NO. RRL10-008

Technical Insight of KURARAY LIQUID RUBBER

Silane modified LBR for SBR / Silica formulation

Elastomer R&D Department
Elastomer Division

kuraray

Agenda

Our silane-modified LBR; GS-L-BR is the latest development of KURARAY LIQUID RUBBER grades.

1) Silane modified LBR (GS-L-BR)

2) Evaluation in SBR / Silica formulation

3) Hypothesis and how to improve Mechanical properties

Silane modified LBR (GS-L-BR-188)

Grade Name [Development Code]	Structure	Mw	Tg (°C)	Number of functional groups / chain	Viscosity at 38°C (Pa • s)
GS-L-BR-188 [SB-006]	Polybutadiene /Graft silane	38,000	-88	4	124

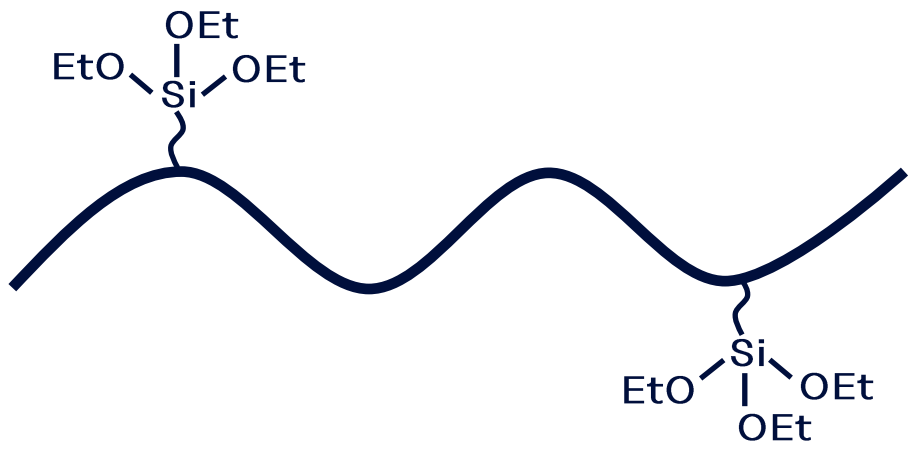


Image of GS-L-BR

- High reactivity with silica
- Improve silica dispersion
- Crosslinkable with base rubber

Agenda

1) Silane modified LBR (GS-L-BR)

2) Evaluation in SBR / Silica formulation

3) Hypothesis and how to improve Mechanical properties

Mechanical properties of GS-L-BR-188

*Precursor of GS-L-BR-188

		Control	Formulation	
f-SSBR		80	80	80
BR		20	20	20
Silica		100	100	100
Si 75®		8	8	8
TDAE		40	28	28
LBR*			12	
GS-L-BR-188				12
Mechanical Properties				
EB	(%)	415	415	335
TB	(MPa)	20.2	18.8	17.9
M100	(MPa)	2.26	2.01	2.37
M300	(MPa)	12.6	11.4	15.1

- GS-L-BR-188 decreases EB and TB.

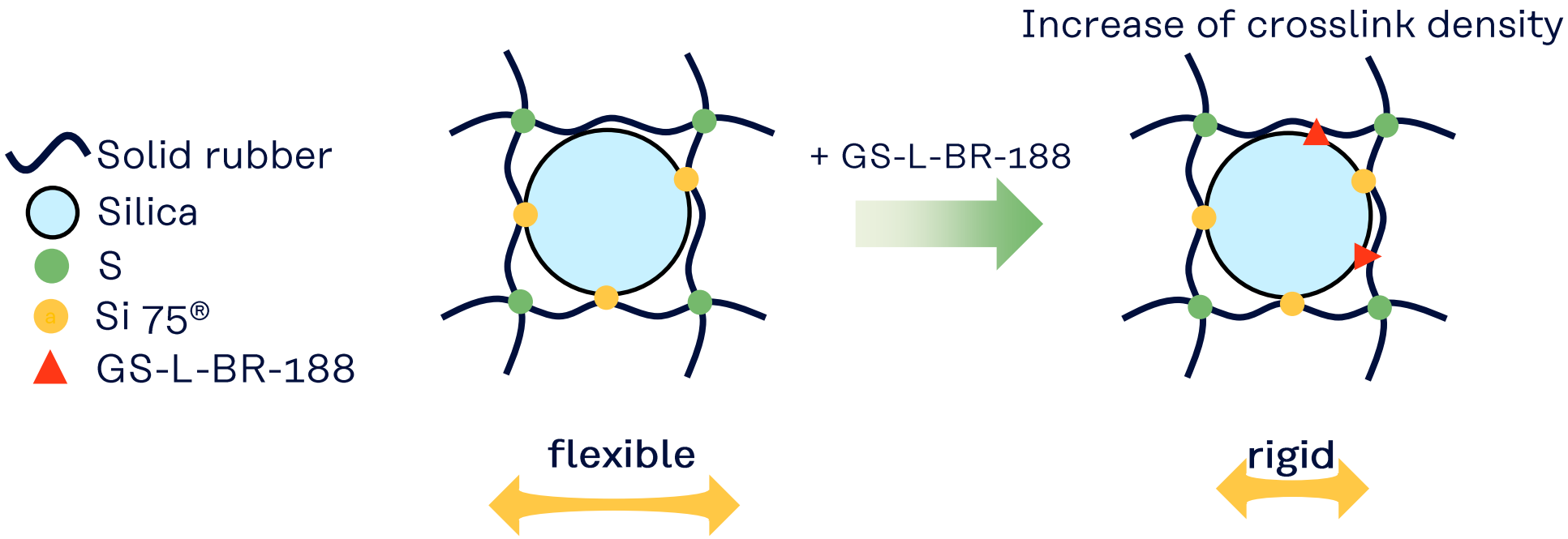
Agenda

1) Silane modified LBR (GS-L-BR)

2) Evaluation in SBR / Silica formulation

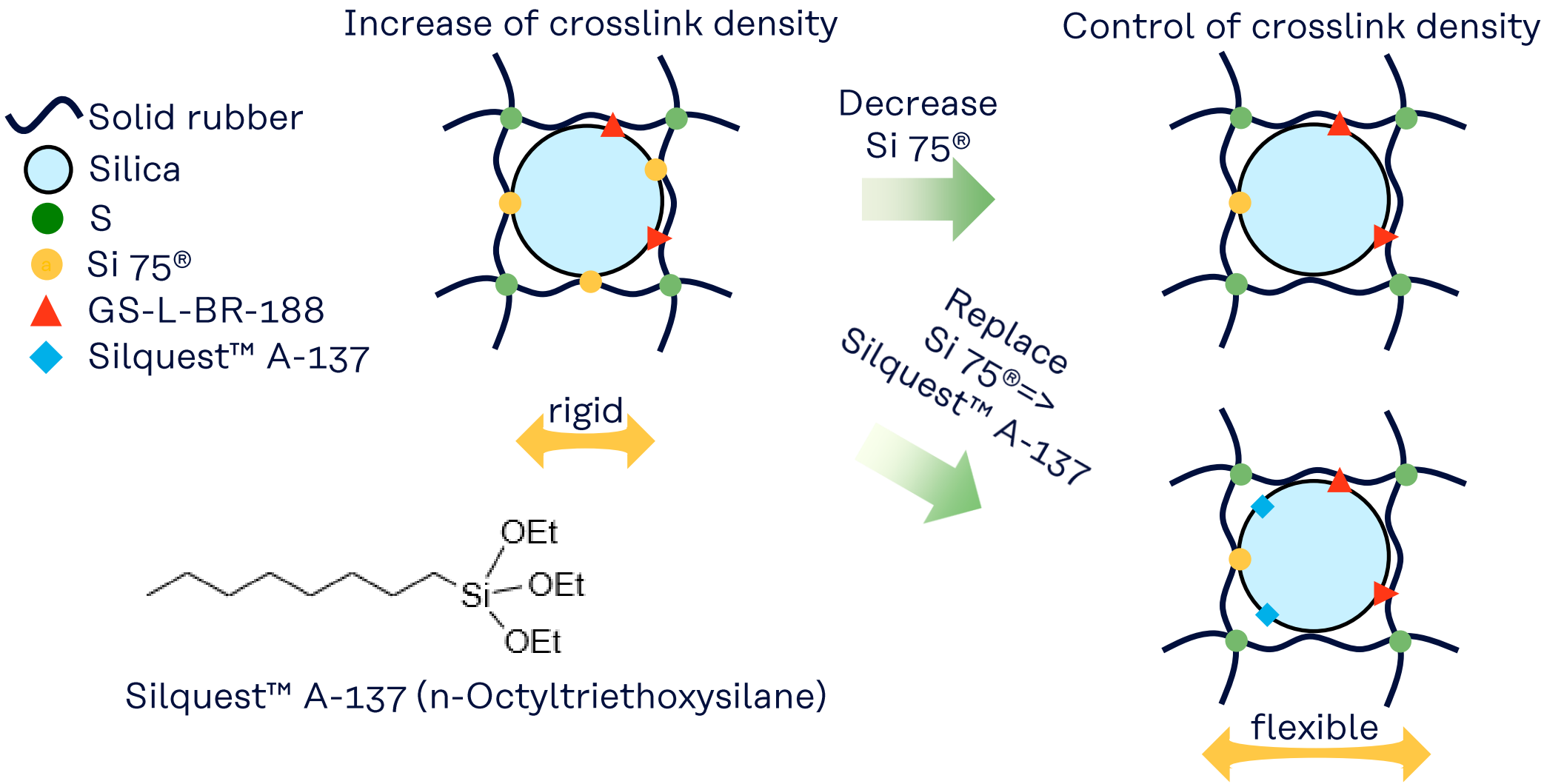
3) Hypothesis and how to improve Mechanical properties

Hypothesis for Mechanical properties



	Control	LBR	GS-L-BR-188
Swell (index)	100	119	96
Crosslink density	—	Low	High

How to improve Mechanical properties



Silquest™ A-137 (n-Octyltriethoxysilane)

Formulation & Mixing Conditions

	Control	Formulation		
No.	1	2	3	4*
f-SSBR	80	80	80	80
BR	20	20	20	20
Silica	100	100	100	100
Si 75®	8	8	4	4
Silquest™ A-137	—	—	—	4.6
TDAE	40	28	28	28
GS-L-BR-188	—	12	12	12
Chemicals	ZnO 3.0, Stearic acid 2.5, 6PPD 2.5, Wax 2.0			
Sulfur	S (oil extended) 1.9			
Accelerator	DPG 0.5, CBS 0.35, TBTD 1.5			

