NO. RRL10-007

Technical Insight of KURARAY LIQUID RUBBER

Accelerate vulcanization of SBR / Silica formulation with GS-L-BR

Elastomer R&D Department
Elastomer Division

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Agenda

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

1) Silane modified LBR (GS-L-BR) and slow vulcanization

2) Add ZnO and Stearic acid later when mixing

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

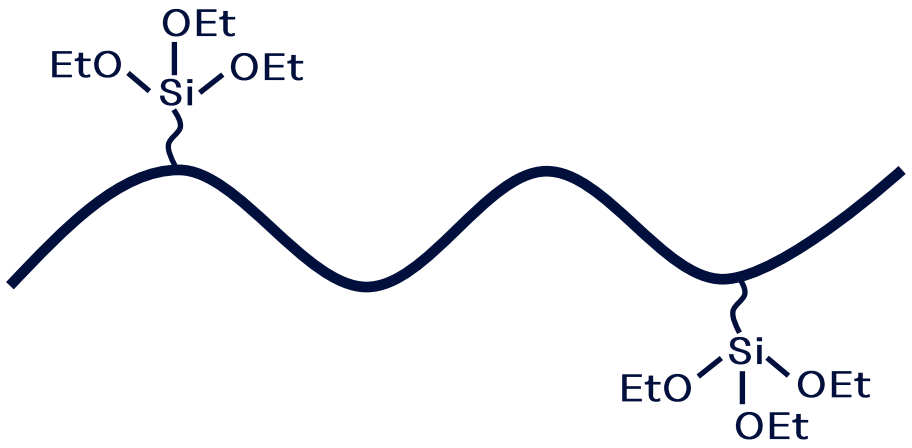


Image of GS-L-BR

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

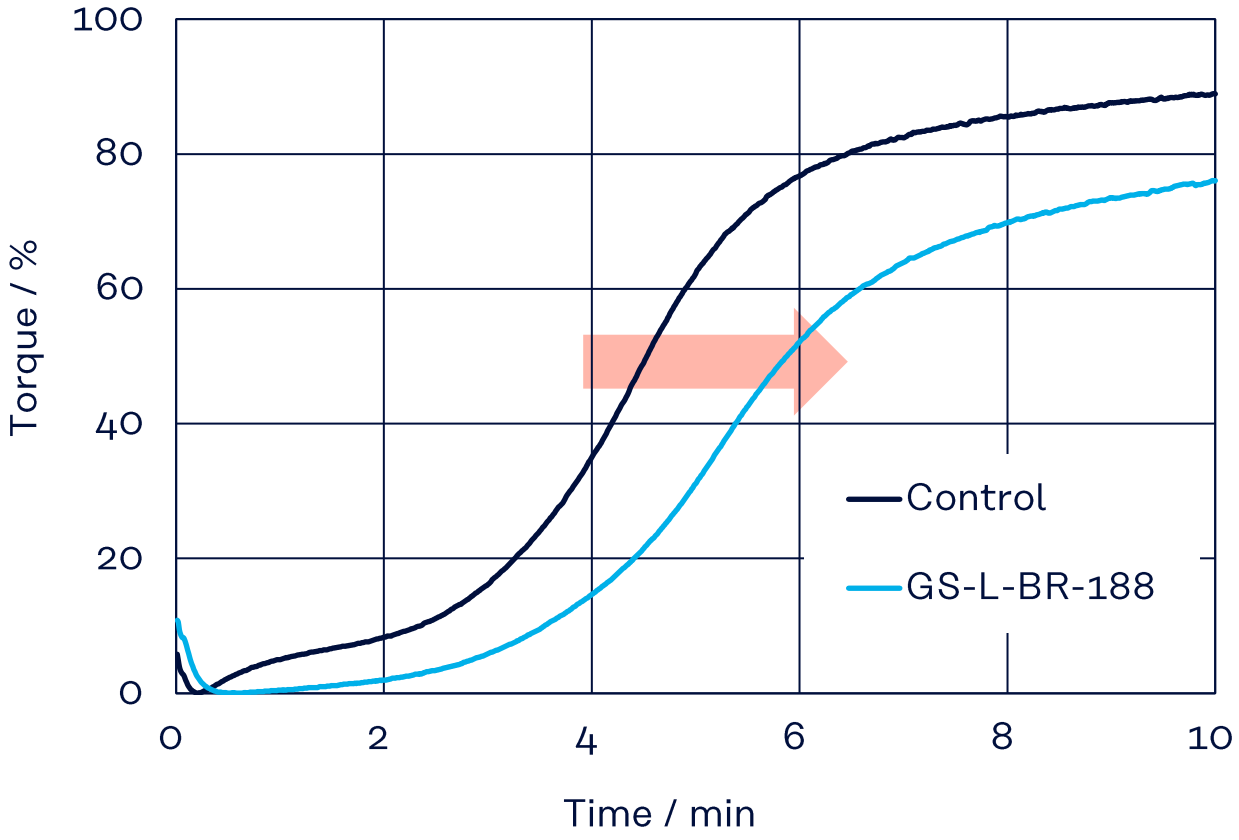
Formulation & Mixing Conditions

	Control	GS-L-BR-188
f-SSBR	80	80
BR	20	20
Silica	100	100
SCA	8	8
TDAE	28	28
GS-L-BR-188	-	12
Chemicals	ZnO 3.0, Stearic acid 2.5, 6PPD 2.5, Wax 2.0	
Sulfur	S 1.5	
Accelerator	DPG 0.5, CBS 0.35, TBTD 1.5	

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 made by Kobe Steel, Ltd.

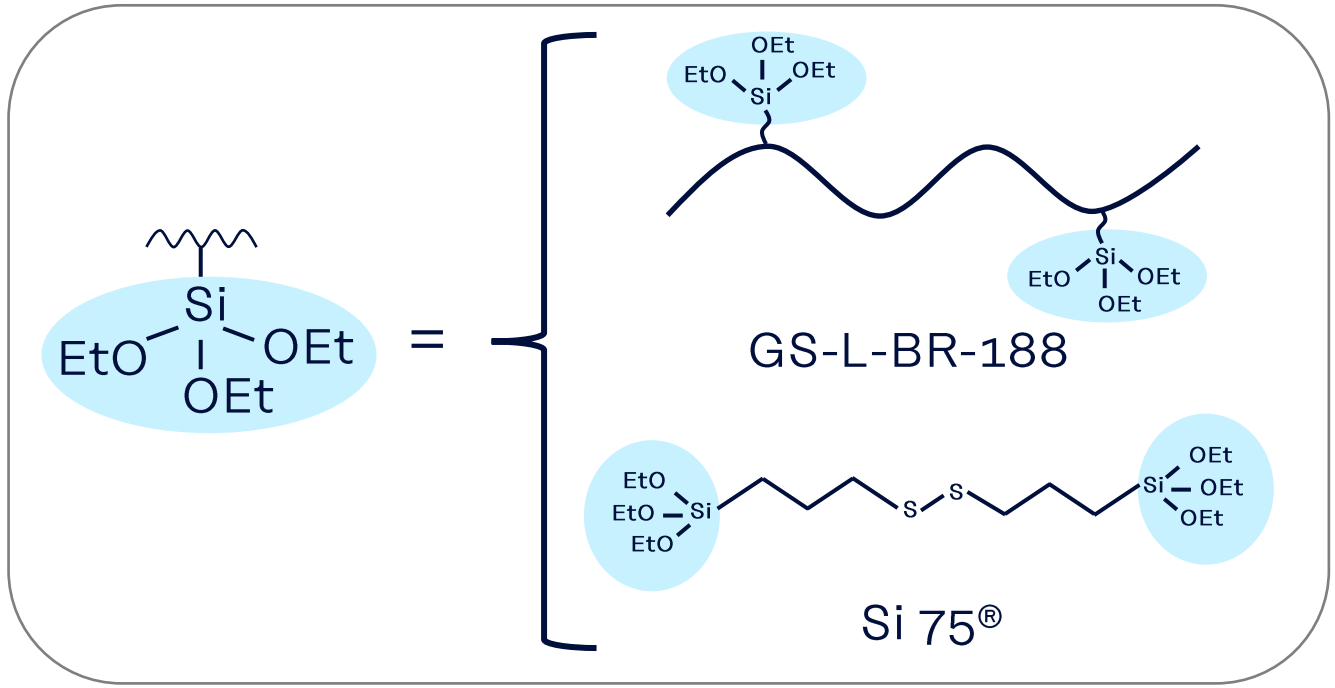
Vulcanization speed with GS-L-BR



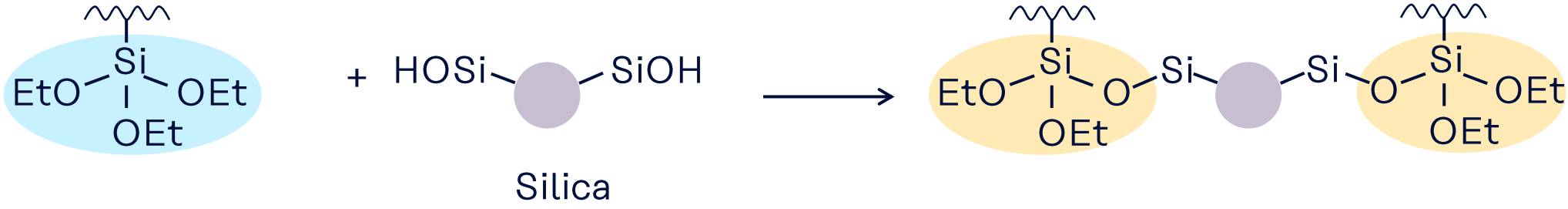
	1	2
	control	GS-L-BR-188
t90 (min)	11.8	23.7

