanization. A classical “cure curve” is obtained. In terms of minimum and maximum $T(\omega_1)$, both tests give essentially the same results, which suggest a perfect homogeneity of the material. Magnification of the earlier part of the curve reveals a marginal difference in time to reach the maximum cure rate, 11.8 and 10.6 s for tests a and b respectively, not significant, since it is within the ± 0.5 s range.

Because vulcanization occurs, viscoelastic properties of the compound evolves during cure, likely in a nonlinear manner because one starts essentially with a “fluid-like” material to end up with a “solid-like” one. New information is thus awaited from the variation of relative torque harmonic components with curing time. With respect to previous works in Fourier transform rheometry, one also expects odd harmonic components to exhibit significant variations because they have been shown to contain most of the information about the nonlinear viscoelastic character of polymer materials^{12,13} As shown in Figure 5, this is indeed the case, since both the 3rd and the 5th relative harmonic components exhibit typical variations as soon as a specific time has been exceeded. The 3rd harmonic component first goes up and down during the earlier period of the test, passes through a minimum value, and then increases towards a plateau as vulcanization reaches completion. One notes a difference between the two tests before the minimum 3rd harmonic is reached; after this minimum, both tests gives the same

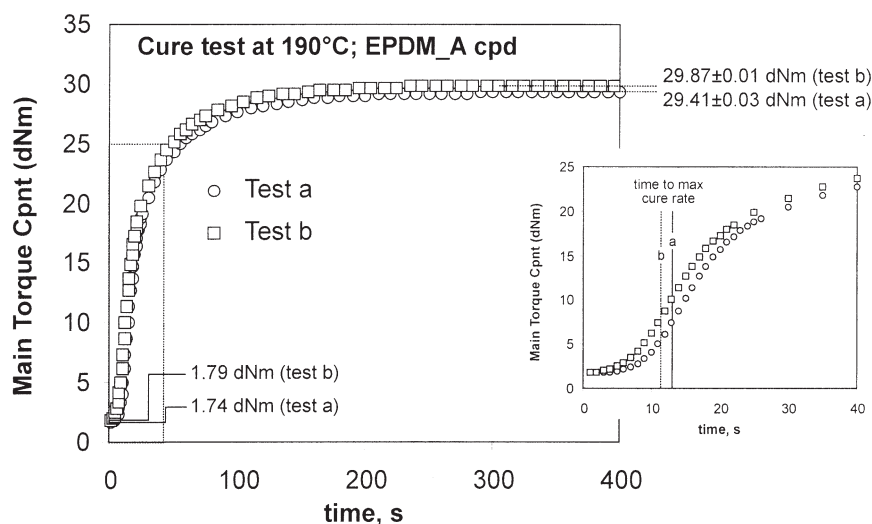


Figure 4 Fourier transform cure curve of an EPDM compound.

Cure test at 190°C; EPDM_A cpd; torque signal; odd harmonic components

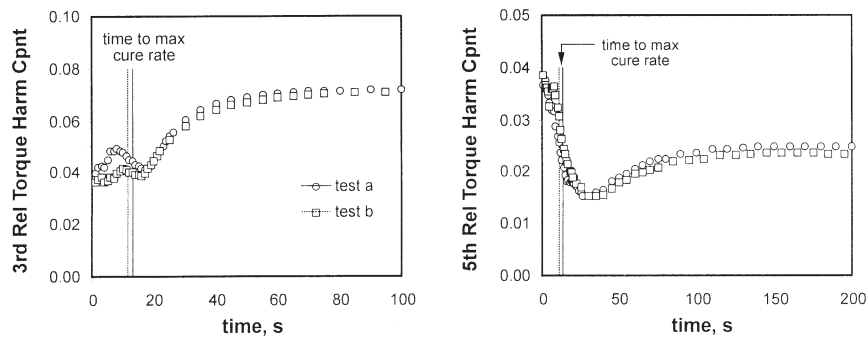


Figure 5 Typical variation of odd harmonic components during a cure test on an EPDM compound.

results. The 5th harmonic first decreases, reaches a minimum value, and then plateaus out as vulcanization is completed.

