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

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) and slow vulcanization

2) Optimization of mixing conditions

Silane modified LBR (GS-L-BR-114)

Grade Name [Development Code]	Structure	Mw	Tg (°C)	Number of functional groups / chain	Viscosity at 38°C (Pa • s)
GS-L-BR-114 [SB-005]	Polybutadiene /Graft silane	6,000	-50	2	6

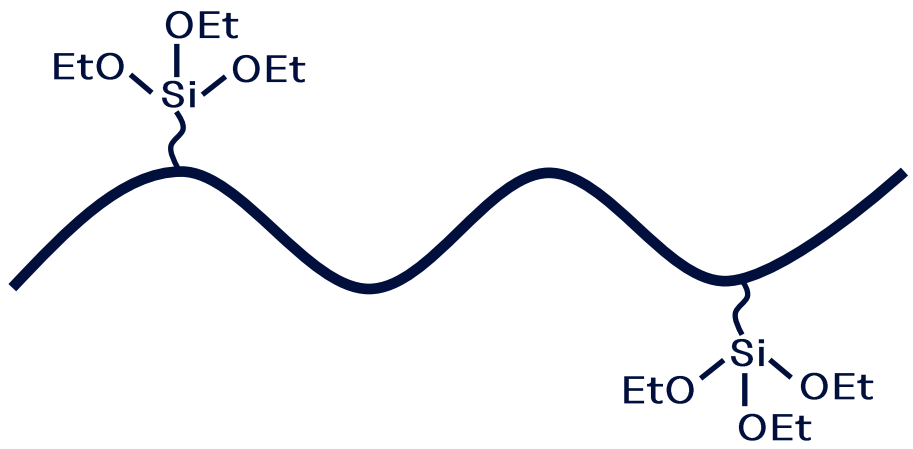


Image of GS-L-BR

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

kuraray

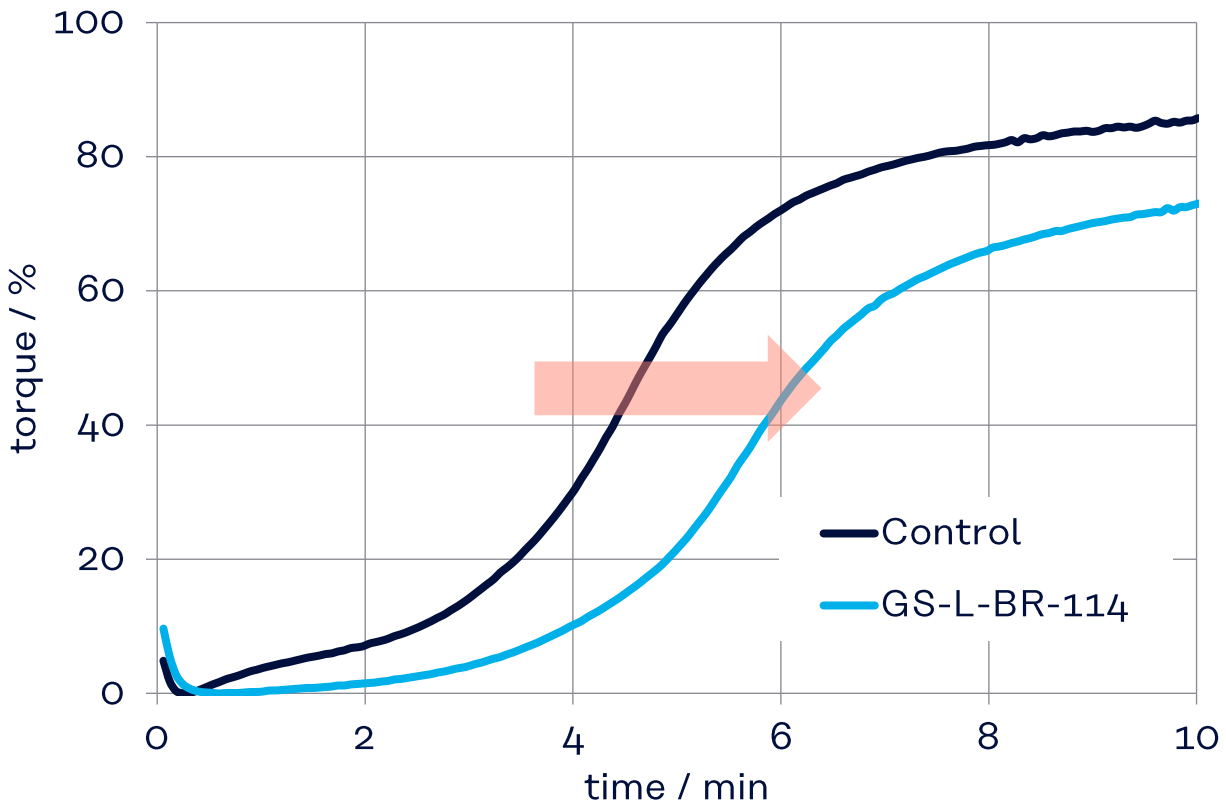
Formulation & Mixing Conditions

	Control	GS-L-BR-114
f-SSBR	80	80
BR	20	20
Silica	100	100
SCA	8	8
TDAE	28	28
GS-L-BR-114	-	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 (by Kobe Steel, Ltd.)

