"Rubber Process Analyzer – RPA. Bridging the gap between polymer and compound rheological properties and true material processing on the shop floor".

Henri G. Burhin
www.polymer-process-consult.be
TA Rubber testing Seminar
Greenville SC, September 2016

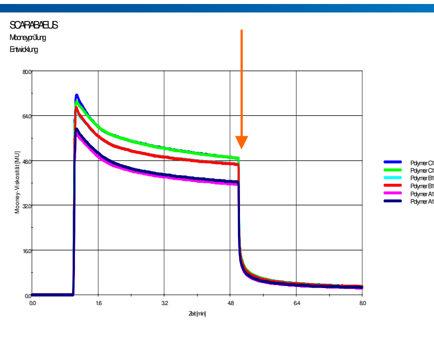
Rubber Process Analyser, presentation outline

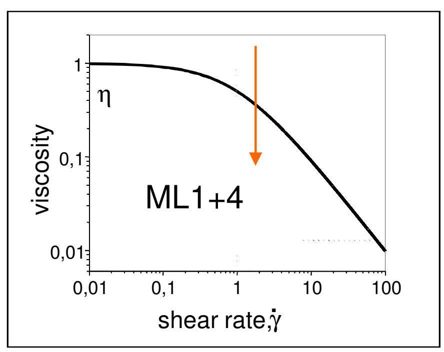
- Instrument design and history
- Testing scope
  - Elastomers (pure gum).
  - Rubber compounds
- Polymer case studies
  - AMW, MWD and LCB
- Compound case studies
  - Mixing
  - Extrusion (surface aspect, output and green-strength).
  - Thixotropy
  - Silica mixing
- Advance curemeter
  - Cure fundamental parameter and cure simulation
  - Sponge compounds.

Rubber Process Analyser

- **History and market position**
  - Development: late 80ies early 90ies
  - Commercialization: 1992
  - Aim: address rubber processing problems
  - Original design: Moving Die Rheometer
  - Retain MDR curemeter capability
    - Isothermal and non isothermal cure
    - Monitoring of sponge compound blowing
- **Became soon popular at large rubber factories (tire manufacturers)**
- **Much less popular at small to medium size companies who found it:**
  - Far too complex to operate and to understand
  - Expensive

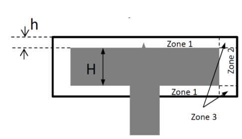
Limitation of Standard Tests (Mooney viscosity)





Mooney Viscosity ML1+4:
Shear rate 1.6 s^{-1} (2 rpm)
But a torque rather than a viscosity.

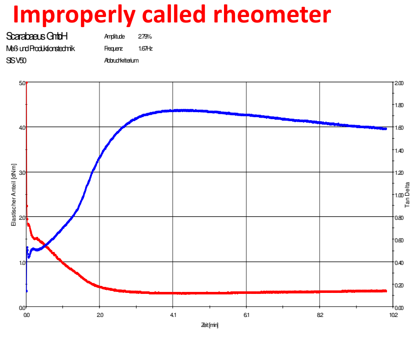
Conversion factors for MU to Nm and RPM to true shear rate in s^{-1}.
1 MU = 0.083 Nm
2 RPM = 1.58 s^{-1} ($\dot{\gamma}$)



Curemeters design and limitations.

Moving Die Rheometer “MDR”

Improperly called rheometer



- Standard test
  - Isotherm
  - Anisotherm
  - S‘ and S‘‘ -> TanDelta

- Rheometer
- Biconic dies
- closed die system
- 100cpm /1.67 Hz
- 0.5° / 7% strain

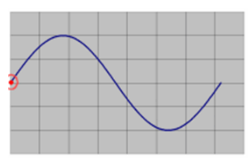
one point method

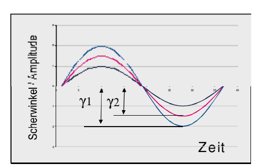
It is important to get more information to help the developer

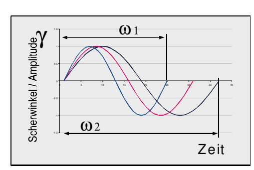
TA Instruments – RPA, a true rheometer

Viscosity is measured with various types of viscometers and rheometers. A rheometer is used for those fluids which cannot be defined by a single value of viscosity and therefore require more parameters to be set and measured than is the case for a viscometer

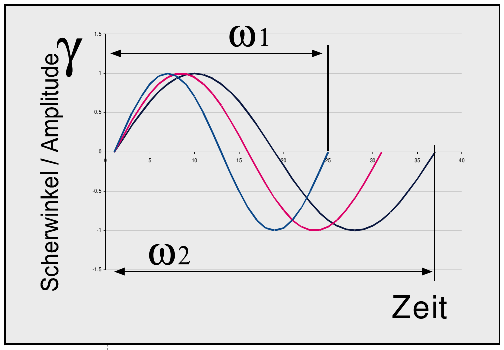
https://en.wikipedia.org/wiki/Rheometer



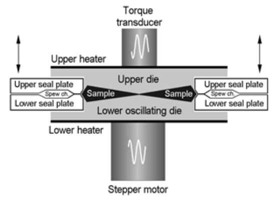


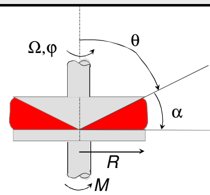


RPA Rheometer (Closed boundary DMA)



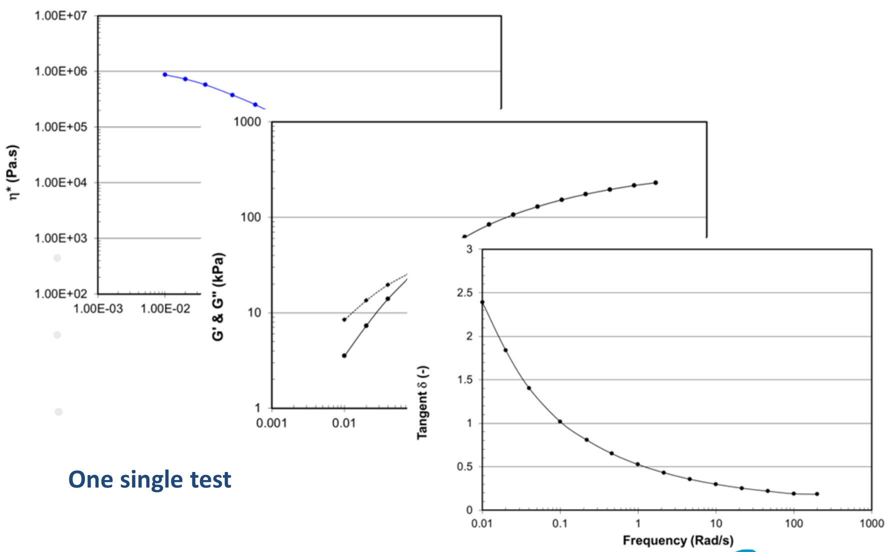
Frequency:
RPA 0.001…50.0 Hz
Step 0.001Hz





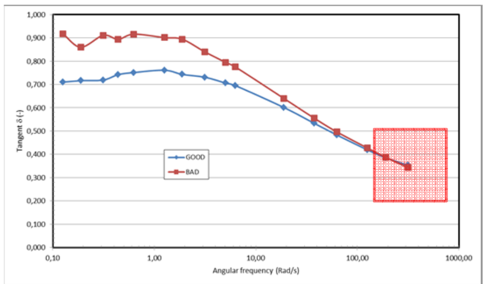
Open boundary DMA
ARES – ARES G2

Dynamic testing typical output from frequency sweep

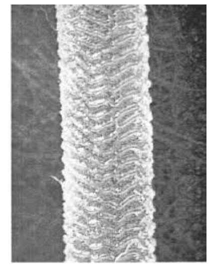


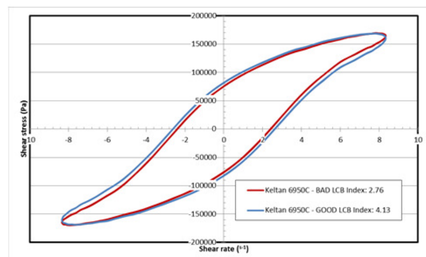
One single test

Effect of Molecular Weight Distribution (MWD) on compound extrusion behavior



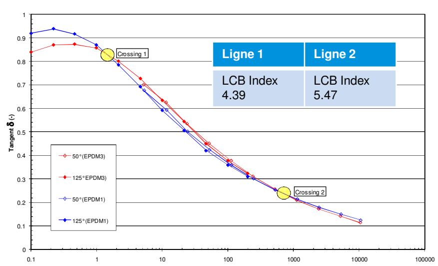
Surface defect as « shark skin »on extrusion



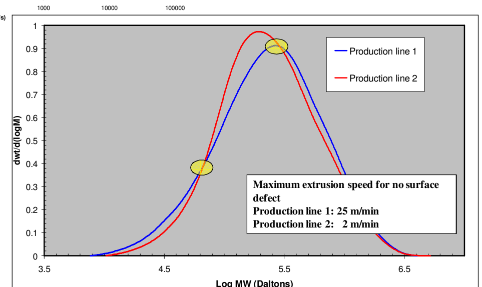


Tentative conclusion
Shark skin effect in extrusion is due to **MWD effect and not LCB effect**.