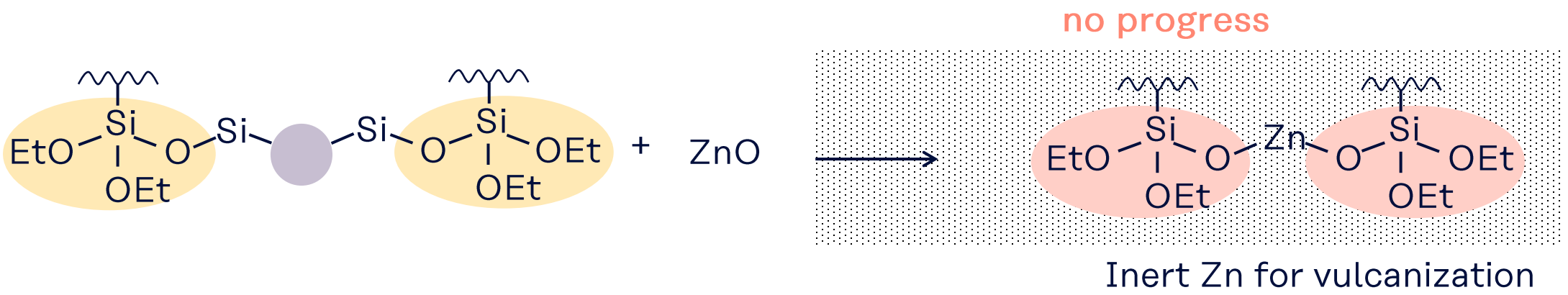
Mechanism of slower vulcanization

Inert Zn for vulcanization



How to prevent inert Zn formation





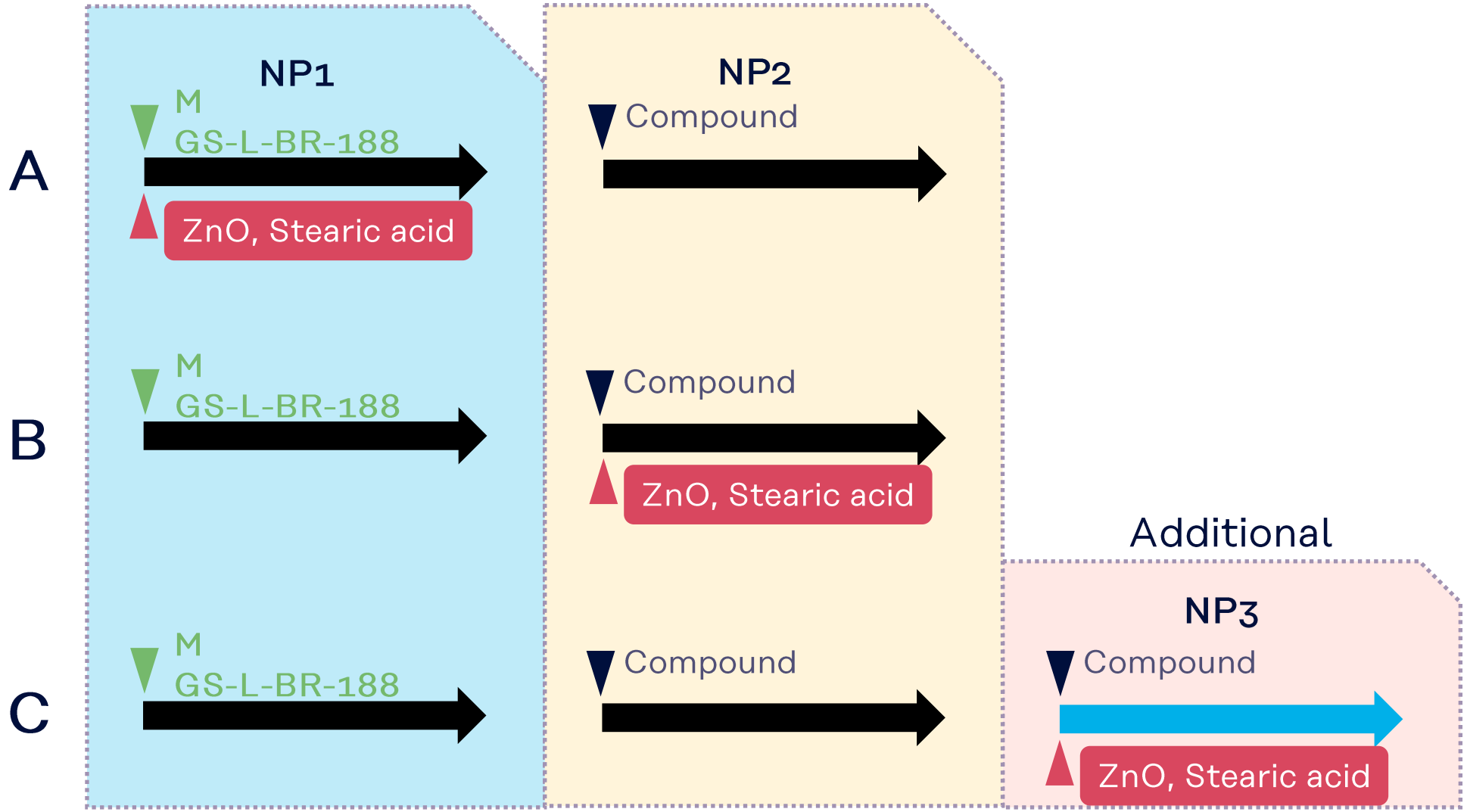
Agenda

1) Silane modified LBR (GS-L-BR) and slow vulcanization

2) Add ZnO and Stearic acid later when mixing

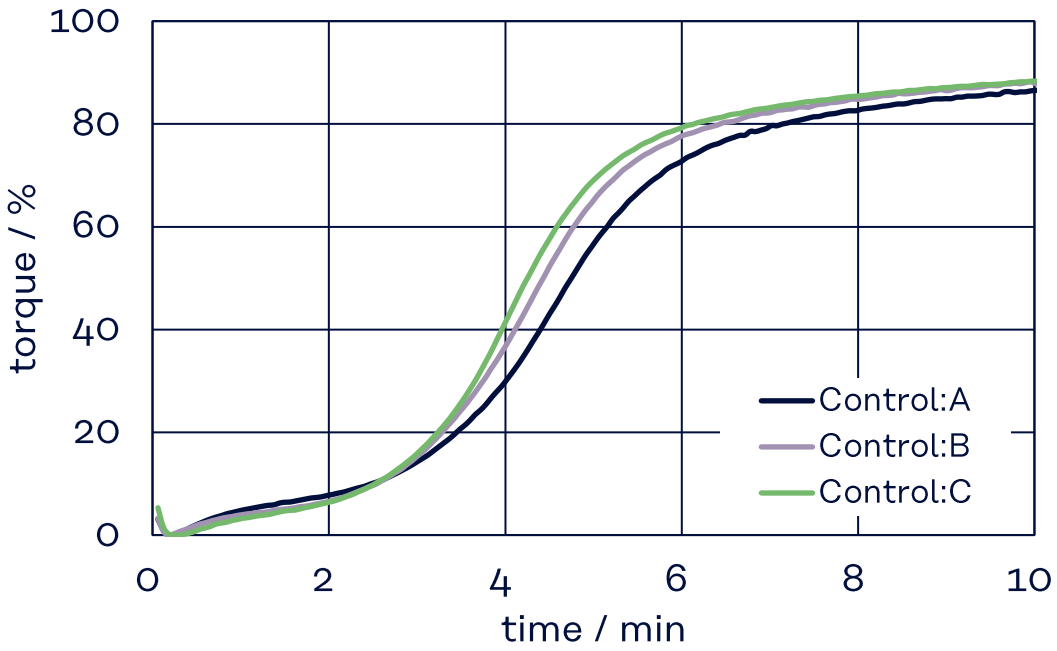
Mixing conditions

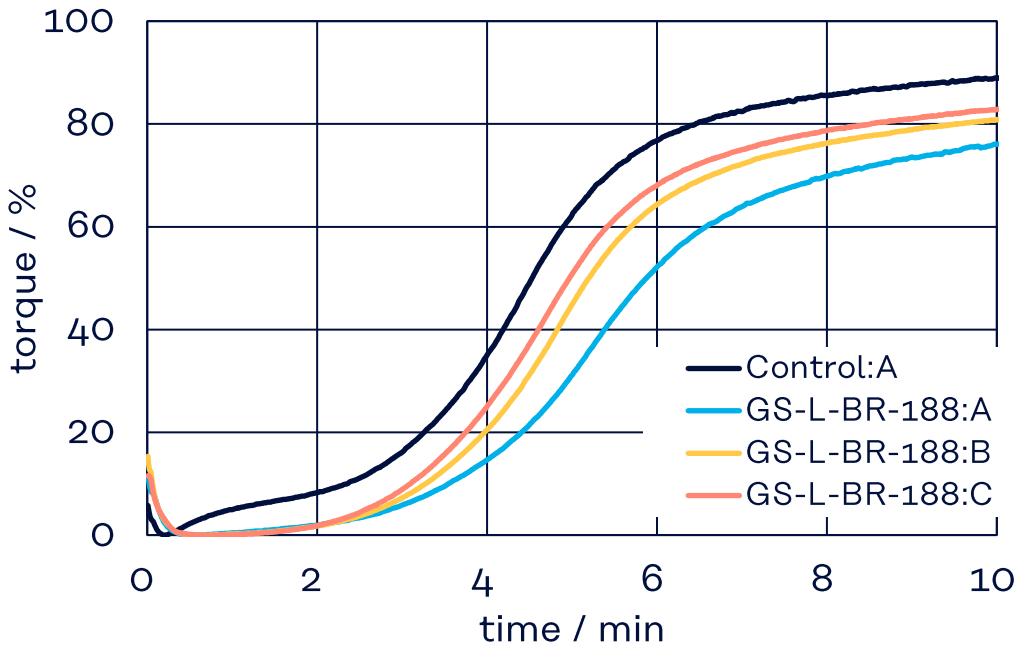
M = Solid rubber
Silica , Si 75®
TDAE , Chemicals



Vulcanization speed

	NP1	NP2	NP3
A	ZnO Stearic acid		
B		ZnO Stearic acid	
C			ZnO Stearic acid





	1	2	3
	control		
Mixing condition	A	B	C
t90 (index)	100	88	88

	1	2	3	4
	control	GS-L-BR-188		
Mixing condition	A	A	B	C
t90 (index)	100	201	171	155

- Adding ZnO and Stearic acid later accelerates vulcanization of SBR / Silica formulation with GS-L-BR.