As shown earlier (Fig. 3), the time to reach the maximum cure rate is detected without ambiguity. It is therefore interesting to consider the (time) position of singularities in odd harmonic components with respect to this information. As shown in Figure 5, the 3rd component passes first through a maximum value, and then through a minimum value before evolving towards a plateau value as vulcanization proceeds. The 5th component passes through a minimum value then becomes asymptotic to a constant value. Both $T(3/1)$, and $T(5/1)$, minimum values are observed at times which are significantly different from the time to reach the maximum cure rate (3rd harm.: 17 and 16 s for tests a and b; 5th harm.: 30 s for both tests; versus 11.2 ± 0.4 s for the time to max cure rate). In other terms, the minimum odd harmonic components correspond to other physical events than the full activation of vulcanizing sites in the compound.

Unexpectedly, as vulcanization proceeds, sharp transitions are also observed on pair harmonics, as illustrated in Figure 6. The 2nd relative harmonic component initially increases, passes through a maximum

then decreases to quickly reach a constant value (about 1% of the main torque component). The 4th harmonic exhibits the same behavior and maximum on both harmonics occur at slightly different times (i.e., 2nd harm.: 10 and 8 s for tests a and b; 4th harm.: 8 and 7 s for tests a and b). As seen in Figure 6, positions of maxima are clearly different from the time for maximum cure rate.

As shown in Figure 7, comparing main torque curves with 2nd harmonic curves shed some light on the meaning of pair harmonic variations. Enlargement was obtained by using a log scale for the time. It is clearly seen that the maximum in the 2nd harmonic component occurs at the end of the scorch period, as defined by the intersection point of an horizontal line drawn through the earlier main torque data and the best straight-line drawn through data points gathered during the torque up-take. One notes also that the time position of the maximum 2nd harmonic appears very sensitive to sample homogeneity; for instance with EPDM A significant differences are observed between tests a and b, while EPDM_C shows no difference. In this respect, EPDM_C is likely to be more homogeneous than EPDM_A.

Cure test at 190°C; EPDM_A cpd; torque signal; pair harmonic components

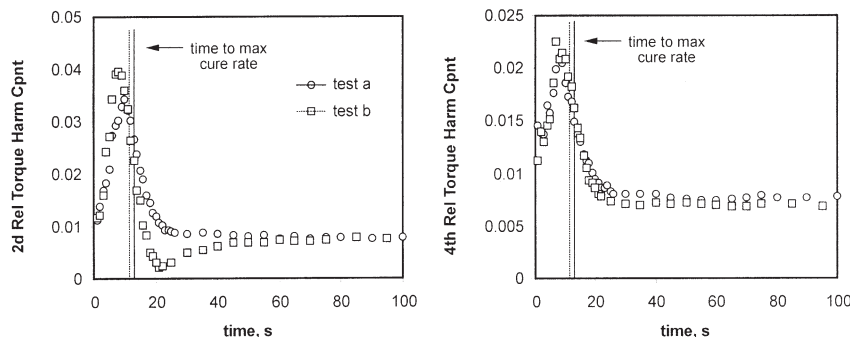


Figure 6 Typical variation of pair harmonic components during a cure test on an EPDM compound.

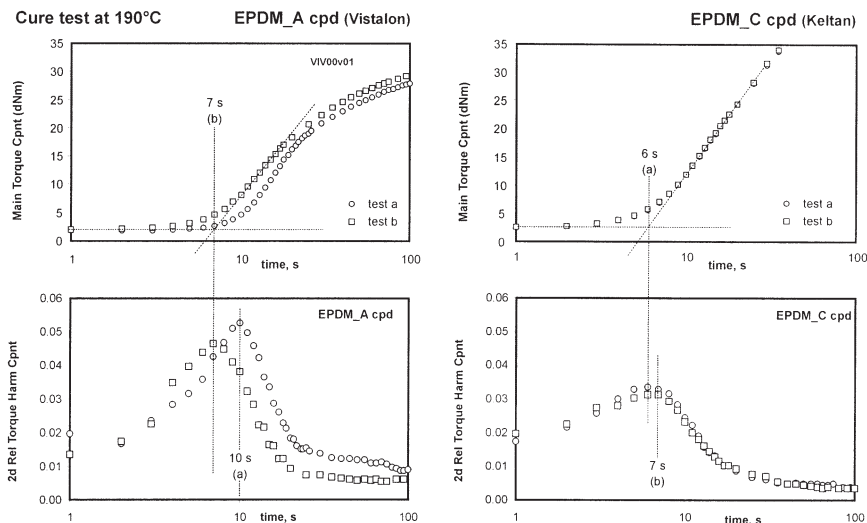


Figure 7 Mean of the time position of the maximum pair harmonic component of measured torque during cure tests (EPDM compounds).

