

Characterization of summer tire tread compounds by Large Amplitude Oscillating Shear (LAOS)

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ABSTRACT

In the last years, characterisation of plastics by Large Amplitude Oscillating Shear (LAOS) became a high-power, widely spread technique. Also for elastomers (especially different EPDM types) this method is applied, using a Fourier Transformation (FT).

Regarding this background investigations with Fourier transformation rheometer were carried out for the non-linear viscoelastic domains for summer tire tread compounds based on the “green tire recipe”, a compound including a silica/silane reinforcing system. In this connection, not only the character of the polymer was changed but also differences in filler and silanes were realised.

In particular was determined, who to detect polymer architecture with this tool and whether there is a potential of this approach to select filler behaviour as surface area and/or structure as well as the bounding type of different silanes in a repeatable way.

INTRODUCTION

In the context of the production of rubber compounds, especially of highly filled Silica/Silane compounds it is often mentioned that processing becomes more difficult. To give a precise definition of “processing” seems difficult since it encloses such different aspects like the behaviour in an internal mixer, on an open mill, a roller die, in an extruder or calender. Despite the

difficulties of a definition, it was always desired to get an idea of processing behaviour by rheological characterization of compounds (with the Mooney measurement as the best-known method). Thus the improvement of understanding of the connection between rheological tests and processing is the main focus in an ongoing project.

One of the test methods applied in the framework of the project is the analysis of Large Amplitude Oscillating Shear (LAOS) which became a widely spread technique to analyse the dynamical behaviour of elastomers (especially different EPDM types), using a Fourier Transformation (FT).^{1,2,3} Also for filled compounds this techniques is used.^{4,5,6}

LAOS

Generally speaking, Large Amplitude Oscillating Shear means to carry out oscillatory measurements at a certain frequency and at high values of shear strain (mostly at 1000 %). At the present time different ways of testing are associated with the term “LAOS” regarding the used strain values as well as the FT analysis technique.

Thus investigations in the present study were done for the entire accessible strain regime, i.e. from the linear to non-linear regime. The Fourier analysis in this study was provided by a discrete Fourier trans-

formation (not FFT) based on 5 cycles each containing 90 data points.

All tests were carried out by a Rubber Process Analyser (RPA from TA) at a fixed temperature of 80 °C and a frequency of 0,2 Hz. The relatively low frequency was chosen to enable large strains.

Figure 1 shows the results at 1 % shear: the graph displays the typical loss ellipse. The results from the measurements at high strains of 1000 % are presented in figure 2 (the material was the same as that used for figure 1): – the stress strain curve deviates significantly from an elliptical shape, which indicates non-linear behaviour.

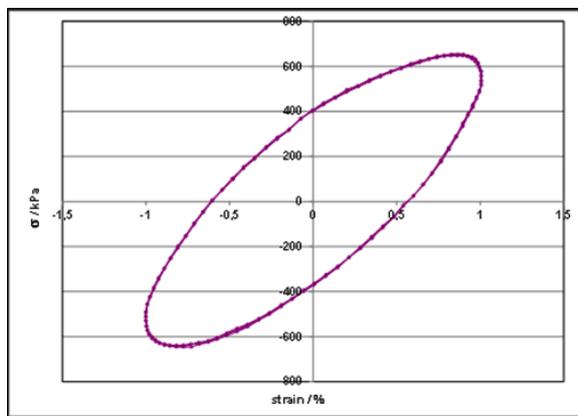


Figure 1. Stress over strain in the linear regime (filled compound, 1 % strain)

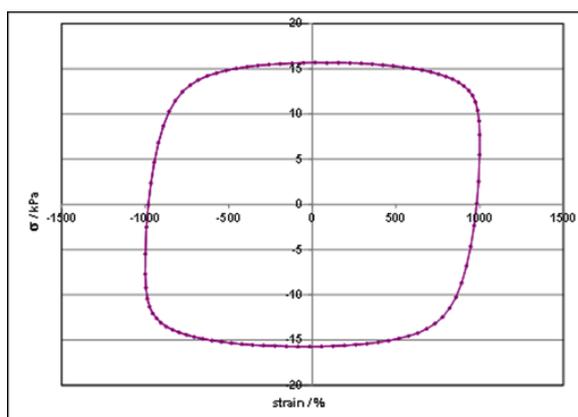


Figure 2. Stress over strain in the non-linear regime (filled compound, 1000 % strain)

