JORNADAS CAUCHO

BOGOTÁ 2025

Cómo desarrollar compuestos de cloropreno libres de nitrosaminas para aplicaciones dinámicas

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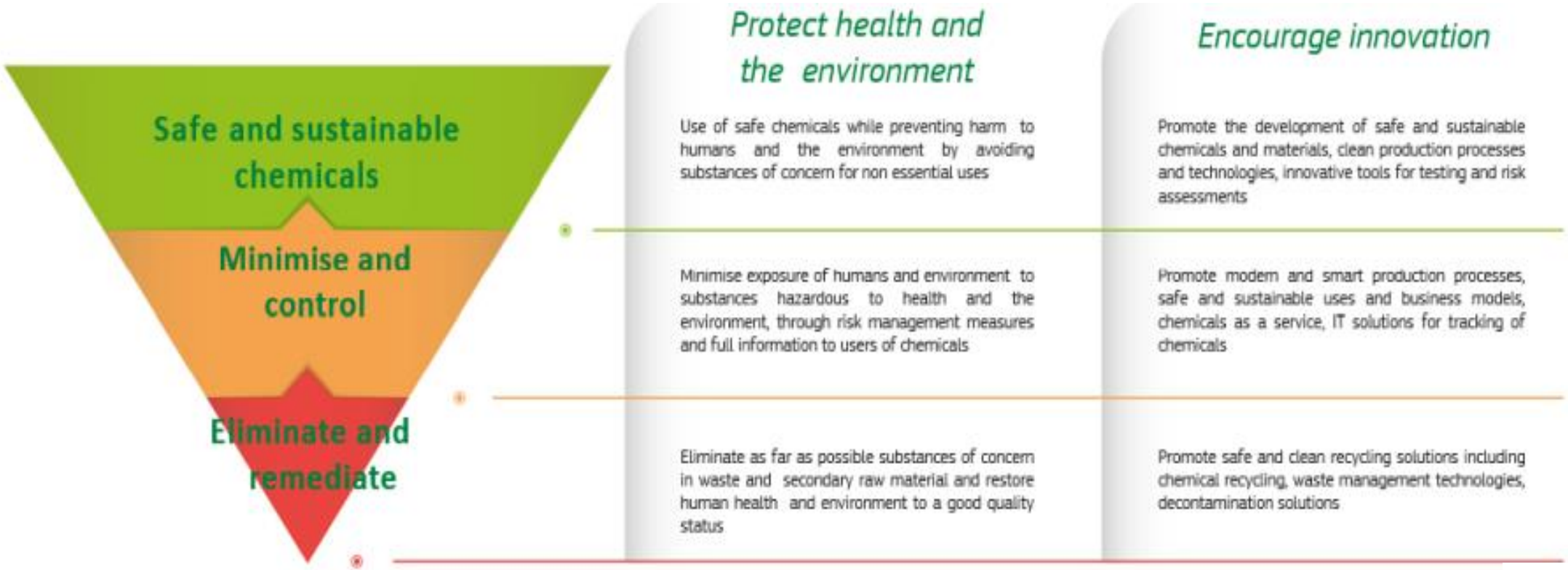
Agenda

- **Nitrosamines**
  - Rubber Industry
  - Health/Environmental Impacts
- **Modified Chloroprene**
- **How to design a Compound**
- **Application**
  - Air Spring
  - Belts

EU Chemicals Strategy for Sustainability

Towards a Toxic-Free Environment



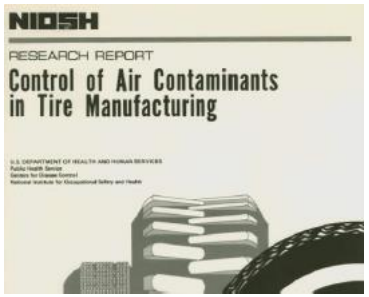
https://ec.europa.eu/environment/pdf/chemicals/2020/10/Strategy.pdf

Health aspects of nitrosamines

Nitrosamines are a known problem in the rubber industry

1956
John Barnes / Peter Magee found that dimethyl nitrosamine causes liver cancer in rats

1979
Fajen *et al.* found first traces of *N*-nitrosamines in rubber plants and connected that to increased findings of cancer at US workers



1990s
- TRGS 552 was introduced
- regulations define hazard nitrosamines and their limits for exposure in air
- critical thiurames and amines in global industry mainly substituted

Ausgabe: September 2018

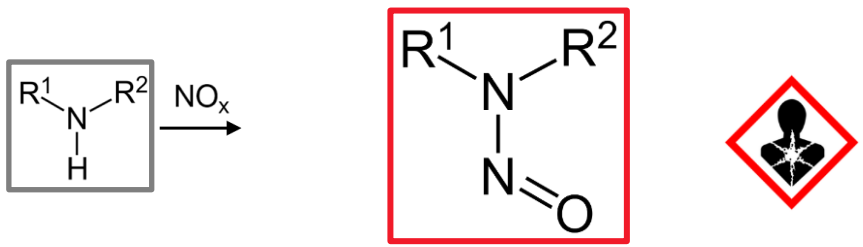
Technische Regeln für Gefahrstoffe	Krebserzeugende N-Nitrosamine der Kat 1A und 1B	TRGS 552

1950 **1990** **2020**

Health aspects of nitrosamines

Nitrosamines are a known problem in the rubber industry

Nitrosamines feature a nitroso group (NO^+) bonded to a deprotonated amine.



Most nitrosamines are volatile and carcinogenic
Regulations are getting more stringent to limits the level of nitrosamines in rubber goods

→ Nitrosamines can be generated during mixing and vulcanization of rubber from accelerators
→ Most of CR sulfur grades are prone to generate nitrosamines due to used polymerization reactants

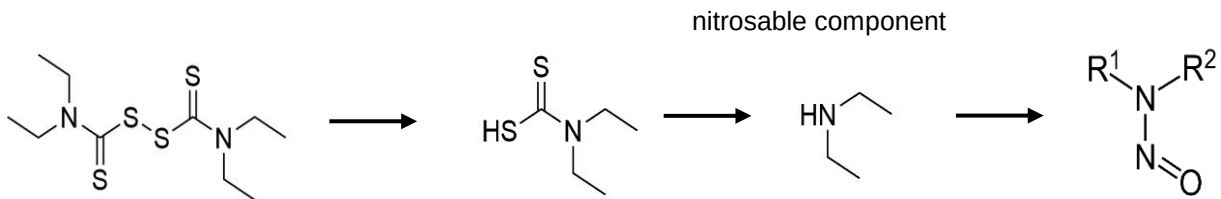
Safe and sustainable alternatives needed

OEHHA
California Office of Environmental Health Hazard Assessment

gadsl
global automotive declarable substance list

Increased public awareness and legislation towards more sustainable product and production standards leads to an increasing need to offer non-critical raw materials

In standard chloroprene sulfur-modified grades thiuram is used as a modifier



→ Thiuram creates toxic nitrosamines

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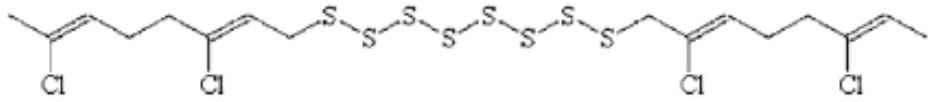
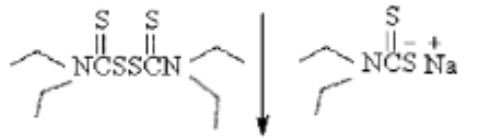
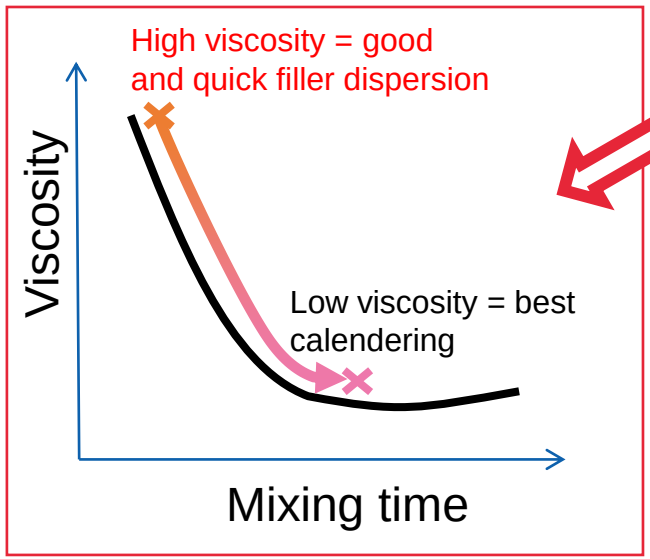
Background: the unique properties of CR sulfur grade