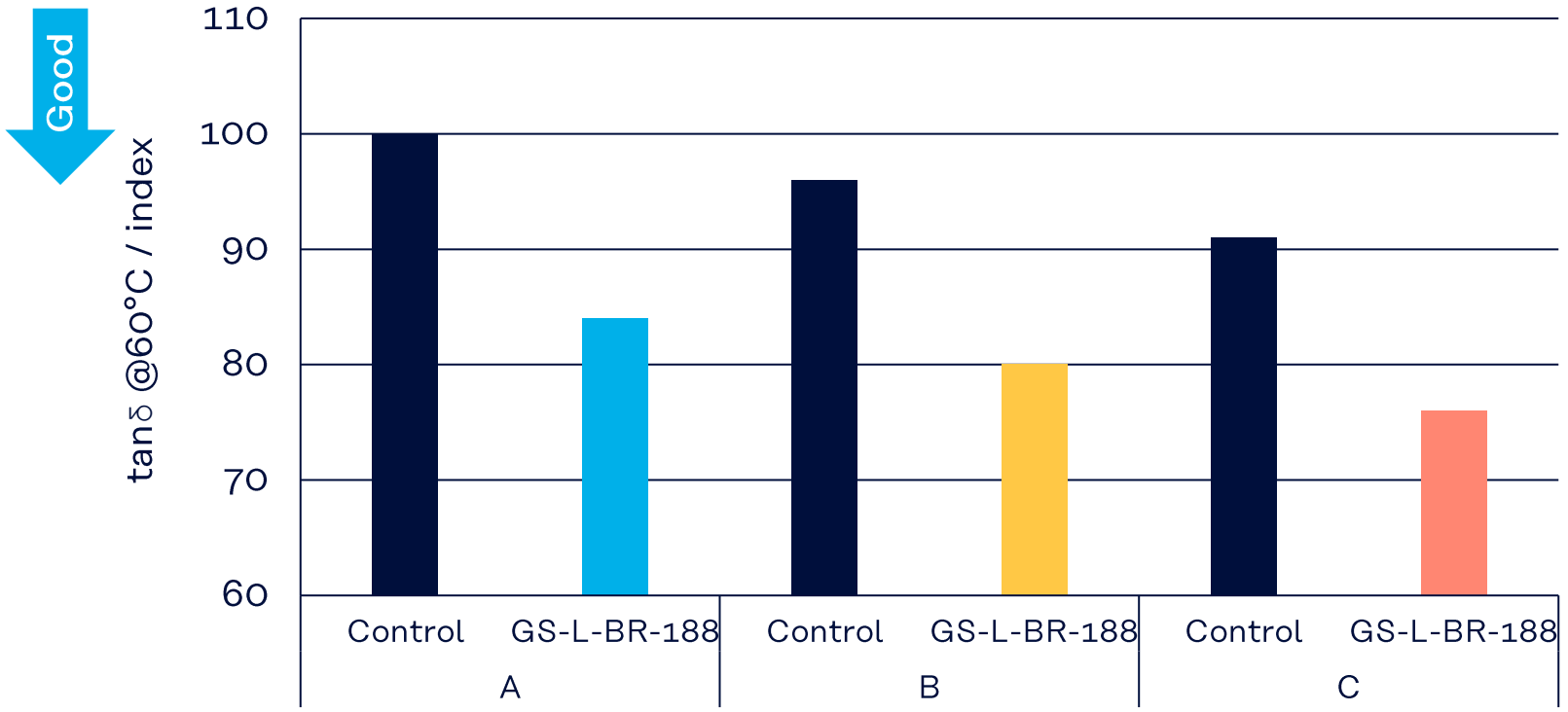
Summary of Properties

	NP1	NP2	NP3
A	ZnO Stearic acid		
B		ZnO Stearic acid	
C			ZnO Stearic acid

			1	2	3	4	5	6
				Control			GS-L-BR-188	
Mixing condition			A	B	C	A	B	C
Mooney Viscosity (ML1+4, 130°C)			100	107	109	79	85	95
Curelastometer (t90, 160°C)		(min)	100	88	88	201	171	155
Mechanical properties								
Hs		Type A	100	100	91	88	86	84
EB		(%)	100	94	97	94	83	87
TB		(MPa)	100	92	100	89	80	83
Payne effect (E'0.5%-5%)		index	100	90	65	36	27	23
DMA (Dynamic Mechanical Analysis)								
E'	0°C	(MPa)	100	91	83	59	57	56
	25°C	(MPa)	100	91	82	73	69	69
	60°C	(MPa)	100	92	82	78	75	76
tanδ	0°C	(-)	100	100	97	66	66	65
	25°C	(-)	100	96	89	67	63	60
	60°C	(-)	100	96	91	84	80	76
Abrasion / FPS, 5%		index	100	102	123	129	142	146
Friction coefficient on wet / RTM, 20°C		index	100	101	97	97	101	101

tanδ at 60°C

	NP1	NP2	NP3
A	ZnO Stearic acid		
B		ZnO Stearic acid	
C			ZnO Stearic acid

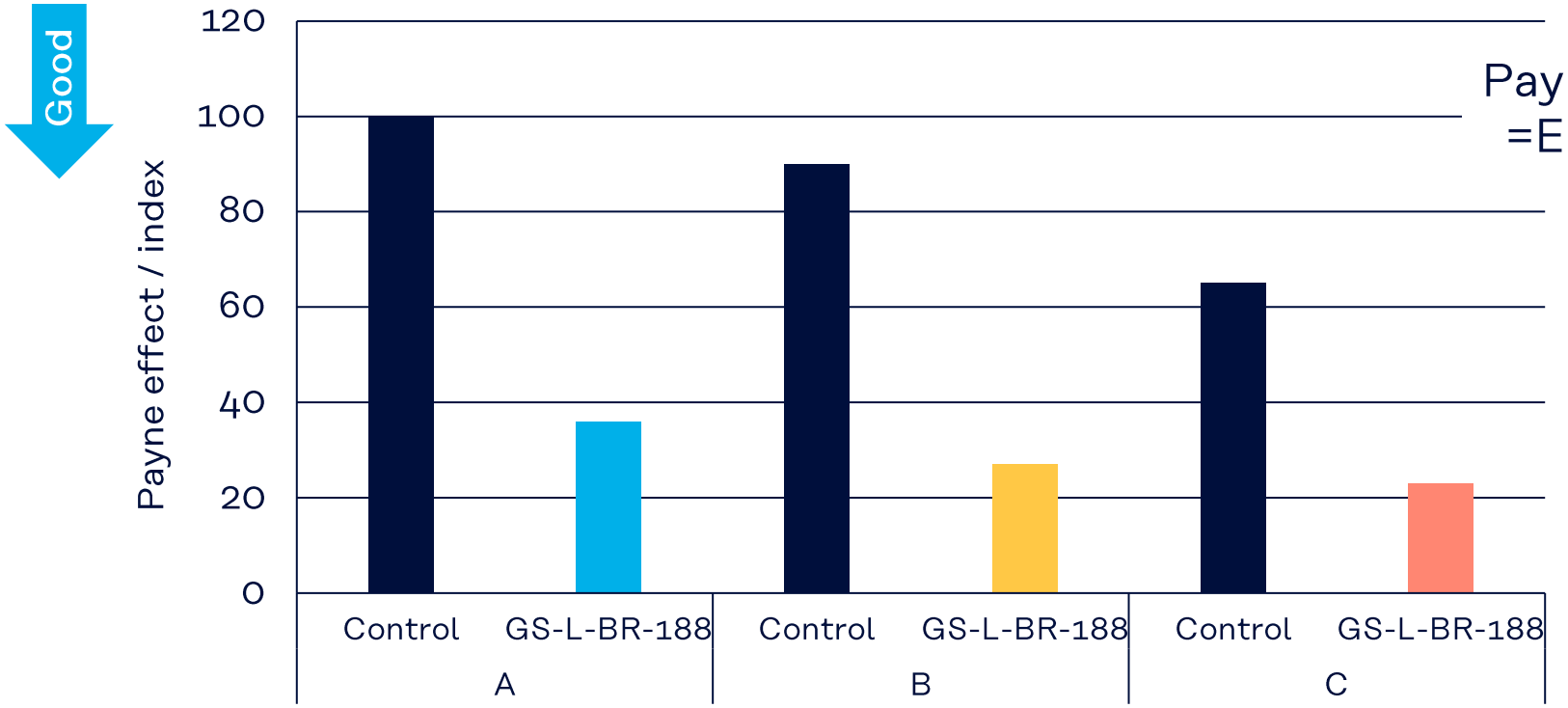


Static strain 10%
Dynamic strain 2%
Frequency 10Hz

- Ethoxysilyl group reacts with silica effectively.
- GS-L-BR improved RR well in each mixing condition.
  tanδ at 60°C: Rolling resistance (RR)

