Faster Processing of High Performance Silica Compounds

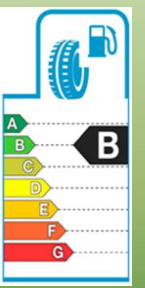
using Struktol® Silica Dispersants

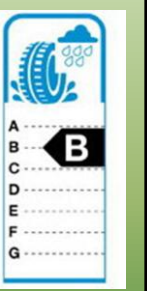
14º Congresso Brasileiro de Tecnologia da Borracha

Dr. Ken Bates
Struktol Company of America

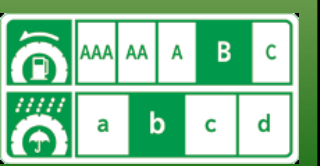
New Tire Labeling for Wet Traction Rolling Resistance

- European Union
  - EC 1222/2009
  - Passenger tire Wet and RR labeling begins in November 2012
  - A(best) thru G(worst) grading system used with both labels
  - Tire companies reportedly competing for the first A-A rating (is it possible?)





- Japan
  - Voluntary RR labeling started in 2010
  - Becomes mandatory in 2012
  - Summer passenger tires only
  - New goal = “AA” Wet with “a” RR



Presentation Outline

- Introduce new Struktol Dispersant Lineup
- Demonstrate performance using two technologies that improve the Wet vs RR tradeoff:
  - 200 m^2/g CTAB Silicas (Zeosil Premium 200MP)
  - End-functional SSBR Polymers (JSR HPR350)
- Illustrate some performance differences of the four Struktol Dispersants in SSBR

Product Information

HT 207	HT 276	JV 46 F	ZB49
Zinc free lubricant	Modified zinc soap	Polar lubricant	Polar lubricant
Produced in Hamburg, Germany	Produced in Hamburg, Germany	Produced in Stow, Ohio	Produced in Stow, Ohio
Drop Point = 65°C	100°C	85°C	105°C
Viscosity reduction Fast cure times Less scorch safety than other products Max tan δ reduction in SSBR	Max Viscosity reduction Long scorch safety Tan δ reduction Especially useful with NR	Viscosity reduction Moderate scorch safety Tan δ reduction	Viscosity reduction Low stiffness reduction in cured product Improves silane-polymer crosslinking Max tan δ reduction in NR

Zeosil® Premium 200MP RECIPES

INGREDIENT	MIX STAGE	CONTROL	HT207	HT276	ZB49	JV46F
Buna VSL 5025-2HM	1	110	110	110	110	110
Lanxess CB24		20	20	20	20	20
Zeosil Premium 200MP		50	50	50	50	50
Stearic Acid		1	1	1	1	1
TDAE Oil		5	5	5	5	5
Struktol SCA985		4	4	4	4	4
N330		8	8	8	8	8
Struktol HT207			3			
Struktol HT276				3		
Struktol ZB49					3	
Struktol JV46F						3
Zeosil Premium 200MP	2	30	50	50	50	50
TDAE Oil		5	5	5	5	5
Struktol SCA985		2.4	4	4	4	4
Struktol HT207			3			
Struktol HT276				3		
Struktol ZB49					3	
Struktol JV46F						3
AOz Wax			1.5	1.5	1.5	1.5
ZnO			2.5	2.5	2.5	2.5
6PPD			2	2	2	2
Zeosil Premium 200MP	3	20	NOT INCLUDED			
Struktol SCA985		1.6				
AOz Wax		1.5				
ZnO		2.5				
6PPD		2				
Santocure CBS	Final	2.2	2.2	2.2	2.2	2.2
Perkacit DPG		2	2	2	2	2
Sulfur		1.5	1.5	1.5	1.5	1.5
Total phr		*268.7*	*274.7*	*274.7*	*274.7*	*274.7*