In summary, Fourier transform treatment of cure test data allows sharp transitions to be observed in both odd and pair harmonics; the former pass through minimum values and the latter through maximum values. Single numbers can consequently be extracted from the analysis of torque harmonics, as given in Tables II and III.

Results appear generally consistent and somewhat dependent on the type of gum used in the formulation. For instance, if one considers the time to reach the maximum in the pair harmonics as an indication of the scorch safety, then the higher the ENB content, the longer is the cure induction time. There may be other relationships between gum characteristics and certain features of the cure process as revealed by FT analysis, but the gum sampling is too narrow (and not selected in this respect) to draw conclusions.

EPDM compounds and effect of processing aid level

Processing aids are expected to have marginal effects on cure behavior. EPDM compounds with various

levels of zinc stearate were consequently tested as a manner to assess the sensitivity of FT analysis of cure tests (Table IV).

Cure tests at 190°C were performed on two samples of each compound; strain frequency and amplitude were 1 Hz and 1° (13.96% strain), respectively. Two samples were tested for each compound. Data acquisition was made during 4 min at the rate of 128 points/s (i.e., 76,800 data points were recorded). FT analysis was performed as described earlier.

Main torque curve features (Table V) are affected in the expected manner by processing aid level, i.e., a marginal decrease of both the maximum torque and the maximum cure rate with increasing processing aid content. The time to reach the maximum cure rate tends to increase with higher processing aid level.

Essentially, the same qualitative observations, as in the previous section, are made on torque harmonic components, i.e. odd harmonics pass through a minimum before plateauing out as vulcanization reaches completion, and pair harmonics exhibit a maximum whose position on the time scale corresponds to the

TABLE II
Sample Series 1: EPDM Compounds with Gum of Different Origins and Pair Harmonics Analysis

Test	2nd Torque harmonic			4th Torque harmonic		
	Max $T(2/1)$	Time to max $T(2/1)$ (s)	Final $T(2/1)$	Max $T(4/1)$	Time to max $T(4/1)$ (s)	Final $T(4/1)$
EPDM_A (Vistalon)						
a	0.0342	10	0.0028	0.0210	8	0.0071
b	0.0396	8	0.0075	0.0225	7	0.0069
EPDM_B (Buna)						
a	0.0426	8	0.0028	0.0204	8	0.0014
b	0.0378	7	0.0027	0.0156	7	0.0011
EPDM_C (Keltan)						
a	0.0334	6	0.0042	0.0096	6	0.0016
b	0.0314	7	0.0036	0.0099	7	0.0016

TABLE III
Sample Series 1: EPDM Compounds with Gum of Different Origins and Odd Harmonics Analysis

Test	3rd Torque harmonic			5th Torque harmonic		
	Max $T(3/1)$	Time to max $T(3/1)$ (s)	Final $T(3/1)$	Max $T(5/1)$	Time to max $T(5/1)$ (s)	Final $T(5/1)$
EPDM_A (Vistalon)						
a	0.0413	17	0.0754	0.0153	30	0.0216
B	0.0389	16	0.0748	0.0153	30	0.0202
EPDM_B (Buna)						
a	0.0182	12	0.0308	0.0309	6	0.0115
b	0.0113	10	0.0315	0.0112	13	0.0115
EPDM_ C (Keltan)						
a	0.0179	10	0.0374	0.0128	70	0.0144
b	0.0208	12	0.0306	0.0119	50	0.0125

end of the induction period (scorch safety). Results are given in Table VI.

Figure 8 shows the effect of processing aid level on the 2nd harmonic component. The time to reach the maximum $T(2/1)$ clearly depends on processing aid level and the observed scatter is likely due to poor material homogeneity. The maximum relative 2nd harmonic does not likely depend on processing aid level.

As shown in Figure 9, the 3rd harmonic component is clearly affected by the level of processing aid; the time to reach the maximum, $T(3/1)$ decreases with zinc stearate content and an increase is observed on the (relative) magnitude of $T(3/1)$. Again, the scatter is attributed to poor material homogeneity.