Payne effect

	NP1	NP2	NP3
A	ZnO Stearic acid		
B		ZnO Stearic acid	
C			ZnO Stearic acid

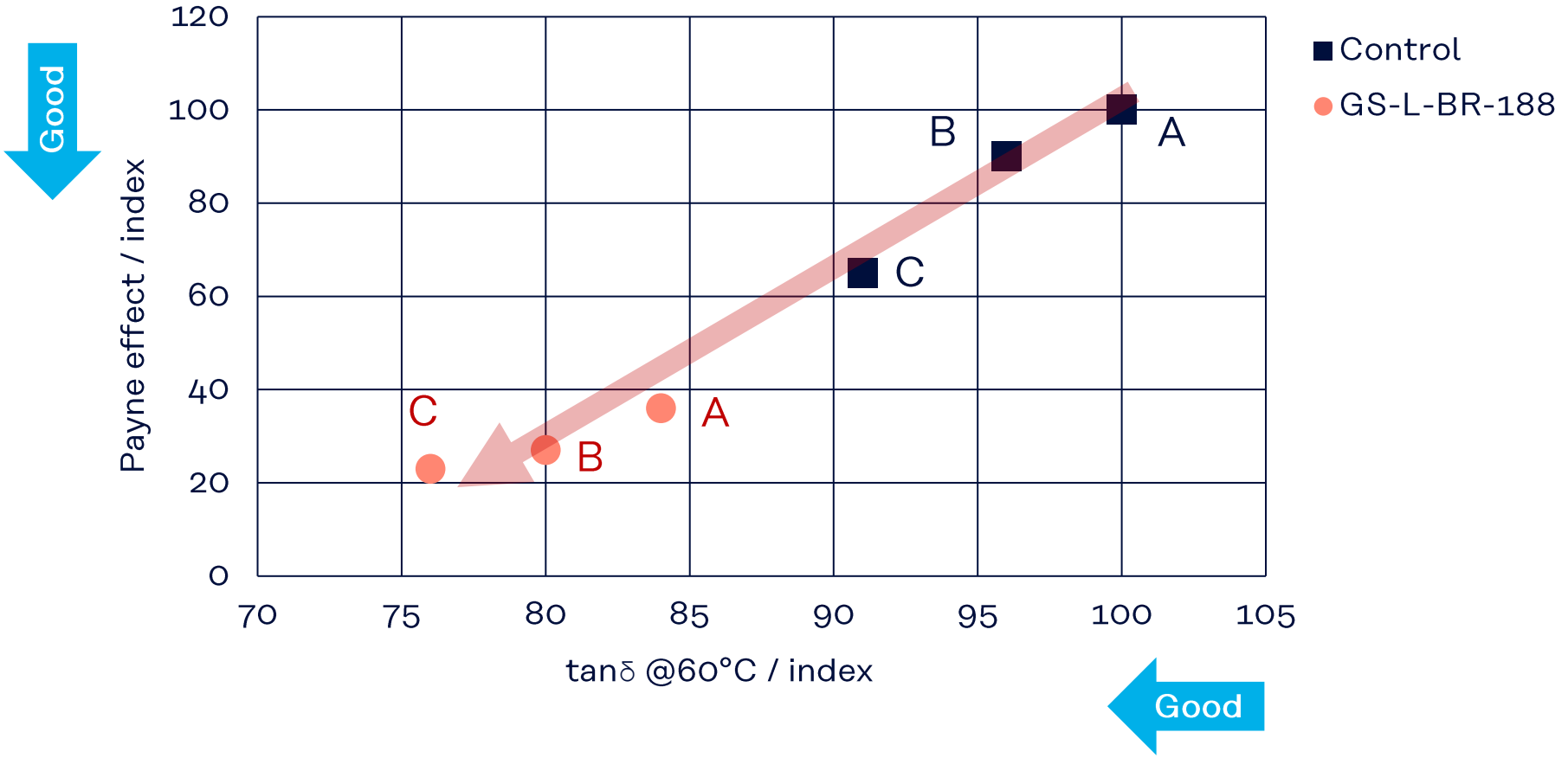


Payne effect
=E′ (strain 0.5%) - E′ (strain 5%)

- Ethoxysilyl group reacts with silica effectively and silica dispersion is improved.

Payne effect vs. tanδ at 60°C

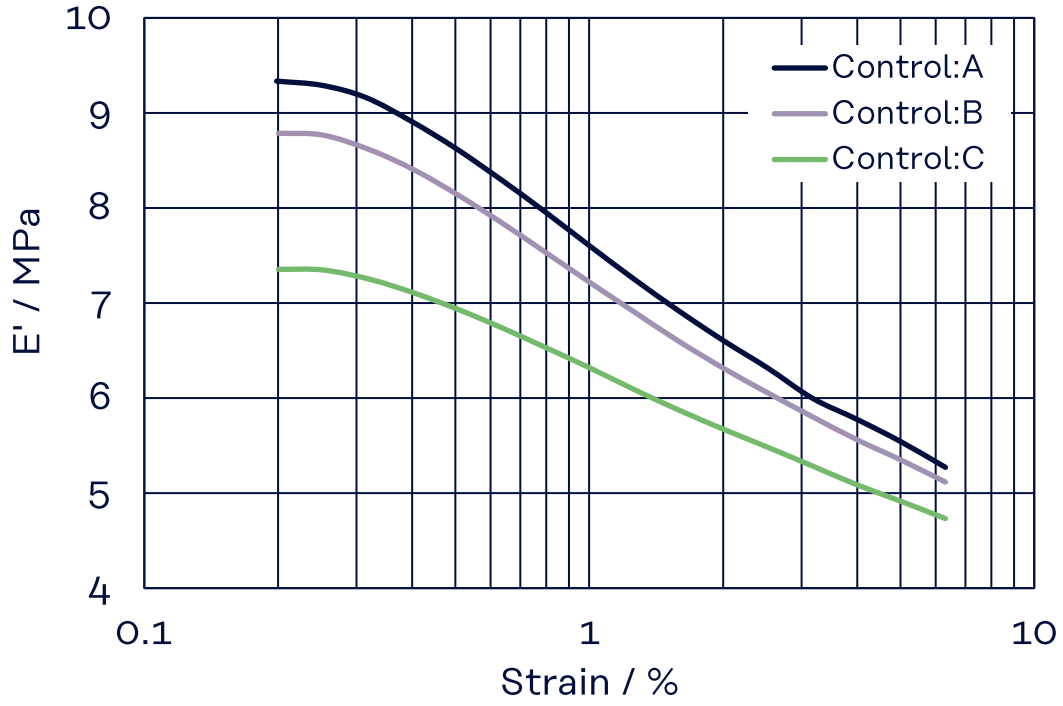
	NP1	NP2	NP3
A	ZnO Stearic acid		
B		ZnO Stearic acid	
C			ZnO Stearic acid

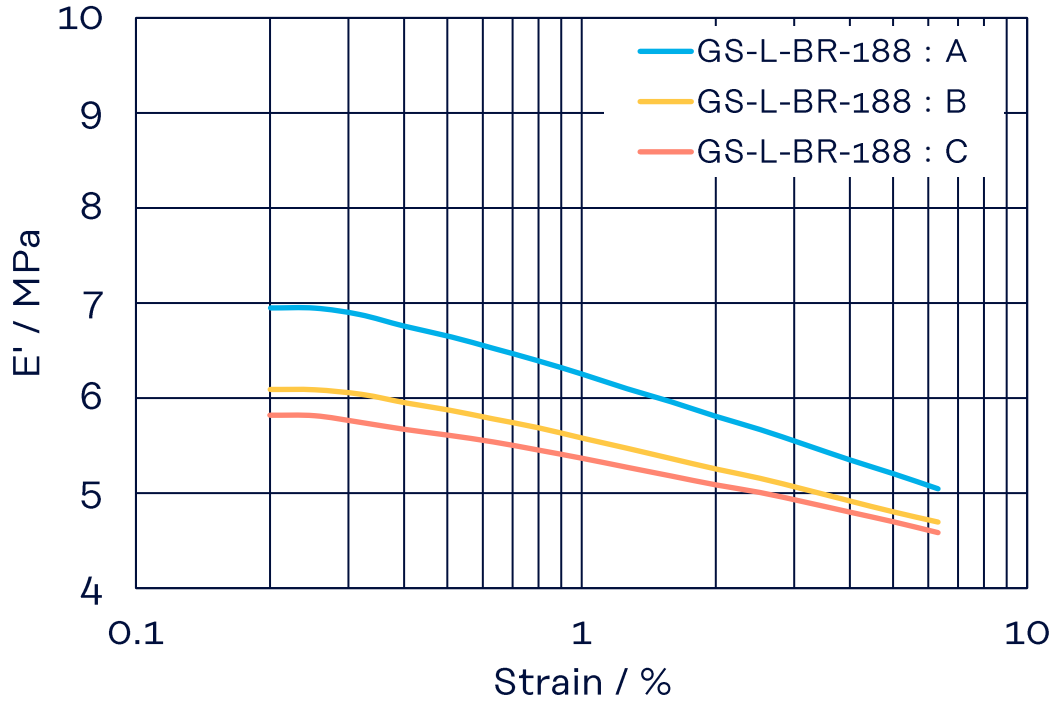


- Tanδ and Payne effect are in a proportional relationship

DMA (E′ vs strain)
[Dynamic Mechanical Analysis]