Mix Procedure for 100phr Zeosil® Premium 200MP Recipe

CONTROL	WITH STRUKTOL ADDITIVE
First pass mix spec: 75 rpm (65% fill) UPSIDE DOWN MIX PROCEDURE REDUCE ROTOR SPEED AT 140C Dump at 300 seconds	**First pass mix spec: 75 rpm (65% fill)** UPSIDE DOWN MIX PROCEDURE REDUCE ROTOR SPEED AT 140C Dump at 300 seconds
Second pass mix spec: 75rpm (65% fill) UPSIDE DOWN MIX PROCEDURE REDUCE ROTOR SPEED AT 140C Dump at 300 seconds	**Second pass mix spec: 75rpm (65% fill)** UPSIDE DOWN MIX PROCEDURE REDUCE ROTOR SPEED AT 140C ADD ZNO, AND 6PPD AT 140C Dump at 300 seconds
Third pass mix spec: 75rpm (65% fill) UPSIDE DOWN MIX PROCEDURE REDUCE ROTOR SPEED AT 140C ADD ZNO, AND 6PPD AT 140C Dump at 300 seconds	**NO THIRD PASS UTILIZED**
Final pass mix spec: 50 rpm (60% fill) ADD MB AND CURATIVES, MIX TO 105C	**Final pass mix spec: 50 rpm (60% fill)** ADD MB AND CURATIVES, MIX TO 105C