Curing behavior with GS-L-BR

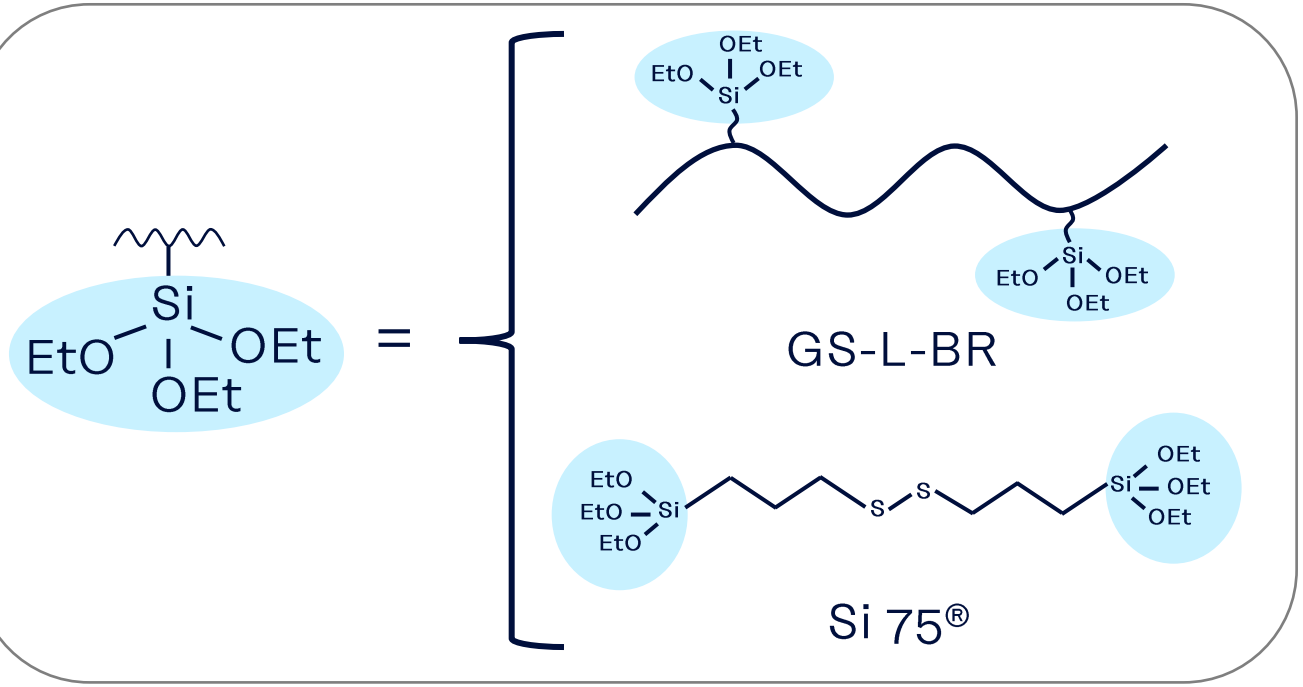


	1	2
	Control	GS-L-BR-114
t90 (index)	100	186

- Addition of GS-L-BR-114 reduces vulcanization speed.

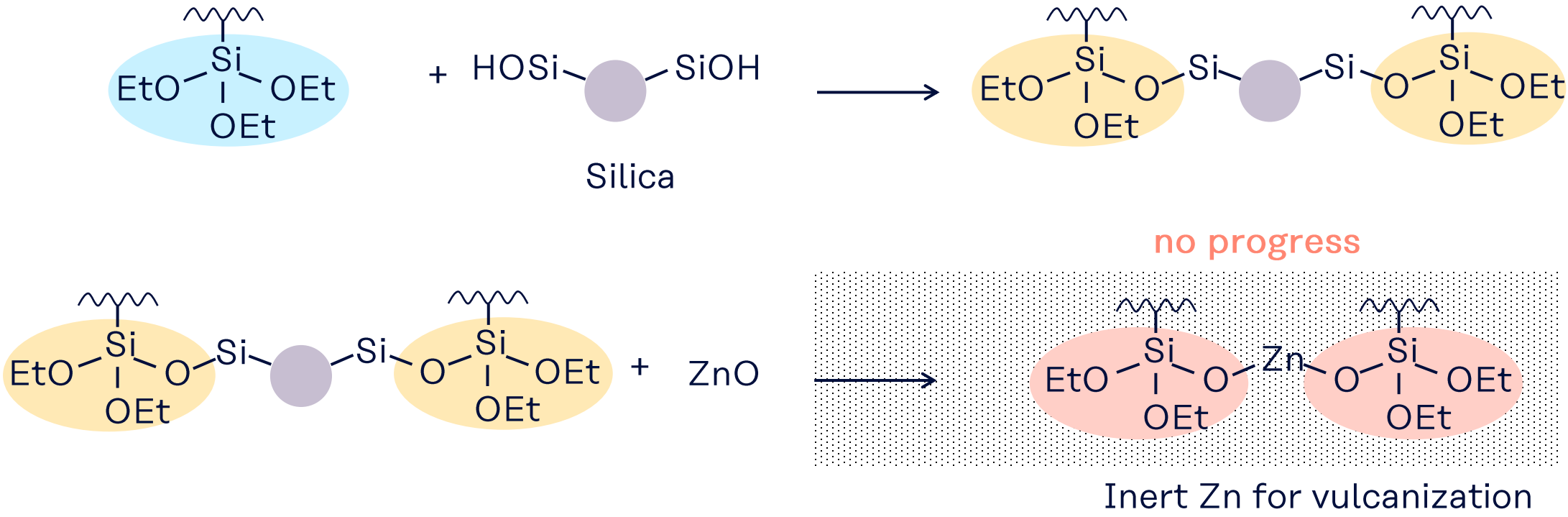
Why vulcanization becomes slow?

Inert Zn for vulcanization



	Control	GS-L-BR
Si(OEt)3	Si 75®	Si 75® GS-L-BR
Amount of Si(OEt)3	few	many
Consumption of ZnO	few	many

How to prevent inert Zn generation?