	NP1	NP2	NP3
A	ZnO Stearic acid		
B		ZnO Stearic acid	
C			ZnO Stearic acid

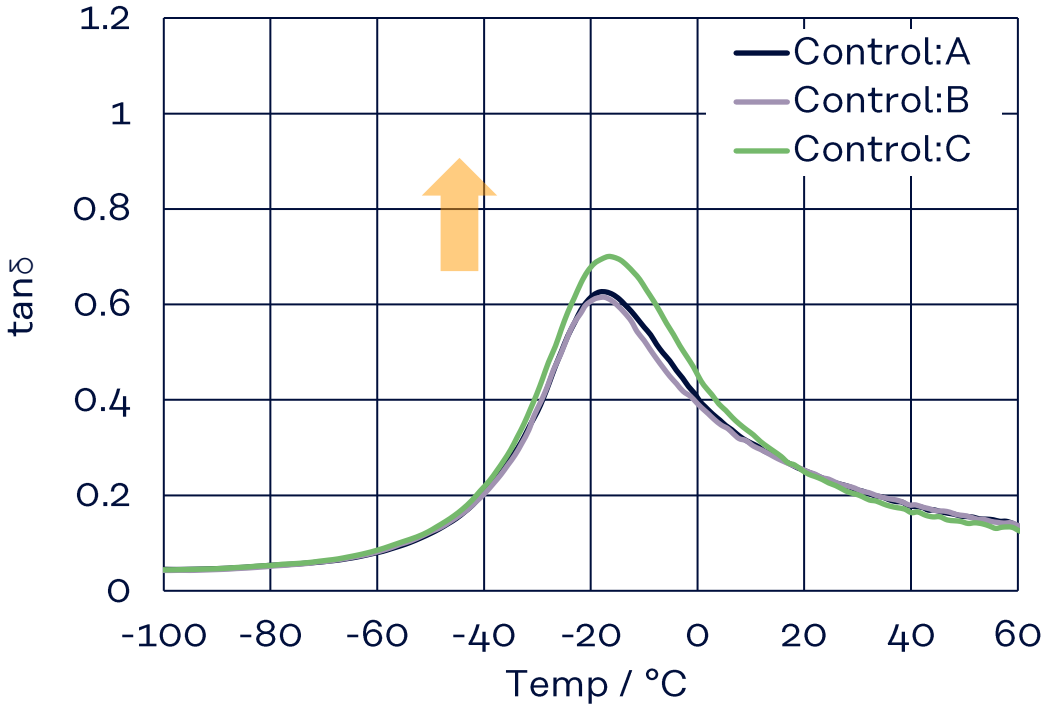


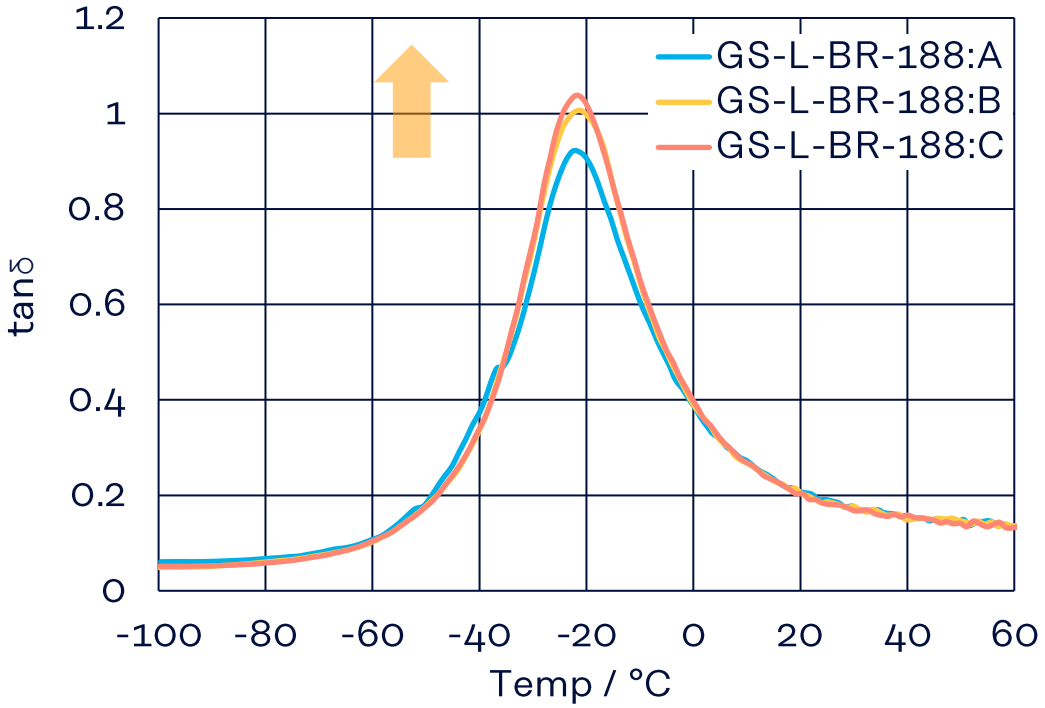


- When ZnO and stearic acid are added later process, rubber shows lower E′.

DMA (tanδ vs. temperature) [Dynamic Mechanical Analysis]

	NP1	NP2	NP3
A	ZnO Stearic acid		
B		ZnO Stearic acid	
C			ZnO Stearic acid



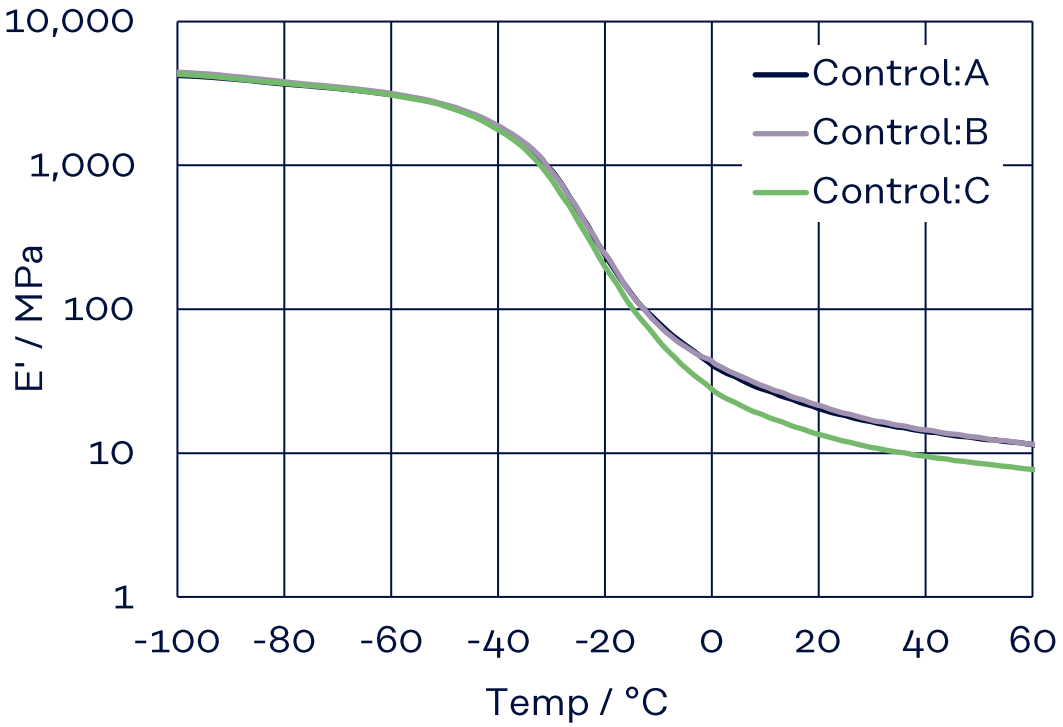


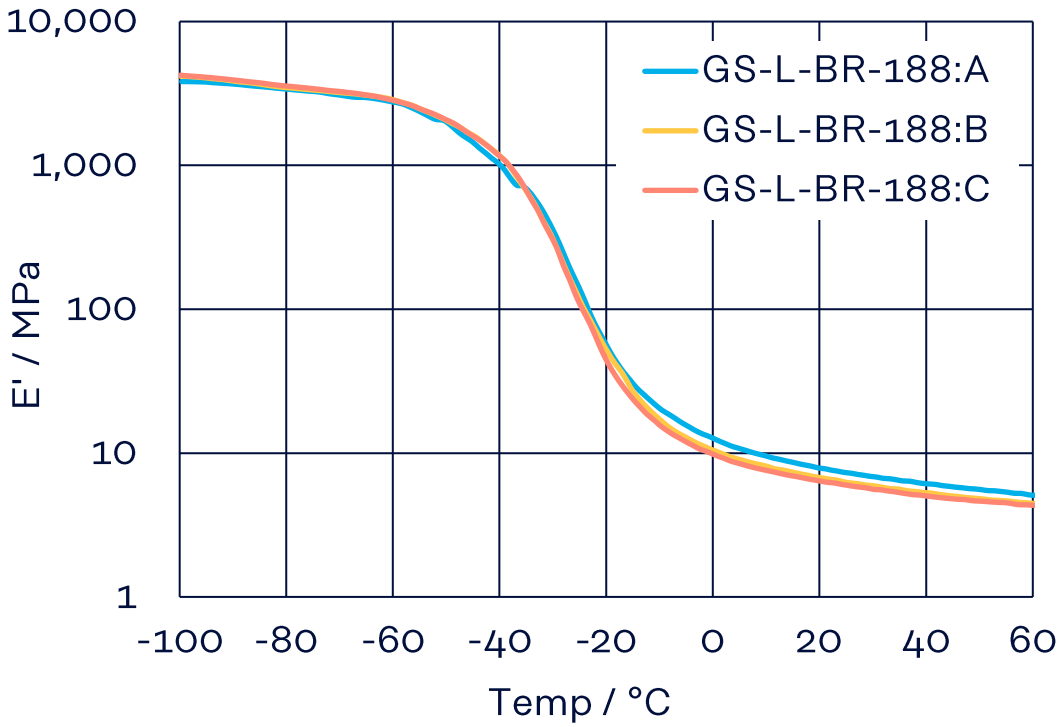
Static strain 0.5%
Dynamic strain 0.1%
Frequency 10Hz

- Ethoxysilyl group reacts with silica effectively and silica dispersion is improved.

DMA (E′ vs temperature) [Dynamic Mechanical Analysis]

	NP1	NP2	NP3
A	ZnO Stearic acid		
B		ZnO Stearic acid	
C			ZnO Stearic acid





Static strain 0.5%
Dynamic strain 0.1%
Frequency 10Hz

Summary

- Adding ZnO and Stearic acid later accelerates vulcanization of SBR / Silica formulation with GS-L-BR.
  - Ethoxysilyl group reacts with silica effectively, and ZnO does not react with ethoxysilyl group.

- When adding ZnO and Stearic acid later,
  - RR was improved.
  - Payne effect was improved.