Providing a harmonic oscillating strain input, the viscoelastic stress response at steady state can be written as a time-domain

Fourier series of odd harmonics⁷:

$$\sigma(t, \omega, \gamma_0) = \gamma_0 \sum_{n:odd} \{G'_n(\omega, \gamma_0) \sin n\omega t + G''_n(\omega, \gamma_0) \cos n\omega t\}. \quad (1)$$

For sufficiently small strain amplitudes γ_0 a linear material response is observed indicated by the fact that the 1st harmonic provides the only significant contribution (see fig. 3). For larger deformation amplitudes, higher odd harmonics appear proving that the material now shows a non-linear response (see fig. 4 for an analysis of the real part of the 1000 % signal in the typical alternating sequence).

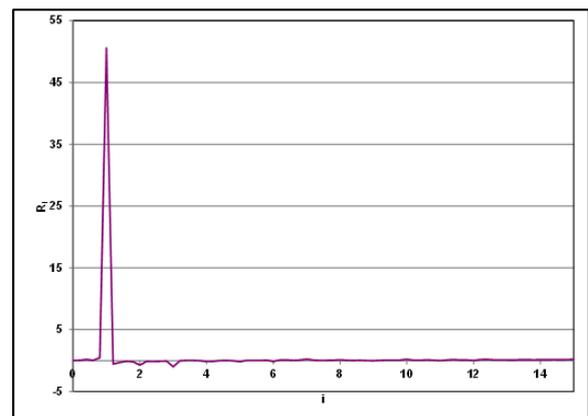


Figure 3. Fourier analysis for linear behaviour (filled compound, 1 %)

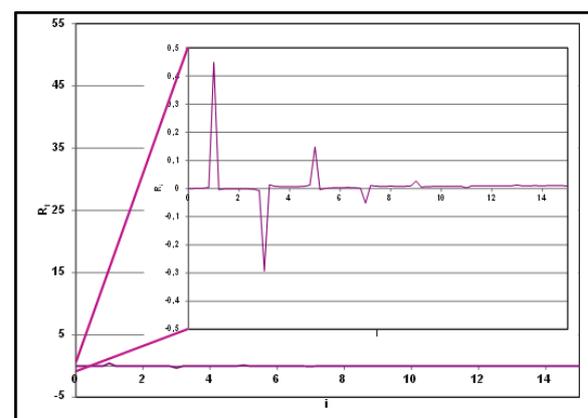


Figure 4. Fourier analysis for non-linear behaviour (filled compound, 1000 %)

To focus explicitly on non-linear effects, the higher Fourier coefficients will be normalized with respect to the linear contributions, i.e.: $r_i = |R_i|/R_1$, $i=3, 5, \dots$

For the present analysis it is sufficient to consider the real (i.e. in phase) part of the signal. This is due to the dominating elasticity achieved for the materials and test conditions under consideration. At 1000 % strain some non-trivial contributions of r_7 are recognized and so, it can be stated that in usual large strain domains (i.e. up to 1000 %) non-linear strain contributions of order 7 and higher can be neglected.