Peptization and reactive chain ends



Promotes chain cleavage





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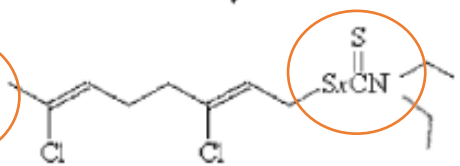
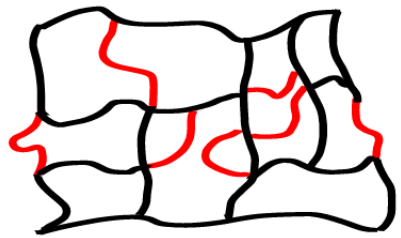


Build reactive chain ends



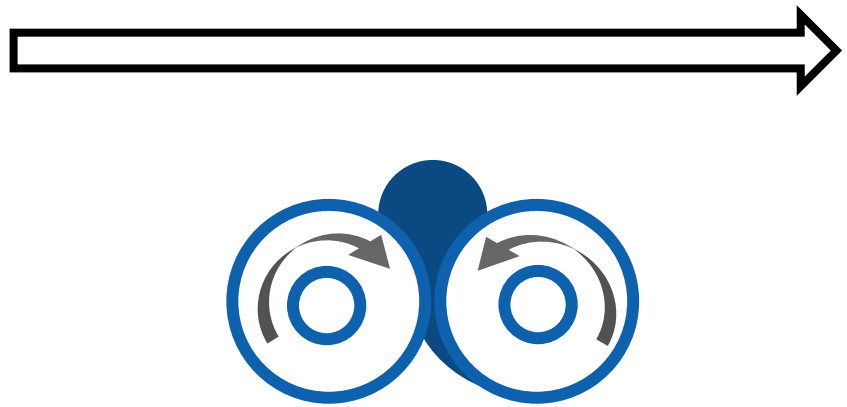
Less dangling chain ends after vulcanization improves the mechanical properties

TETD does not fully react during mixing

80% remains unreacted after compounding

	PHR
Baypren 611	100
Carbon black	30
OCD	1.0
Stearic acid	0.5
MgO	4.4
ZnO	5

20% of the TETD reacts



80%*

of the TETD in the CR sulfur grade remains unreacted in the compound

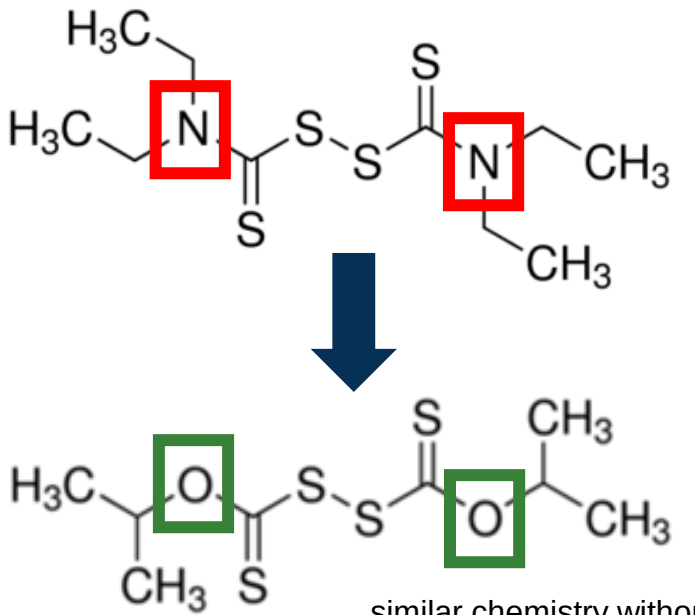
* In our ISO compound experiment. Value may vary depending on the recipe and the mixing procedure

New CR - different chemistry for a similar effect

Based on well established chemicals

Replace the amine by an alcohol…

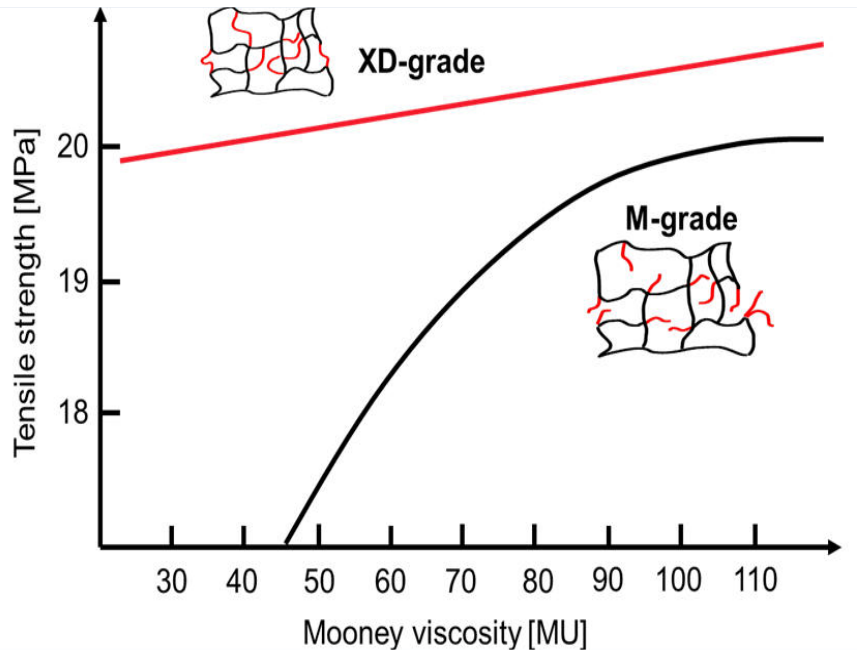
Thiuram replaced by the same class of chemical used in XD Grades



similar chemistry without secondary amines

…known from the XD-Grades

Better tensile strength
XD Grades 30% more fatigue resistant than M-Grades

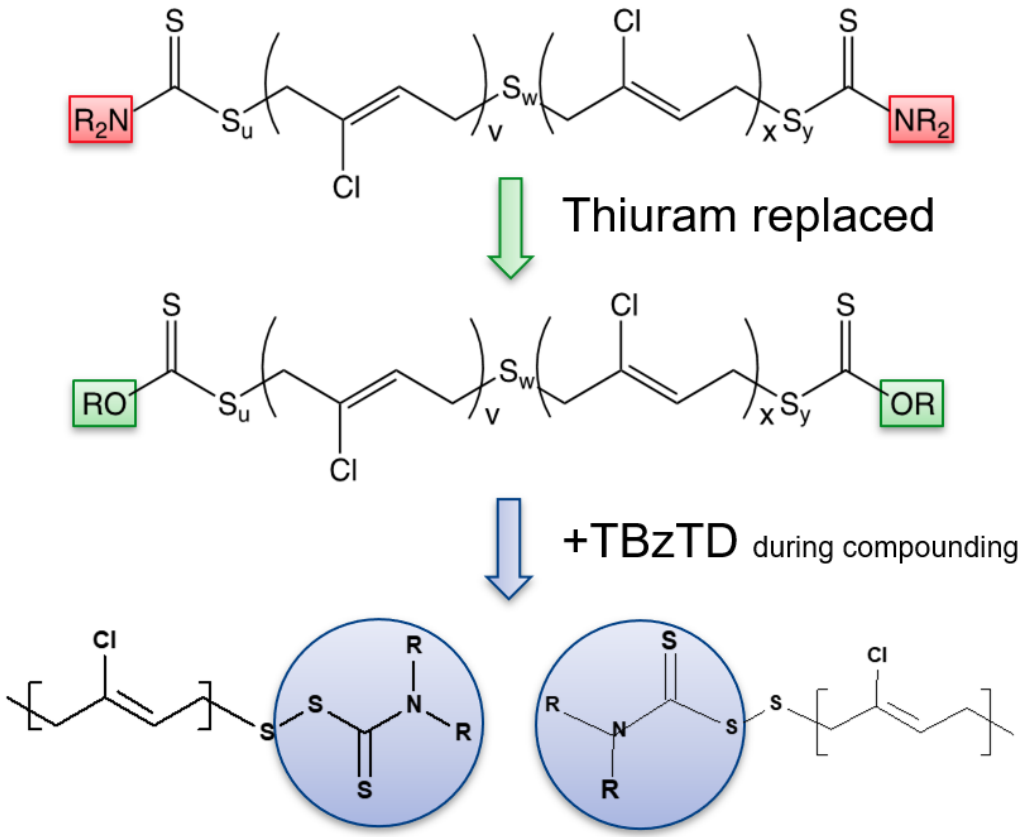


CR nitrosamine free - close to sulfur grades

Addition of safe a thiuram in the compound makes it even more alike

Key features preserved

- ❑ Sulfur in chain functionality for mastication is preserved
- ❑ Reactive end group preserved
- ❑ Raw material ageing similar to standard sulfur grades
- ❑ No toxic thiuram in the material: adding TBzTD to the compound introduce end chain functionalization chemically almost identical to standard sulfur grades