4-Pass Mixing of 200MP Control Compound

PASS #1

total silica = 50 phr / energy = 0.35 kW-hr

PASS #2

total silica = 80 phr / 0.37 kW-hr

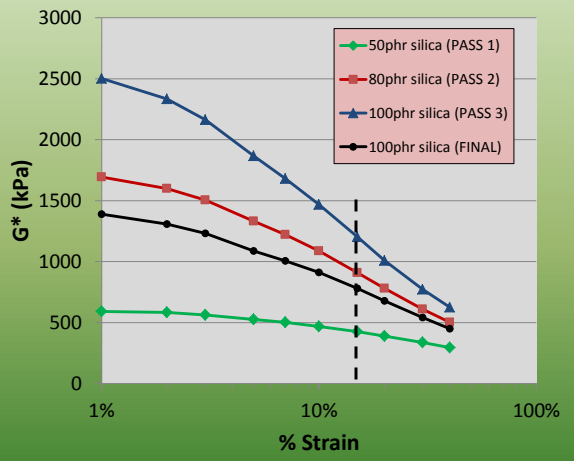
PASS #3

total silica = 100 phr / 0.41 kW-hr

FINAL PASS

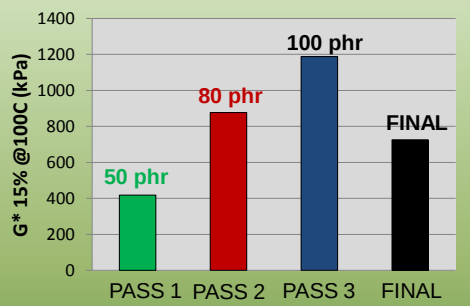
total silica = 100 phr / 0.14 kW-hr

Payne Effect after Each Mix Stage

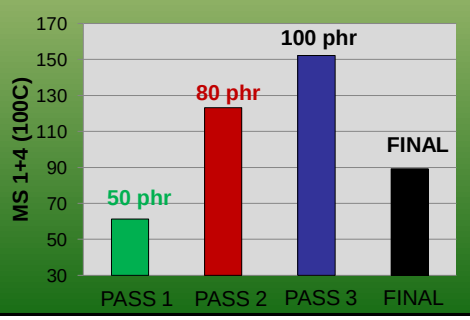


MIXING VISCOSITY PROFILE

RPA Strain Sweep



Mooney Small Rotor



3-Pass Mixing of Compounds with ZB49

PASS #1

total silica = 50 phr / energy = 0.35 kW-hr

PASS #2

total silica = 50 phr / energy = 0.36 kW-hr

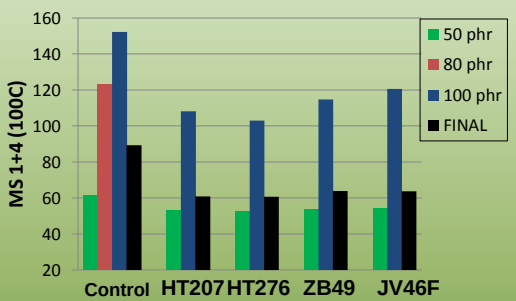
PASS #3

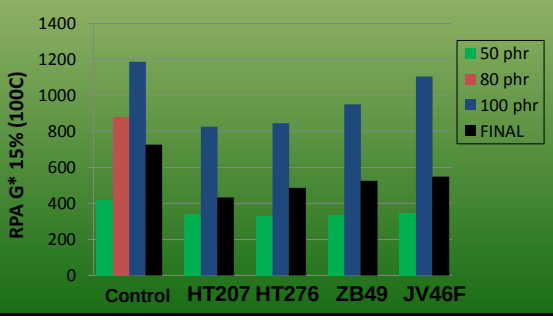
total silica = 50 phr / energy = 0.12 kW-hr

35% Savings in Mix Energy

VISCOSITY PROFILE with PROCESS AIDS

- 2nd pass Mooney of control over 120 MS 1+4
- All process aid batches give lower 2nd pass viscosity (even with higher silica loading)

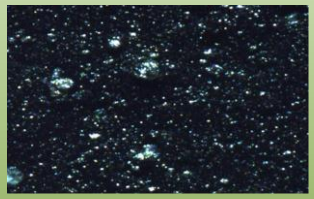




- 2nd pass RPA G*15% of control over 800 kPa
- Similar G*15% values obtained with 2nd pass compounds including processing aid
- Best viscosity reduction obtained with HT207 and HT276

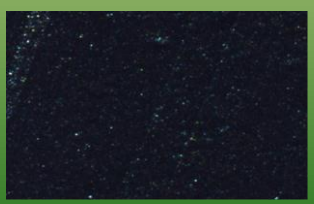
DISPERSION KINETICS*

Control Batch



Z = 45%

Z = 64%

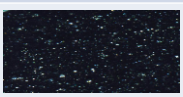
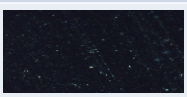
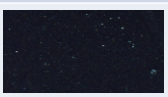
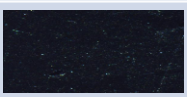
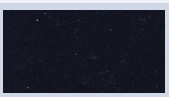
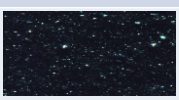
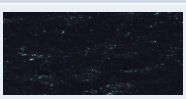
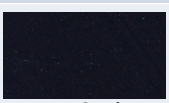
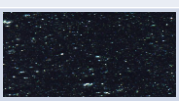
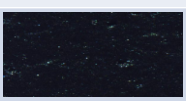
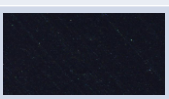