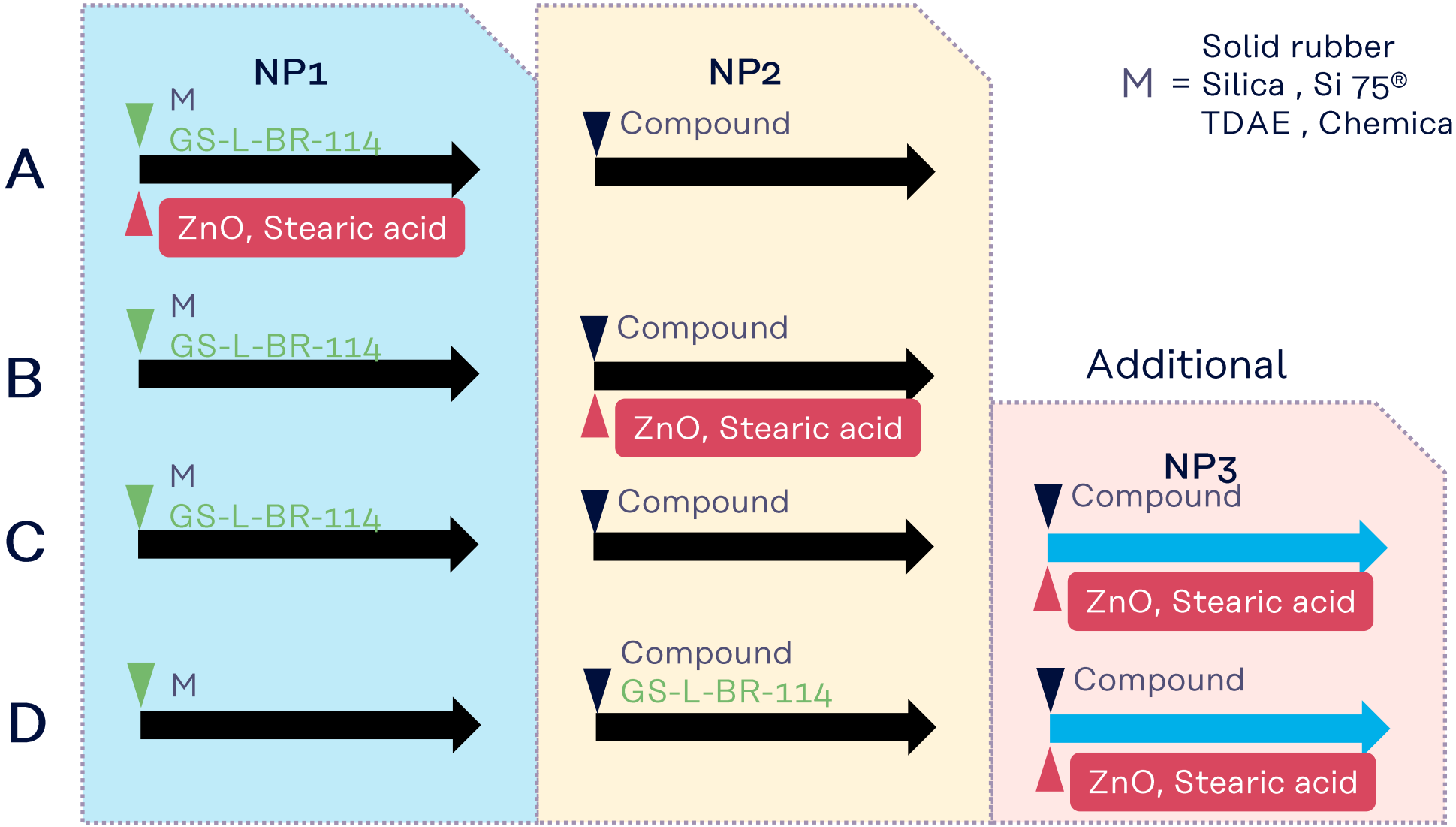


Agenda

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

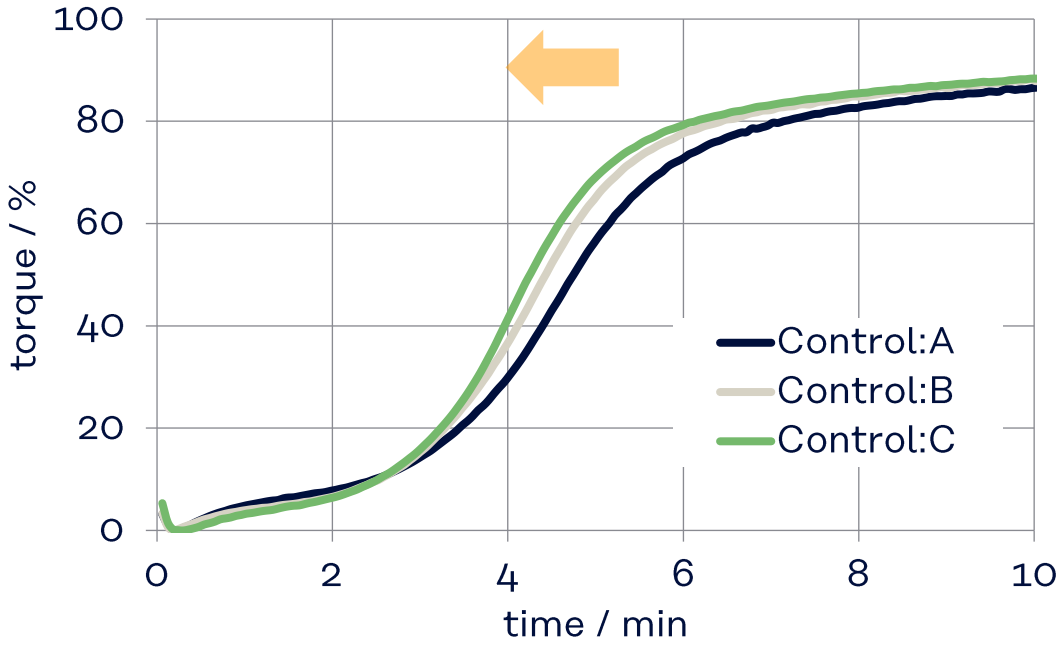
2) Optimization of mixing conditions

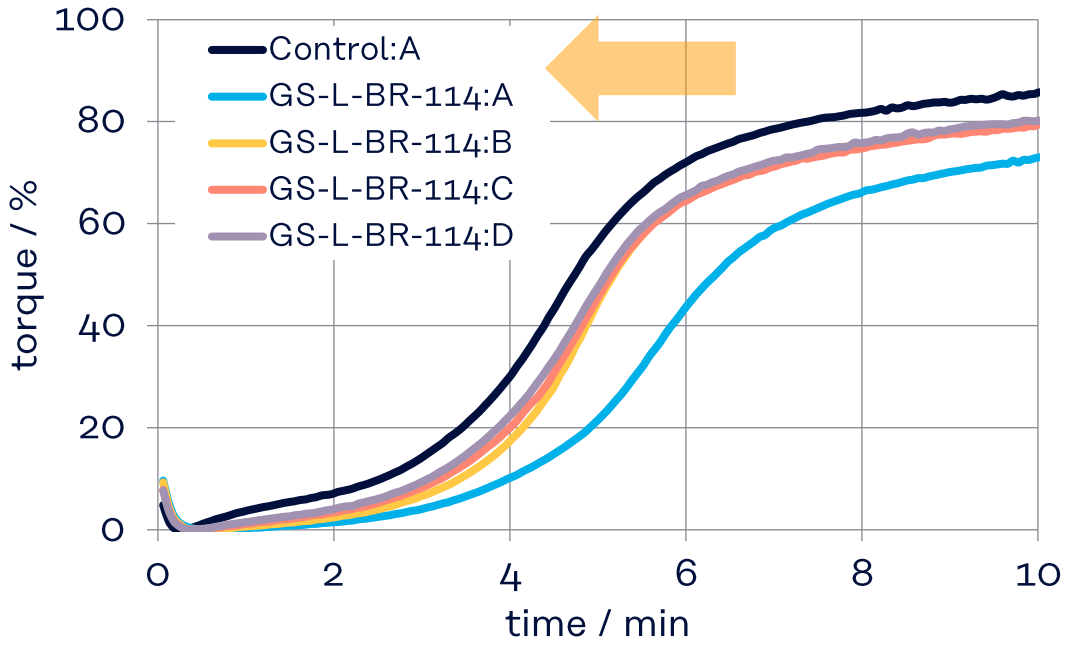
Mixing conditions



Curing behavior

	NP1	NP2	NP3
A	LR ZnO, Stearic acid		
B	LR	ZnO, Stearic acid	
C	LR		ZnO, Stearic acid
D		LR	ZnO, Stearic acid





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

	1	2	3	4	5
	Control	GS-L-BR-114			
Mixing condition	A	A	B	C	D
t90 (index)	100	186	155	148	140

- Adding ZnO and Stearic acid at later mixing stage accelerates vulcanization speed in GS-L-BR formulation.

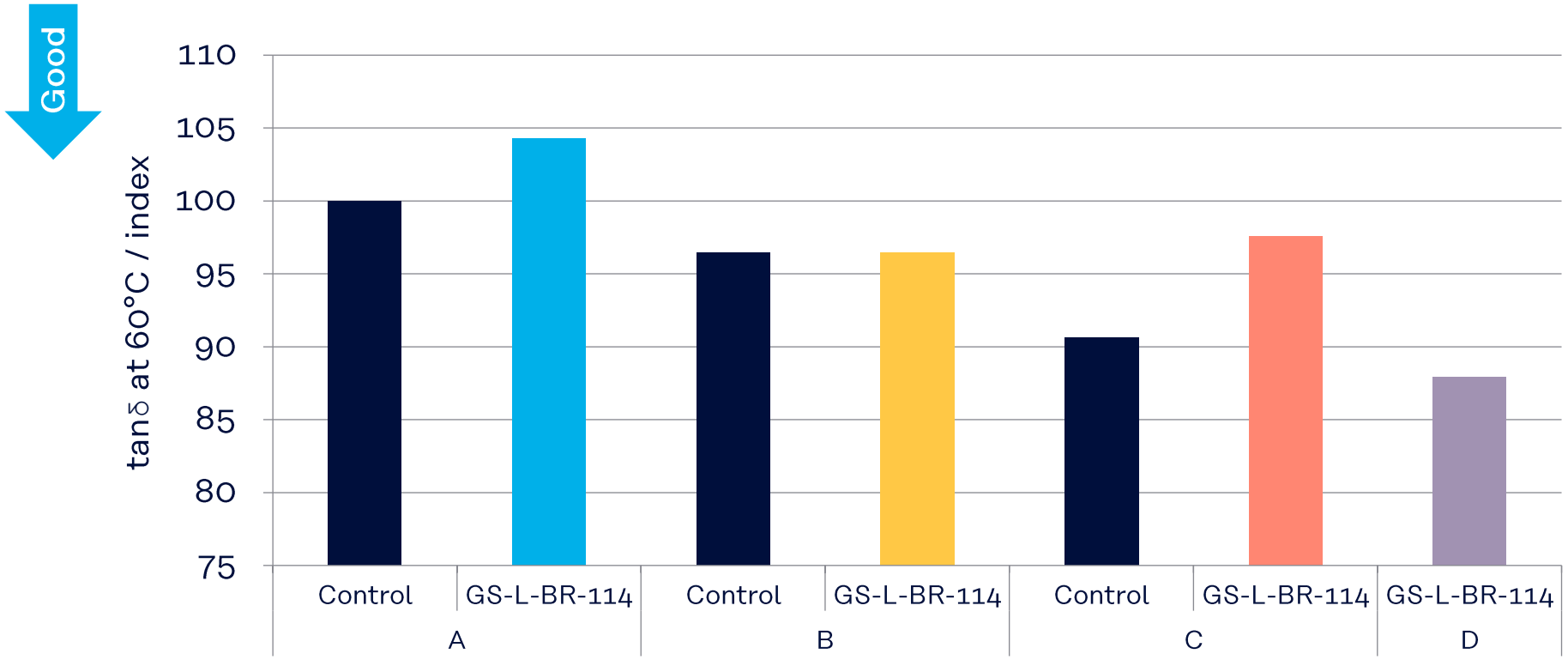
Summary of Properties

	NP1	NP2	NP3
A	LR ZnO, Stearic acid		
B	LR	ZnO, Stearic acid	
C	LR		ZnO, Stearic acid
D		LR	ZnO, Stearic acid

			1	2	3	4	5	6	7
				Control			GS-L-BR-114		
Mixing condition			A	B	C	A	B	C	D
Mooney Viscosity (ML1+4, @130°C)			100	107	109	72	78	78	80
Curelastometer (t90, 160°C)		(min)	100	88	88	186	155	148	140
Mechanical properties									
Hs		Type A	68	68	62	63	61	62	61
EB		(%)	100	94	97	110	109	101	105
TB		(MPa)	100	92	100	95	97	94	100
Payne effect (E'0.5%-5%)		index	100	90	65	98	75	79	60
DMA (Dynamic Mechanical Analysis)									
E'	0°C	(MPa)	100	91	83	111	98	98	89
	25°C	(MPa)	100	91	82	105	91	93	84
	60°C	(MPa)	100	92	82	97	86	87	81
tanδ	0°C	(-)	100	100	97	99	100	99	97
	25°C	(-)	100	96	89	103	99	99	90
	60°C	(-)	100	96	91	104	96	98	88
Abrasion / FPS, 5%		index	100	102	123	86	93	97	95
Friction coefficient on wet / RTM, 20°C		index	100	101	97	98	98	99	99