Unfilled EPDM compound

Filler and other compounding ingredients affect the viscoelastic response of elastomer materials. To support our view that the aforementioned effects are essentially reflecting events associated with the curing process, and a model compound was investigated. A peroxide-cured gum EPDM compound, as described in Table VII, was therefore prepared by thoroughly mixing ingredients on a laboratory rolls-mill at 60°C until optimal dispersion was obtained. After sheeting out (2 mm thickness), cylindrical samples were die cut

TABLE IV
Sample Series 2: EPDM Compounds with Various Level of Processing Aid

Vistalon 2504 N	100
N550 carbon black	70
Plasticizer	20
ZnO	5
Stearic acid	0.5
Sulfur	2
Activators (4)	3.5
Zn stearate	0.5, 1, 2, 4

and their weight adjusted to meet the RPA cavity volume plus about 5%.

Cure tests at 180°C were performed on five samples with strain frequency and amplitude fixed at 1 Hz and 1° (13.96% strain), respectively. Data acquisition was made for 10 min at the rate of 128 points/s (i.e. 76,800 data points were recorded). FT analysis was performed as previously described.

As expected, main torque components from the five tests yield cure curves (Fig. 10) that exhibit a perfect reproducibility, thus demonstrating the optimal dispersion of curing ingredients. Standard cure data are easily extracted from such curves and the maximum cure rate is found to be 0.190 ± 0.001 dN m/s, occurring at 54.3 ± 0.4 s.

As shown in Figure 11, sharp transitions are observed on odd and pair harmonics, for instance the 3rd and the 2nd harmonic components. As seen in the upper graph, despite an initially large scatter, the 3rd relative harmonic component first clearly increases, then passes through a maximum value, and eventually reaches a constant value ($2.39\% \pm 0.09\%$). In contrast with the observation previously made on filled compounds, there is no clear occurrence of a mini-

TABLE V
Sample Series 2: Effect of Processing Level on Cure Curve Features

Proc. aid (phr)	Test	Max torque (dN m)	Max cure rate (dN m/s)	Time to max CR (s)	T90 (s)
0.0	a	31.39	1.385	13.0	98
0.0	b	31.67	1.385	8.9	73
0.5	a	32.40	1.274	11.8	65
0.5	b	33.35	1.218	10.6	78
1.0	a	30.12	1.207	12.9	71
1.0	b	32.00	1.174	10.7	68
2.0	a	28.46	1.122	8.0	74
2.0	b	30.46	1.075	14.3	76
4.0	a	26.86	0.964	13.8	75
4.0	b	28.57	1.021	15.5	78

TABLE VI
Sample Series 2: Effect of Processing Aid Content on Torque Harmonic Components During a Cure Test

Proc. aid (phr)	Test	Pair harmonic components				Odd harmonic components			
		Max $T(2/1)$ (dN m)	Time to max $T(2/1)$ (s)	Max $T(4/1)$ (dN m)	Time to Max $T(4/1)$ (s)	Min $T(3/1)$ (dN m)	Time to min $T(3/1)$ (s)	Min $T(5/1)$ (dN m)	Time to min $T(5/1)$ (s)
0.0	a	0.0527	10	0.0145	10	0.0198	18	0.0151	35
0.0	b	0.0464	7	0.0159	8	0.0162	15	0.0127	235
0.5	a	0.0285	10	0.0134	10	0.0124	12	0.0093	75
0.5	b	0.0233	8	0.0102	7	0.0266	15	0.0096	75
1.0	a	0.0370	10	0.0139	9	0.0190	10	0.0103	14
1.0	b	0.0141	7	0.0076	5	0.0256	7	0.0098	50
2.0	a	0.0312	9	0.0126	8	0.0314	9	0.0103	35
2.0	b	0.0246	11	0.0076	13	0.0257	13	0.0100	50
4.0	a	0.0255	11	0.0122	11	0.0164	11	0.0102	30
4.0	b	0.0338	12	0.0132	13	0.0370	12	0.0098	35

mum $T(3/1)$ value after the peak, whose average value for the five tests is $3.40\% \pm 0.04\%$. One notes that the peak $T(3/1)$ occurs at 14.4 ± 0.9 s, largely before the maximum cure rate is reached. The lower part of Figure 11 shows the early variation of the 2nd harmonic component. A large scatter is at first observed, but there is a remarkable occurrence of either a maximum (with 4 samples) or a minimum (1 sample) before a final value of $0.71\% \pm 0.04\%$ is reached. A sharp transition on $T(2/1)$ thus occurs at 22.2 ± 1.2 s. It must be noted that because the strain frequency is 1 Hz, one cannot expect to detect events with a better accuracy than 1 s, as indeed observed.