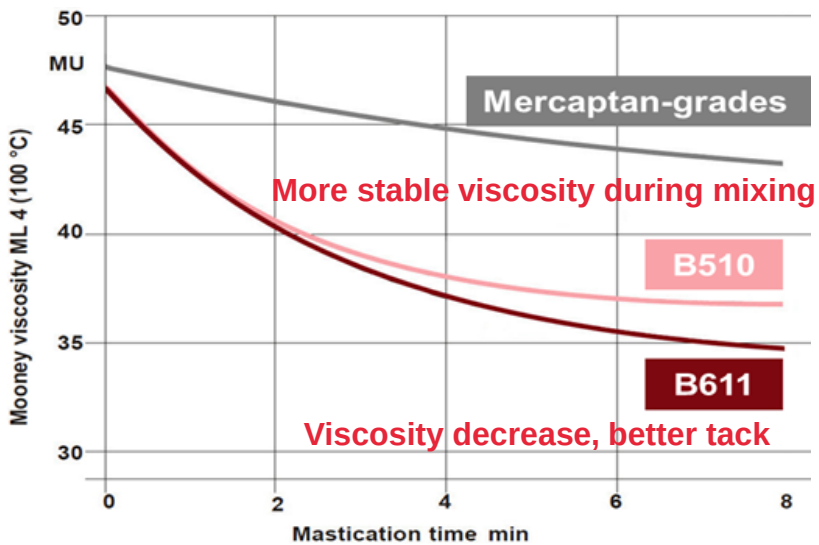
Designing CR compounds

CR sulfur grades – limited possibilities

The amount of sulfur has a major impact on the mastication of the polymer:

Two options for compounding:

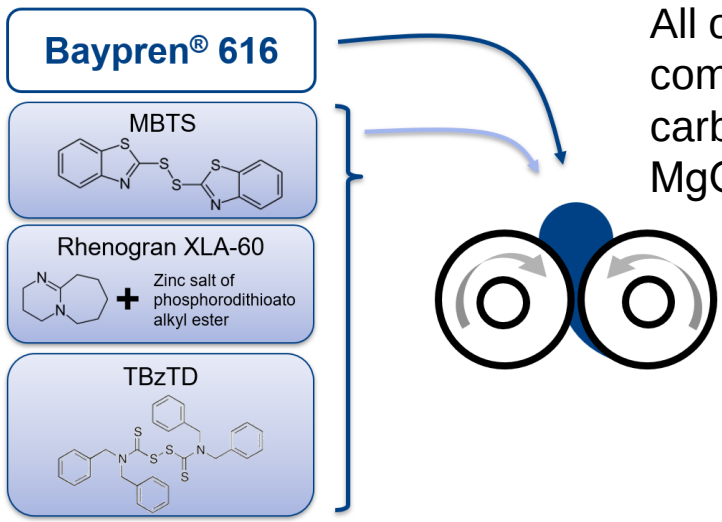
1. Select the right grade
2. Use a combination to achieve the balance dispersion / final viscosity / tack



CR nitrosamine free - additives based strategy

3 new degrees of freedom to adjust the

- Compound viscosity
- Vulcanization characteristic
- Mechanical properties
- Adhesion to fabric…



All on top of the usual components like carbon black, ZnO, MgO, plasticizer…

How to design a compound?

1

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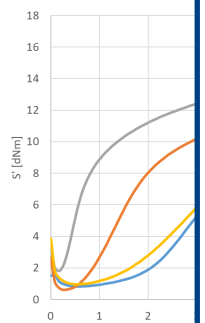

2

- Surface graph
- Optimize 2 va
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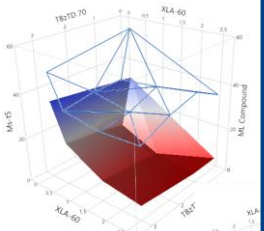
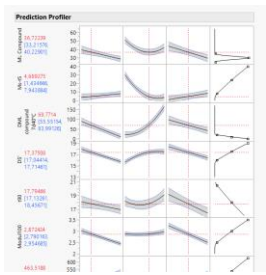
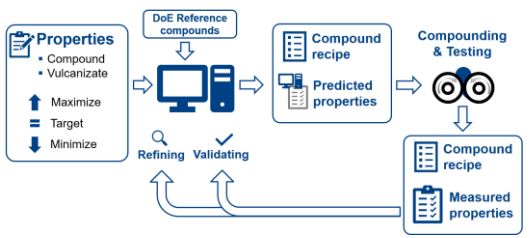


3

- Full statistical treatment
- Optimize all variables at once





Optimizing a multi-parameter system
From one-at-a-time to statistic driven optimization