Z = 83%

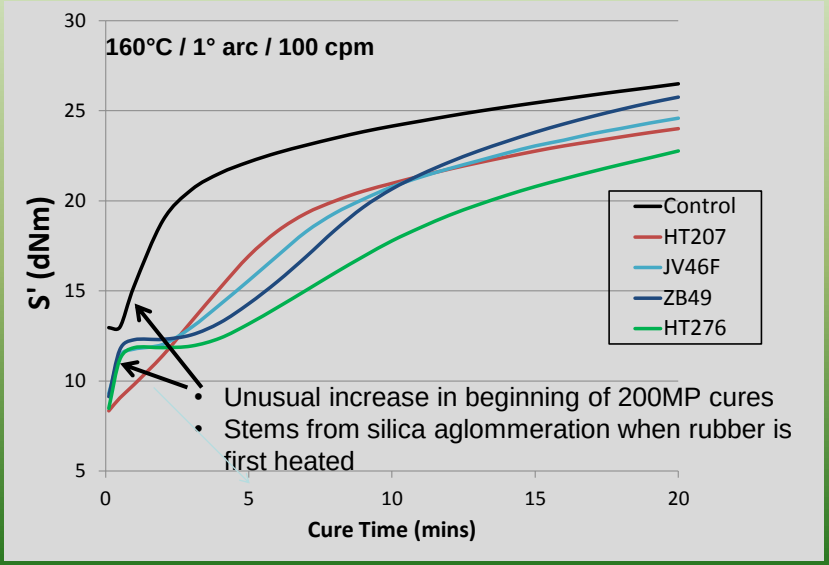
Z = 89%

* **Dispergrader α View** courtesy of Alpha Technologies

DISPERSION KINETICS

	PASS 1	PASS 2	PASS 3	FINAL
Control	Z = 45%	Z = 64%	Z = 83%	Z = 89%
HT207	 Z = 61%	 Z = 83%	N/A	 Z = 94%
HT276	Z = 61%	 Z = 84%	N/A	 Z = 94%
ZB49	 Z = 64%	 Z = 79%	N/A	 Z = 95%
JV46F	 Z = 61%	 Z = 84%	N/A	 Z = 93%

MDR CURING RESULTS



CURING SUMMARY

COMPOUND	Delta S'(dNm)	t90(mins)
Control	13.5	13.6
HT207	15.7	**14.0**
JV46F	15.3	15.0
ZB49	**16.6**	15.6
HT276	14.3	16.2

COMPOUND PERFORMANCE

TEST PARAMETER	CONTROL	HT207	HT276	ZB49	JV46F
Mooney Scorch t5 @125C	11.7	21.6	> 60	53	42
Spiral Mold Flow @ 160C (g)	1.29	1.42	1.39	1.36	1.37
Tensile (MPa)	13.2	17.2	14.3	16.6	17.2
Elongation %	268	427	468	457	472
Sh. A Hardness	78	74	75	79	77
DIN Abrasion loss	215	164	166	182	171
Tear Strength Die C (N/mm)	28.1	33.0	34.1	35.1	33.1
G* 10% @50C (MPa)	3.20	2.48	2.66	2.80	2.75
tan δ max @50C (0.5-20% strain)	0.241	0.209	0.266	0.245	0.231

= IMPROVEMENT

= DRAWBACK

HPR350 Functional SSBR RECIPES

4-Pass Mixing of Functional SSBR

INGREDIENT	MIX STAGE	Functional SSBR Control	Nonfunct. SSBR Control	HT207	HT276	ZB49	JV46F
JSR HPR350	1	80	---	80	80	80	80
Buna VSL 5025-2 HM		0	110	0	0	0	0
Lanxess CB24		20	20	20	20	20	20
Zeosil 1165MP		**50**	**50**	**50**	**50**	**50**	**50**
Stearic Acid		1	1	1	1	1	1
TDAE Process Oil		20	5	20	20	20	20
Struktol SCA985		4	4	4	4	4	4
Stearic Acid		1	1	1	1	1	1
N330		8	8	8	8	8	8
Struktol HT207		0	0	3	0	0	0
Struktol HT276		0	0	0	3	0	0
Struktol ZB49		0	0	0	0	3	0
Struktol JV46F		0	0	0	0	0	3
Zeosil 1165MP	2	**30**	**30**	**50**	**50**	**50**	**50**
TDAE Process Oil		20	5	20	20	20	20
Struktol SCA985		2.4	2.4	4	4	4	4
Struktol HT207		0	0	3	0	0	0
Struktol HT276		0	0	0	3	0	0
Struktol ZB49		0	0	0	0	3	0
Struktol JV46F		0	0	0	0	0	3
AOz Wax		0	0	1.5	1.5	1.5	1.5
ZnO		0	0	2.5	2.5	2.5	2.5
6PPD		0	0	2	2	2	2
Zeosil 1165MP	3	**20**	**20**	NOT INCLUDED			
Struktol SCA985		1.6	1.6				
AOz Wax		1.5	1.5				
ZnO		2.5	2.5				
6PPD		2	2				
CBS	FINAL	2.2	2.2	2.2	2.2	2.2	2.2
DPG		2	2	2	2	2	2
Sulfur		1.5	1.5	1.5	1.5	1.5	1.5
Totals:		***269.7***	***269.7***	***275.7***	***275.7***	***275.7***	***275.7***