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APPENDIX

Summary of Properties

	NP1	NP2	NP3
A	ZnO Stearic acid		
B		ZnO Stearic acid	
C			ZnO Stearic acid

			1	2	3	4
			Control		GS-L-BR-188	
Mixing condition			A	A	B	C
Mooney Viscosity (ML1+4, 130°C)			57.4	45.2	48.9	54.7
Mechanical properties						
Hardness		Type A	69	61	59	58
EB		(%)	355	335	295	310
TB		(MPa)	20.2	17.9	16.1	16.7
M100		(MPa)	2.96	2.87	2.69	2.63
M300		(MPa)	16.5	15.7	16.9	15.7
Tear Resistance		(kN/m)	49.9	46.5	42.1	44.0
DMA (Dynamic Mechanical Analysis)						
E′	0°C	(MPa)	13.8	8.16	7.85	7.76
	25°C	(MPa)	7.48	5.42	5.17	5.17
	60°C	(MPa)	5.39	4.18	4.06	4.11
tanδ	0°C	(-)	0.658	0.431	0.433	0.425
	25°C	(-)	0.324	0.216	0.205	0.195
	60°C	(-)	0.164	0.138	0.132	0.125
Payne effect (0.5%E′-5.0%E′)		index	100	36	27	23

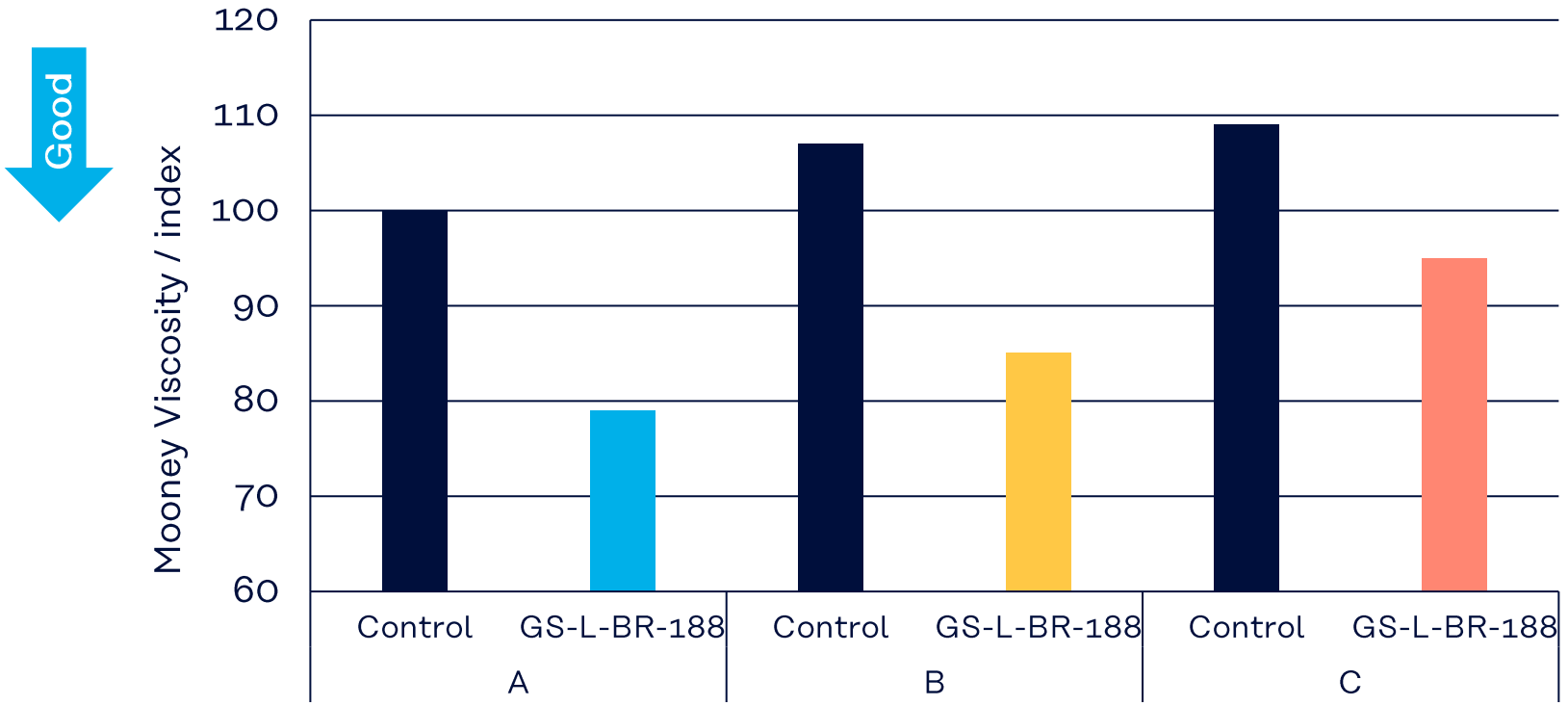
Summary of Properties -formulation without GS-L-BR

	NP1	NP2	NP3
A	ZnO Stearic acid		
B		ZnO Stearic acid	
C			ZnO Stearic acid

			1	2 Control	3
Mixing condition			A	B	C
Mooney Viscosity (ML1+4, 130°C)			56.3	60.2	61.2
Mechanical properties					
Hardness		Type A	68	68	62
EB		(%)	360	340	350
TB		(MPa)	21.4	19.8	21.5
M100		(MPa)	2.95	2.86	2.63
M300		(MPa)	16.6	17.0	17.5
Tear Resistance		(kN/m)	51.5	53.3	46.9
DMA (Dynamic Mechanical Analysis)					
E′	0°C	(MPa)	12.7	11.6	10.6
	25°C	(MPa)	6.88	6.29	5.65
	60°C	(MPa)	5.15	4.72	4.23
tanδ	0°C	(-)	0.671	0.671	0.652
	25°C	(-)	0.314	0.303	0.281
	60°C	(-)	0.163	0.157	0.148
Payne effect (0.5%E′-5.0%E′)		index	100	90	65

Mooney Viscosity

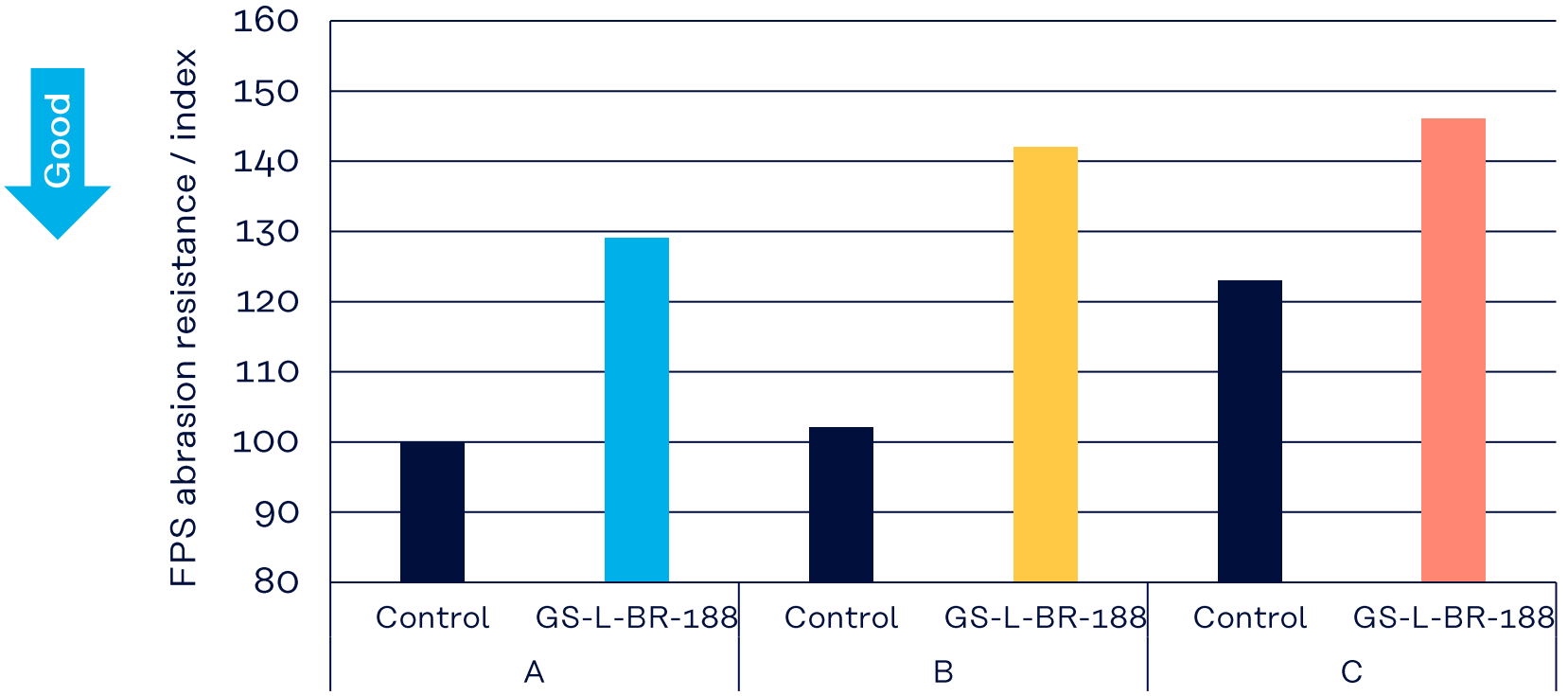
	NP1	NP2	NP3
A	ZnO Stearic acid		
B		ZnO Stearic acid	
C			ZnO Stearic acid



- Mooney Viscosity increases by adding ZnO and stearic acid later.