Rolling resistance

	NP1	NP2	NP3
A	LR ZnO, Stearic acid		
B	LR	ZnO, Stearic acid	
C	LR		ZnO, Stearic acid
D		LR	ZnO, Stearic acid

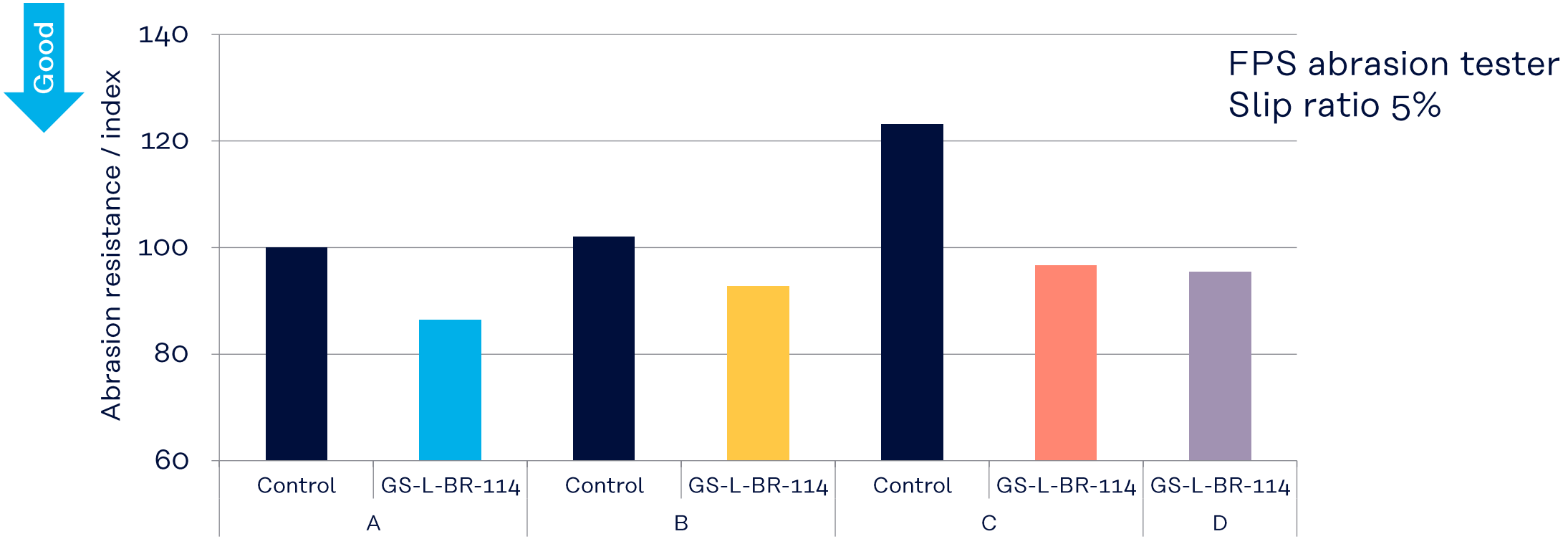


Static strain 10%
Dynamic strain 2%
Frequency 10Hz

- Ethoxysilyl group reacted with silica effectively and silica-polymer interaction was improved.
  tanδ at 60°C: Rolling resistance

Abrasion resistance

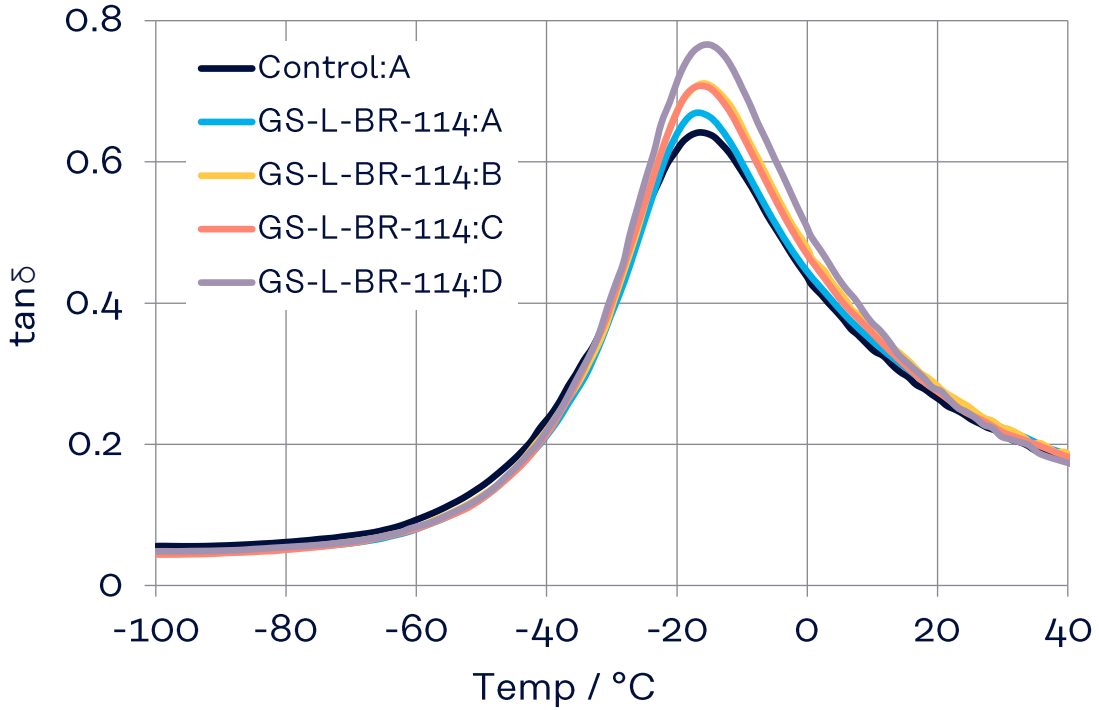
	NP1	NP2	NP3
A	LR ZnO, Stearic acid		
B	LR	ZnO, Stearic acid	
C	LR		ZnO, Stearic acid
D		LR	ZnO, Stearic acid