*Si(OEt)3 amount of silane coupling agent in No. 4 is same as No. 2

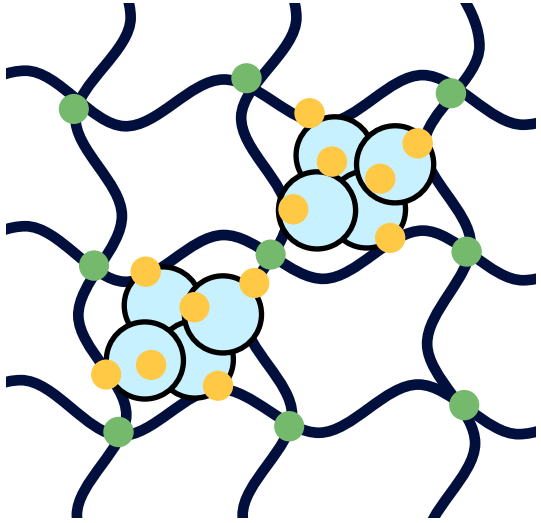
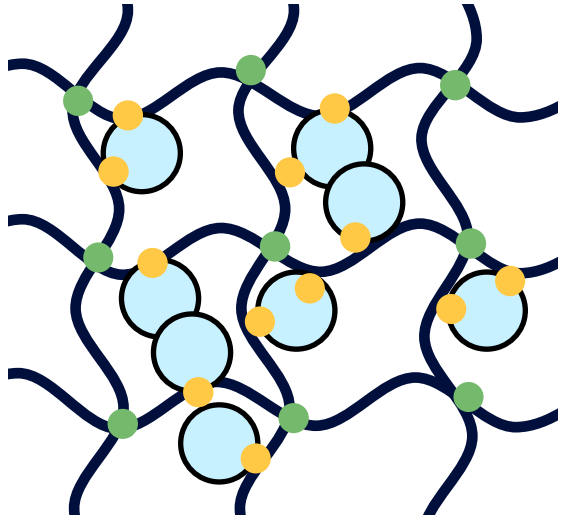
Mixing Conditions		
NP1	sec	Banbury-type mixer*
	0	Solid rubber (60°C)
	20	Silica, SCA, TDAE, LR, Chemicals
	180	Sweep
	360	Dump out (150-160°C)
NP2		Banbury-type mixer*
	0	1st mixed compound(90°C)
	240	Dump out (150-160°C)
FM		Banbury-type mixer*
	0	Compound, Sulfur, Accelerators (50°C)
	75	Dump out (90-100°C)

*MIXTRON® BB Mixer (by Kobe Steel, Ltd.)

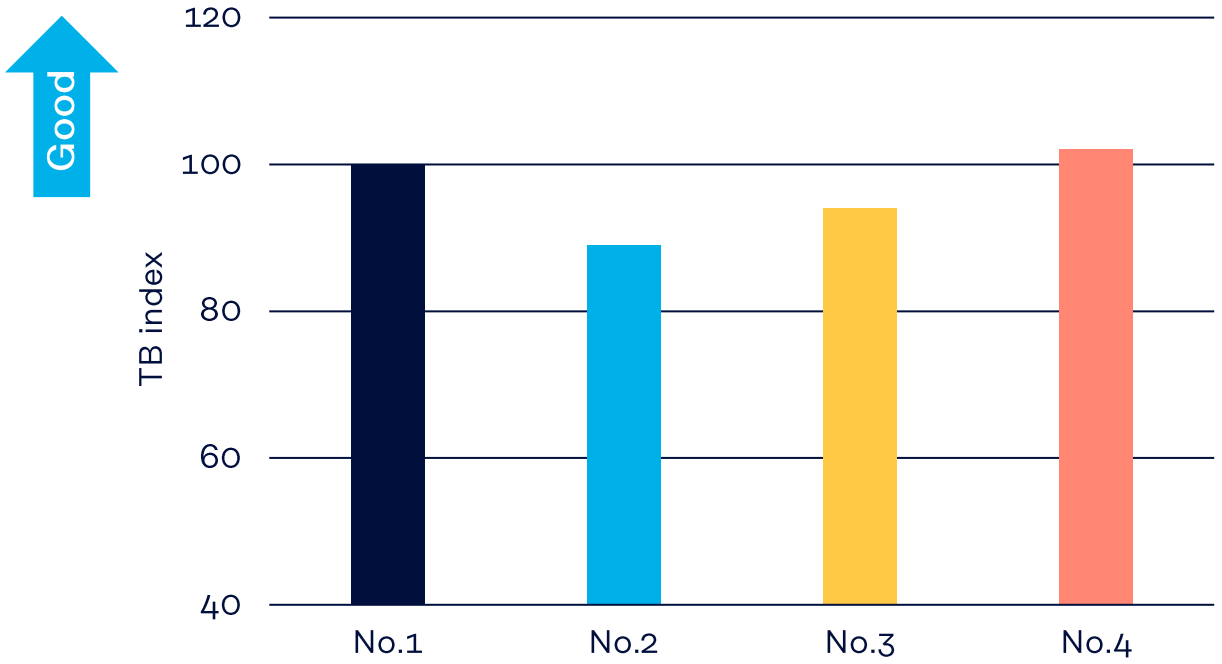
Summary of properties

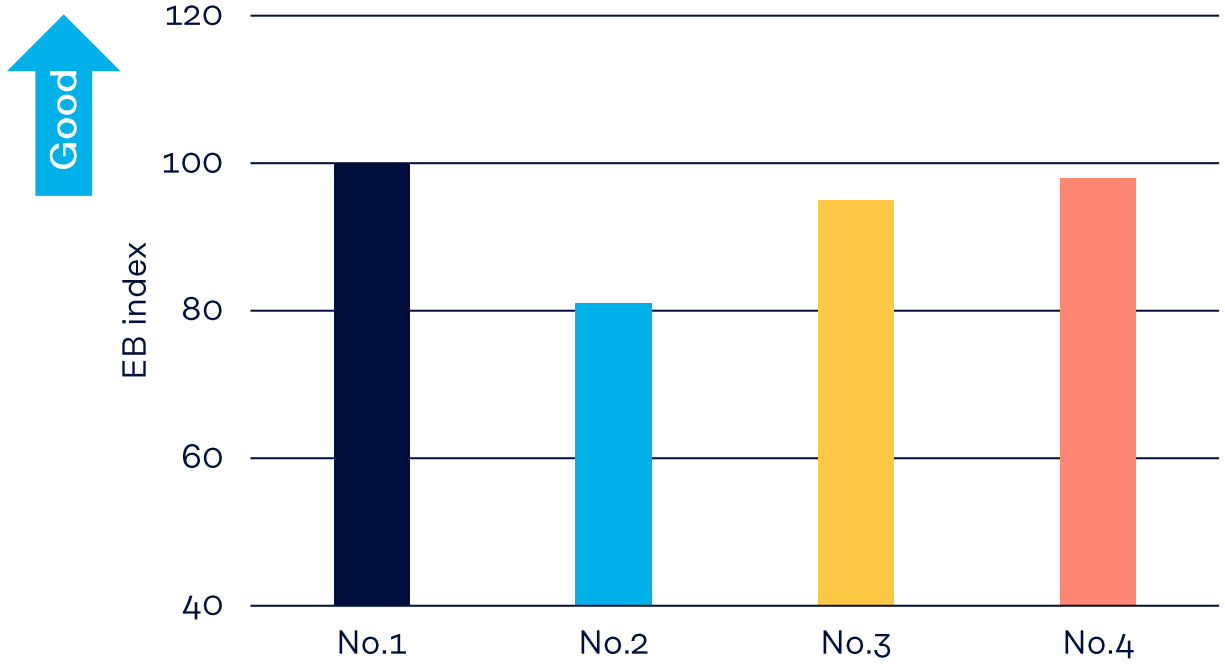
No.			1	2	3	4
			Control	GS-L-BR-188	GS-L-BR-188 Half Si 75®	GS-L-BR-188 Half Si 75® +Silquest™ A-137
Mooney Viscosity (ML1+4, @130°C)			40.3	45.2	59.0	42.7
Mechanical properties						
Hs		Type A	60	61	55	57
EB		(%)	415	335	395	405
TB		(MPa)	20.2	17.9	19	20.7
M100		(MPa)	2.26	2.87	2.09	2.24
M300		(MPa)	12.6	15.7	11.7	12.6
Tear strength		(kN/m)	47.0	46.5	44.4	50.1
DMA (Dynamic Mechanical Analysis)						
E'	0°C	(MPa)	9.43	8.16	7.3	6.88
	25°C	(MPa)	5.12	5.42	4.83	4.61
	60°C	(MPa)	3.73	4.18	3.75	3.63
tanδ	0°C	(-)	0.638	0.431	0.427	0.42
	25°C	(-)	0.298	0.216	0.207	0.203
	60°C	(-)	0.157	0.138	0.14	0.139
Payne effect (0.5%E'-5.0%E')		index	100	59	43	38
Friction coefficient on Wet @20°C		index	100	100	101	101
Swell		index	100	96	111	105