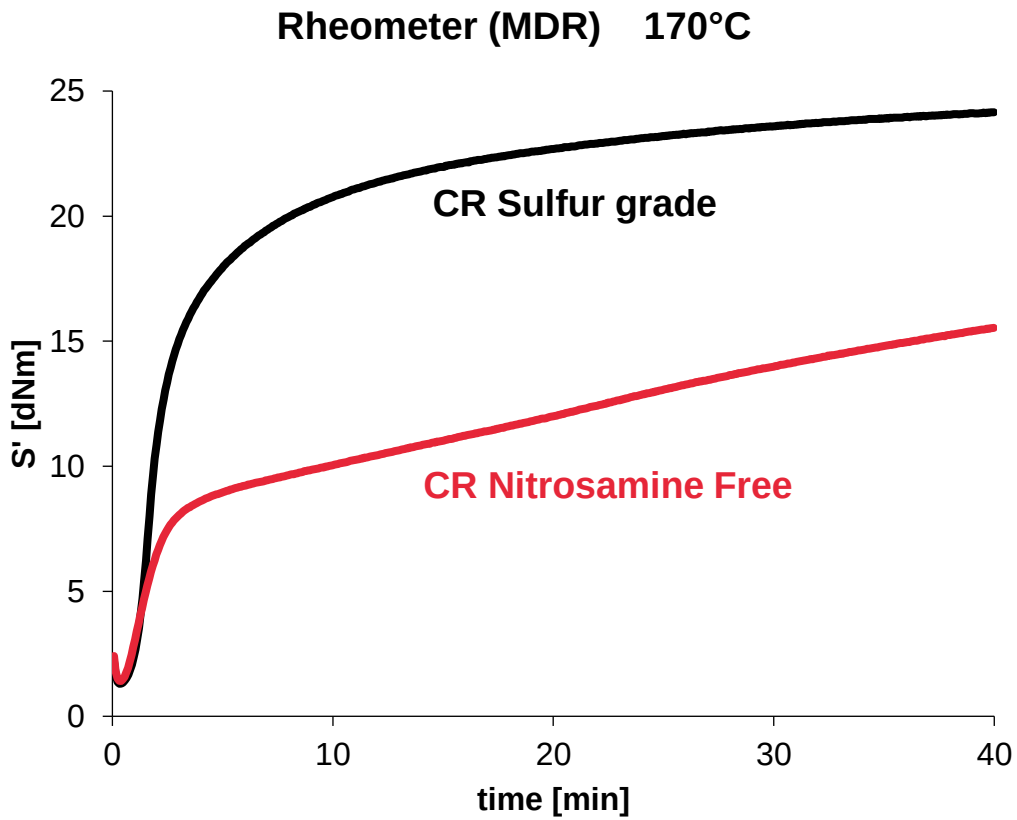
Compound evaluation

Different modifier: crosslinking density and speed lower

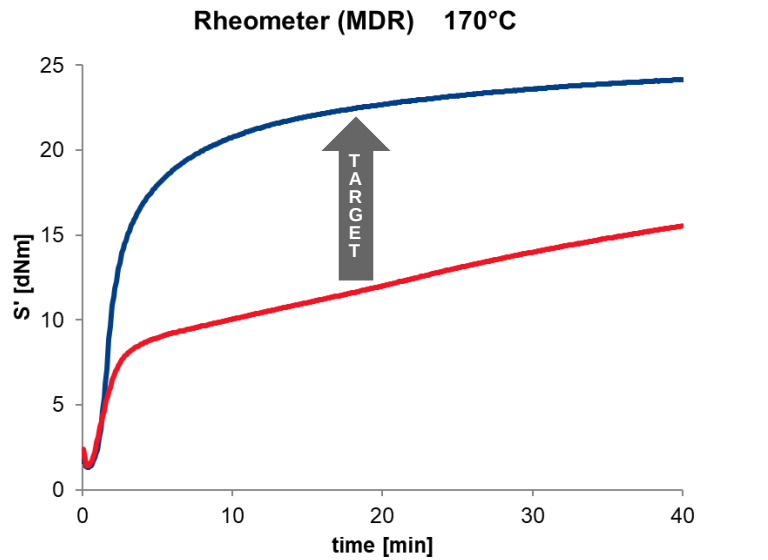
Compound ingredients

Ingredient	Reference	Test
CR Sulfur	100	
CR Nitrosamine Free		100
Carbon black N772	30	30
Stearic acid	1	1
MgO	4.4	4.4
ZnO	5	5

Lower crosslink density observed



Increase of crosslink density can be achieved by additives



With statistical analysis (Design of Experiment*) important ingredients with major influence were identified

→ curing additives can be added to adjust properties to the desired needs

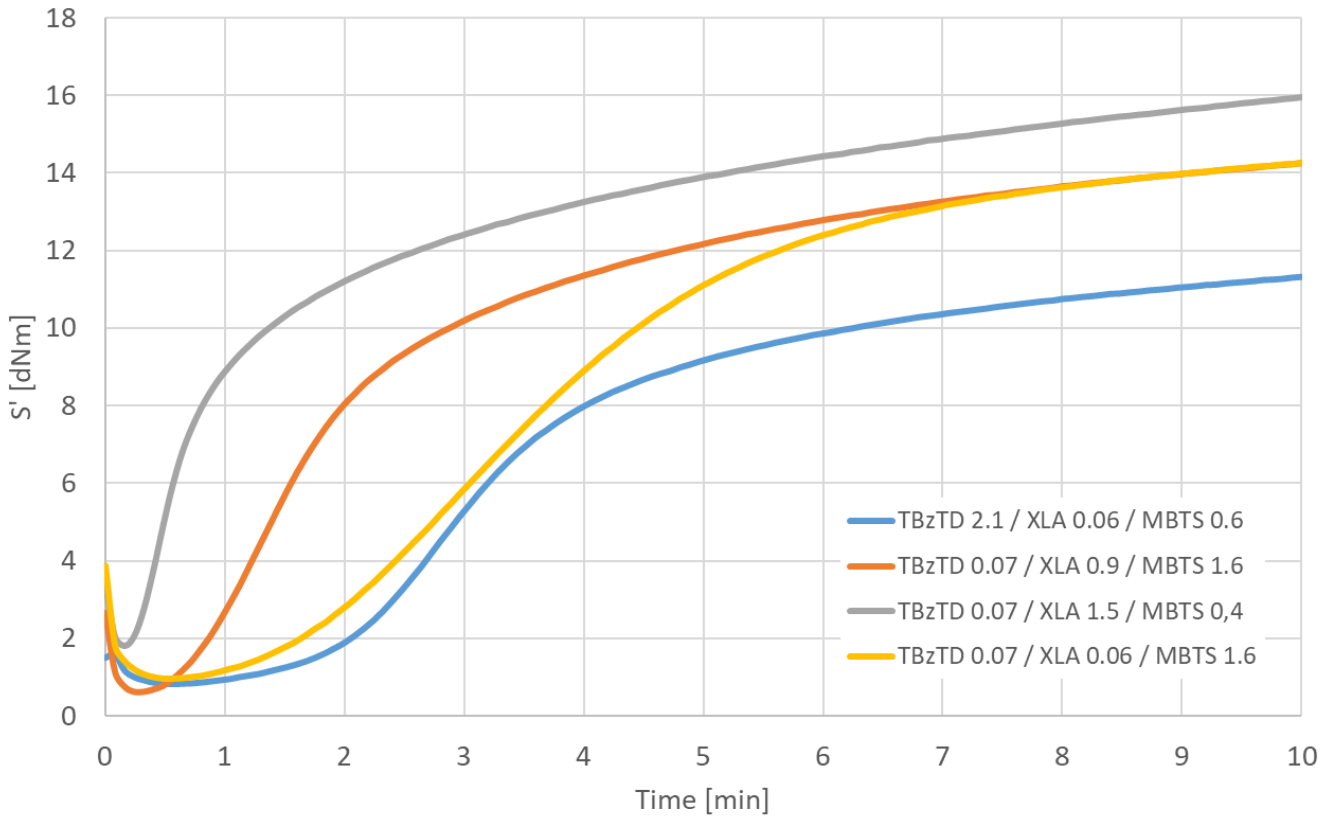
→ evaluation in an air spring and belt application recipe

*https://en.wikipedia.org/wiki/Design_of_experiments

Initial Screening of compounding additives

Influence on the vulcanization

Component	phr
CR Nitrosamine Free	100
Cabon black	40
DOS	5
MgO	4
TBzTD	Variable
Stearic acid	0.5
Antioxidants	3.5
ZnO	5
Rhenogran® XLA-60	Variable
MBTS	Variable



Application examples

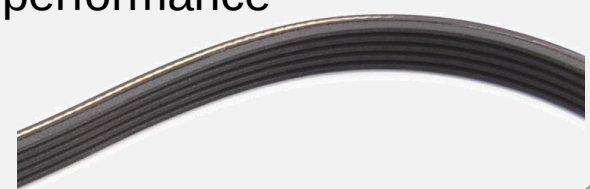
Using the DoE results, formulation suggestion was developed to meet requirements of different applications

Air Springs

- ✓ Matching cure speed
- ✓ Improved friction properties
- ✓ Same dynamic performance
- ✓ Cord adhesion

Belts

- ✓ Matching cure speed
- ✓ Same moduli
- ✓ Same dynamic performance
- ✓ Cord adhesion
- ✓ Abrasion