COMPOUNDS

On basis of the “green tire recipe” compounds with variations of BR-type, filler and

Table 1. General ingredients
“Green tire recipe”

Ingredient	Silica compounds		Carbon black compounds	
	/ phr		/ phr	
Buna VSL 4526-2	96,25		96,25	
BR	30		30	
Silica	80		-	
Carbon black	-		72	
OCTEO or Si 266®	4 or 5,8		-	
ZnO	2		2	
Stearic acid	1		1	
Vivatec 500	8,75		8,75	
WulkanoX HS/LG	1,5		1,5	
WulkanoX 4020	2		2	
Protector G3108	2		2	
Rhenogran DPG-80	2,5		-	
Perkacit TBzTD PDR-D	0,2		-	
Wulkacit CZ	1,6		1,6	
Sulfur	2		1,4	

Table 2. Assignment of variations to the compounds

	BR	Silica	Silane	Carbon black
Comp. 1	Buna CB 22	ULTRASIL® VN2 GR	OCTEO	
Comp. 2	Buna CB 22	ULTRASIL® VN2 GR	Si 266®	
Comp. 3	Buna CB 22	ULTRASIL® 7000 GR	OCTEO	
Comp. 4	Buna CB 22	ULTRASIL® 7000 GR	Si 266®	
Comp. 5	Buna CB 22			N339
Comp. 6	Buna CB 22			N326
Comp. 7	Buna CB 22			N234
Comp. 8	Buna CB 1220	ULTRASIL® VN2 GR	OCTEO	
Comp. 9	Buna CB 1220	ULTRASIL® VN2 GR	Si 266®	
Comp. 10	Buna CB 1220	ULTRASIL® 7000 GR	OCTEO	
Comp. 11	Buna CB 1220	ULTRASIL® 7000 GR	Si 266®	
Comp. 12	Buna CB 1220			N339
Comp. 13	Buna CB 1220			N326
Comp. 14	Buna CB 1220			N234

silane are produced. Table 1 shows the general ingredients.

Table 2 shows the assignment of the variations to the compounds; different coloured and shades fields should underline the systematic of the variations.

The compounds were mixed on a GK 90 E from Werner + Pfleiderer (with intermeshing PS5 geometry) in three stages.

RESULTS

In rubber properties

Physical tests of uncured and cured samples were carried out. Significant observations are shortly summarized without further discussion:

- Mooney viscosity:
 - Increasing for linear BR-type.
 - Increasing for bifunctional silane.
 - Increasing for higher surface area of the both silica and carbon black.
 - Increasing for higher carbon black structure.
- Cure behaviour:
 - Curing time is increasing for linear BR-type.
 - The Influence of the different types of silanes is much more pronounced for linear BR-type.
- Filler dispersion:
 - A better filler dispersion was found for the highly branched BR-type.
 - Dispersion of low surface area – low structure carbon black is extremely challenging.
- Hardness:
 - Slightly increasing for linear BR-type.
 - Significantly increasing for use of bifunctional silane.
 - Generally increasing for high structure and/or high surface of filler.
- Reinforcement:
 - Decreasing slightly for linear BR-type.
 - Significantly increasing for use of bifunctional silane.

Processing

Garvey die tests are regarded as a significant method to estimate the extrusion behaviour of compounds being an important aspect of processing. Thus these kind of tests were carried for a various screw speeds (up to 100 rpm). Figures 5a to 5c display pictures of Garvey die profiles of several compounds at screw speed of 45 rpm.



Figure 5a. Profile of compound 6 N 326, CB 22



Figure 5b. Profile of compound 4 ULTRASIL[®] 7000, Si 266[®], CB 22



Figure 5c. Profile of compound 11 ULTRASIL[®] 7000, Si 266[®], CB 1220

It is remarkable that the BR-type (linear vs. branched) influences the extrusion quality tremendously: if one assigns the Si 266[®]/ULTRASIL[®] 7000 GR filler system to be challenging from the processing perspective and N326 to achieve good extrusion behaviour, the change of the BR polymer from linear to branched dominates these influences (e.g. CB1220 provides smooth stripes even for the Si 266[®]/ULTRASIL[®] 7000 GR system).

LAOS

It is known that LAOS is an appropriate tool for a reliable evaluation of (long chain) branching in case of pure polymer melts. The branching variation in the present study is provided by the BR types, which show pronounced differences in the non-linear regime (see figure 6).

Since the BR is underrepresented (30 PHR vs. 96 PHR of oil extended S-SBR) in the compounds the influence of blending

was first checked. Figure 7 shows that that the dynamic behaviour of the S-SBR dominates the LAOS analysis.