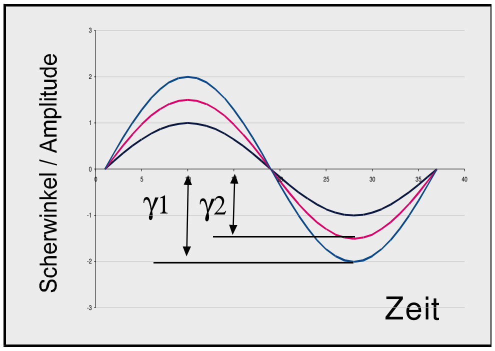
Effect of Molecular Weight Distribution (MWD) on compound extrusion behavior



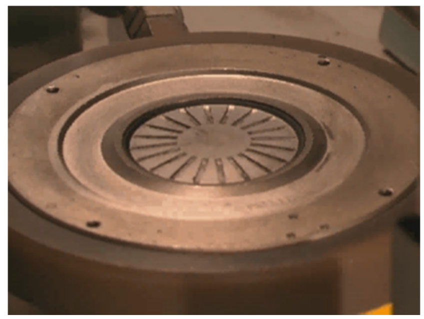
- LCB contend of both polymers was very similar
- The extrudability problem (shark skin) was found in the large reduction of small molecules in the problem polymer
- Very small molecules act in compound as excellent processing aid
- The higher tangent δ value at high frequency for the good processing polymer confirmed this result.



RPA Rheometer Strain sweep
From small strain to large strain (SAOS to LAOS)



Strain:
RPA 0.005…360.0 °
Step 0.01°



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Comparison of Butyl IIR (RPA)
Technical information

Instrument:	RPA *flex*
Company:	TA Instruments
Sample A) :	Synthetic Butyl Edbrisic - BK
B) :	Synthetic Butyl Exxon
Film:	Dartek - polyamid film

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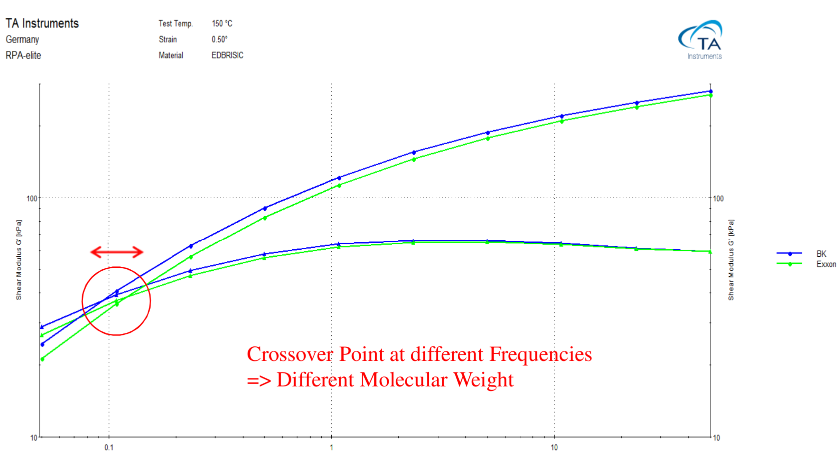
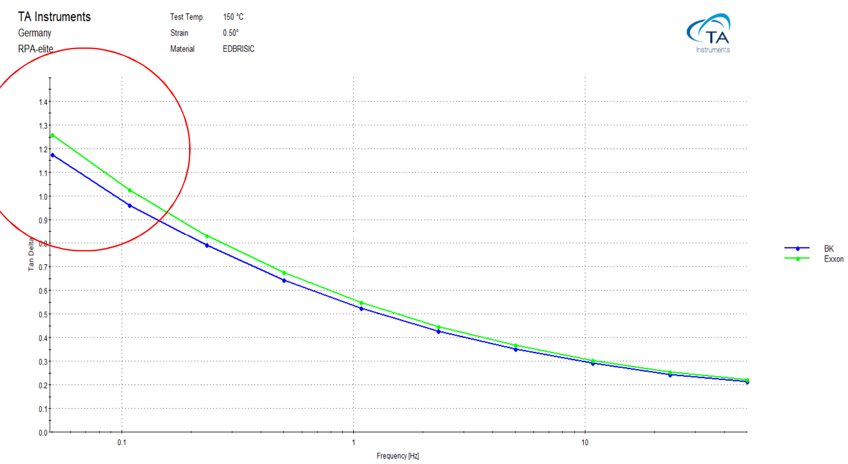
Comparison of Butyl (RPA)
Test Program

Method	Temperature [°C]	Frequency [Hz]	Strain [°of arc]
Frequency-Sweep	150	0.05 - 50	0.5
Strain-Sweep	150	0.2	0.5 - 90

Comparison of Butyl (RPA)
Frequency - Sweep, 150°C, 0.5°of arc, G', G"



Comparison of Butyl (RPA)
Frequency - Sweep, 150°C, 0.5°of arc, tan δ



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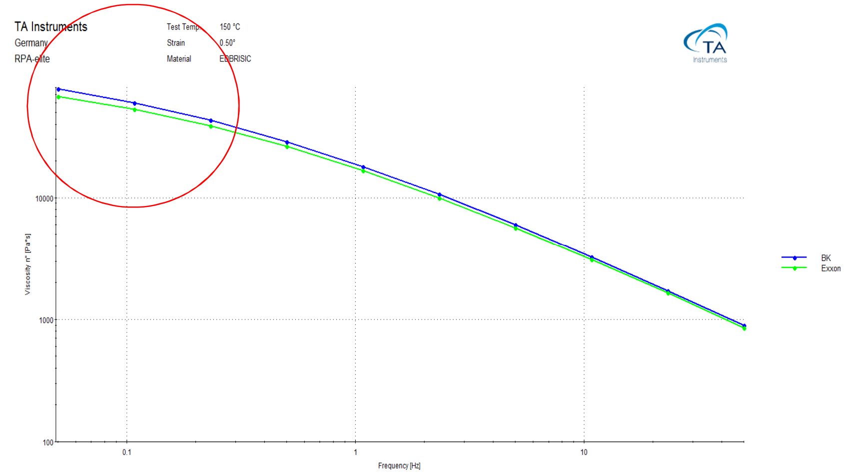
Comparison of Butyl (RPA)
Frequency - Sweep, 150°C, 0.5°of arc, η" (Log-Scale)