MIXER PHOTOS – PASS #1

Functional
total silica = 50phr

Nonfunctional
total silica = 50phr

ZB49
total silica = 50phr

MIXER PHOTOS – PASS #2

Functional
total silica = 80phr

Nonfunctional
total silica = 80phr

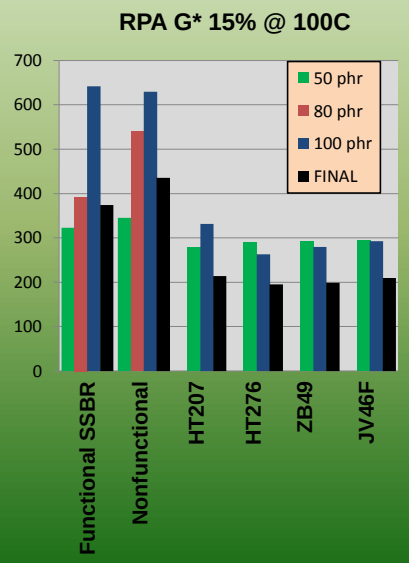
ZB49
total silica = 100phr

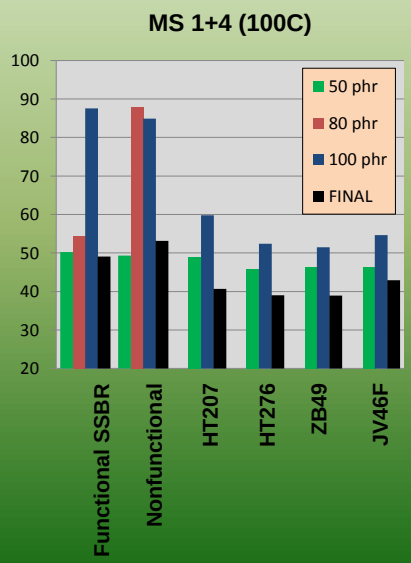
MIXER PHOTOS – PASS #3

Functional
total silica = 100phr

Nonfunctional
total silica = 100phr

VISCOSITY AFTER EACH MIX PASS



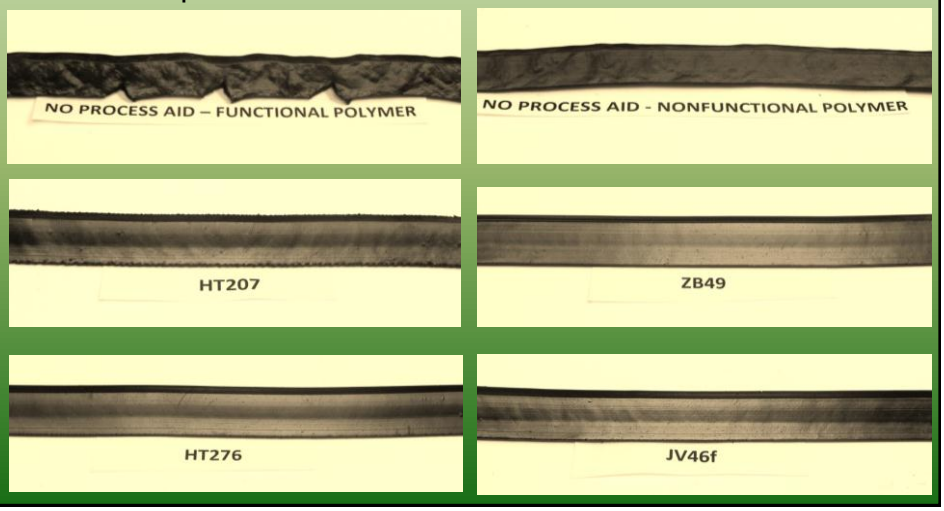


Dispergrader Z-Values

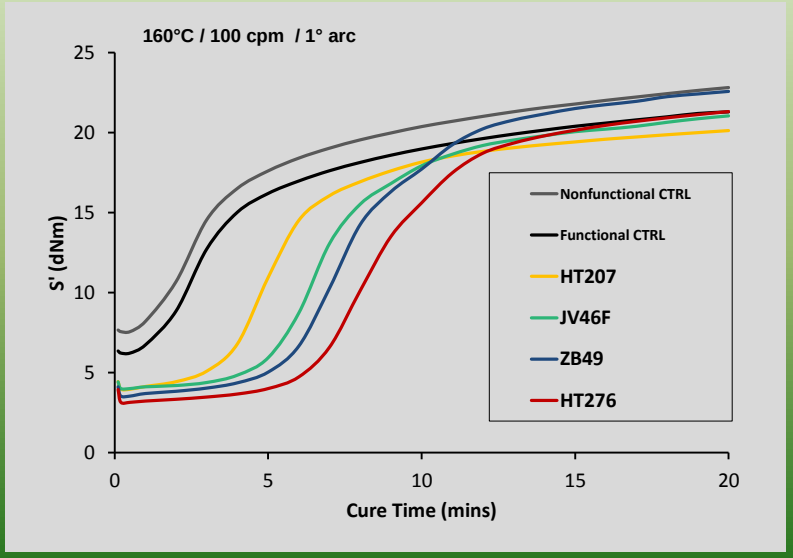
Compound	PASS #1	PASS #2	PASS #3	FINAL
FUNCTIONAL CONTROL	76%	73%	88%	96%
NONFUNCTIONAL CONTROL	65%	77%	83%	94%
6phr HT207	80%	88%	N/A	94%
6phr HT276	81%	92%	N/A	92%
6phr ZB49	79%	95%	N/A	91%
6phr JV46F	81%	91%	N/A	93%

Garvey Die Extrusions

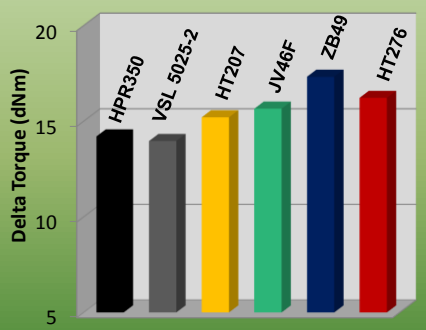
- All zones of extruder barrel maintained at 125C
- Screw speed = 60 RPM

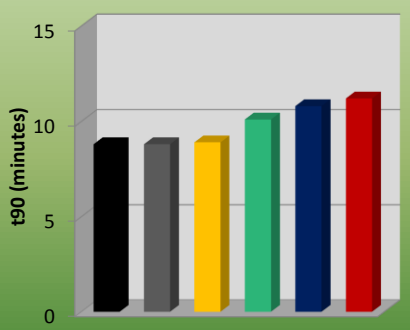


MDR Curing Behavior



Curing Summary - Functional SSBR





★ ENHANCED CURING WITH ZB49

★ NO INFLUENCE ON T90 WITH HT207

COMPOUND PERFORMANCE