FPS abrasion resistance

	NP1	NP2	NP3
A	ZnO Stearic acid		
B		ZnO Stearic acid	
C			ZnO Stearic acid

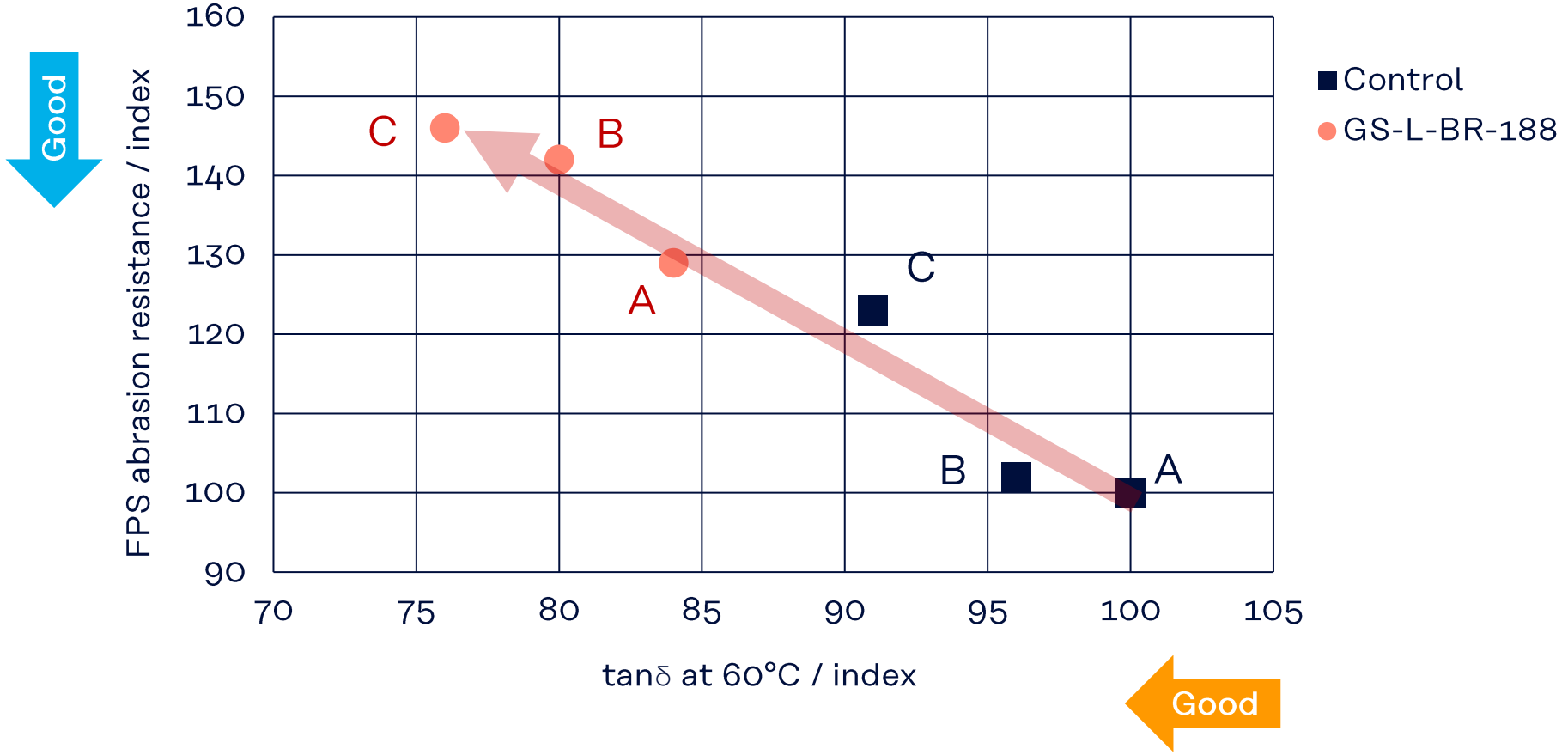


FPS abrasion tester
Slip ratio 5%

- Abrasion Resistance deteriorates by adding ZnO and stearic acid later.

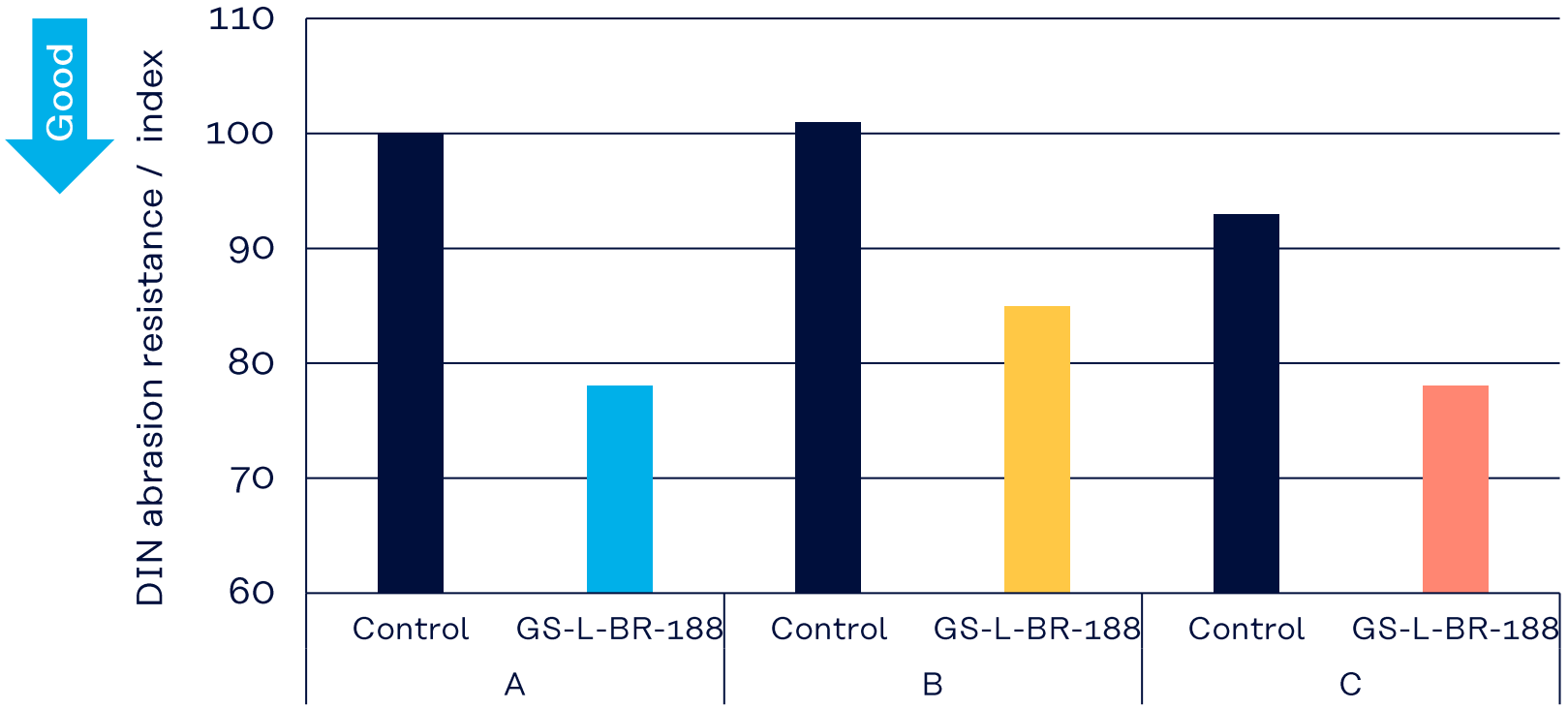
Rolling resistance vs abrasion resistance