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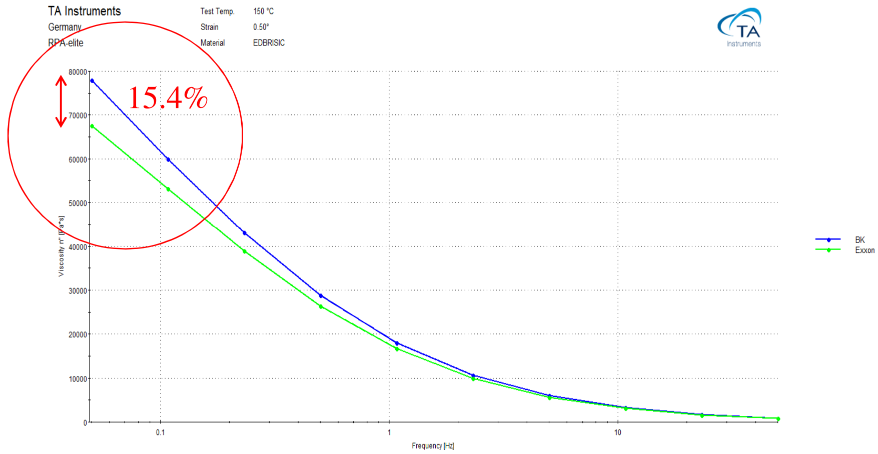
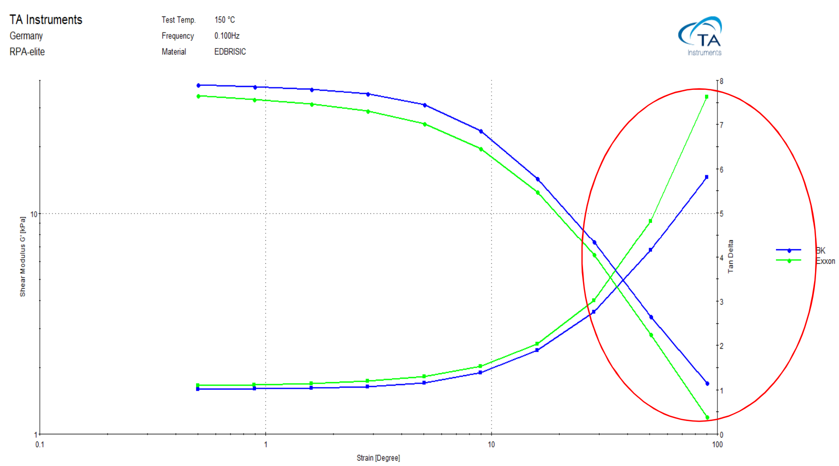
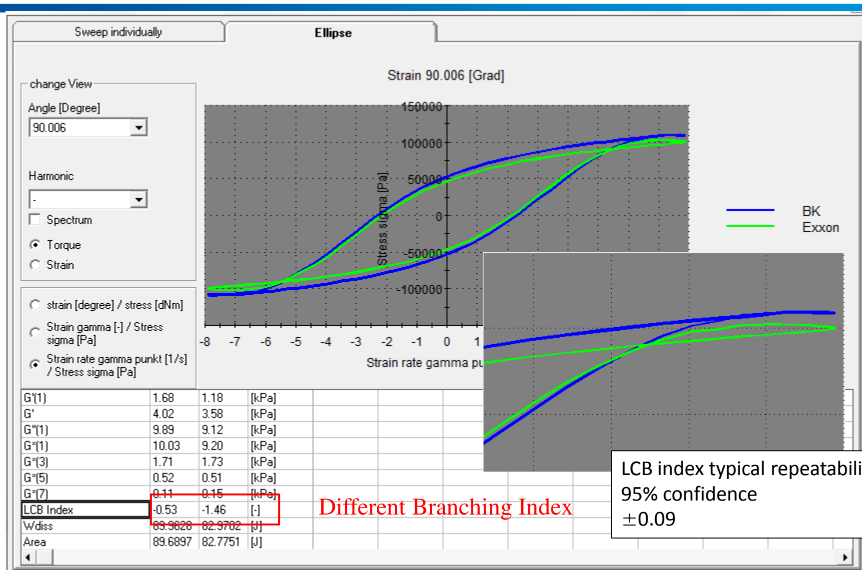
Comparison of Butyl (RPA)
Frequency - Sweep, 150°C, 0.5°of arc, η" (Lin-Scale)



Comparison of Butyl (RPA)
Strain - Sweep, 150°C, 0.1 Hz, G', Tan δ



Comparison of Butyl (RPA)
Strain - Sweep, 150°C, 0.1 Hz, Long Chain Branching

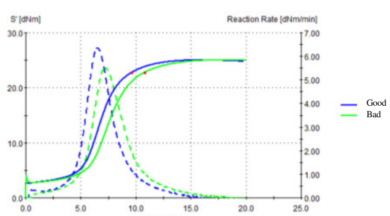


LCB index typical repeatability
95% confidence
±0.09

Rubber compound process troubleshooting

Rubber compound extrusion.
Serious processing problem in production
Summary of observations:

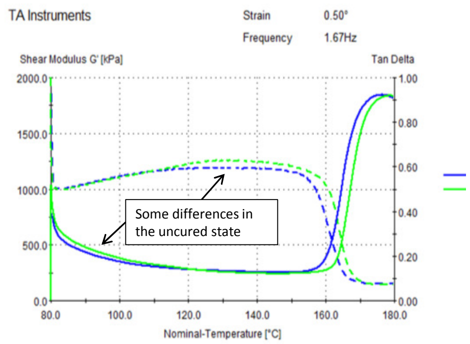
- All batches passed standard QC tests.
- QC test involves rheometer only (MDR).
- One batch gave higher extrusion head pressure and temperature, higher swell and surface defect ("Orange skin") suggesting possible scorch in the extruder.
- The faulty batch was compared to a trouble free batch.



		S' Min	S' Max	Peak Rate (S'/min)	Time to Peak Rate (S')
	Unit	[dNm]	[dNm]	[dNm/min]	[min]
	Good	2.60	25.04	6.36	6.43
	Bad	2.73	25.06	5.56	7.16

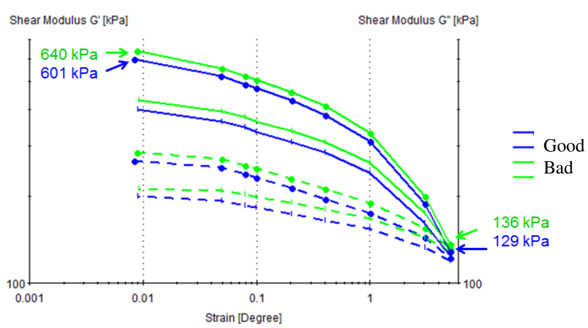
Both compounds have identical or almost identical ML and MH.
The faulty compound exhibits a lower cure rate (?)
The faulty compound exhibits a significantly LONGER scorch time (??????)

Rubber compound process troubleshooting



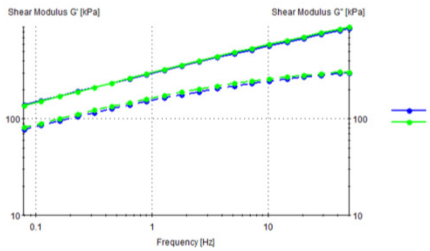
Non isothermal cure test confirms identical ML and MH and longer cure time for the faulty batch
Some differences are observed on G' and Tangent δ before cure suggesting that viscoelastic properties of uncured compounds being different.

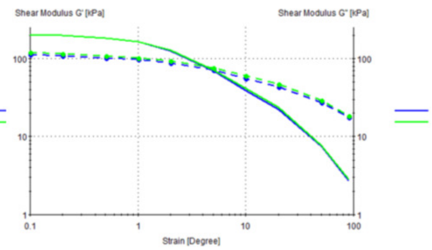
Rubber compound process troubleshooting

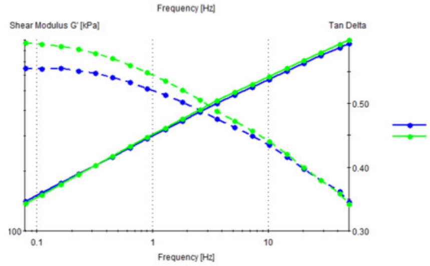


Bad compound shows higher modulus at both low and high strain.
This suggest that filler dispersion is not the cause of the problem.
The problem therefore stays in either polymer quality of filler content.

Rubber compound process troubleshooting

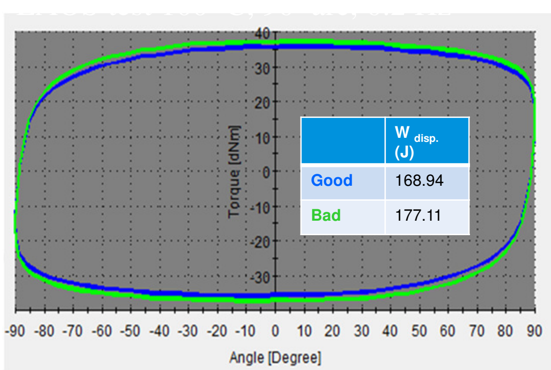






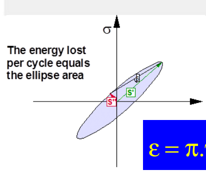
Bad and good batches show almost identical viscoelastic properties in both frequency and strain sweep.
Only some significant difference is observed at very low shear rate (frequency) on Tangent δ.

Rubber compound process troubleshooting



	$W_{disp.}$ (J)
Good	168.94
Bad	177.11

The bad compound has been found to dissipate almost 10% higher energy per cycle in non-linear conditions.
Premature scorch for this compound is produced by large heat generation in the extruder.



$$\varepsilon = \pi.\gamma_0.\sigma_0.\sin\delta$$

ISO Standard method 4664-1
Where ε is the ellipse area or the energy lost per oscillation
γ_0 is the maximum strain
σ_0 is the maximum stress

Practical example, linear and branched Polymer

	Keltan 6950	Nordel 5565
Mooney ML 1+4 [MU]	65	65
Ethylen [%]	48	50
ENB content [%]	9	7.5
Distribution	medium	medium
Degree of branching	Branched	Linear