Silica dispersion and crosslink density

	Half Si 75®	Half Si 75® + Silquest™ A-137
		
Silica dispersion	Bad	Good
Crosslink density	Low	High

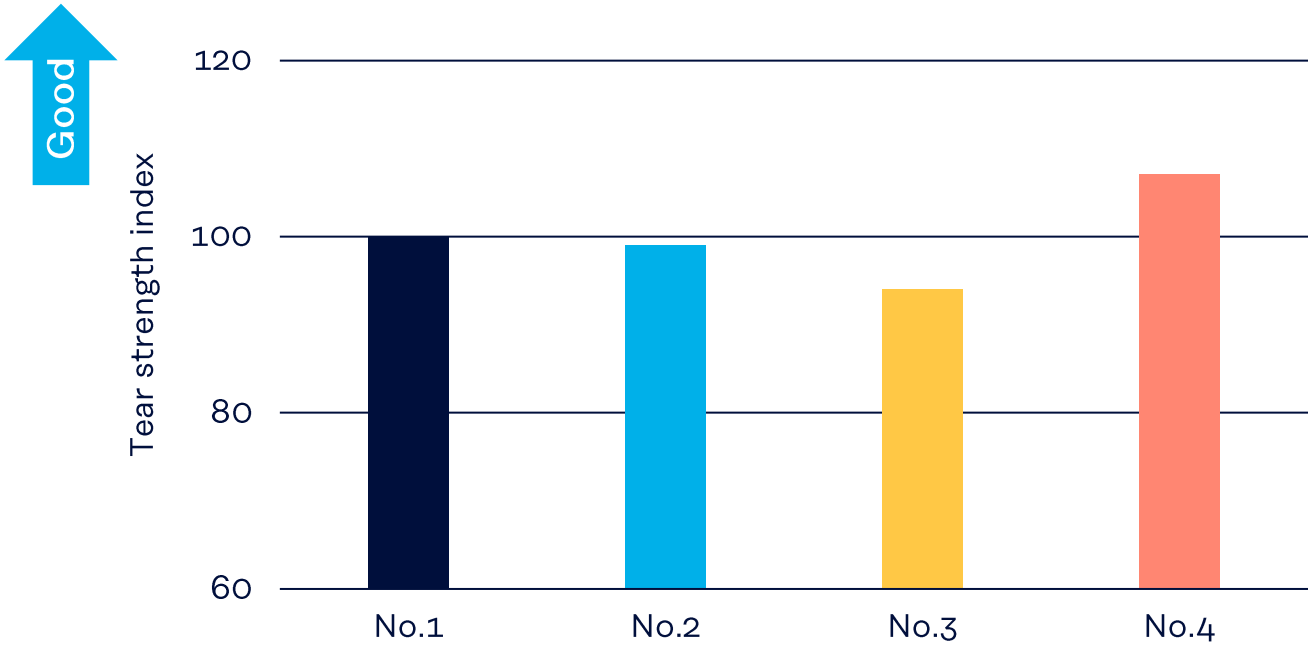
Tensile Strength and Elongation at Break





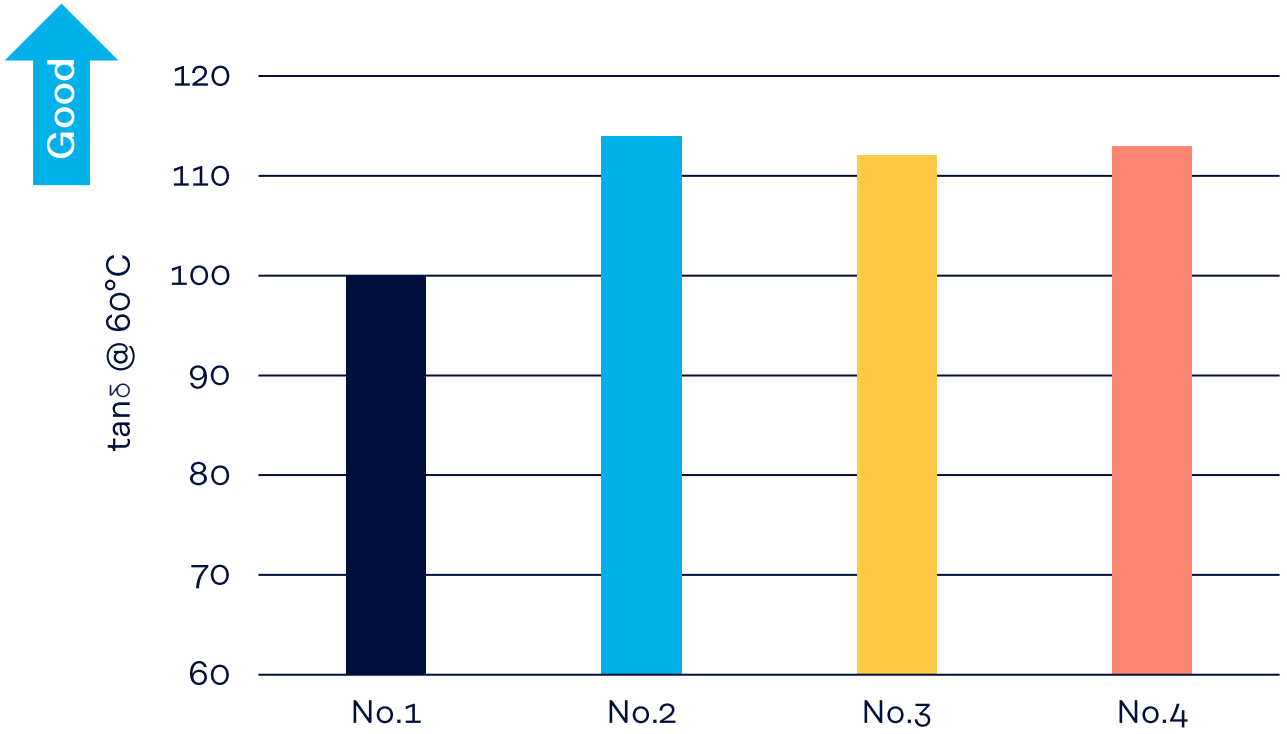
- Mechanical properties are improved by controlling crosslink density.

Tear Strength



- Tear strength is improved by controlling crosslink density.

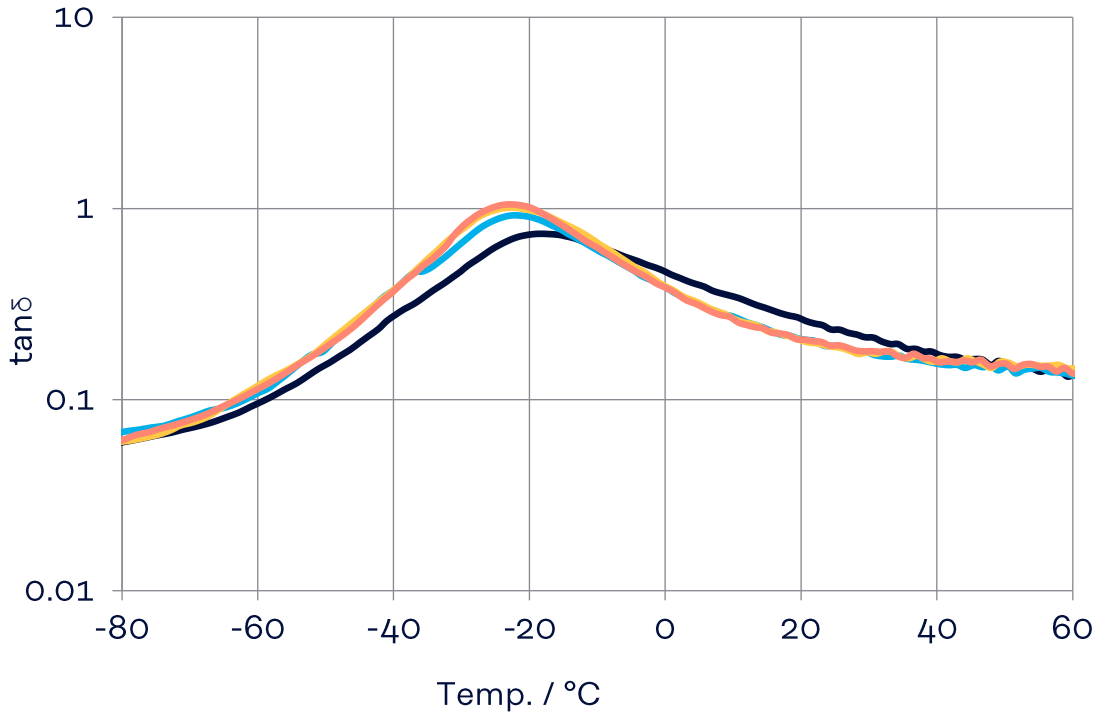
DMA [Dynamic Mechanical Analysis]

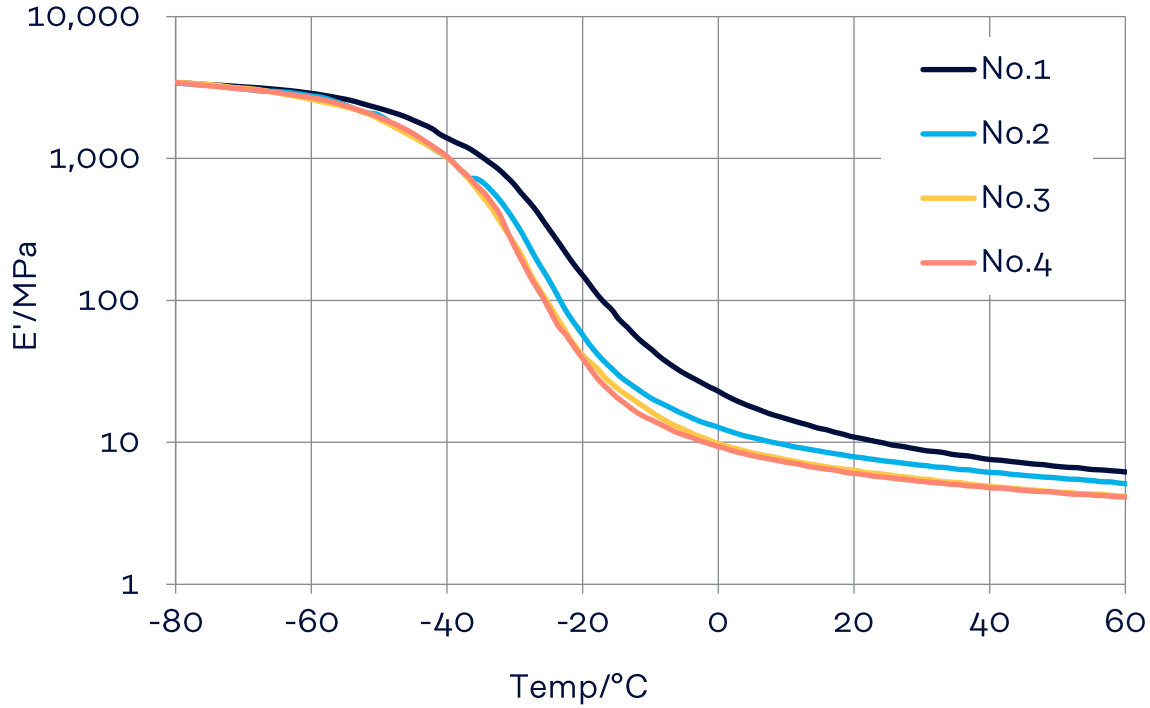


- Maintain RR even if controlling crosslink density.