DISCUSSION

Fourier transform analysis of harmonic torque signals recorded during a cure test brings clearly new information. Despite some differences due to compounding ingredients, there is a remarkable coherence in the occurrence of sharp transitions on both odd and pair harmonics that, for the sake of discussion, are illustrated by Figure 12, using data obtained with the

unfilled EPDM compound. Sharp transitions seen on both the 3rd and the 2nd harmonic components occur at times, which are markedly different from the time for the maximum cure rate to be reached. The transition on $T(3/1)_i$ seems to be related to the minimum torque, while the transition on $T(2/1)_i$ seems to somewhat correspond to the “scorch” time.

Providing curatives are thoroughly dispersed in the compound, and vulcanization occurs when heating brings enough energy for a set of complex chemical reactions to be activated that will eventually result in a tridimensional polymer network. With respect to the various chemical mechanisms that have been suggested for vulcanization, it is fairly obvious that the process does not occur instantaneously but according to an overall kinematics that is considered well reflected by the so-called “cure curve”, as recorded with any vulcameter. Essentially, the vulcameter addresses the viscoelastic character of the material, at least a single point of the complex modulus function (at fixed frequency, strain amplitude, and temperature). The measured complex modulus varies during cure because the material is changing, evolving from a (vis-

Cure test at 190°C; EPDM cpds; torque signal; 2d harmonic component

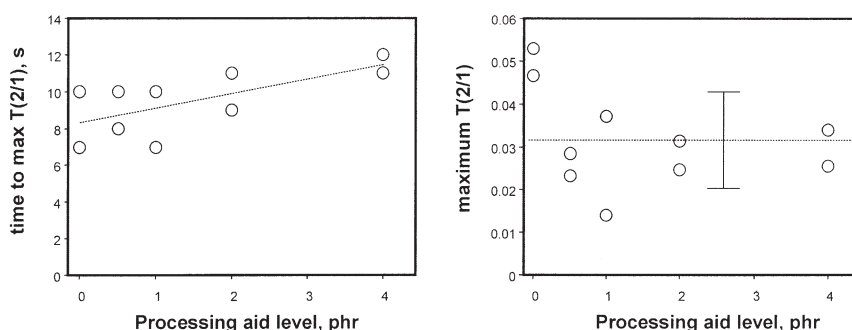


Figure 8 Effect of processing aid level on pair harmonic components of the measured torque during a cure test; the vertical bar in the right graph indicates the standard deviation of the data and supports the comment that no significant effect is observed.

Cure test at 190°C; EPDM cpds; torque signal; 3d harmonic component

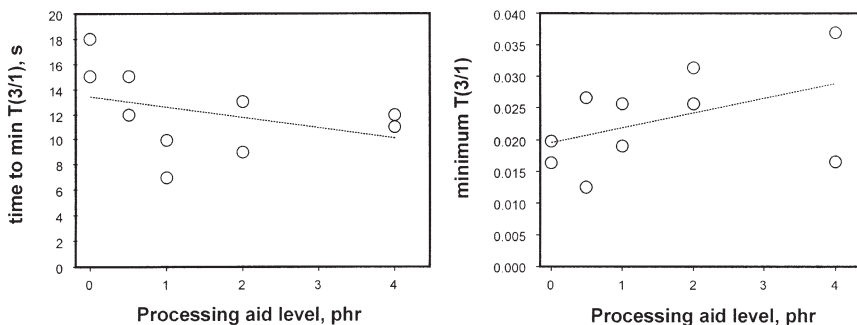


Figure 9 Effect of processing aid level on odd harmonic components of the measured torque during a cure test.

coelastic) pseudo-liquid state towards a solid state, viscoelastic as well. Sharp transitions occurring on both odd and pair harmonics are likely reflecting critical changes in the structure of the material as vulcanization proceeds.

Let us, for instance, consider a compound sample, within the cavity of a vulcameter, that is suddenly submitted to thermal activation in such a manner that complex chemical events take place that will eventually result in full vulcanization. All curatives have been thoroughly dispersed in the compound but, in practice, the dispersion, even if close to ideal, does not exclude the likeness that active vulcanizing species are somewhat locally clustered. Vulcanization can be viewed as an auto-catalytic process in this sense that, once initiated locally in the material, crosslinking proceeds preferably in the vicinity of just made crosslinks. In other terms, crosslinking is not an instantaneous bulk process, as indeed reflected by the S shape of the cure curve, but is the result of a sequel of local chemical events, initiated at random and autocatalytically propagating at the rate of consumption of chemical species. Crosslinking is therefore similar to the well-known nucleation process in crystallization.