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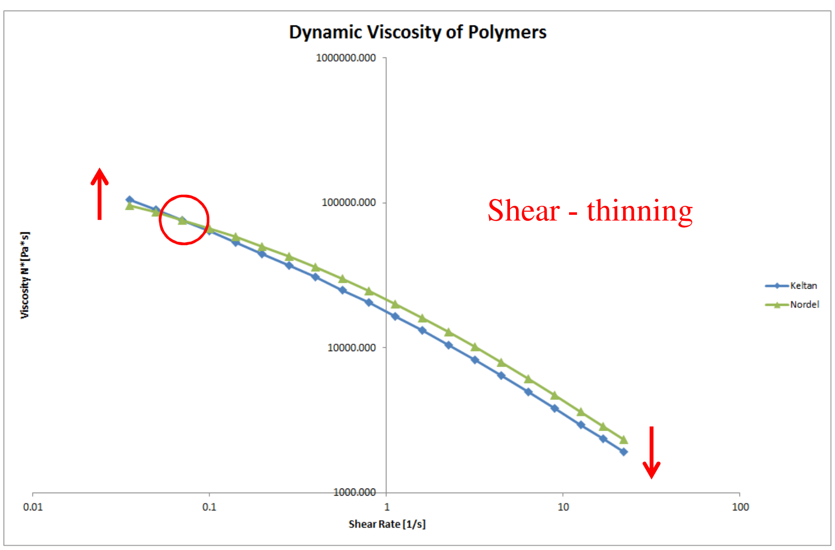
Practical example, linear and branched Polymer Frequency Sweep



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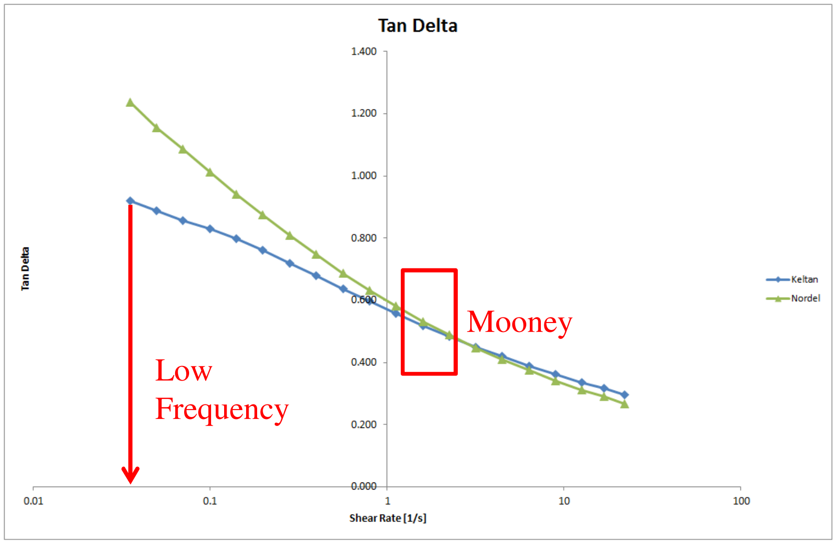
Practical example, linear and branched Polymer Frequency Sweep



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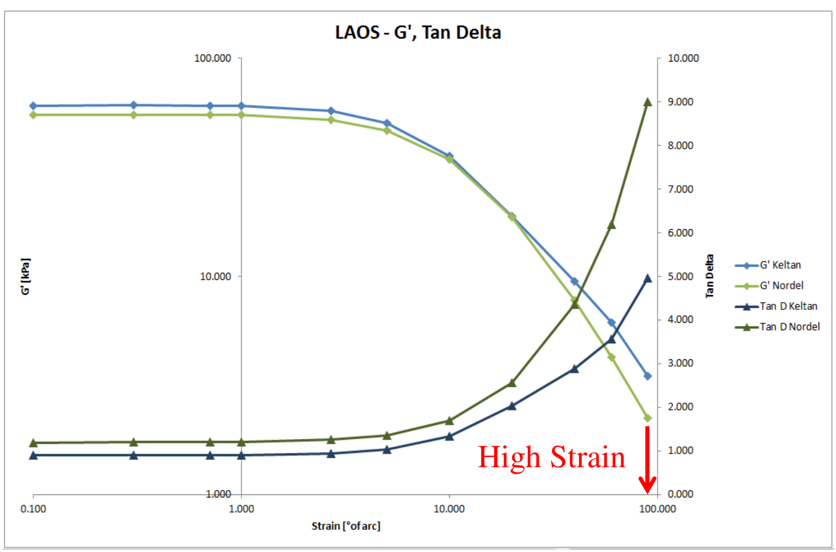
Physical description of Polymers Strain Sweep - LAOS



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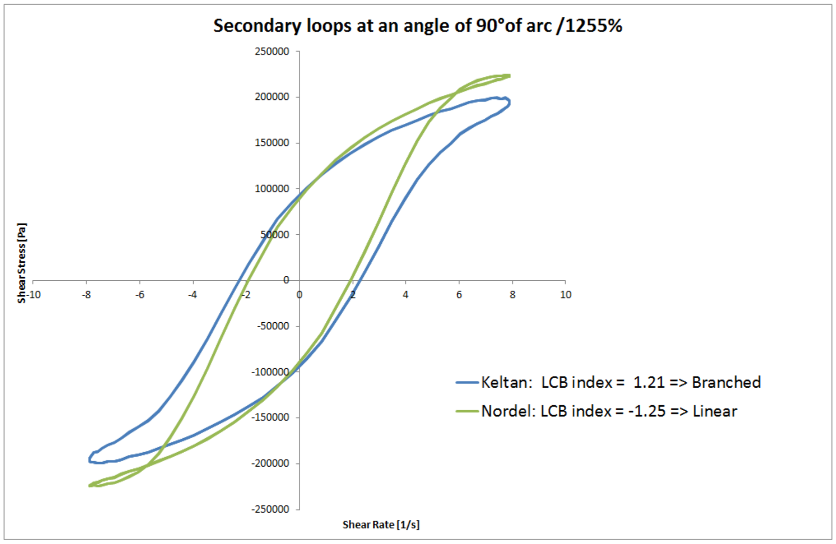
Physical description of Polymers
Strain Sweep - LAOS



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Recipe of Compounds

	Keltan compound	Nordel compound
	phr	phr
EPDM (LCB)	100	
EPDM, linear		100
Fast Extrusion Furnace (FEF) carbon black	95	95
Chalk	50	50
Paraffinic Oil	65	65
ZnO	6	6
Stearic acid	1	1
Drying agent	9	9
Antiaging agent	0,5	0,5
Sulfur and accelerator	4,5	4,5

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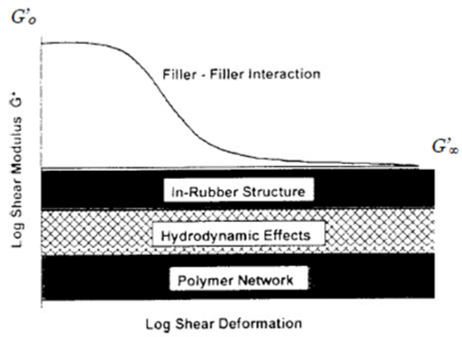
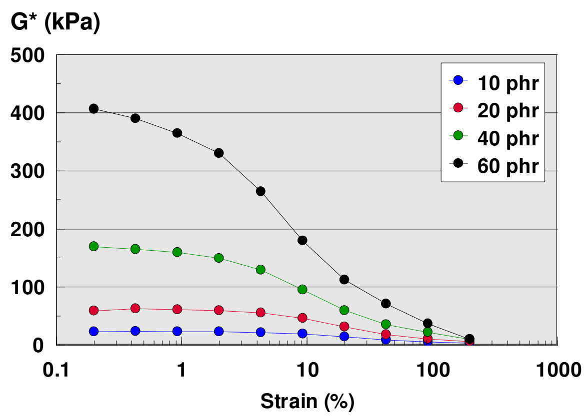
Physical description of filled Polymers
Strain Sweep - PAYNE



A. R. Payne, Rubber Plast. Age 42, 963 (1961)

Pic. 2.2.: schematic representation of the composition of the dynamic modulus of various proportions by Payne [16]

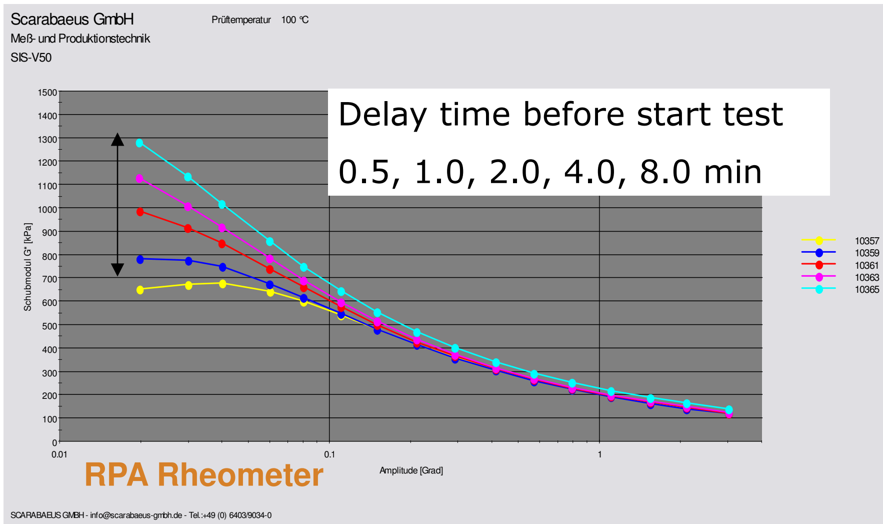
Payne diagram, increasing filler content