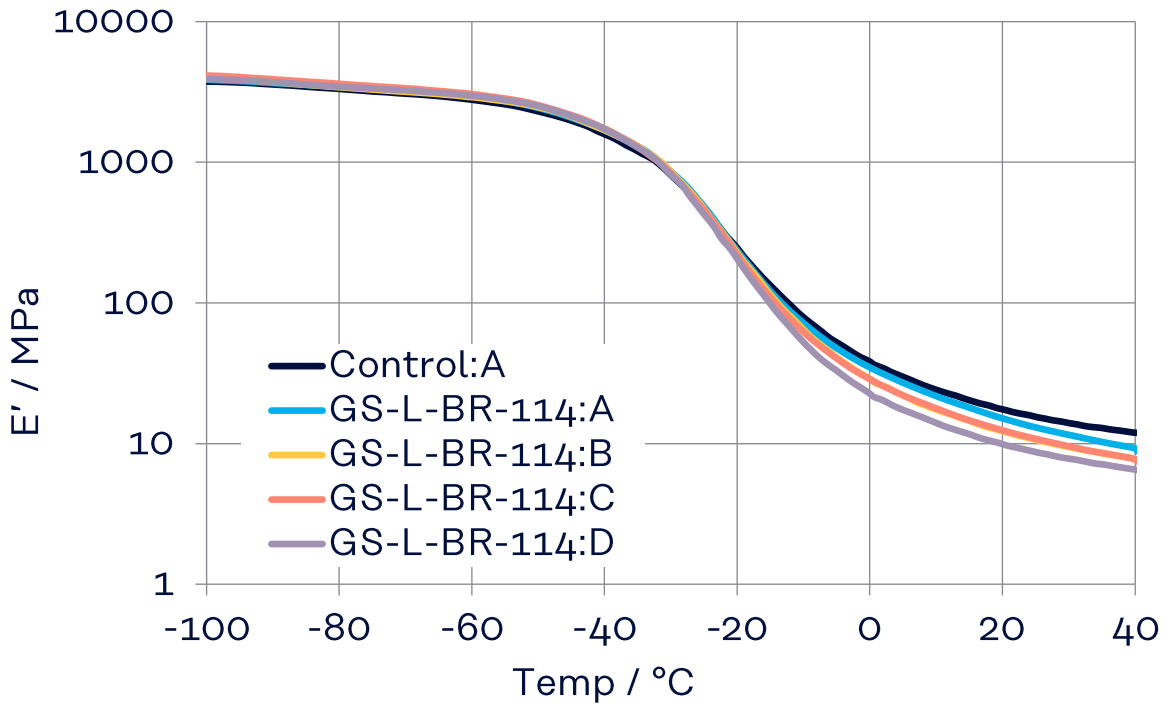


- Abrasion resistance of controls were deteriorated when ZnO was added later.
- GS-L-BR-114 maintained abrasion resistance under all mixing conditions.

DMA [Dynamic Mechanical Analysis]

	NP1	NP2	NP3
A	LR ZnO, Stearic acid		
B	LR	ZnO, Stearic acid	
C	LR		ZnO, Stearic acid
D		LR	ZnO, Stearic acid

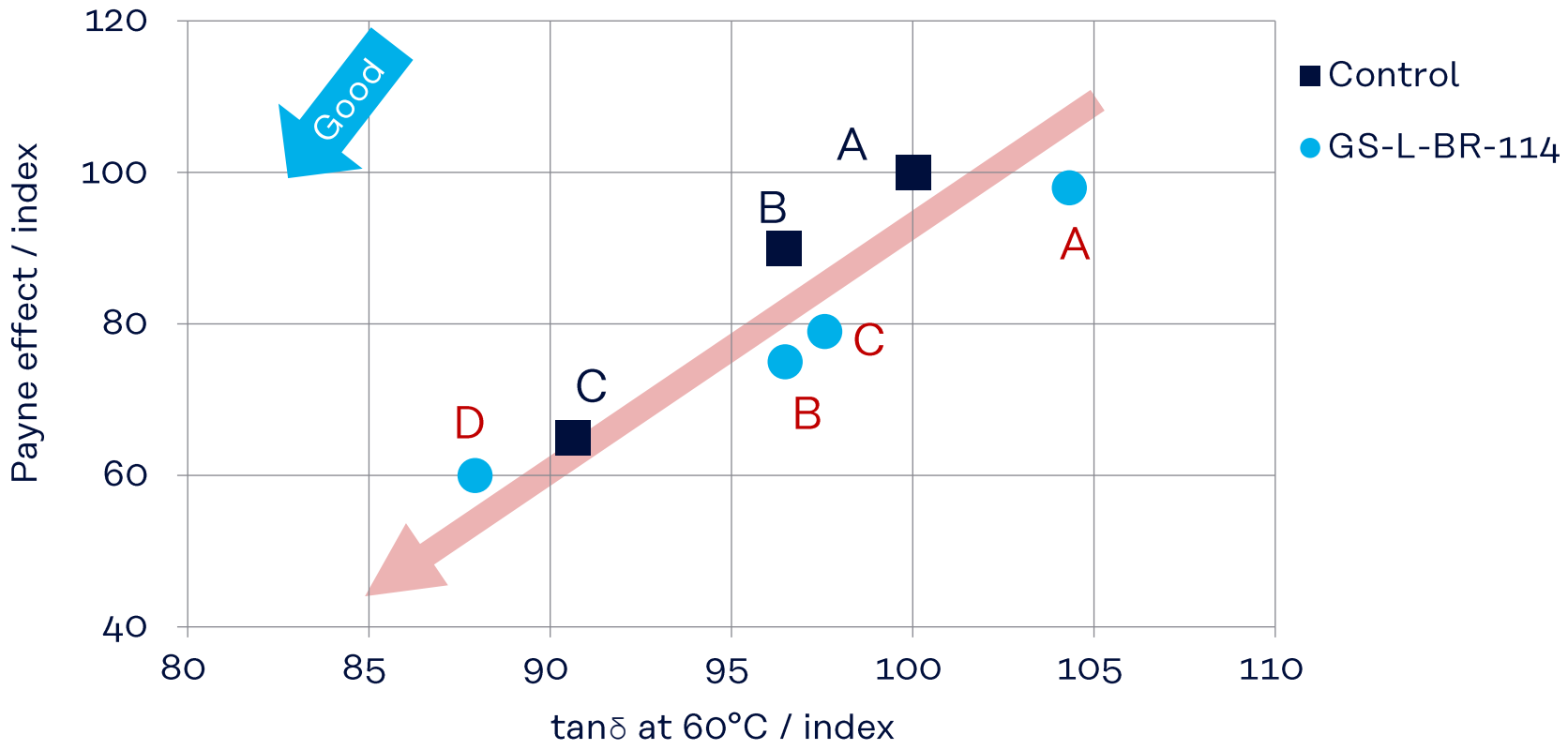




- Adding GS-L-BR-114 at NP3 exhibited the best silica dispersion.