Within the cavity of the vulcameter, during the so-called "scorch period," one thus has a heterogeneous viscoelastic systems submitted to a harmonic strain, at constant amplitude and frequency, in which there is an uneven dispersion of cured zones growing

in size. Heterogeneity is therefore worsening during the earlier period of the vulcanization process, with in addition transient thermal conditions as heat flux is progressing from test cavity walls towards the middle of the sample. This initial worsening heterogeneity clearly reflects in the earlier variation of odd and pair harmonics. As cured zones grow in size, they eventually come into contact and overlap, and homogeneity improves as a tridimensional network is subsequently created. Consequently, at the end of the vulcanization process, torque harmonics stabilize and reach constant values that reflect the nonlinear viscoelastic character of the cure compounds, as indeed observed.

With this schema in mind, it is now possible to offer an explanation for the critical variations observed on both pair and odd harmonics. Odd harmonics correspond to distortions in the strain signal that are essentially reflecting the nonlinear viscoelastic character of the polymer matrix when strained at sufficiently large amplitude (i.e. larger than a few percent for high MW materials). A sharp transition is observed on odd harmonics as the material passes from a nonlinear viscoelastic "fluid" state to a "solid" one.

TABLE VII
Peroxide-Curing Gum EPDM Compound

Sample code	EPR00
Buna EP5450	100
Dicumyl peroxyde	2
Tri-allyl cyanurate	0.5
Gum characteristics (supplier's data)	
Ethylene (%)	52
ENB (%)	4.0
MWD	Narrow
ML (1 + 4) at 125°C	46

Cure test at 180°C; unfilled EPDM cpd

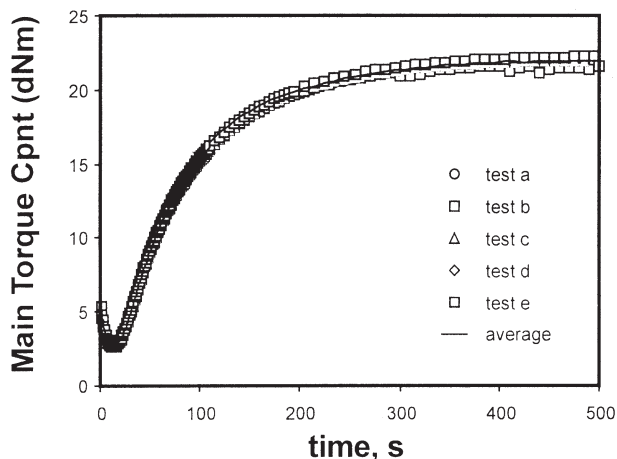


Figure 10 Cure curves from FT main torque component.

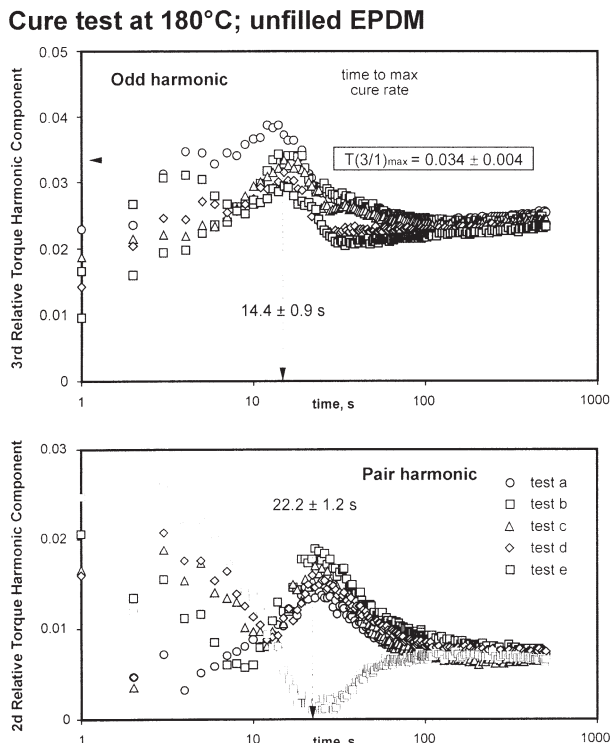


Figure 11 Early variations of the 3rd and 2nd harmonic components during a cure test on an unfilled EPDM compound (five samples tested); note that a logarithm time scale has been used for easier observation.