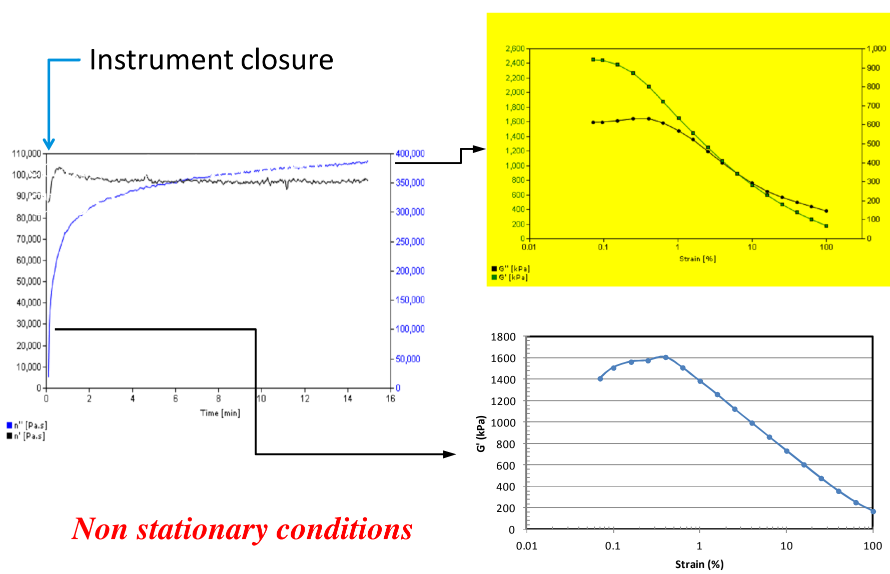
Variation of G* of reinforced rubber compound in the strain domain

Henri Buhrin, "Visco-elasticity Properties of Polymers and Compounds. From Linear to Non Linear Visco-elasticity, Benefit and Potential"

Compound, Reinforcing fillers



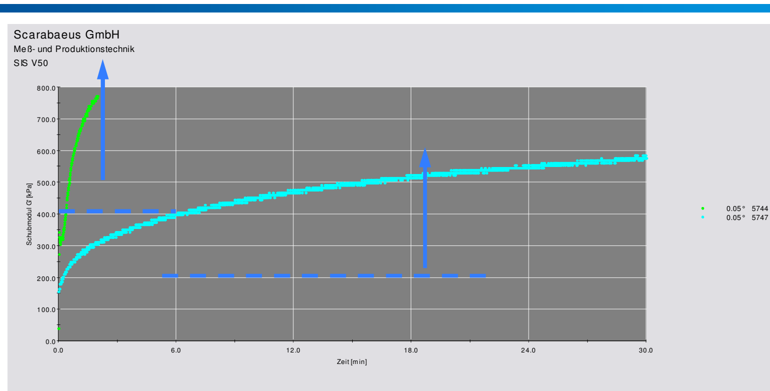
Uncured compound thixotropy in DMA measurements.



Uncured compound thixotropy in DMA measurements.

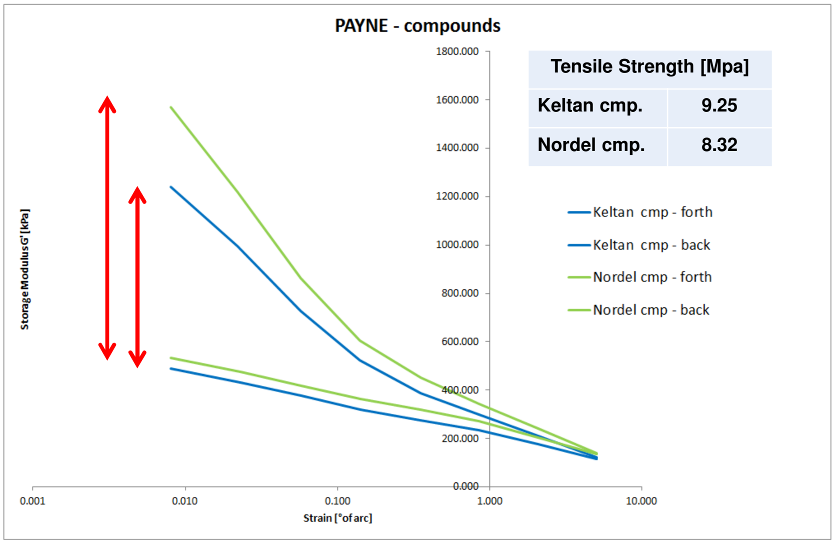
What is thixotropy ? – Viscosity time dependence

Compound, Reinforcing fillers



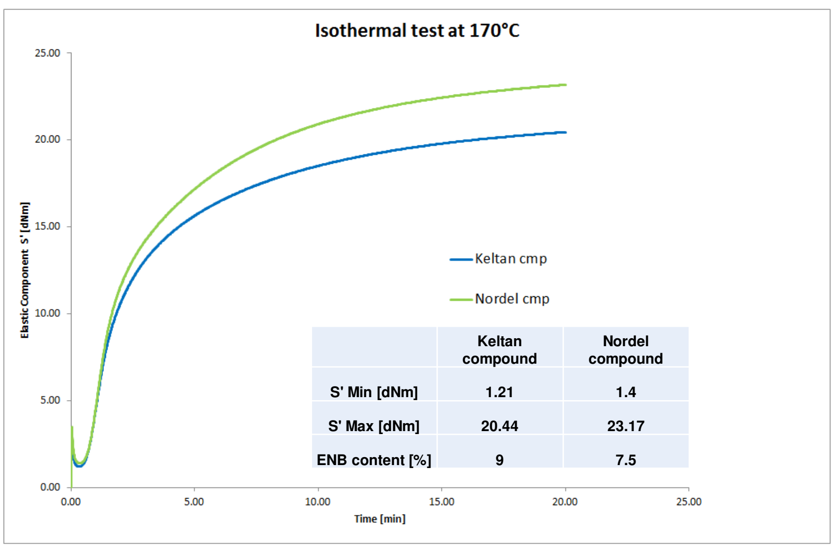
Heinrich, dN/dt=kN^2 ,1995

Physical description of filled Polymers
Strain Sweep - PAYNE



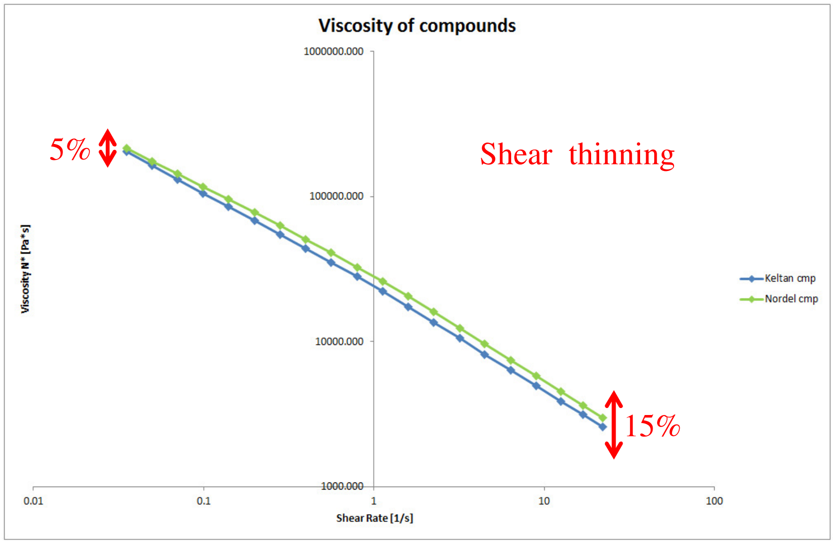
Tensile Strength [Mpa]	
Keltan cmp.	9.25
Nordel cmp.	8.32

Kinetic description of filled Polymers
Vulcanisation



	Keltan compound	Nordel compound
S' Min [dNm]	1.21	1.4
S' Max [dNm]	20.44	23.17
ENB content [%]	9	7.5

Physical description of filled Polymers Frequency Sweep



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Extrusion – Machine parameters

Extrusion	Keltan compound	Nordel compound
Temp. extruder [°C]	70	70
Pressure die [bar]	**91.3** ↔	**102**
Current [A]	**111.5** ↔	**124**
Speed [m/min]	10.5	10.5
Temp. Mass [°C]	114	114-125

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Additional use of Payne diagram
Tread compound formulation