Payne effect vs. rolling resistance (RR)

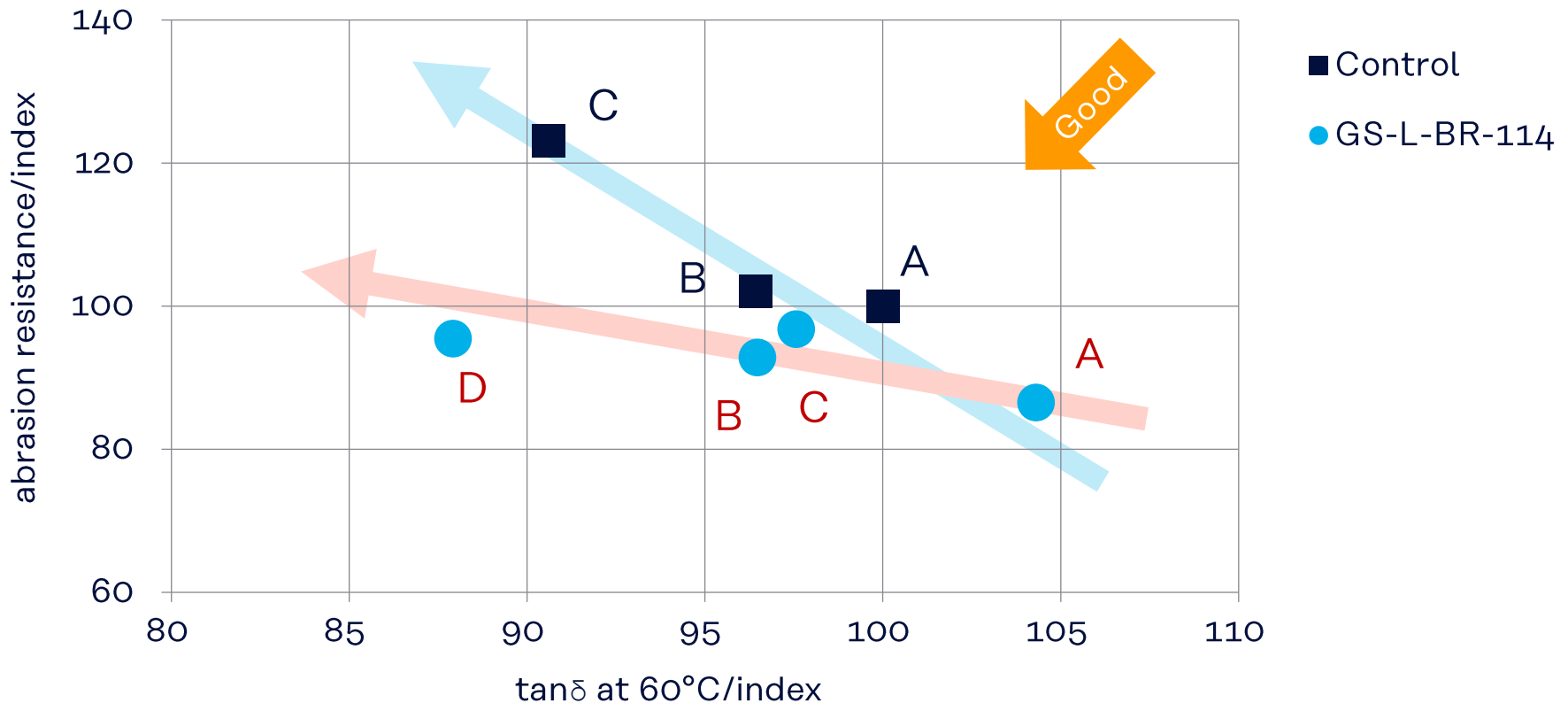
	NP1	NP2	NP3
A	LR ZnO, Stearic acid		
B	LR	ZnO, Stearic acid	
C	LR		ZnO, Stearic acid
D		LR	ZnO, Stearic acid



- Payne effect and RR were improved by adding ZnO at later mixing stage.

Rolling resistance (RR) vs. abrasion resistance

	NP1	NP2	NP3
A	LR ZnO, Stearic acid		
B	LR	ZnO, Stearic acid	
C	LR		ZnO, Stearic acid
D		LR	ZnO, Stearic acid



- GS-L-BR-114 improved the balance between RR and abrasion resistance.

Summary

- Vulcanization speed was optimized by adding ZnO and stearic acid at later mixing stage.
- Regardless of GS-L-BR addition, Payne effect and RR were improved by adding ZnO at later mixing stage.
- GS-L-BR-114 with optimized mixing conditions improved the balance between RR and abrasion resistance.

Kuraray Co., Ltd.
Elastomer Division
Tokiwabashi Tower
2-6-4, Otemachi
Chiyoda-ku, Tokyo 100-0004, Japan

✉ elastomer@kuraray.com

→ www.kuraray.com

→ www.elastomer.kuraray.com

Precautions should be taken in handling and storage. Please refer to the appropriate Safety Data Sheet for further safety information. In using KURARAY LIQUID RUBBER, please confirm related laws and regulations, and examine its safety and suitability for the application.
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.