DMA [Dynamic Mechanical Analysis]

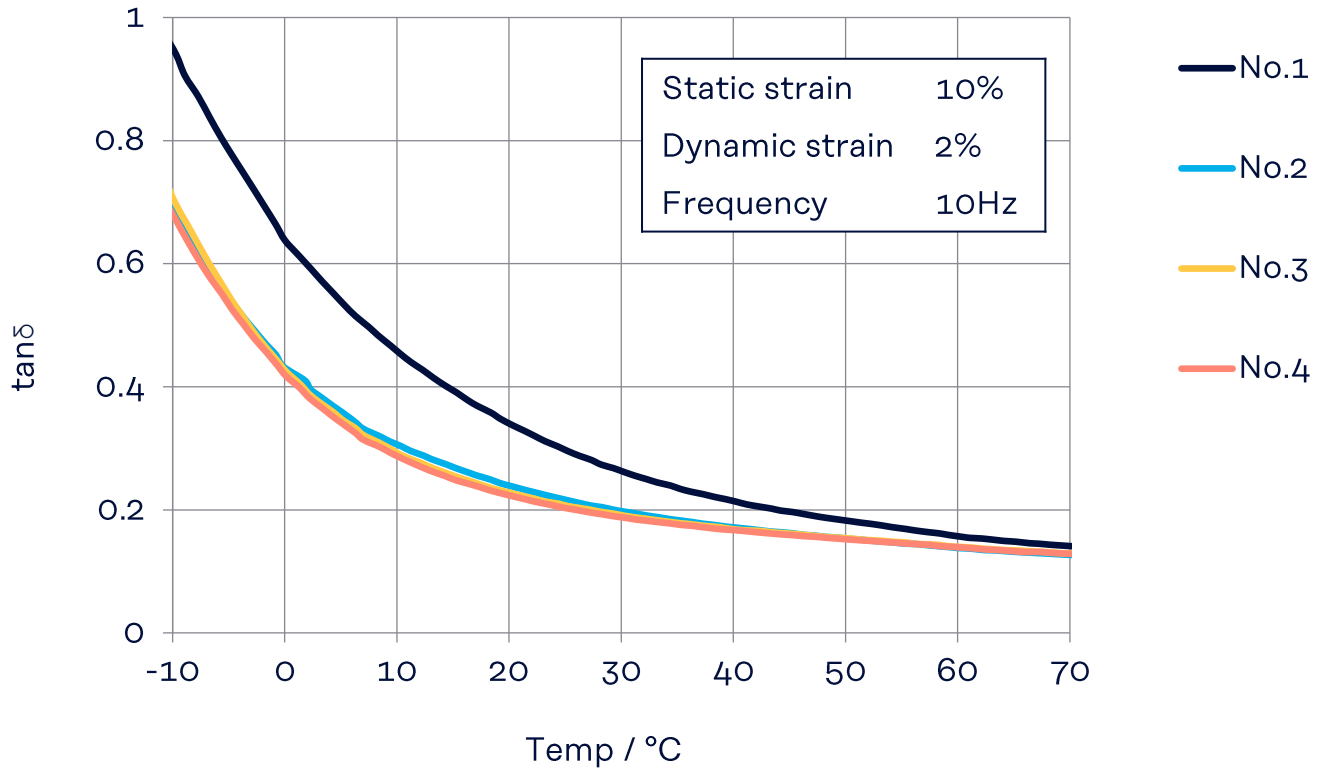
Static strain	0.5%
Dynamic strain	0.1%
Frequency	10Hz





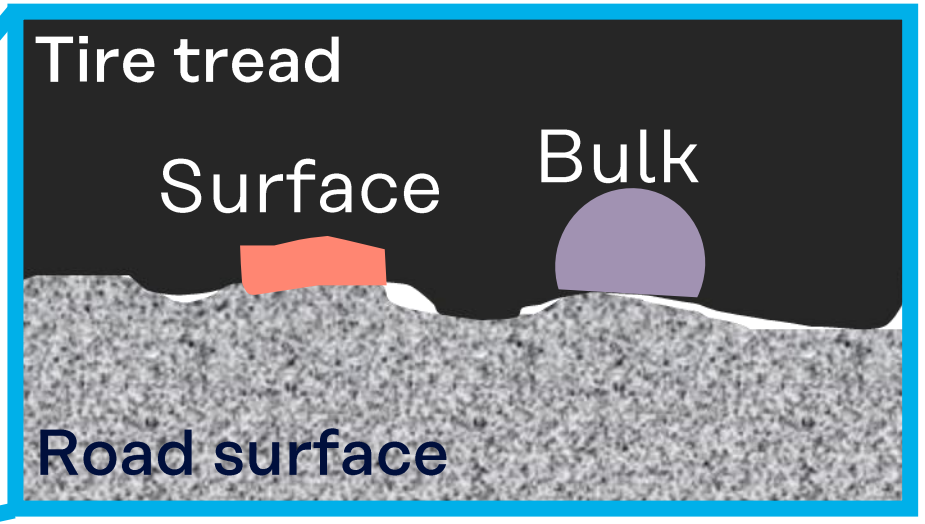
- No change was observed in viscoelasticity.

DMA [Dynamic Mechanical Analysis]



- No change was observed in viscoelasticity.
- Since tanδ at 0°C is low, there is a concern about decrease in wet grip.

Background



Grip = Adhesion + Hysteresis

In general, tanδ at 0°C is used as wet grip index.
However actual wet grip is improved by multiple factors.
Effect of Liquid Rubbers to Adhesion factor was evaluated.

Measurement of Friction Performance

RTM friction tester

Size:
Diameter 80mm
Width 16mm

Road surface :
Ice, Safety walk, Asphalt

Mode :
Ice, Wet, Dry grip, RR

RTM measures grip performance comprised of Adhesion & Hysteresis.