TEST PARAMETER	Functional SSBR	Nonfunct. SSBR	HT207	HT276	ZB49	JV46F
Mooney Scorch t5 @125C	15.7	13.1	30	56.3	46.5	42.7
Spiral Mold Flow @ 160C (g)	1.48	1.47	1.73	1.80	1.78	1.73
Tensile (MPa)	14.8	12.6	17.9	17.1	17.8	18.1
Elongation %	316	224	378	382	393	408
Sh. A Hardness	72	74	73	69	71	68
DIN Abrasion loss	173	188	137	163	148	138
Tear Strength Die C (N/mm)	31	31	37.6	38.7	38.5	37.4
G* 10% @50C (MPa)	2.10	2.29	1.61	1.60	1.83	1.63
tan δ max @50C (0.5-20% strain)	0.204	0.209	0.176	0.198	0.197	0.181

= IMPROVEMENT

= DRAWBACK

CONCLUSIONS

- A silica loading of 100 phr is easily achieved when a Struktol silica dispersant is incorporated into the recipe.
- A mixing time and energy savings of 30-35% is obtained with dispersant use.
- The high viscosity of Zeosil Premium 200MP silica can be reduced by 30 MS1+4 (~50 ML1+4) points through each mixing step with dispersant use.
- The rough extrusion profile of highly-filled HPR350 SSBR can be eliminated with a Struktol dispersant.
- Struktol HT207 is recommended for use with Zeosil Premium 200MP.
- Struktol ZB49 is recommended for use with HPR350 SSBR.

MUITO OBRIGADO !!!