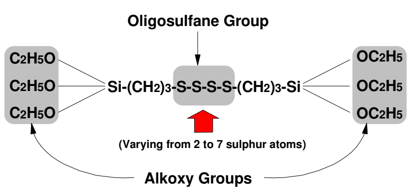
Silica compound

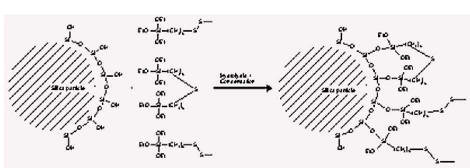
Ingredient	PHR
Buna VSL 4020-1	103.1
Buna CB 10	25.0
Ultrasil 3370GR	80.0
Silane X50S	12.5
High aromatic oil	5.0
ZnO	2.5
Stearic acid	1.0
6 PPD	2.0
Wax	1.5

Patent Application EP 0501 227, Michelin, R. Rauline, February 25th, 1991

Silica silane chemistry

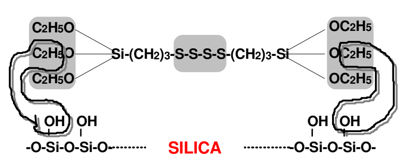
TESPT (Si69 DEGUSSA)
Bifunctional organosilanes

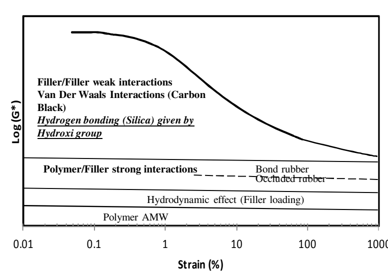




Silica "silanisation"

Mixing from 140°C to 160°C





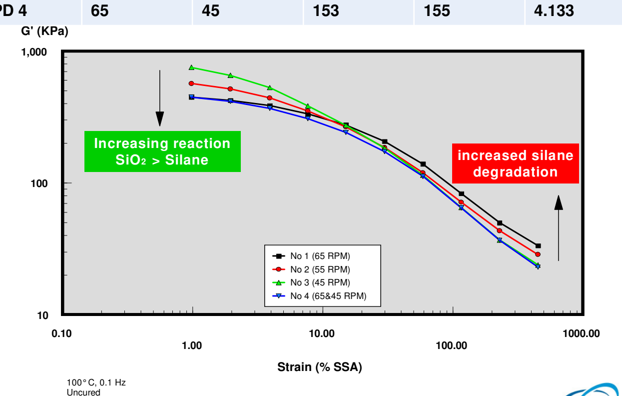
Masterbatch mixing procedure

Internal mixer: 3 L Tangential

Time (mins)	Addition	Temp (°C)	Energy (W.h)
0	Add polymers	65	0
½	Add ZnO, ¾ silica, ¾ X50S and stearic acid	?	20
	Add rest of silica, rest X50S, wax, 6PPD and oil	?	550
	Sweep	?	700
	Dump at 750 W.h	?	750
Remill			
0	Add masterbatch	65	0
	Dump at 650 W.h	?	650

Mixing conditions and Payne diagram

	Mixer speed step 1	Mixer speed step 2	Dump temp step 1	Dump temp step 2	Total mixing energy
CPD 1	65	65	155	180	4.123
CPD 2	55	55	145	161	4.076
CPD 3	45	45	146	146	4.067
CPD 4	65	45	153	155	4.133



Mooney viscosity versus visco-elasticity

At first, Mooney viscometer was used for QC of silica compounds

	MS(1+4) 100℃	G’@1% strain (kPa)	S’@450% strain (dNm)
CPD 1	68.7	448	27.69
CPD2	65.4	568	23.75
CPD3	68.1	754	19.75
CPD4	60.5	448	19.04

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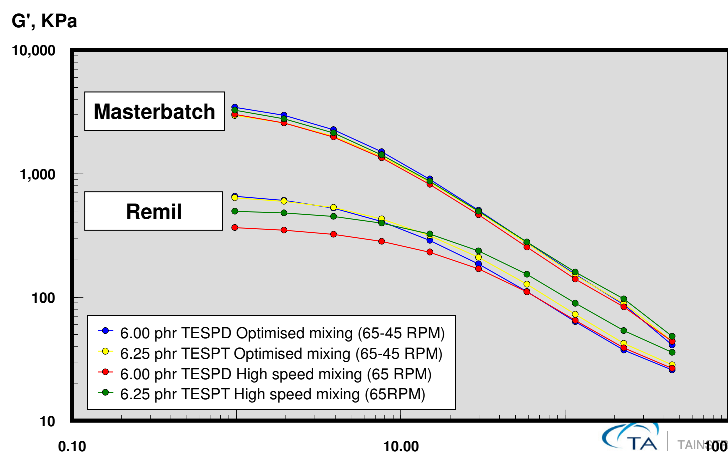
TESPT versus TESPD

Silica silane reaction can essentially be measured after mixing second stage



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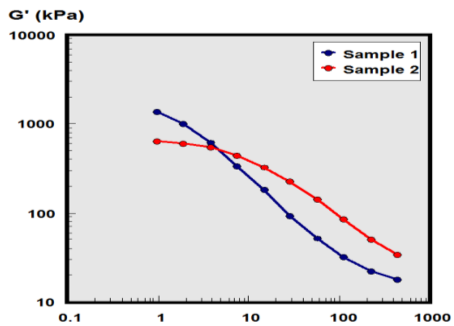
Silica mixing test conclusion

Careful visco-elasticity measurements on masterbatch can rapidly and easily:

- Fully characterize Payne diagram
- Payne diagram low strain elastic modulus provides essential information of silica/silane chemical reaction
- Payne diagram high strain elastic modulus or better elastic torque provides information on the uncured compound processability

2 industrial uncured compounds

- Compound 1 can be processed but won't provide adequate cured properties
- Compound 2 will provide adequate cured properties but cannot be processed.



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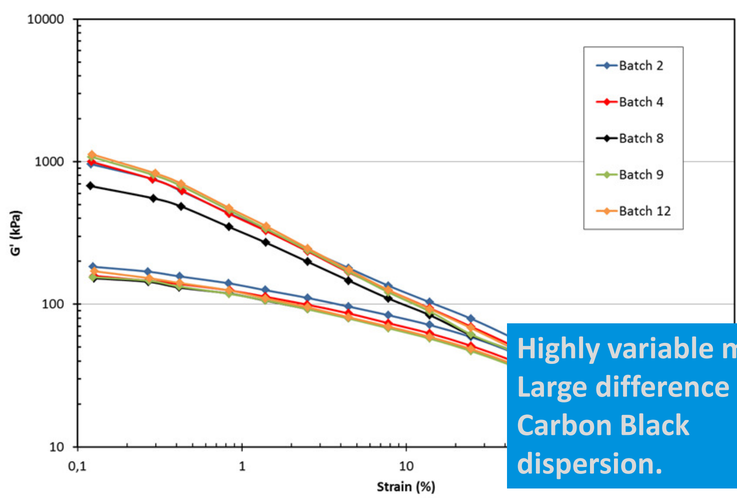
Physical description of filled Polymers Strain Sweep – Injection molding compounds



Highly variable mixing
Large difference in Carbon Black dispersion.

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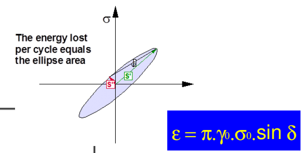
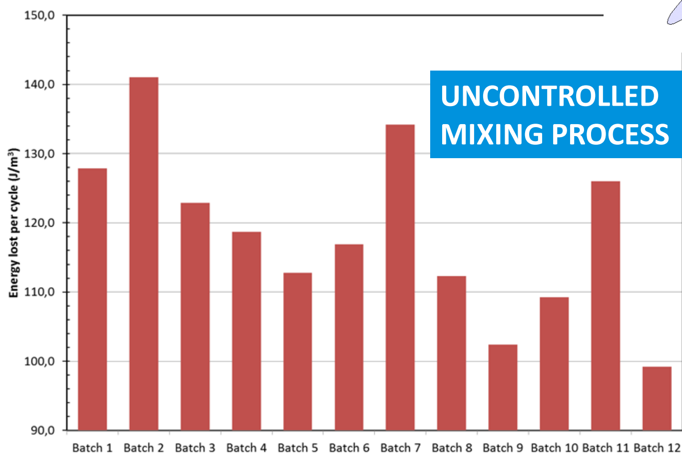
Physical description of filled Polymers
Strain Sweep

Energy dissipation in process
LAOS – 90˚ Arc – 100˚C, 0.1 Hz





Instrument repeatability, Compound homogeneity and production variation

Relevant QC

- Instrument repeatability
  - Additional mixing compound
  - Sample number: 15
  - CV (Std Dev/Mean) ≈ 0.75%
- Production compound homogeneity
  - Batch number: 1
  - Sample number: 12
  - CV ≈ 0.75%
- Production variability
  - Batch number: 18
  - CV from 15.43% to 4.72%