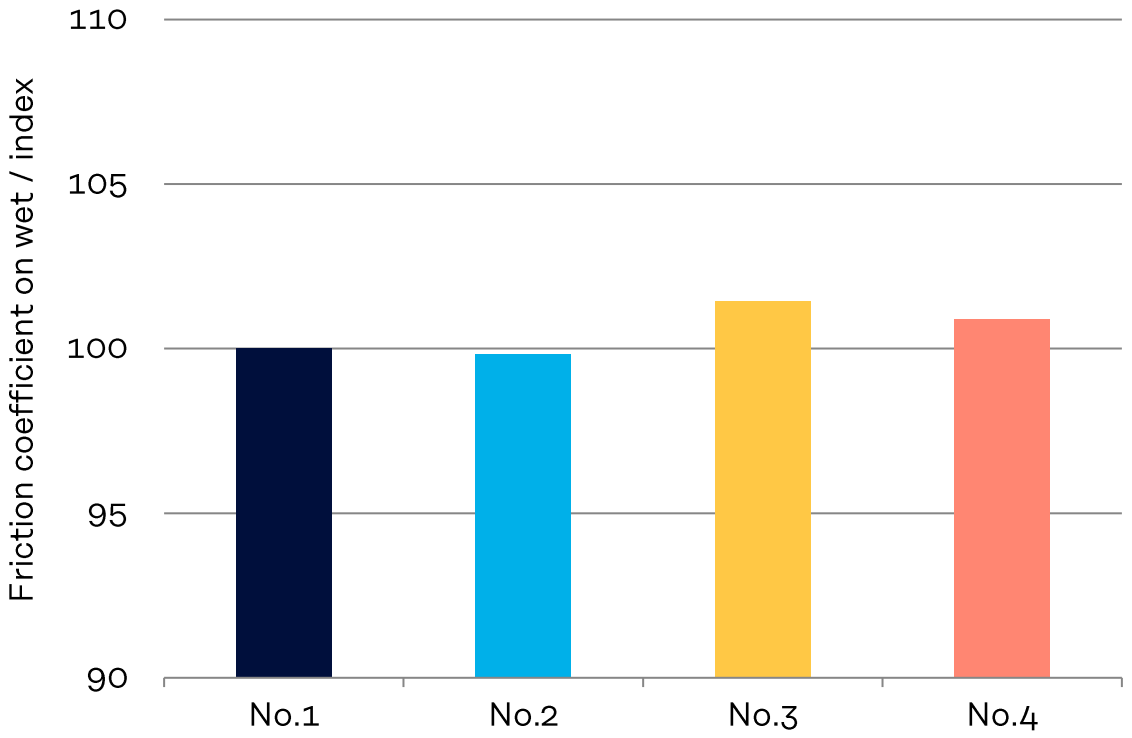
Friction Coefficient on Wet Surface

Measured friction performance by RTM friction tester

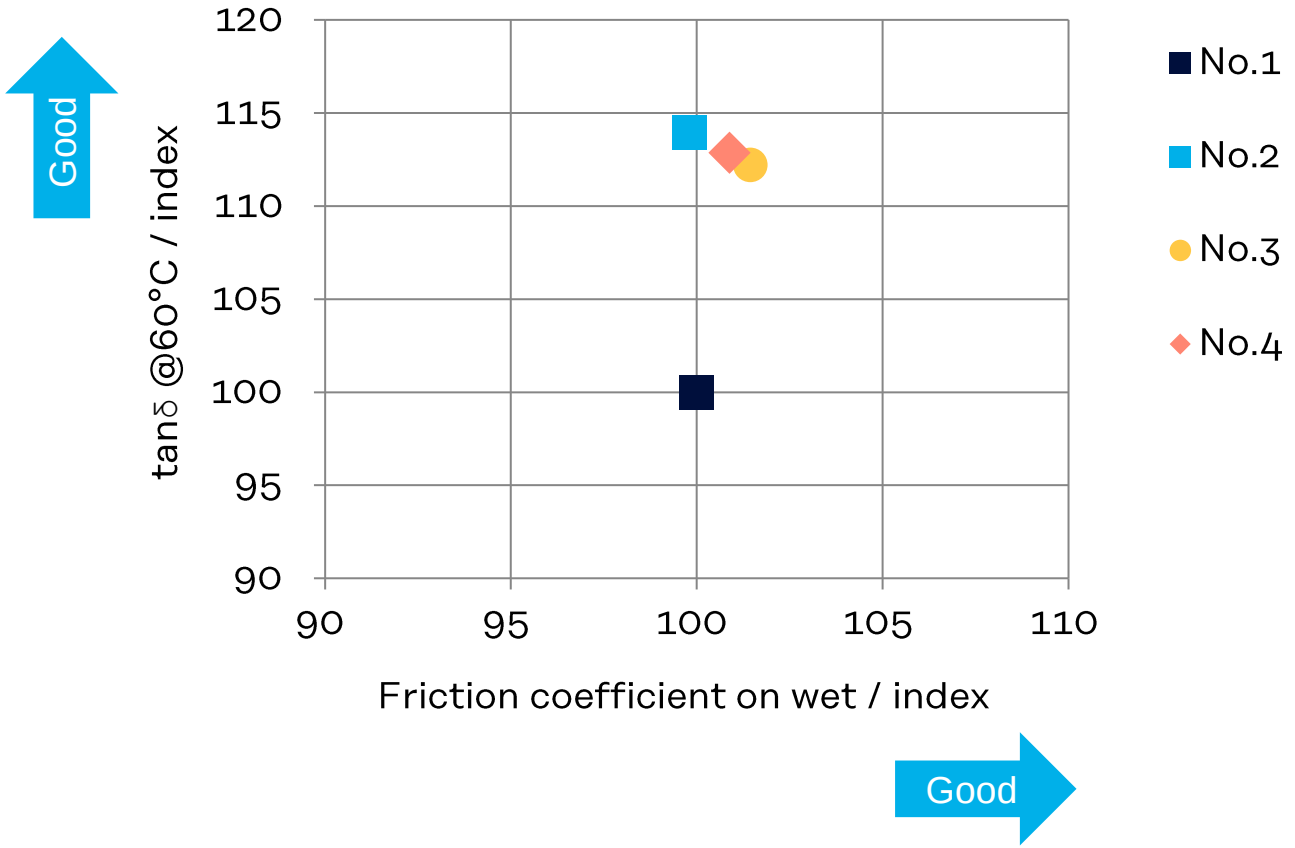
Temp	20°C
Water temp	20°C
Initial circumferential speed	30km/h
Load	50N
Slip rate	0 to 40%

Friction coefficient : Peak top value was read

- GS-L-BR-188 shows similar wet grip to control despite its low tanδ.

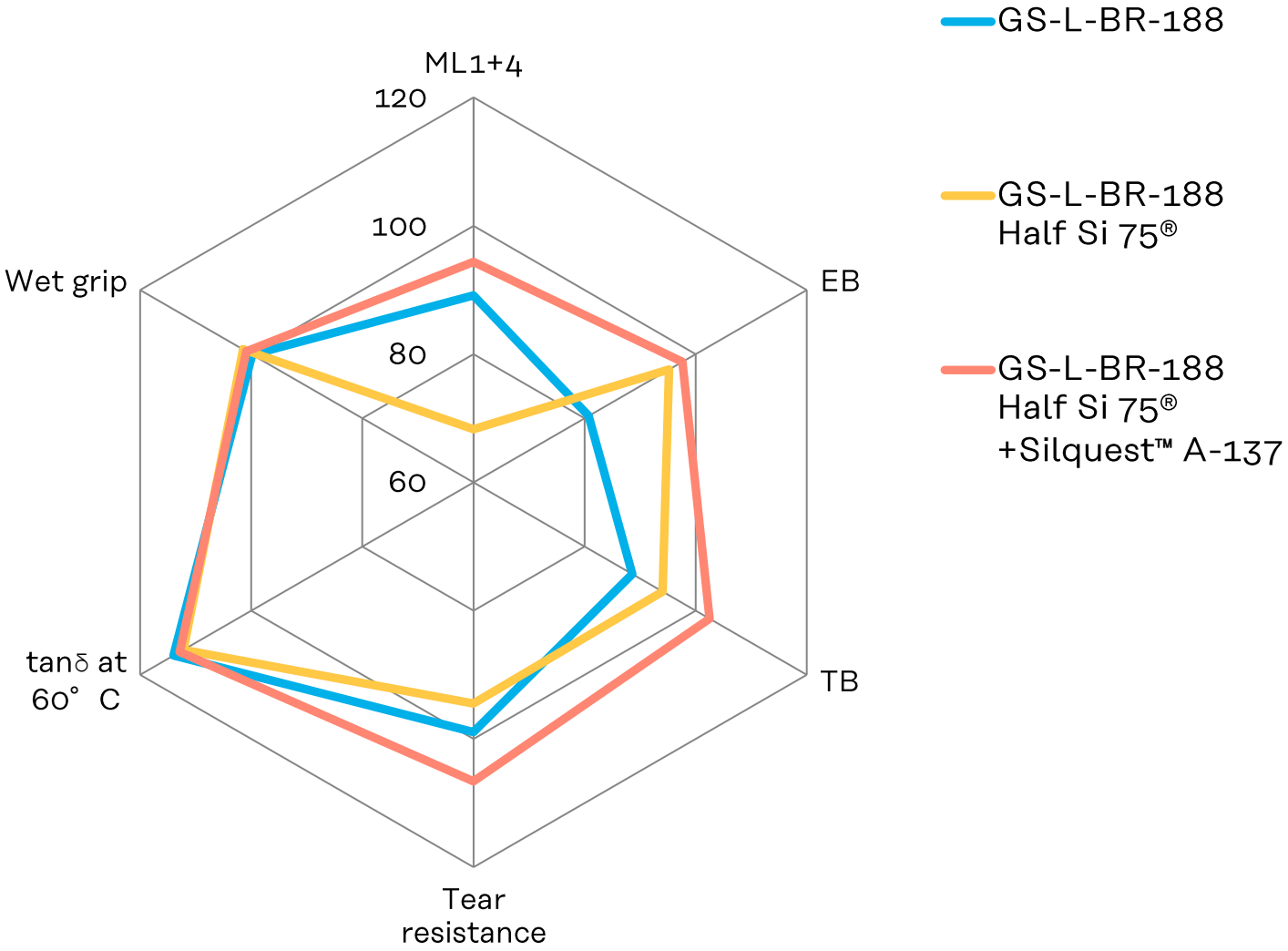


Friction on Wet vs tanδ @60°C



- GS-L-BR-188 shows good rolling resistance/wet grip balance.

Test results



Summary

GS-L-BR

- Improve dispersibility of silica
- Crosslinkable with base rubber
- Improve silica-polymer interaction

GS-L-BR-188

- Enhanced interaction between silica-polymer is good for rolling resistance
- Good Wet/RR balance from RTM evaluation
- Adjusting SCA improve mechanical properties by improving silica dispersion and interaction between silica and rubber

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For medical, health care and food contact applications, please contact your Kuraray representative for specific recommendations. Even so, users must conduct their own assessment, revisions, registrations as well rely in their own technical and legal judgment to establish the safety and efficacy of their compound and/or end product with KURARAY LIQUID RUBBAR for any application. KURARAY LIQUID RUBBER should not be used in any devices or materials intended for implantation in the human body. Nothing contained herein constitutes a license to practice under any patent and it should not be construed as an inducement to infringe any patent and the user is advised to take appropriate steps to be sure that any proposed use of the product will not result in patent infringement.