detailed compounding studies available upon request

Comparison between compounds

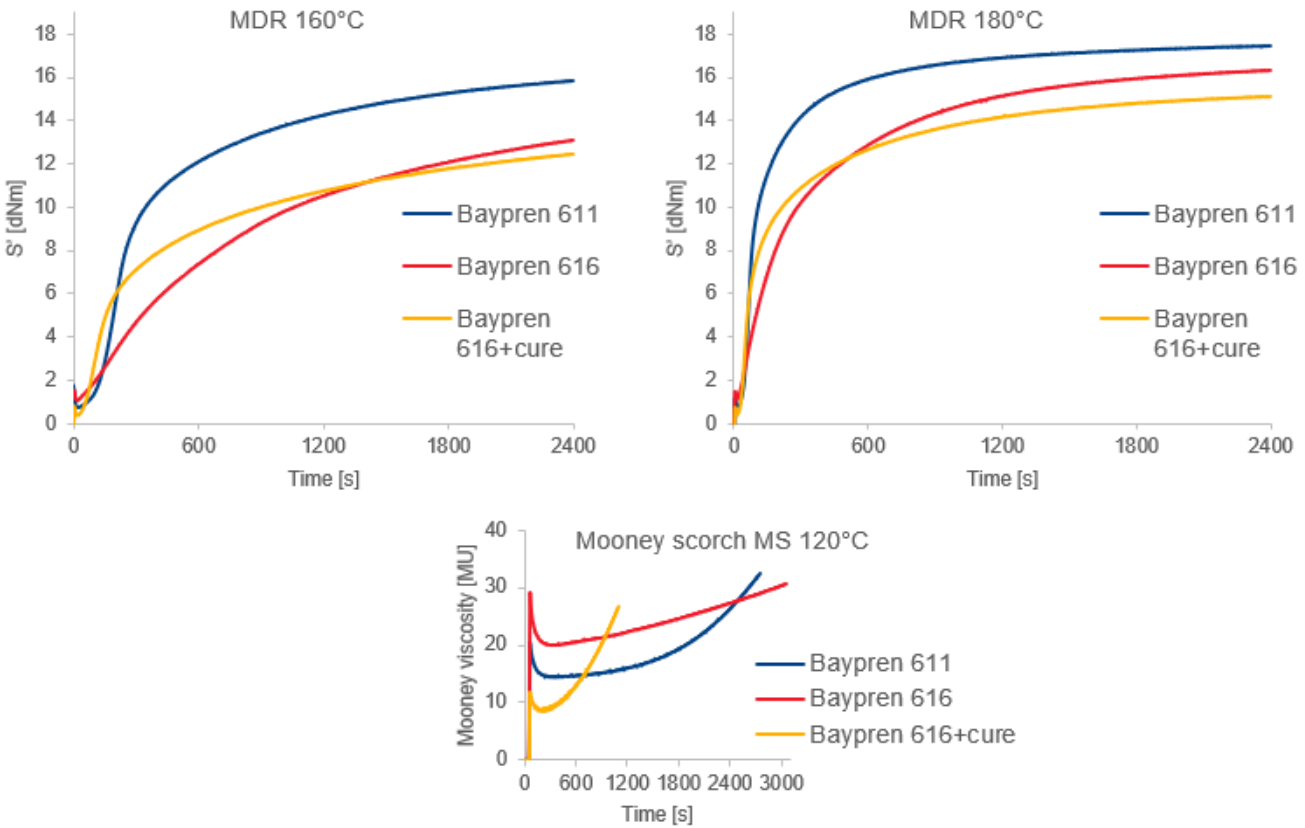
Example application air springs

	B611	B616	B616 cure
BAYPREN® 611 (polymer Mooney 40 MU)	100		
BAYPREN® 616 VP (polymer Mooney 58 MU)		100	100
CARBON BLACK N 772	40	40	40
PLASTICIZER DOS	10	10	10
ANTIOXIDANTS	3.5	3.5	3.5
PARAFFIN WAX	1	1	1
STEARIC ACID	0.5	0.5	0.5
MAGNESIUM OXIDE	4	4	4
ZINC OXIDE	5	5	5
CURING AGENTS			4
Total phr	164	164	168
compound Mooney viscosity ML1+4/100°C [MU]	**34**	**45**	**22**

- Typical air spring recipe was used
- Compound viscosity is determined by the polymer viscosity
- Using the adjusted cure package, a strong decrease of compound Mooney for Baypren® 616 VP is achieved
- This can give advantages in processing

Curing characteristics of compounds

Slower cure speed can be adjusted by additives

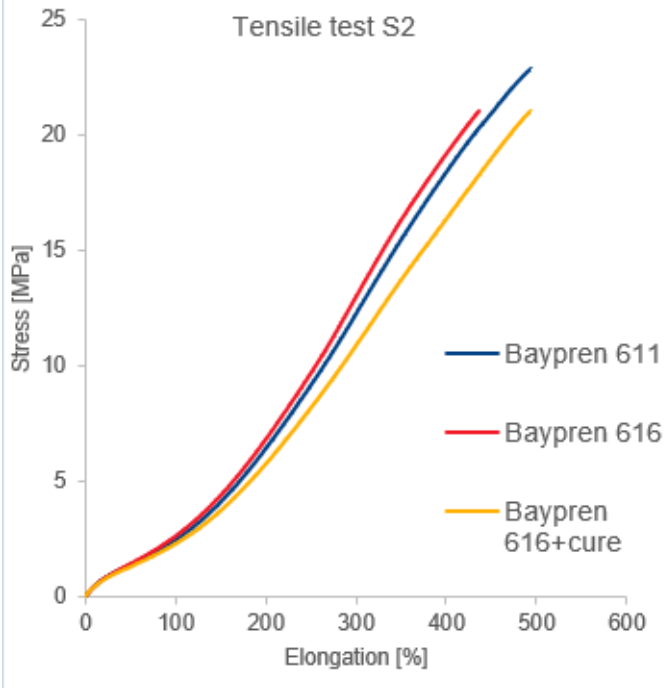


- Slower cure speed and higher marching modulus for Baypren® 616 VP vs. standard Baypren® 611
- Final state of cure similar at elevated temperatures
- Cure speed can be adjusted by modified curative package
- Scorch safety of Baypren® 616 VP is similar to Baypren® 611
- Scorch safety is reduced with modified curative package

Mechanical properties of cured rubber

Original and after hot air ageing

	B611	B616	B616 cure
Hardness [Shore A]	60	59	58
M50 [MPa]	1.4	1.5	1.4
M100 [MPa]	2.5	2.7	2.4
M300 [MPa]	12.1	13	11.2
EB median [%]	494	438	493
TS median [MPa]	22.9	21.1	21.1
abrasion loss [mm³]	78	74	79
tear Graves [N/mm]	37	34	38



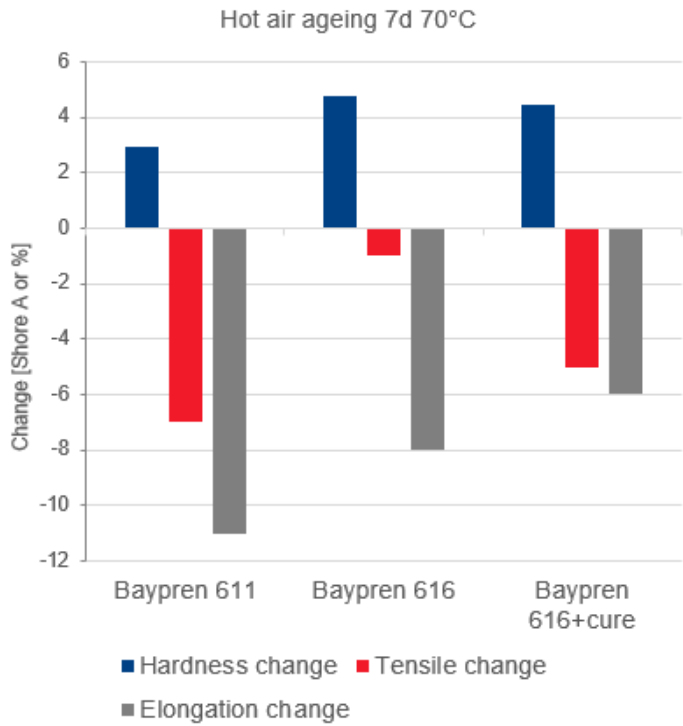
- Same hardness
- Marginally lower tensile strength for Baypren® 616 VP without and with modified cure
- Elongation at break and moduli similar
- Despite lowest compound Mooney with modified cure package, tensile properties are not affected
- Abrasion and tear resistance of Baypren® 616 VP identical with Baypren® 611