	NP1	NP2	NP3
A	ZnO Stearic acid		
B		ZnO Stearic acid	
C			ZnO Stearic acid



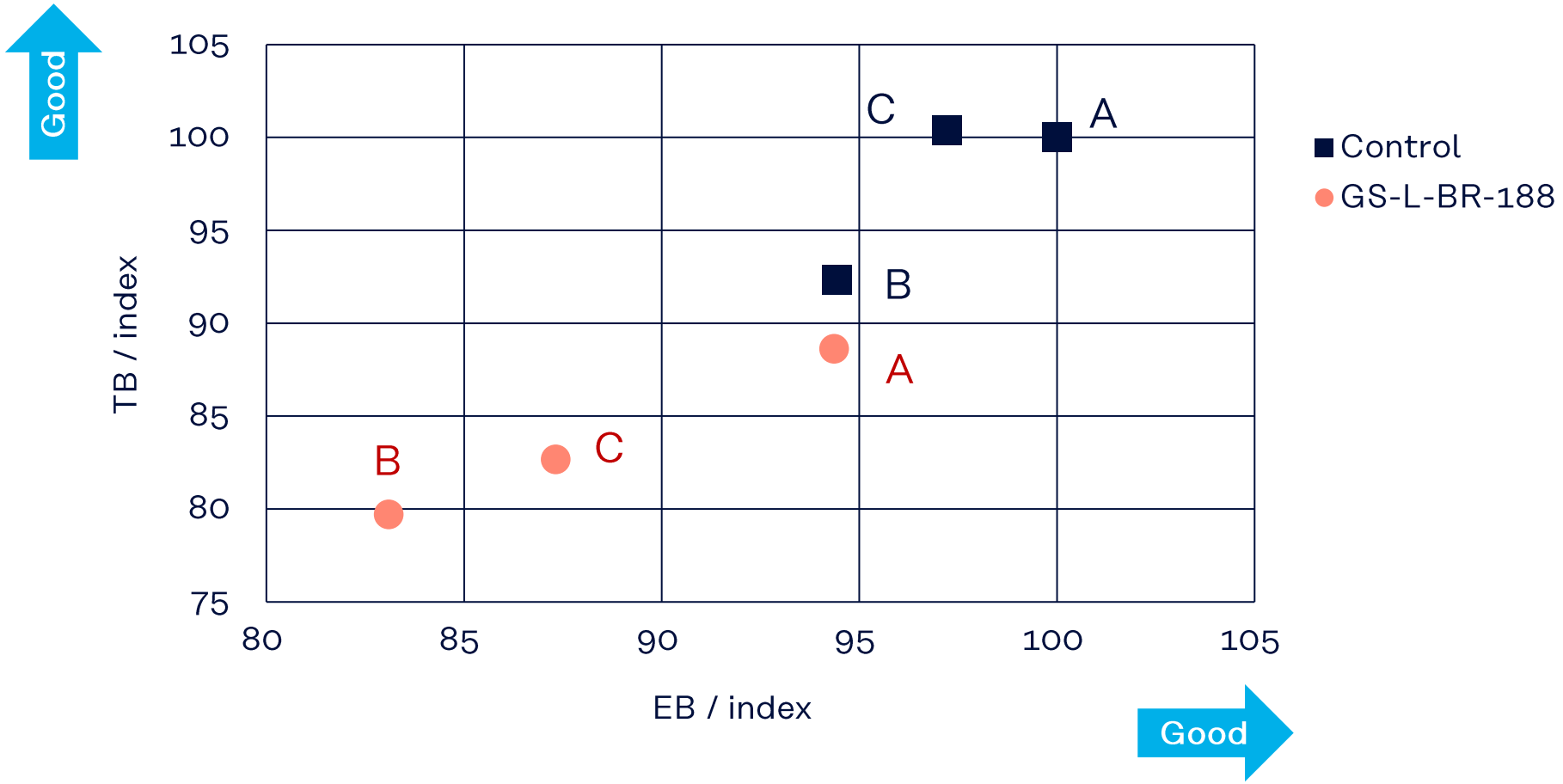
DIN abrasion resistance

	NP1	NP2	NP3
A	ZnO Stearic acid		
B		ZnO Stearic acid	
C			ZnO Stearic acid



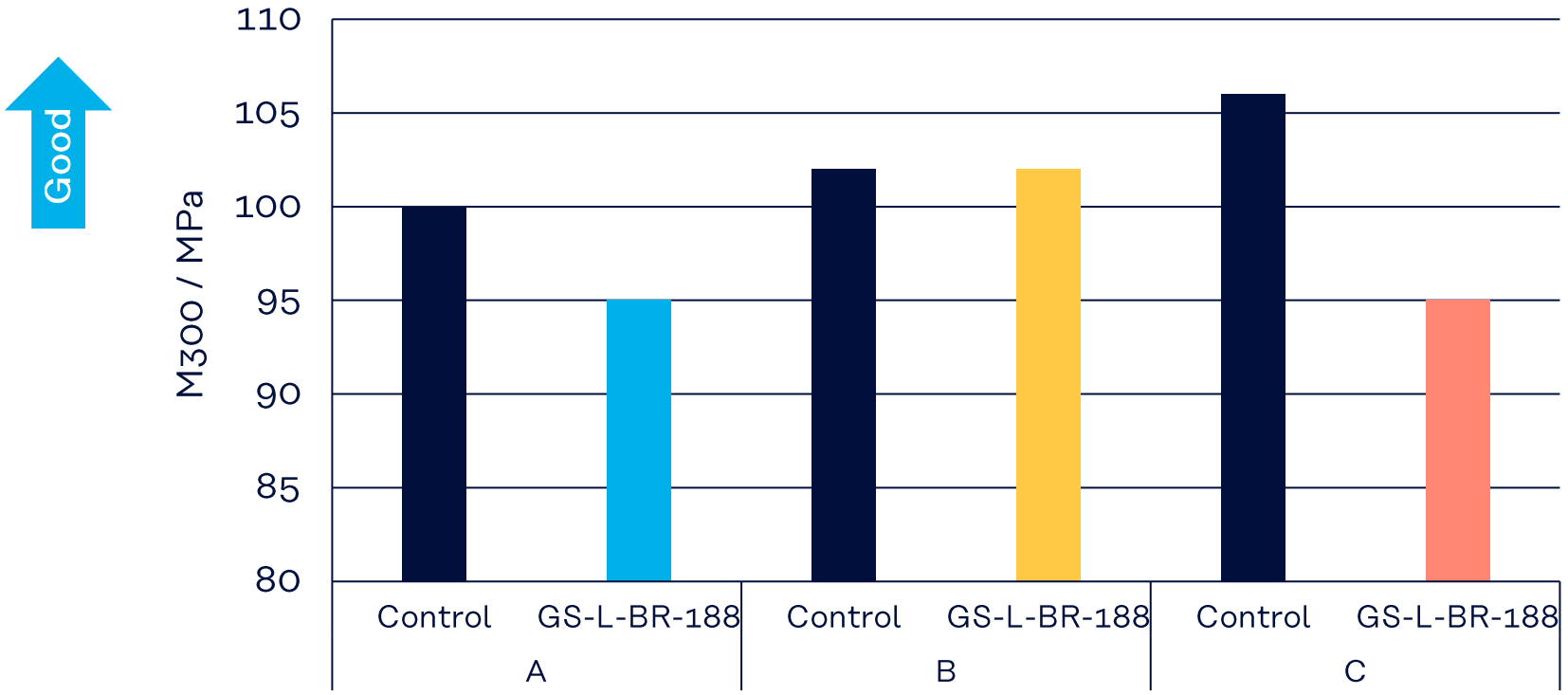
Tensile property

	NP1	NP2	NP3
A	ZnO Stearic acid		
B		ZnO Stearic acid	
C			ZnO Stearic acid



Analysis of 300% modulus [M300] for Silica-polymer interaction

	NP1	NP2	NP3
A	ZnO Stearic acid		
B		ZnO Stearic acid	
C			ZnO Stearic acid



Silanol groups slow vulcanization speed

	NP1	NP2	NP3
A	ZnO Stearic acid		
B		ZnO Stearic acid	
C			ZnO Stearic acid

$ZnO + 2(OH^-) + H_2O \rightarrow Zn(OH)_2 + 2OH^-$
$RCOOH + OH^- \rightarrow RCOO^- + H2O$
$Zn(OH)_2 + 2RCOO^- \rightarrow (RCOO)_2Zn + 2OH^-$

※RCOOH : Stearic acid

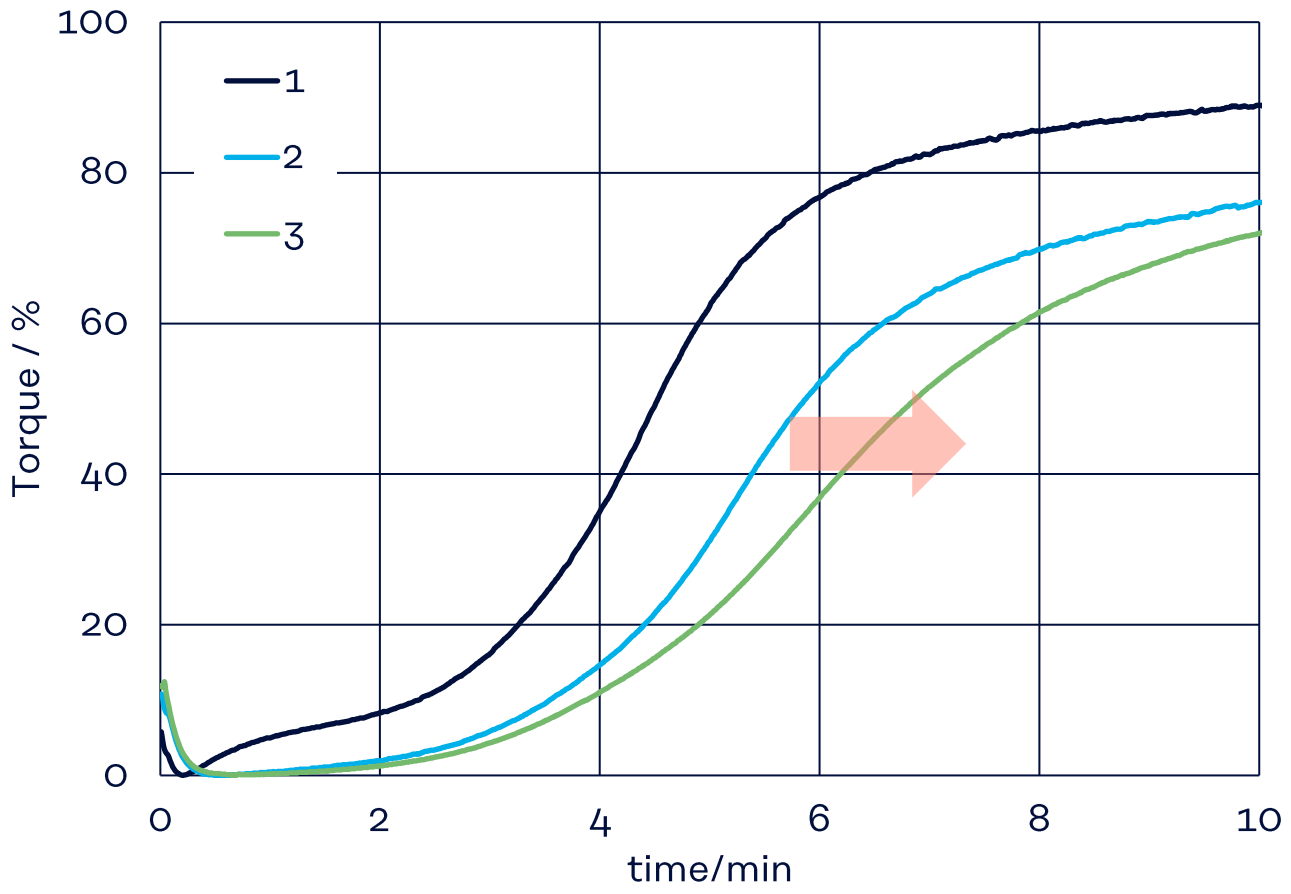
Add silanol groups

$ZnO + 2(OH^-) + H_2O \rightarrow Zn(OH)_2 + 2OH^-$
~~$RCOOH + OH^- \rightarrow RCOO^- + H2O$~~
~~$Zn(OH)_2 + 2RCOO \rightarrow (RCOO)_2Zn + 2OH$~~

$Si\text{-}OH + OH^- \rightarrow Si\text{-}O^- + H_2O$
$Zn(OH)_2 + Si\text{-}O^- \rightarrow (Si\text{-}O)_2Zn + 2OH^-$

Add many ZnO and Stearic acid

	Formulation		
	1	2	3
f-SSBR	80	80	80
BR	20	20	20
Silica	100	100	100
SCA	8	8	8
TDAE	28	28	28
GS-L-BR-188		12	12
ZnO/Stearic acid	3.0/2.5		4.5/3.75
Other chemicals	6PPD 2.5,Wax 2.0		
Sulfur Accelerator	S 1.5, DPG 0.5, CBS 0.35,TBTD 1.5		
t90 (min)	11.76	23.67	24.55



Raw materials

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	
TDAE	VIVATEC 500	H&R GmbH Co. KGaA	