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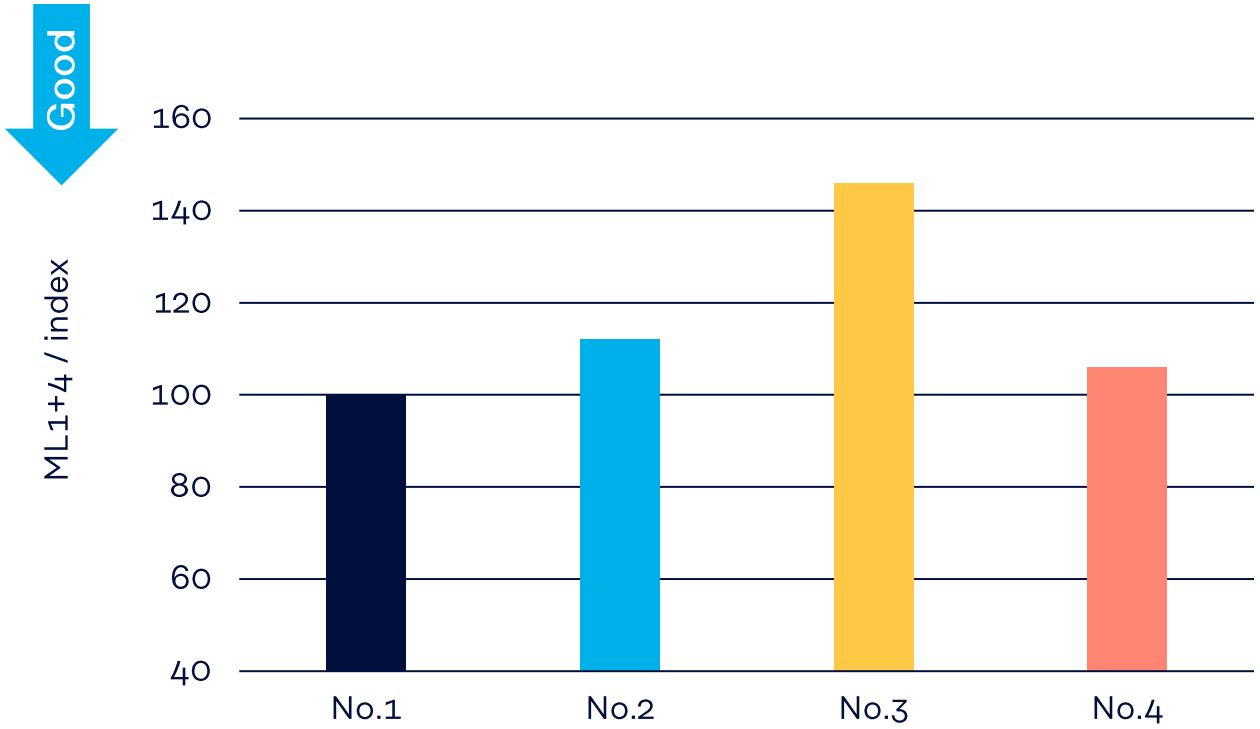
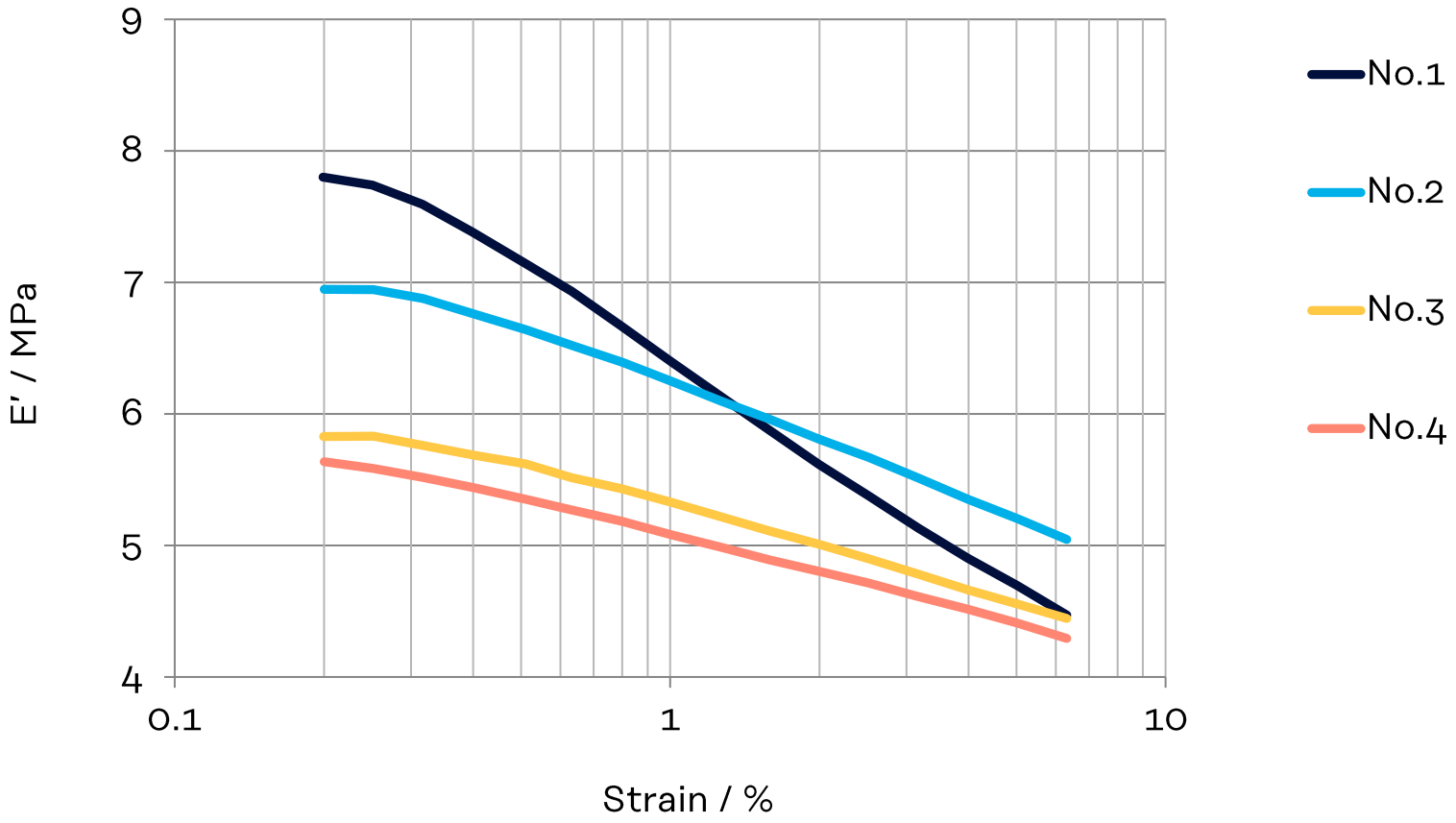
APPENDIX