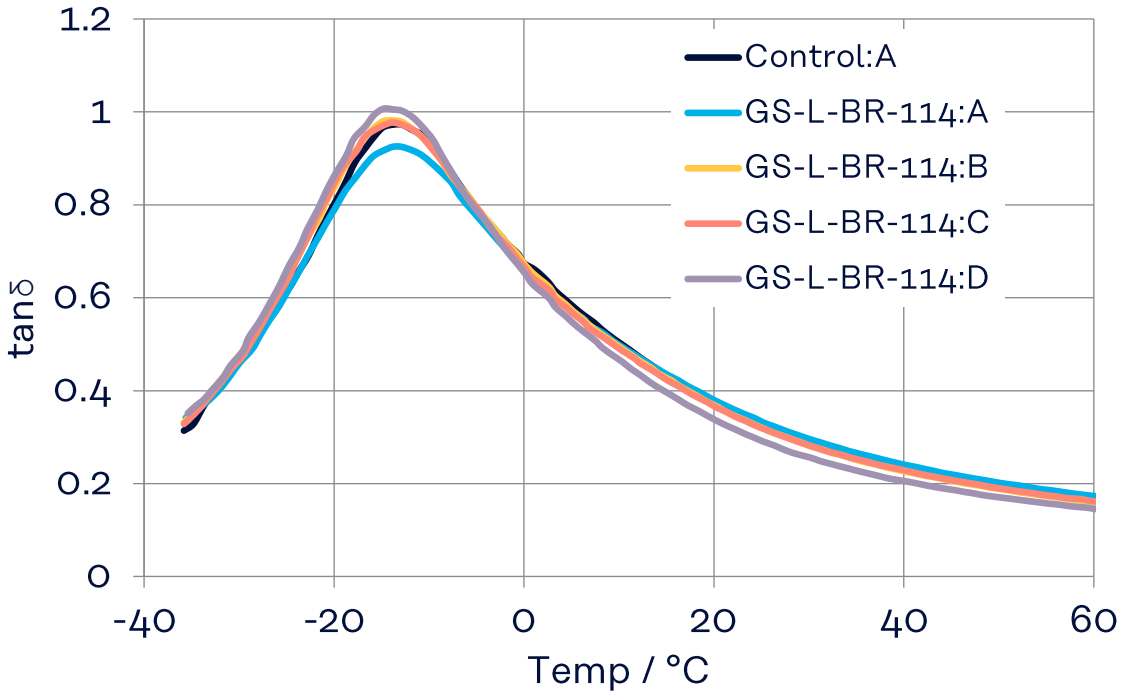
kuraray

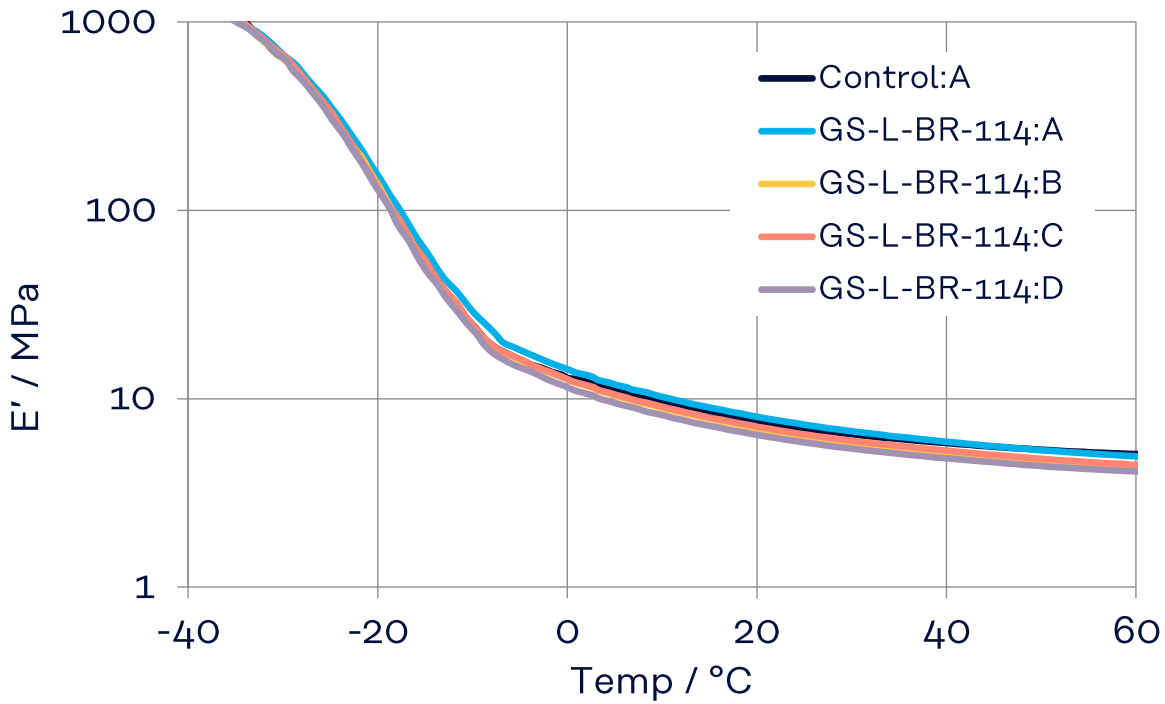
APPENDIX

DMA [Dynamic Mechanical Analysis]

	NP1	NP2	NP3
A	LR ZnO, Stearic acid		
B	LR	ZnO, Stearic acid	
C	LR		ZnO, Stearic acid
D		LR	ZnO, Stearic acid

Static strain 10%
Dynamic strain 2%
Frequency 10Hz





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

Mixing conditions

	sec		A	B	C	D
NP1	0	(60°C)	Solid rubber			
	20		Silica, SCA, TDAE,6PPD, wax, LR ZnO, Stearic acid	Silica, SCA, TDAE, 6PPD, wax, LR	Silica, SCA, TDAE, 6PPD, LR	Silica, SCA, TDAE, 6PPD
	180	Sweep				
	360	Dump out(150°C)				
NP2	0	(90°C)	1st mixed compound			
	20			ZnO, stearic acid		LR
	240	Dump out(150°C)				
NP3	0	(90°C)	2nd mixed compound			
	20				ZnO, stearic acid	ZnO, stearic acid
	240	Dump out (120°C)				

Silanol groups slow vulcanization speed

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

※RCOOH : Stearic acid

Add silanol groups

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

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

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	