Pair harmonics are likely associated with the presence of dispersed “particles” whose rigidity is higher than the one of the matrix, as it is readily observed with filled (noncuring) rubber compounds. A sharp transition is also observed as vulcanization proceeds because local curing zones grow in size, come in contact, and eventually fuse together.

CONCLUSIONS

Using a purposely modified Rubber Process Analyzer, a new approach of the curing test has been successfully developed that consists in recording the complete torque signal as it varies during the test, and in splitting it into a sequence of single oscillations those are treated through Fourier transform calculations. For each single oscillation, essentially three types of information are obtained: the main torque component $T(\omega_1)_i$ (i.e., the amplitude of the torque signal at this precise time i of the curing process), the odd $T(3/1)_i$, $T(5/1)_i \dots$, and pair $T(2/1)_i$, $T(4/1)_i \dots$, relative harmonic components that reflect, in fact, torque signal distortions with respect to a pure sine. How the odd and pair harmonic components vary as vulcanization proceeds, discloses hidden information about the vulcanization process.

Using a limited series of EPDM compounds, a number of data have been obtained that support the view that variations in odd harmonic component essentially reflect the passage from a viscoelastic “fluid” state towards a viscoelastic “solid” one, as vulcanization proceeds. This transition does not coincide with the time for the maximum cure rate to be reached and is likely to be affected by (non curatives) compounding ingredients and the macromolecular characteristics of the gum polymer, while no systematic investigation was so far conducted regarding such aspects. Variations in pair harmonic components are believed to be associated with changes in compound’s heterogeneity in agreement with the view that curing sites are distributed at random and increase in size until a full tridimensional network is formed.

The report is a preliminary description of a promising technique for extracting original information from the well-established vulcametry test. It requires

Cure test at 180°C; unfilled EPDM

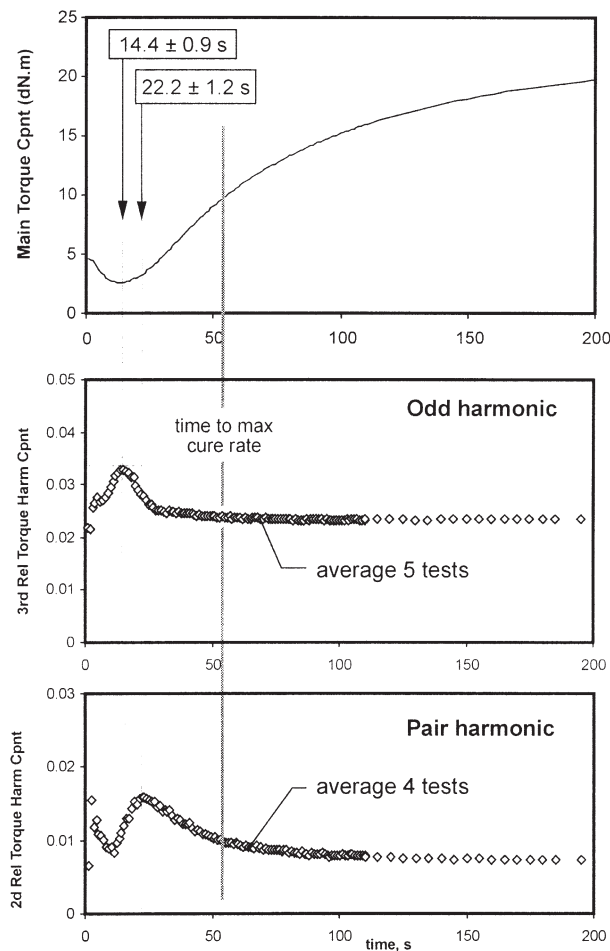


Figure 12 Cure curve (main torque component) versus harmonic components early variations for a peroxide curing unfilled EPDM compound; the gray zone indicates the standard deviation in repeating tests.