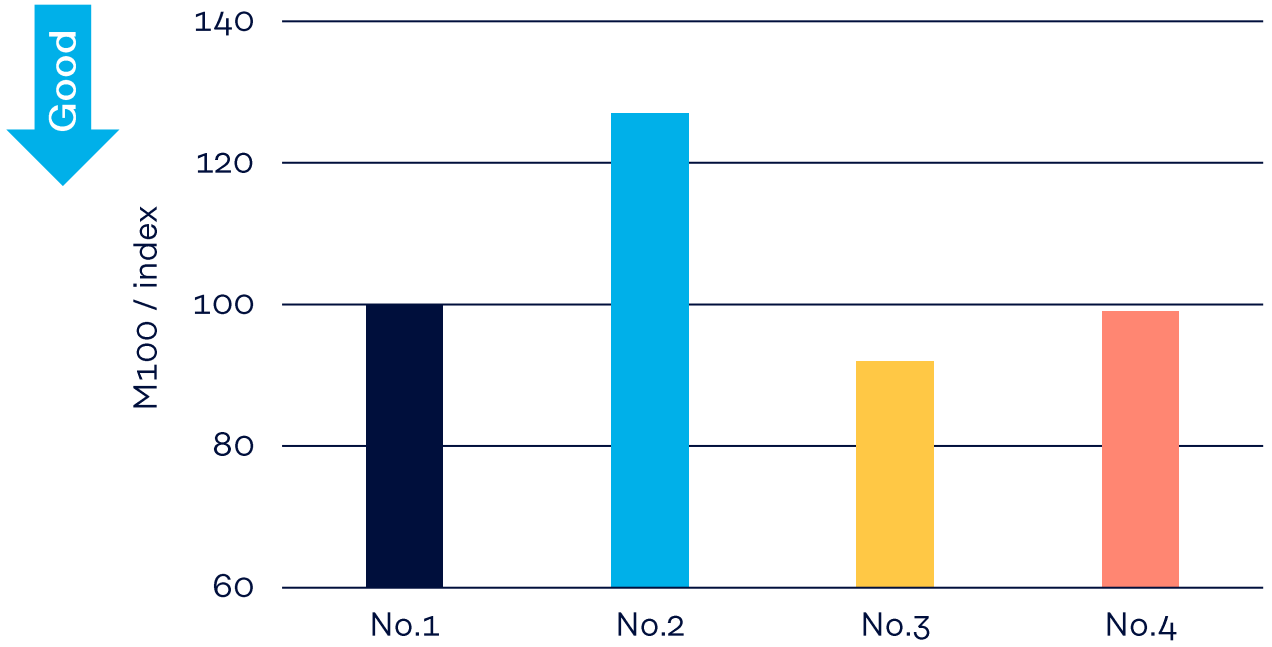
Mooney Viscosity



Payne effect

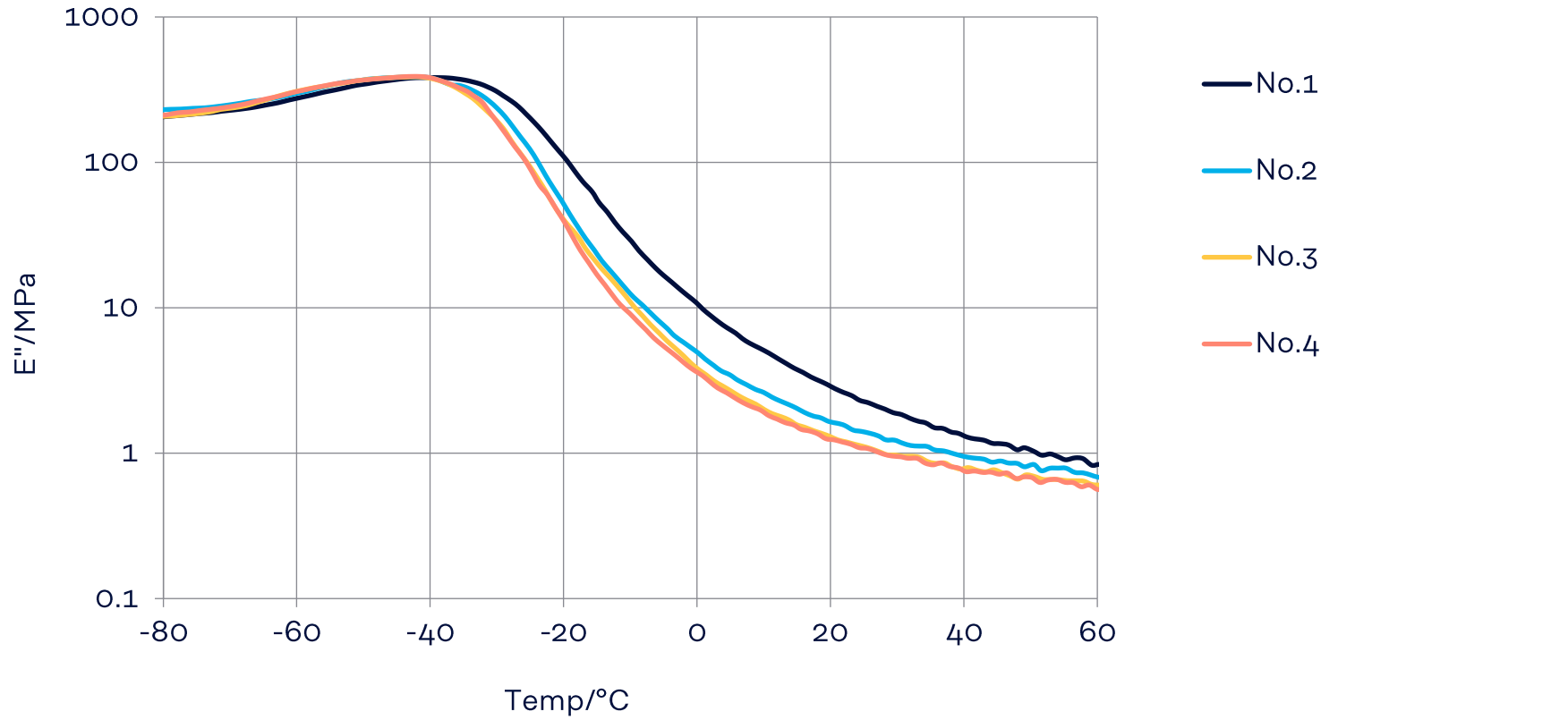


Analysis of Modulus100 [M100] for silica-silica interaction

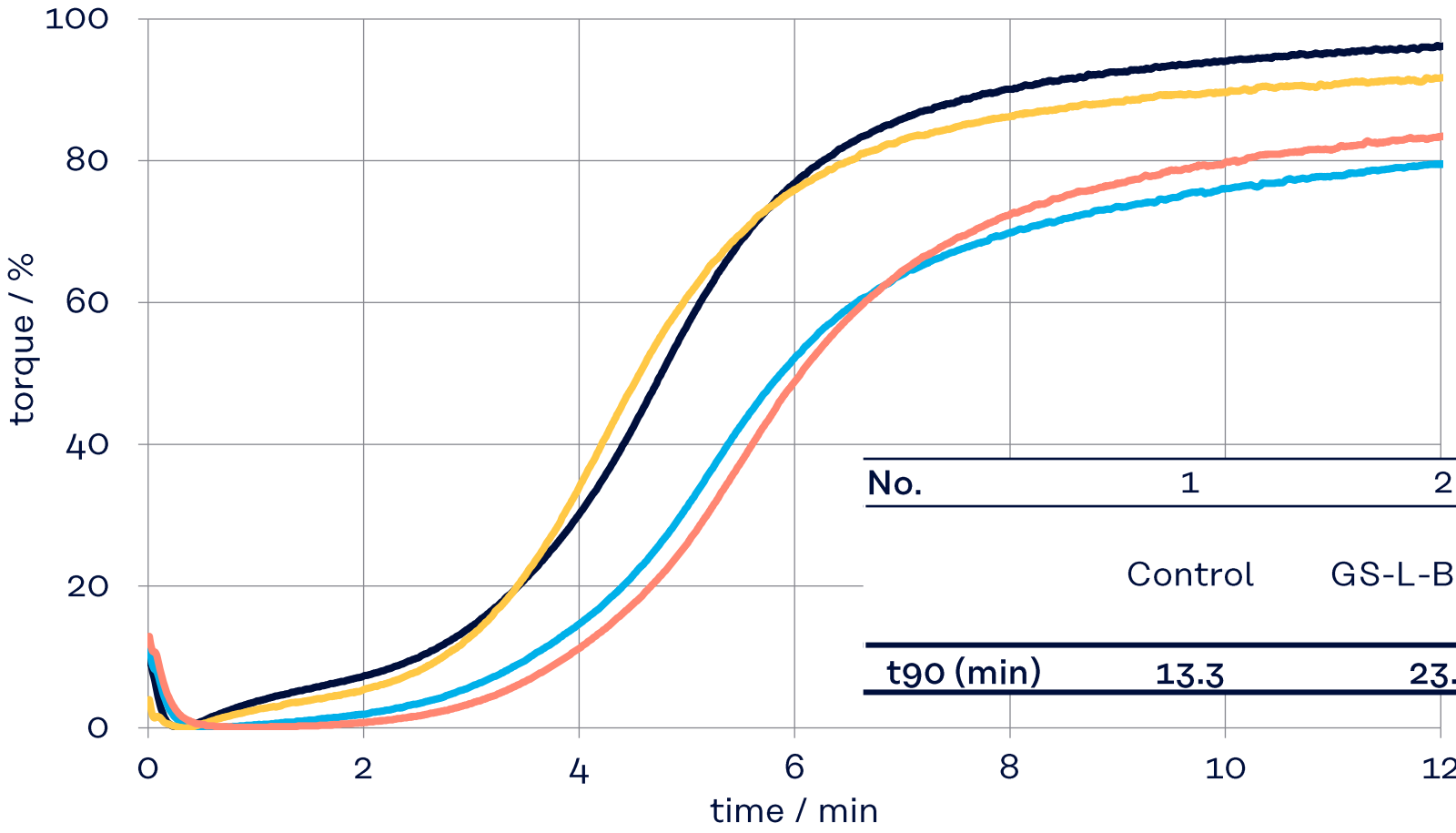


DMA [Dynamic Mechanical Analysis]

Static strain	0.5%
Dynamic strain	0.1%
Frequency	10hz



Vulcanization speed



No.	1	2	3	4
	Control	GS-L-BR-188	GS-L-BR-188 Half Si 75®	GS-L-BR-188 Half Si 75® +Silquest™ A-137
t90 (min)	**13.3**	**23.7**	**10.2**	**19.5**

Silane modified LBR (GS-L-BR)

Grade Name [Development Code]	Structure	Functional Group	Mw	Tg (°C)	Number of functional group / chain	Viscosity at 38°C (Pa • s)
GS-L-BR-114 [SB-005]	Polybutadiene /Graft silane	Triethoxysilane	6,000	-50	2	6
GS-L-BR-188 [SB-006]	Polybutadiene /Graft silane	Triethoxysilane	38,000	-88	4	124

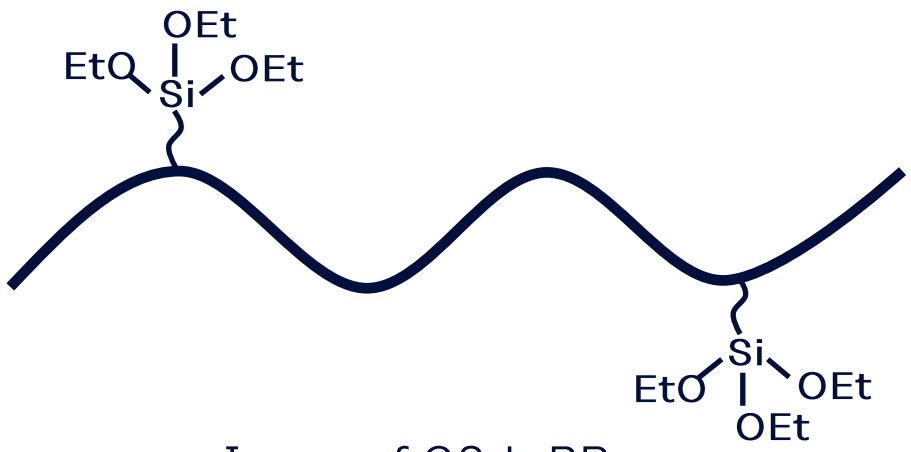


Image of GS-L-BR

- High reactivity with silica
- Improve dispersibility of silica
- Crosslinkable with base rubber

Formulation & Mixing Conditions

	Control	Formulation			
No.	1	2	3	4*	5*
f-SSBR	80	80	80	80	80
BR	20	20	20	20	20
Silica	100	100	100	100	100
Si 75®	8	8	4	4	4
Silquest™ A-137	—	—	—	4.6	4.6
TDAE	40	28	28	28	28
GS-L-BR-188	—	12	12	12	12
GS-L-BR-114	—	—	—	—	6
Chemicals	ZnO 3.0, Stearic acid 2.5 6PPD 2.5, Wax 2.0				
Sulfur	S (oil extended) 1.9, DPG 0.5				
Accelerator	CBS 0.35, TBTD 1.5				

*Si(OEt)3 amount of silane coupling agent in No. 4 and No. 5 is same as No. 1 and No. 2.

Mixing Conditions		
NP1	sec	Banbury-type mixer*
	0	Solid rubber (60°C)
	20	Silica, SCA, TDAE, LR, Chemicals
	180	Sweep
	360	Dump out (150-160°C)
NP2		Banbury-type mixer*
	0	1st mixed compound(90°C)
	240	Dump out (150-160°C)
FM		Banbury-type mixer*
	0	Compound, Sulfur, Accelerators (50°C)
	75	Dump out (90-100°C)

*MIXTRON® BB Mixer (by Kobe Steel, Ltd.)

Summary of properties

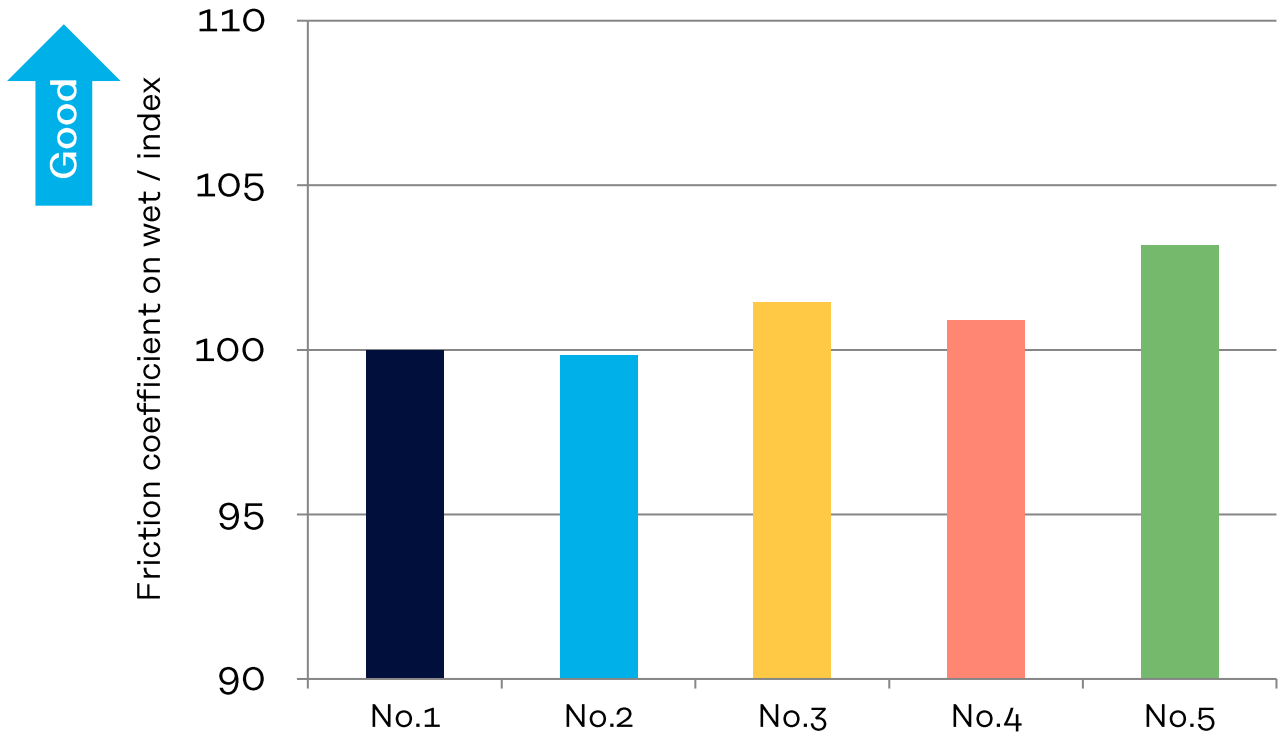
No.			1	2	3	4	5
			Control	GS-L-BR-188	GS-L-BR-188 Half Si 75®	GS-L-BR-188 Half Si 75® +Silquest™ A-137	GS-L-BR-188/114 Half Si 75® +Silquest™ A-137
Mooney Viscosity (ML1+4, @130°C)			40.3	45.2	59.0	42.7	38.5
Mechanical properties							
Hs		Type A	60	61	55	57	59
EB		(%)	415	335	395	405	390
TB		(MPa)	20.2	17.9	19	20.7	18.2
M100		(MPa)	2.26	2.87	2.09	2.24	2.35
M300		(MPa)	12.6	15.7	11.7	12.6	12.5
Tear strength		(kN/m)	47.0	46.5	44.4	50.1	50.2
DMA (Dynamic **Mechanical** Analysis)							
E'	0°C	(MPa)	9.43	8.16	7.3	6.88	7.98
	25°C	(MPa)	5.12	5.42	4.83	4.61	5.18
	60°C	(MPa)	3.73	4.18	3.75	3.63	3.97
tanδ	0°C	(-)	0.638	0.431	0.427	0.420	0.443
	25°C	(-)	0.298	0.216	0.207	0.203	0.220
	60°C	(-)	0.157	0.138	0.14	0.139	0.145
Payne effect (0.5%E'-5.0%E')		index	100	59	43	38	52
Friction coefficient on Wet @20°C		index	100	100	101	101	103
Swell		index	100	96	111	105	105