Mechanical properties of cured rubber

Original and after hot air ageing

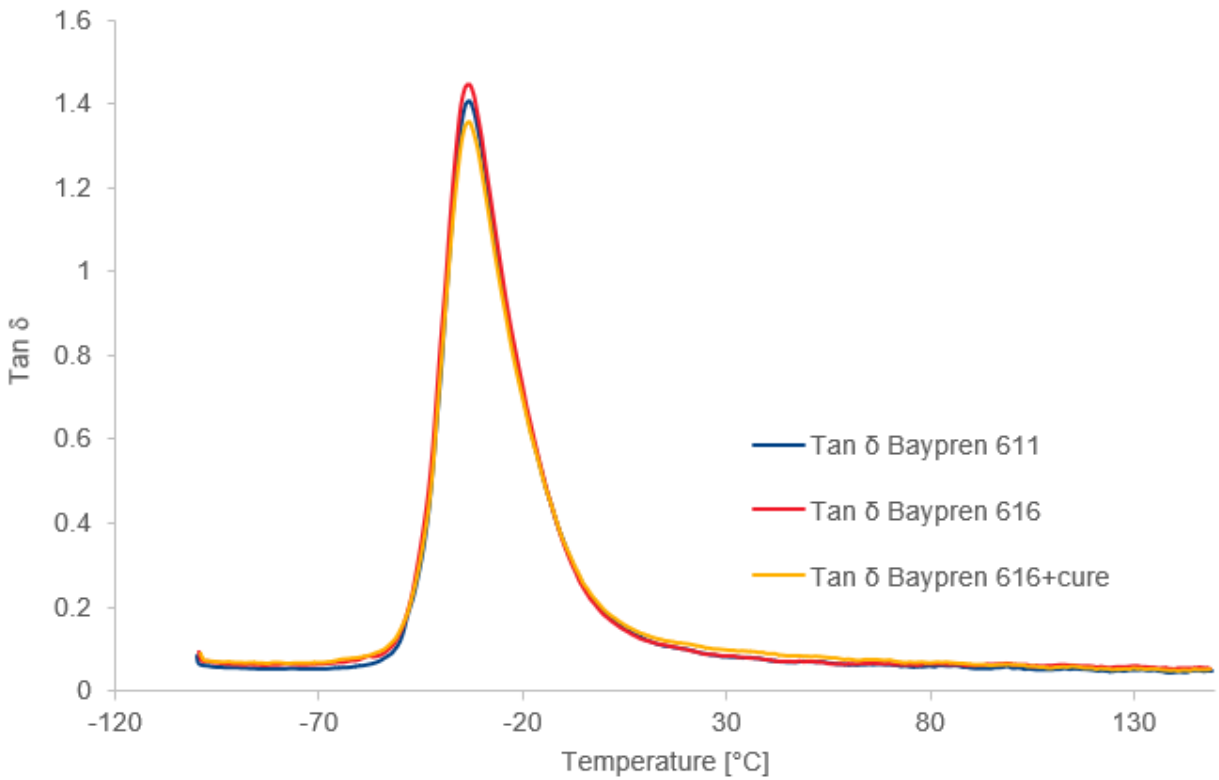
	B611	B616	B616 cure
EB original [%]	494	438	493
TS original [MPa]	22.9	21.1	21.1
M50 aged 7d 70°C [MPa]	1.6	1.8	1.5
M100 aged 7d 70°C [MPa]	2.8	3.2	2.6
EB aged 7d 70°C [%]	441	404	464
TS aged 7d 70°C [MPa]	21.3	20.8	20
compression set* 24h 70°C [%]	15	16	16

Compression Set DIN ISO 815 method A, sample type B



- Hot air ageing at 70°C similar for all three compounds
- Compression set identical

Dynamic properties

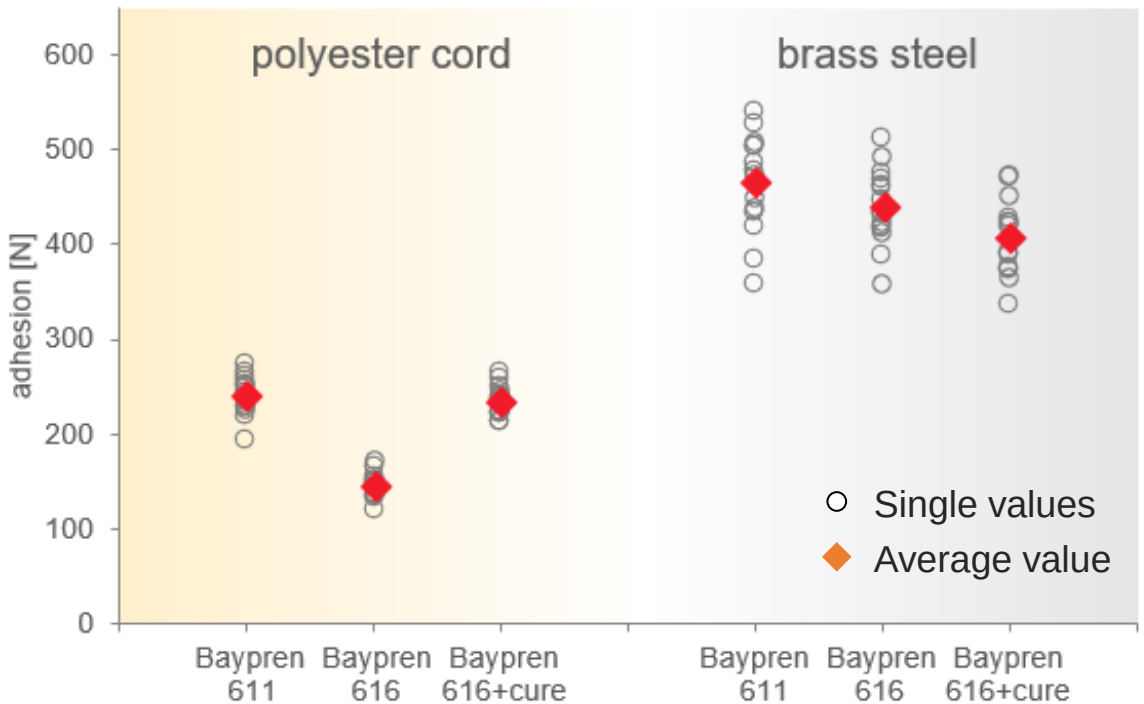


	B611	B616	B616cure
Goodrich flexometer set [%]	0.8	0.4	0.4
Goodrich flexometer Temperature rise [°C]	19.9	20.8	21.9
Eplexor T sweep temperature tan d max [°C]	-33.2	-33.2	-33.2
MTS frequency sweep dynamic stiffness	1.206	1.23	1.236
MTS amplitude sweep tan d max	0.135	0.126	0.147

- Goodrich heat build-up similar for all three compounds
- No differences in Eplexor temperature sweep seen → Tg the same for all three compounds
- Dynamic stiffness from MTS frequency sweep is identical

Cured properties: cord adhesion T-test

Adhesion to polyester cord and brass steel can be adjusted



- Slightly lower adhesion of standard Baypren® 616 VP compound for polyester cord
- Adhesion is improved when using modified cure package
- Similar adhesion of standard Baypren® 616 VP compound for brass steel
- Adhesion is slightly reduced when using modified cure package

➢ Curatives need to be adjusted according to application needs

	B611	B616	B616 cure
adhesion to cord T-test [N]	239	143	232
adhesion to brass T-test [N]	462	438	404