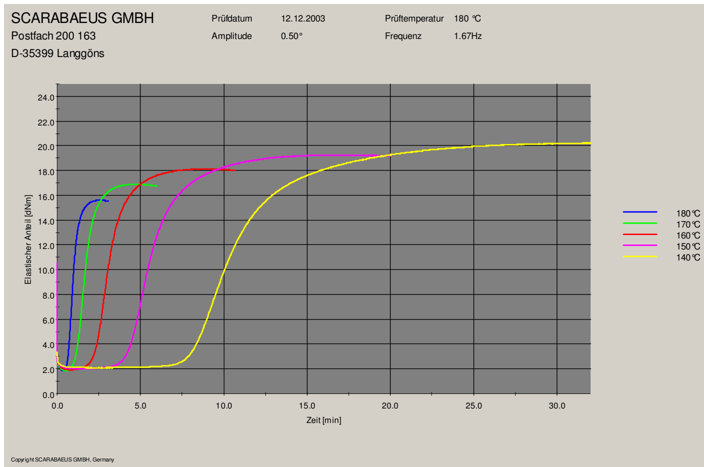
Irrelevant QC
Poor material homogeneity

More variation within one batch than between batches

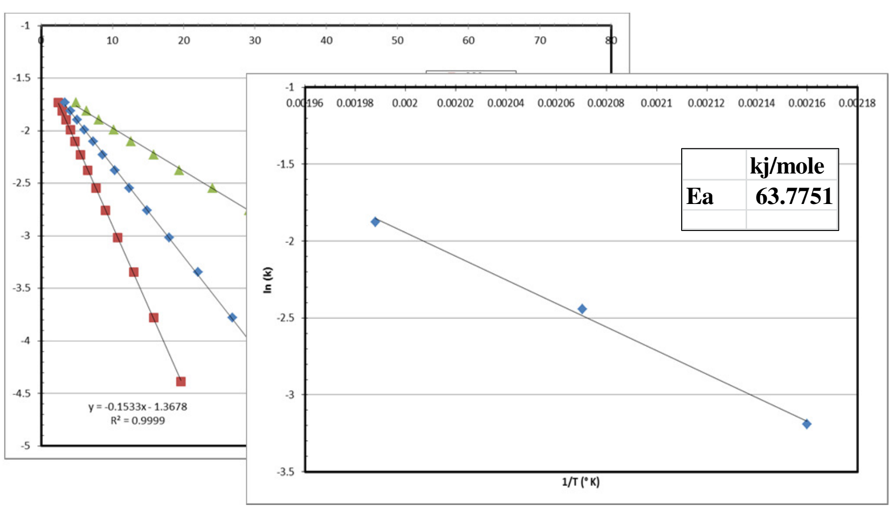
Complex modulus (G*)
@ low frequency

Mean	1232.5	**Within batch**
Std Dev	166.1	
CV (%)	13.5	
Mean	940.0	**Between batch**
Std Dev	50.7	
CV (%)	5.4	

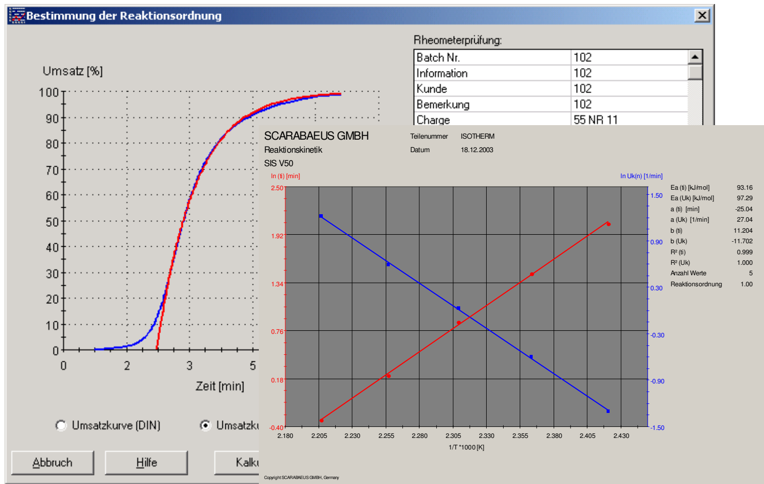
Enhanced Calculation MDR: Cure Kinetic



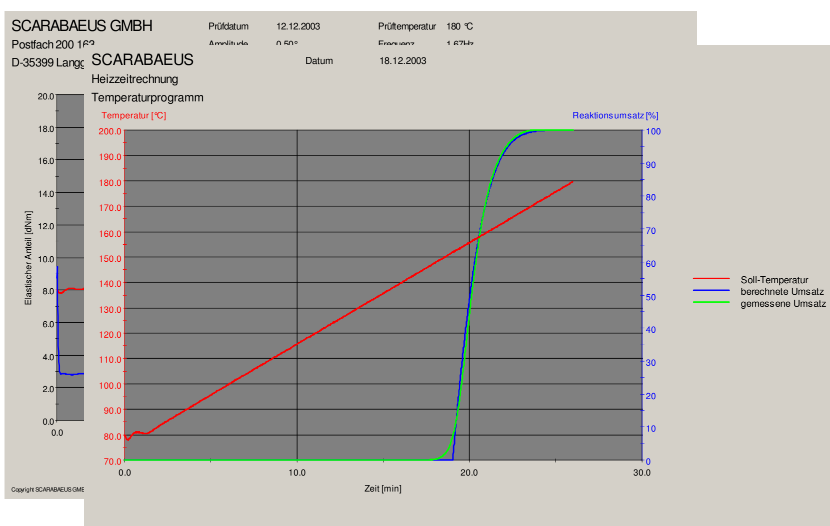
Enhanced Calculation MDR: Cure Kinetic



Enhanced Calculation MDR: Cure Kinetic

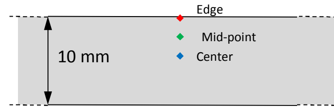


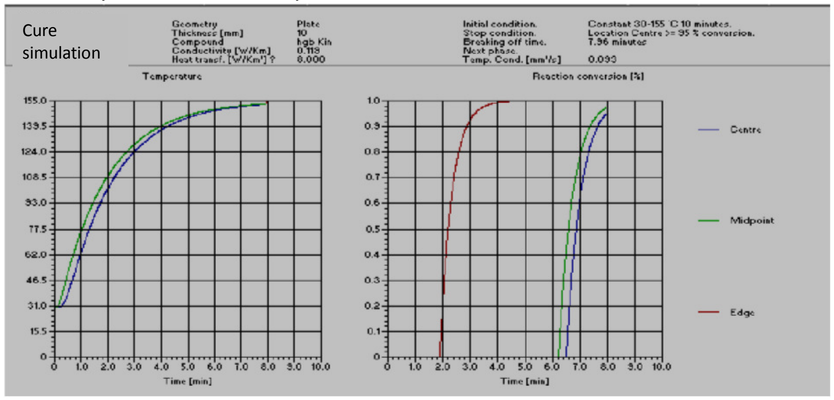
Cure simulation based on kinetics. verification



Cure simulation based on kinetic parameters

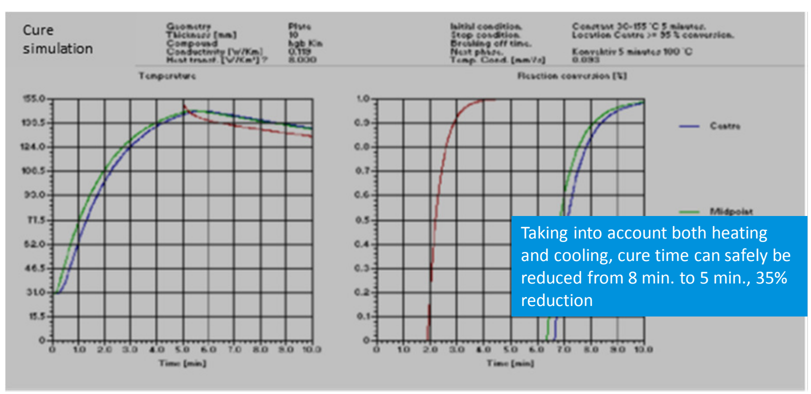
Rubber slab: 10 mm thick
155˚ C cure temperature
Compound initial temperature: 30˚ C
Arbitrary heat conductivity values





Cure simulation – Cure time optimization

Rubber slab: 10 mm thick
155˚ C cure temperature
Compound initial temperature: 30˚ C



Taking into account both heating and cooling, cure time can safely be reduced from 8 min. to 5 min., 35% reduction