NBR/N550 cpd; cure tests at 150°C; strain angle : 1°

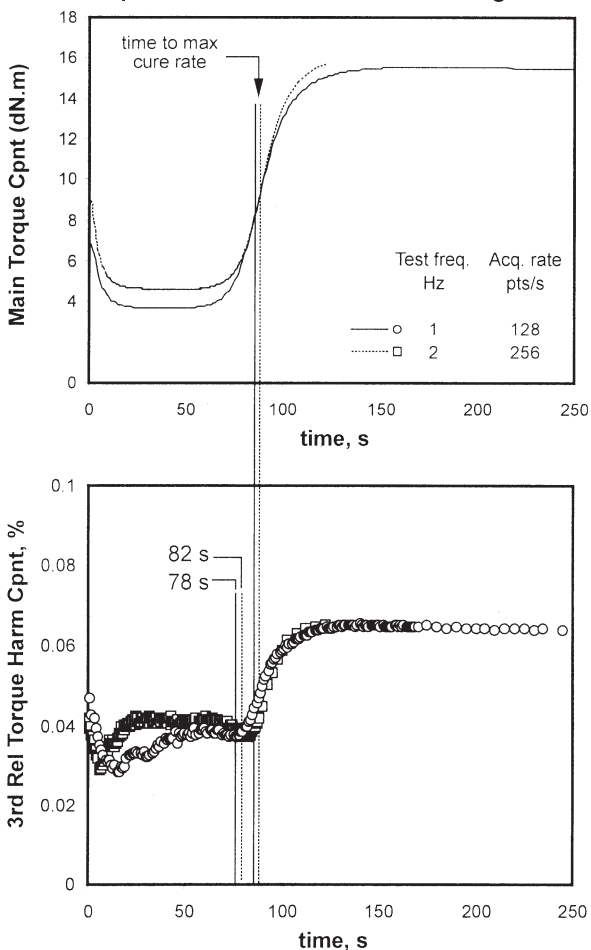


Figure A.1 Cure curve (main torque component) and 3rd relative harmonic components as recorded while performing vulcanization tests either at 1 or 2 Hz frequency on a carbon black-filled NBR compound (sulfur cure system).

no special testing skills or protocols, except a suitable modification of the instrument for a full capture of the (harmonic) torque signal and, of course, the appropriate calculation routines. Further works, with purposely designed curatives formulations, are expected to demonstrate the full potential of this technique.

APPENDIX

Torque variation during a cure test essentially reflects the modification of the material structure as vulcanization proceeds. To practically demonstrate that the strain frequency has no effect on the observed variation, i.e., the main torque component and the harmonics, tests on a NBR/N550 carbon black filled compound (sulfur cure system) were made at test frequencies 1 and 2 Hz, i.e., below and above the standard cure test condition (1.67 Hz). As shown in Figure A.1, except a slight (and expected) vertical shift of the main torque component, no significant frequency effect is detected on the time position of critical events of the cure process, for instance the time to maximum cure rate or the end of the scorch period through the singularity in the $T(3/1)$ versus strain curve.

References

1. Decker, G. E.; Wise, R. W.; Guerry, G. *Rubber Chem Technol* 1963, 36, 451.
2. Göttfert, O. *Kautsch Gummi Kunstst* 1976, 29, 261.
3. Göttfert, A. In ACS Rubber Division Meeting, New York, April 8–11, 1986. Paper No. 64.
4. Pawlowski, H. A.; Perry, A. L. In PRI Conference, Birmingham, UK, March 12–16, 1984.
5. Sezna, J. A.; Pawlowski, H. A.; De Coninck, D. In ACS Rubber Division Meeting, Detroit, MI, October 17–20, 1998. Paper No. 78.
6. Standard Test Method for Rubber Property—Vulcanization Characteristics Using Oscillating Disk Cure Meters, ASTM D-2084, ASTM, 2001.
7. Standard Test Method for Rubber Property—Vulcanization Using Rotorless Cure Meters, ASTM D-5289, ASTM, 2002.
8. Coran, A. Y. *Rubber Chem Technol* 1964, 37, 689.
9. Ding, R.; Leonov, A. I.; Coran, A. Y. *Rubber Chem Technol* 1996, 69, 81.
10. Leblanc, J. L.; de la Chapelle, C. *Rubber Chem Technol* 2003, 76, 287.
11. Leblanc, J. L.; de la Chapelle, C. *Rubber Chem Technol* 2003, 76, 979.
12. Wilhelm, M. *Macromol Mater Eng* 2002, 287, 83.
13. Leblanc, J. L. *Rubber Chem Technol* 2005, 78, 54.