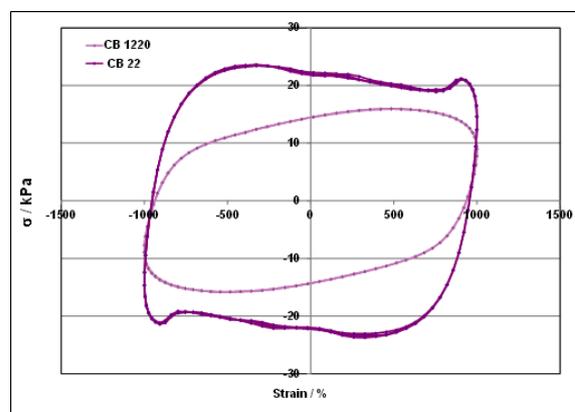


Figure 6. Lissajous figures of pure CB22 (linear: higher n.l. contributions) and CB1220 (branched: smaller n.l. contributions) melts

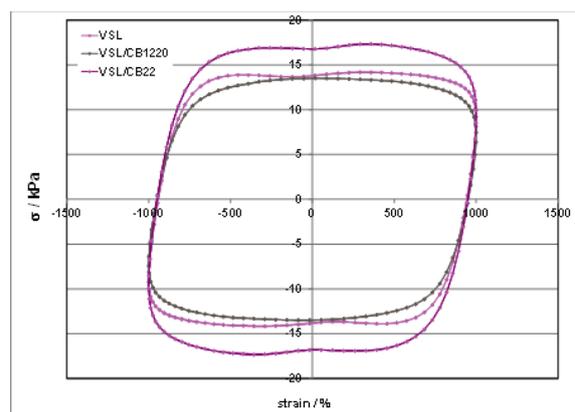


Figure 7. Lissajous figures of pure S-SBR and pure blend systems

These observations suggest that non-linear analysis is not able to differentiate in between the BR polymers for the compounds considered. This is indeed the case as

figure 8 might document by the example of the systems Si 266[®]/ULTRASIL[®] 7000 GR.

Therefore, the further discussion focuses on the systematic analysis of differentiations with regard to filler variations based on the CB1220 compounds.

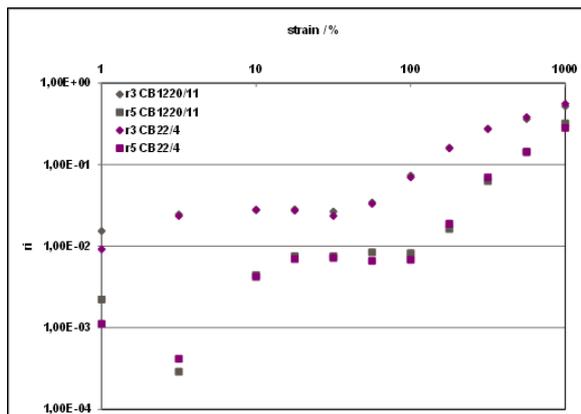


Figure 8. LAOS analysis of Si 266[®]/ULTRASIL[®] 7000 GR filled compounds

Figure 9 shows the r_3 values for the silica-filled compounds. For both silica types, one systematically finds a slight crossover at about 100 % shear for the mono- respectively bi-functional silane (which is recognized for the CB22 systems in the same manner). Whether this effect is of significance regarding the accuracy of the tests should be investigated in the future.

Similar observations can be made for the influence of the surface area of the silica (and for r_5 and r_7 but at a reduced level of significance).