Comparison between compounds

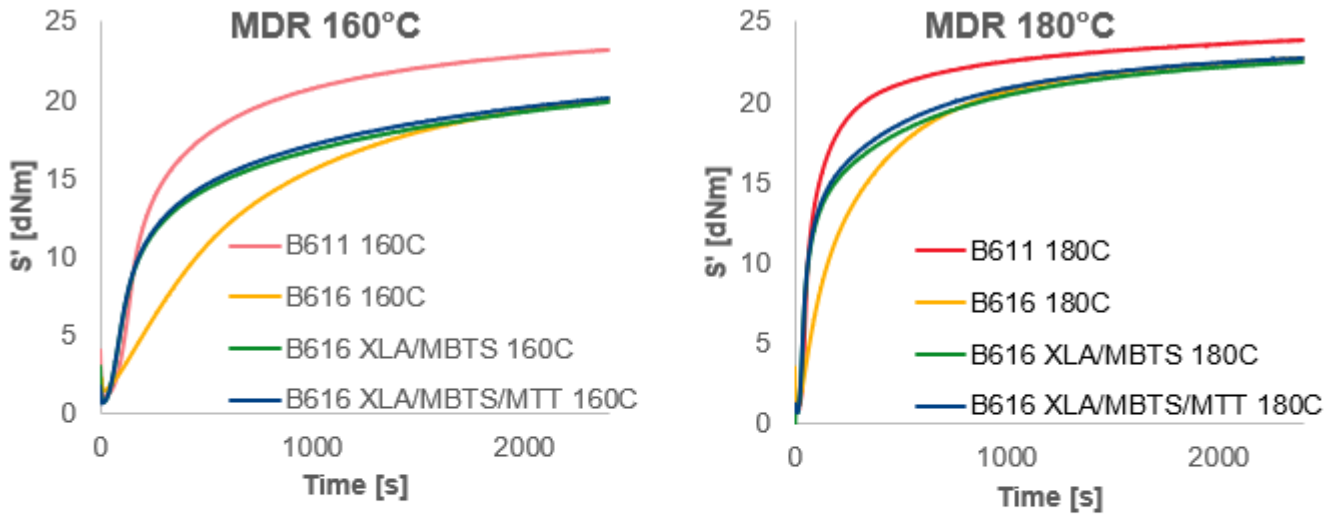
Example application belts

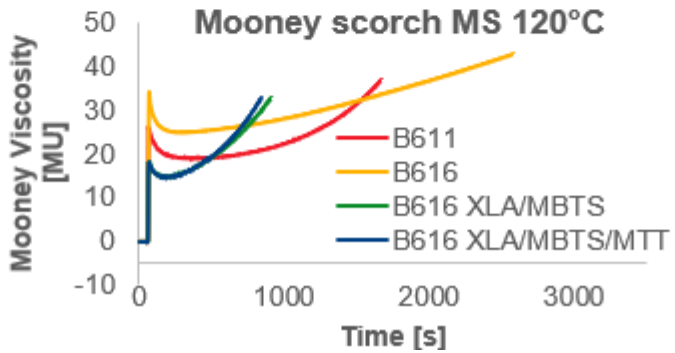
	B611	B616	B616 XLA/ MBTS	B616 XLA/ MBTS/ MTT
BAYPREN® 611 (polymer Mooney 37 MU)	100			
BAYPREN® 616 VP (polymer Mooney 58 MU)		100	100	100
Carbon black N 660	50	50	50	50
VULKASIL S	10	10	10	10
Plasticizer DOS	10	10	10	10
Antioxidants	7.5	7.5	7.5	7.5
Stearic Acid	0.5	0.5	0.5	0.5
Magnesium Oxide	4.4	4.4	4.4	4.4
Zinc Oxide	5	5	5	5
RHENOGRAN MTT-80	0.3	0.3		0.3
RHENOGRAN XLA-60			1.67	1.67
RHENOGRAN MBTS-80			1.25	1.25
	187.7	**187.7**	**190.32**	**190.62**
compound Mooney viscosity ML1+4/100°C	**44**	**55**	**36**	**35**

- Typical belt recipe was used
- Compound viscosity is determined by the polymer viscosity
- With the adjusted curing package a strong decrease of compound Mooney for B616 is achieved, even below B611
- This can give advantages in processing
- MTT does not influence Mooney

Curing characteristics of compounds

Slower cure speed can be adjusted by additives

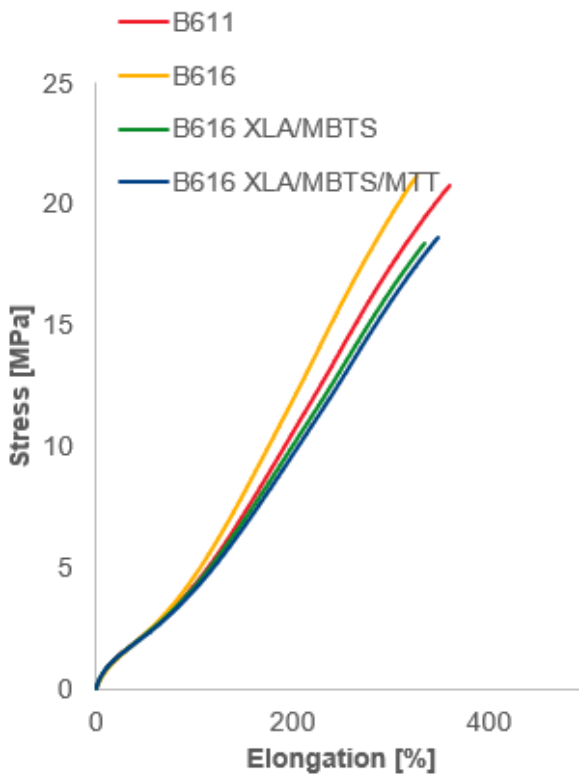




- Slower cure speed and higher marching modulus for Baypren® 616 VP vs. standard Baypren® 611
- Final state of cure similar at elevated temperatures
- Cure speed can be adjusted by modified curative package
- Scorch safety of Baypren® 616 VP is similar to Baypren® 611
- Scorch safety is reduced with modified curative package

Mechanical properties of cured rubber

Original and after hot air ageing



	B611	B616	B616 XLA/MBTS	B616 XLA/MBTS/MTT
Hardness [Shore A]	70	68	71	71
M50 [Mpa]	2.3	2.3	2.3	2.2
M100 [Mpa]	4.3	4.6	4.3	4.1
M300 [Mpa]	17.3	19.4	16.7	16.1
EB median [%]	362	328	335	348
TS median [Mpa]	20.8	21.2	18.4	18.6
Abrasion loss [mm³]	75	100	76	75
Tear Graves [N/mm]	33	31	33	33

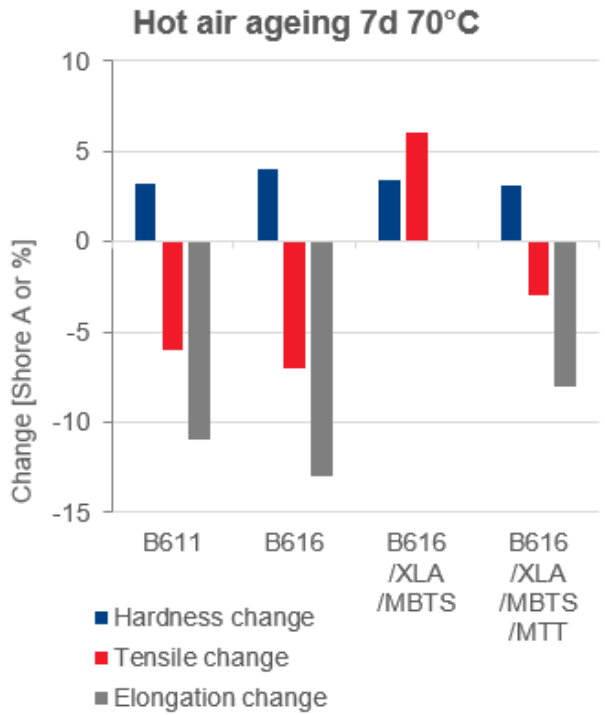
- Similar hardness
- Marginally higher tensile strength for Baypren® 616 VP without and lower tensile strength with modified cure
- Elongation at break and modulus 50 and 100 similar
- Abrasion and tear resistance of Baypren® 616 VP with adjusted curing package same as Baypren® 611
- Adhesion to cords can be adjusted by curing package

Mechanical properties of cured rubber

Original and after hot air ageing

	B611	B616	B616 XLA/ MBTS	B616/ XLA/ MBTS / MTT
EB [%]	362	328	335	348
TS [MPa]	20.8	21.2	18.4	18.6
M50 aged 7d 70°C [Mpa]	2.6	2.8	2.7	2.6
M100 aged 7d 70°C [Mpa]	4.9	5.6	4.9	4.8
EB aged 7d 70°C [%]	323	284	336	319
TS aged 7d 70°C [Mpa]	19.6	19.7	19.5	18.1
CS* 24h/100°C [%]	28	25	36	33