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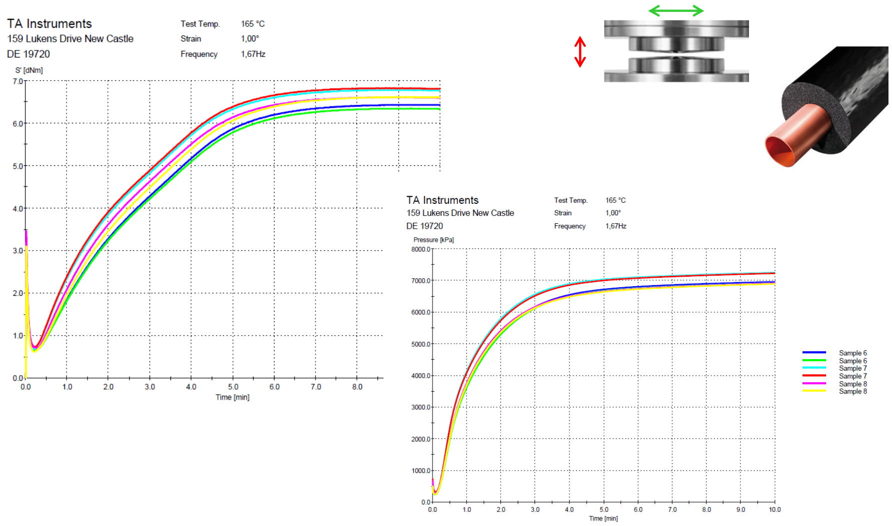
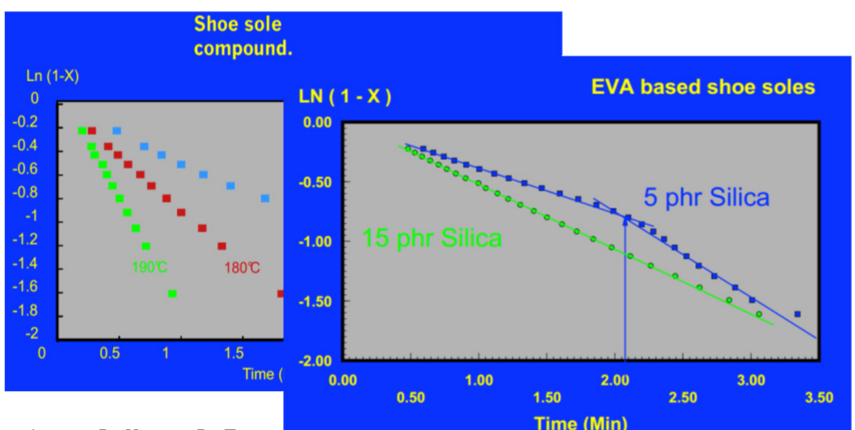
MDR - Application on sponge rubber



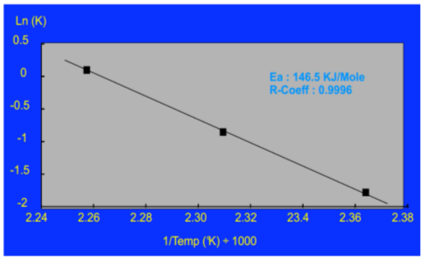
Use of kinetic analysis on different MDR curves

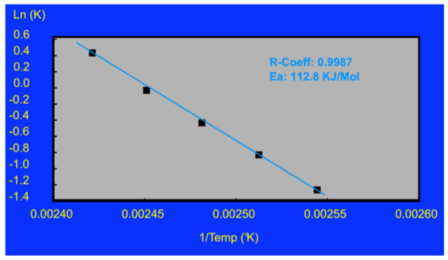
Conversion rate constant on pressure curve



Boyle Law: $P \cdot V = n \cdot R \cdot T$
Pressure is linearly proportional to n so P can be used to calculate conversion rate constant of gas formation in the compound.
Detection of dual decomposition reaction in silica compound based on filler level

Activation energy of blowing agent decomposition



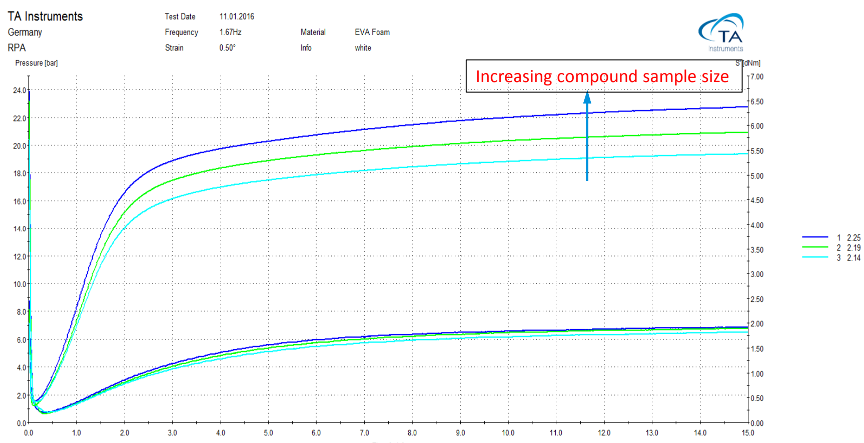


Insulation foam
NBR-PVC blend with Cellogen AZ

Car door seal
EPDM compound with Cellogen OT

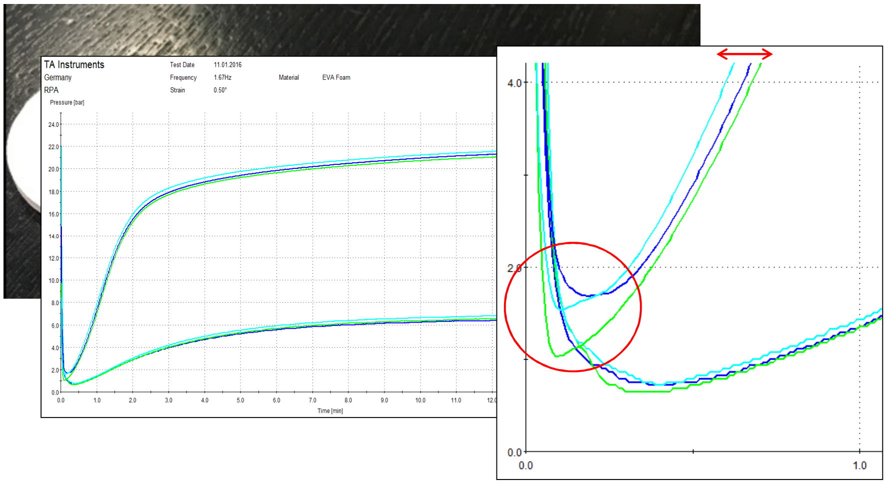
Results – Different sample weight, same shape

Accurate cure and blowing agent decomposition testing prerequisite:
- Identical material quantity
- Identical shape with minimizing material flow in the test chamber.



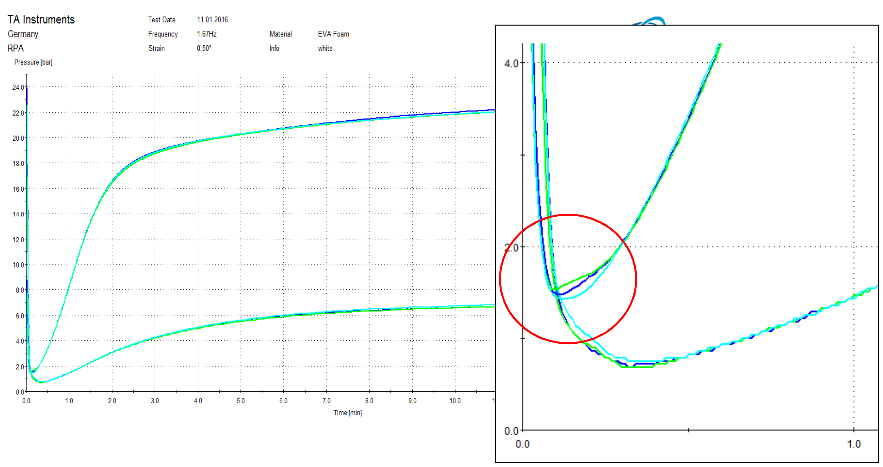
Effect different sample shape, same weight

Different sample high and different Diameter



Results – Same sample weight, same shape

Optimum repeatability and accuracy can only be archieved on cure and pressure with sample weight ±0.01 g and sample diameter ±1 mm



RPA summary and conclusion

- Since its commercialization, the RPA has found a growing importance in rubber testing.
- At first, at big rubber manufacturers such as tire companies
- But these were the most reluctant to share useful information on how to use this novel instrument.
- The level of complex physical properties of rubber compound and even pure polymers have hindered wide and fast distribution
- Available literature may present some of RPA useful technique in showing how things are different but often failed to explain why.
- In this presentation I tried to present some of critical RPA tests in connection to material fundamental properties.
- These properties include processing related characteristics such as viscosity, green-strength (sagging resistance), surface aspect, mixing etc.
- We have also seen precise relationship between RPA measurements and polymer characteristics (AMW, MWD, LCB etc.) affecting compound processing.
- The RPA effective testing power remains essentially within it high and flexible programmability thus offering a unique testing versatility.
- So the RPA is capable to replace a large amount of conventional techniques.
- It can as well considerably deepen rubber behavior understanding.

Thank You

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