Friction Coefficient on Wet Surface

Measured friction performance by RTM friction tester

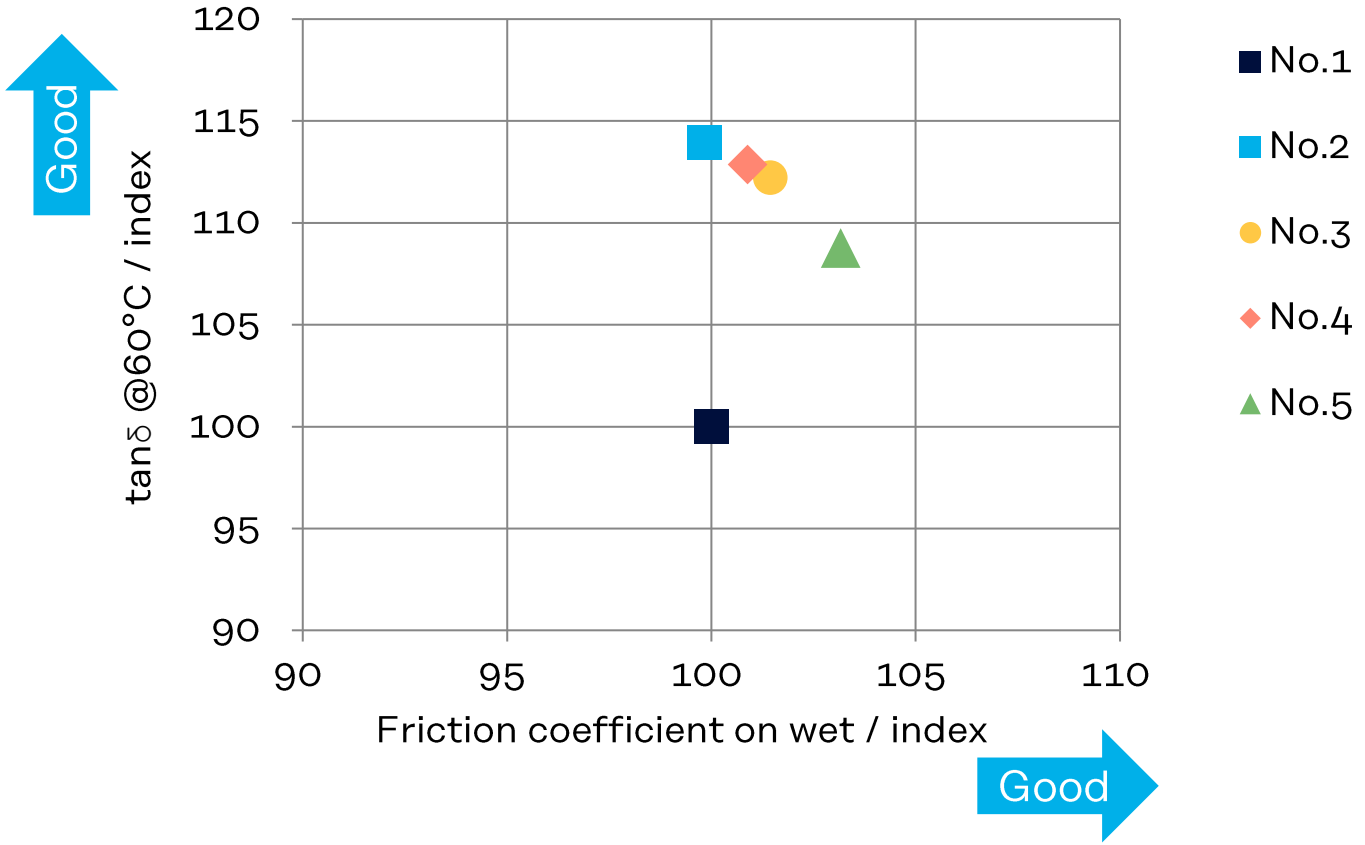
Temp	20°C
Water temp	20°C
Initial circumferential speed	30km/h
Load	50N
Slip rate	0 to 40%

Friction coefficient : Peak top value was read



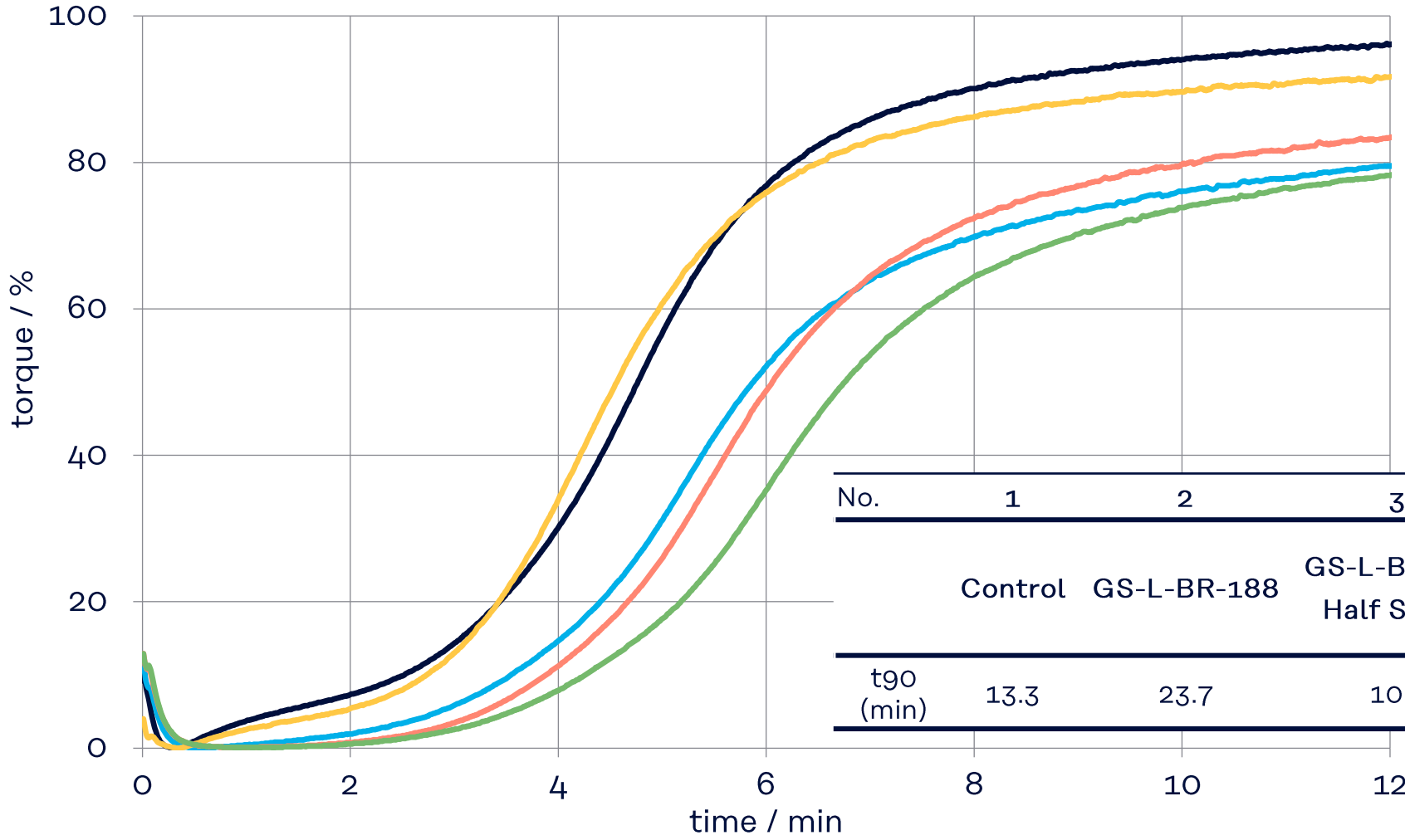
- GS-L-BR-188 shows similar wet grip to control despite its low tanδ.

Friction on Wet vs tanδ @60°C



- GS-L-BR-188 shows good RR/Wet balance.

Vulcanization speed



No.	1	2	3	4	5
	Control	GS-L-BR-188	GS-L-BR-188 Half Si 75®	GS-L-BR-188 Half Si 75® +Silquest™ A-137	GS-L-BR-188/114 Half Si 75® +Silquest™ A-137
t90 (min)	13.3	23.7	10.2	19.5	25.3

Raw material

Material	Product Name	Manufacturer	Note
Styrene-butadiene rubber	JSR HPR355	JSR Corporation	Styrene content: 27% Mooney Vis. @100°C: 44 Tg: -24°C
Butadiene Rubber	JSR BR01	JSR Corporation	Cis content: 95% Mooney Vis. @100°C: 45
Silica	ULTRASIL® 7000GR	Evonik Industries AG	Specific surface area (N2) 175 m^2/g
Silane Coupling Agent	Si 75®	Evonik Industries AG	
Silane Coupling Agent	Silquest™ A-137	Momentive Performance Materials Inc	
TDAE	VIVATEC 500	H&R GmbH Co. KGaA	