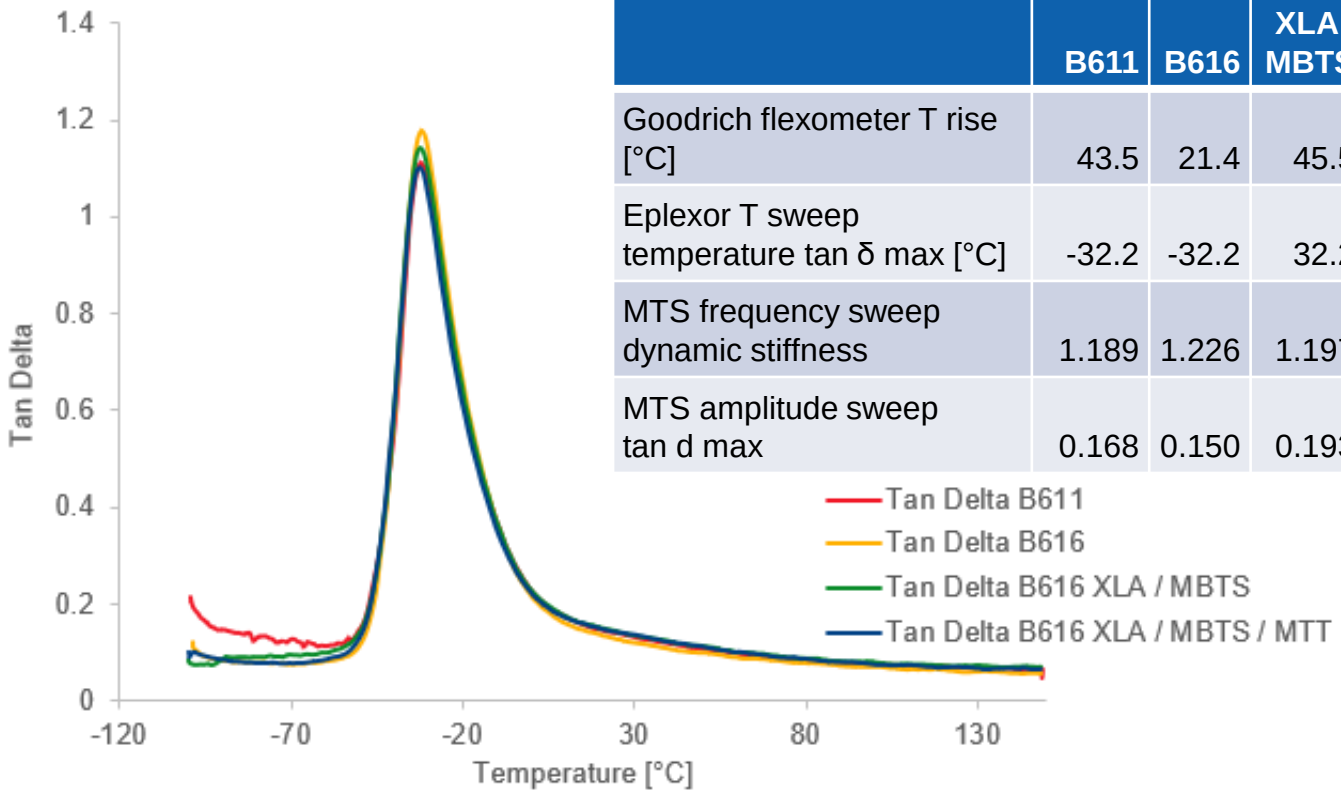
* Compression Set DIN ISO 815 method A, sample type B



- Similar aging performance Baypren® 611 as Baypren® 616 VP
- Curing package gives slightly improved ageing performance
- Compression set similar with Baypren® 611 and Baypren® 616 VP and is somewhat higher with adapted curing package

Dynamic properties

	B611	B616	B616 XLA / MBTS	B616 XLA /MBTS /MTT
Goodrich flexometer T rise [°C]	43.5	21.4	45.5	44
Eplexor T sweep temperature tan δ max [°C]	-32.2	-32.2	32.2	32.2
MTS frequency sweep dynamic stiffness	1.189	1.226	1.197	1.188
MTS amplitude sweep tan d max	0.168	0.150	0.193	0.182

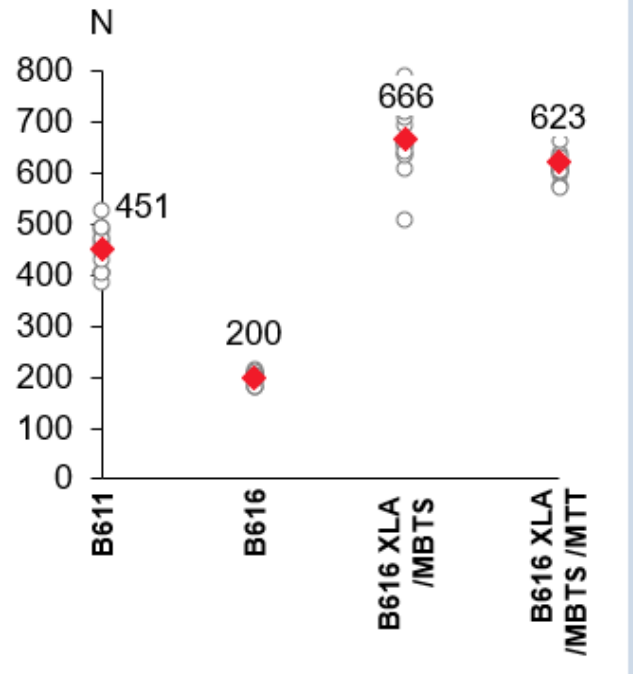


- Goodrich heat build-up of Baypren® 616 VP and Baypren® 611 is similar with adjusted curing system
- No differences in Eplexor temperature sweep seen → maximum tan δ = T_g are the same
- Dynamic stiffness from MTS frequency sweep is identical

Cured properties: cord adhesion T-test + separation

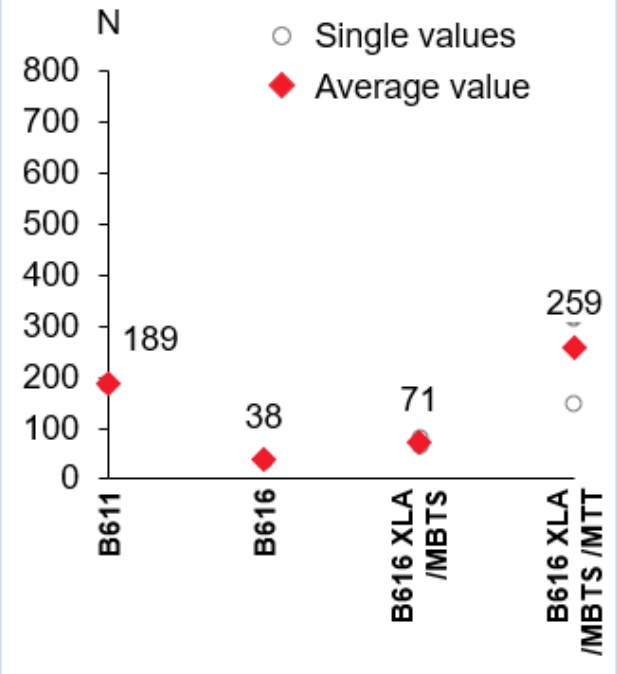
Adhesion can be adjusted

Cord adhesion polyester cord



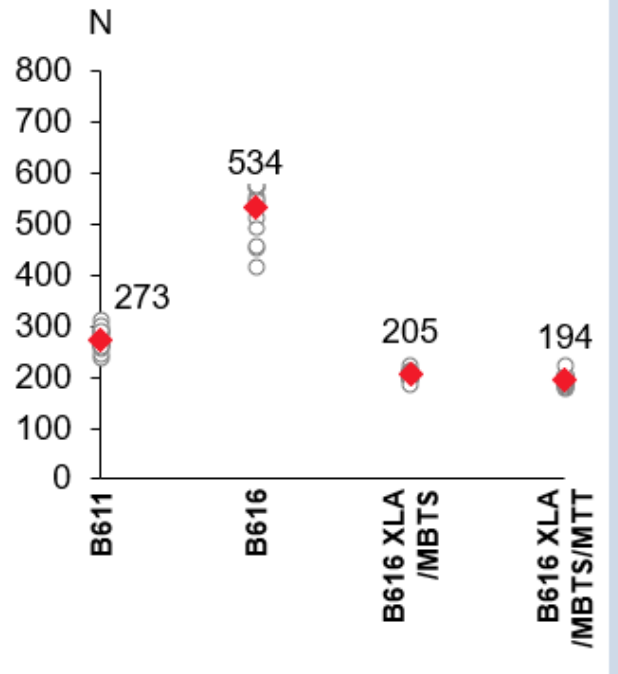
Baypren® 616 VP with adjusted curing package gives best adhesion

Separation rubber fabric PA



Separation force fabric varies strongly and can be adjusted with curing package.

Cord adhesion brass steel



Baypren® 616 VP gives best adhesion to brass steel

Summary

1. CR sulfur grade without thiurams has different crosslinking reactivity and can be adjusted with curing additives

2. Mechanical and dynamical properties are similar to the standard sulfur grade.

Influence of different additives after statistical evaluation

	ZnO	MBTS	XLA 60	TBzTD	MBTS TBzTD
Mooney viscosity	0	-	--	-	0
scorch time	0	+	-	+	0
delta S	++	-	+	-	0
TS	-	0	-	0	0
EB	--	++	0	++	0
M 100	+	-	0	0	0
Hardness	++	--	0	-	--
CS 100°C, 24h	--	++	--	0	0
MTS-dynamic creep	-	0	0	0	+
MTS-Internal temperature	0	+	0	-	++
cord adhesion	++	--	++	--	0

+ = value increases
- = value decreases

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Gracias / Thank you

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Performance Elastomers

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