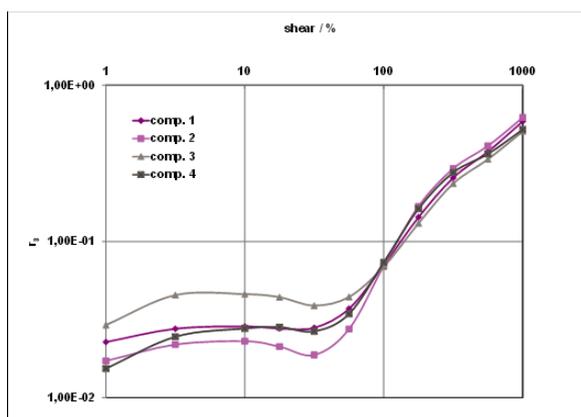


Figure 9. r_3 values of the silica filled compounds in the VSL 4526-2 / CB 1220 – blend

For carbon black filled compounds the influence of structure seems to be not recognisable by LAOS (see fig. 10), but regarding the surface area a behaviour analogous to that in case of silica is found: a higher surface area leads to higher r_3 values for lower strains where the values are more or less similar at strain values about 100 %.

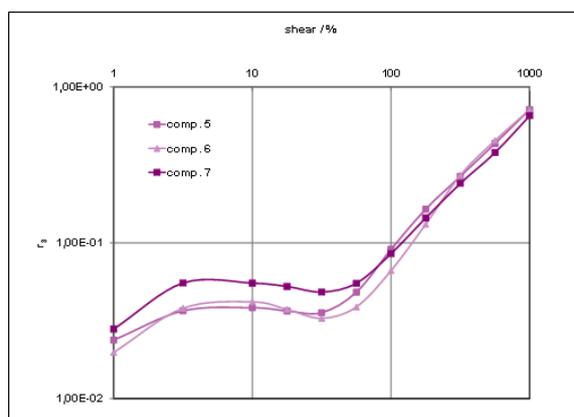


Figure 10. r_3 values of the carbon black filled compounds in the VSL 4526-2 / CB 1220 – blend

Comparing the high surface carbon black (N234) with the high surface silica (ULTRASIL[®] 7000 GR), it is remarkable that for the use of mono-functional silane the r_3 -values are similar to the values of the carbon black filled compound, whereas a large difference is found for the bi-functionally bounded silica (see fig. 11).

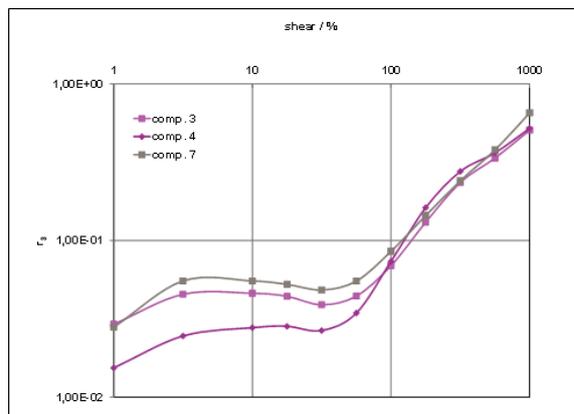


Figure 11: Comparison of r_3 values of the carbon black vs. silica filled compounds

CONCLUSION

Large oscillation strain analysis allows for a reliable differentiation of polymer melts where the effects noticed by the relative Fourier coefficients are usually dominated by the branching structure of the polymer. In S-SBR - BR blends the main part (here S-SBR) seems to determine the non-linear behaviour (as mirrored by LAOS analysis) and masks the differences introduced by the polymer architecture of the BR types (linear vs. branched) nearly completely.

The results for filled compounds show that the differences of the BR types in the polymer phase remain nearly completely undetected by analysis of the large strain regime (i.e. for strain above 100 %). This is particularly remarkable because the polymer variations induce a large impact on processing, here shown by the example of Garvey die extrusion. Thus processing behaviour seems not to be predictable by "classical" (i.e. high strain) LAOS analysis.

In the case of filled compounds Fourier analysis of strains in the intermediate range (10 % to 100 % strain) shows potential with regard to the estimation of filler polymer interaction (silica vs. CB, influences of silane type or surface area). Since the capability of differentiations is maintained up to the large strain regime in a reliable manner (a significant "crossover" was detectable), a further analysis of the method with regard to deeper understanding of filler polymer interaction is promising (as a kind of "Advanced Payne test"). Whether a further inspection of the intermediate strain regime also bears information directly utilizable for an estimation of processing behaviour will also be subject of further investigations.

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