Technical Insights of KURARAY LIQUID RUBBER

Liquid Farnesene Rubber in Winter Tire Formulation

Elastomer R&D Department
Elastomer Division

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L-FBR grades for Winter Tire (NR/BR formulation)

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Agenda

- Introduction of L-FBR Grade
- Comparison with Various Softeners
  - Softening effect at low temperature
  - Toluene extraction test

Replacement of Process Oils

- Process oils are used in winter tire tread as Low temperature softener to improve ice grip performance.
- Process oils migrate to other parts or tread surface and cause aging deterioration over time.

- L-FBRs achieves good softening effect at low temperature without migration.

List of Softener

Category	Product Description	Tg (°C)	Supplier
L-FBR	L-FBR-742 (Middle Mw type)	-78	Kuraray
	L-FBR-746 (High Mw type)	-78	Kuraray
LFR	L-FR-101 (Low Mw polyfarnesene)	-73	Kuraray
	L-FR-103 (Middle Mw polyfarnesene)	-73	Kuraray
	L-FR-107L (High Mw polyfarnesene)	-73	Kuraray
LBR	LBR-307 (Low Mw polybutadiene)	-94	Kuraray
	LBR-305 (Middle Mw polybutadiene)	-94	Kuraray
Oil	TDAE (VIVATEC 500)	-50	H&R GmbH Co. KGaA

Formulation

	Control	Formulation
Natural Rubber	70	70
BR	30	30
Softener		
TDAE	20	10
Liquid Rubber	-	10
Carbon Black (N220)	35	35
Silica	35	35
Silane coupling agent	2.8	2.8
ZnO	3.5	3.5
Stearic acid	2.0	2.0
Anti oxidant 6C [1)]	1.5	1.5
Anti oxidant RD [2)]	1.0	1.0
Sulfur	2.0	2.0
Accelerator NS [3)]	1.0	1.0
Accelerator DPG [4)]	1.0	1.0

1st Stage	Banbury mixer
0′00″	NR, BR (60 °C)
0′20″	CB, Silica, Softener, AO, ZnO, Stearic acid
5′30″	Dump out (150-160 °C)
2nd Stage	**Banbury mixer**
0′00″	Compound, Sulfur, Accelerators (50 °C)
0′75″	Dump out (95-105°C)

1) N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine
2) Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline
3) N-tert-Butyl-2-benzothiazolesulfenamide
4) 1,3-Diphenylguanidine

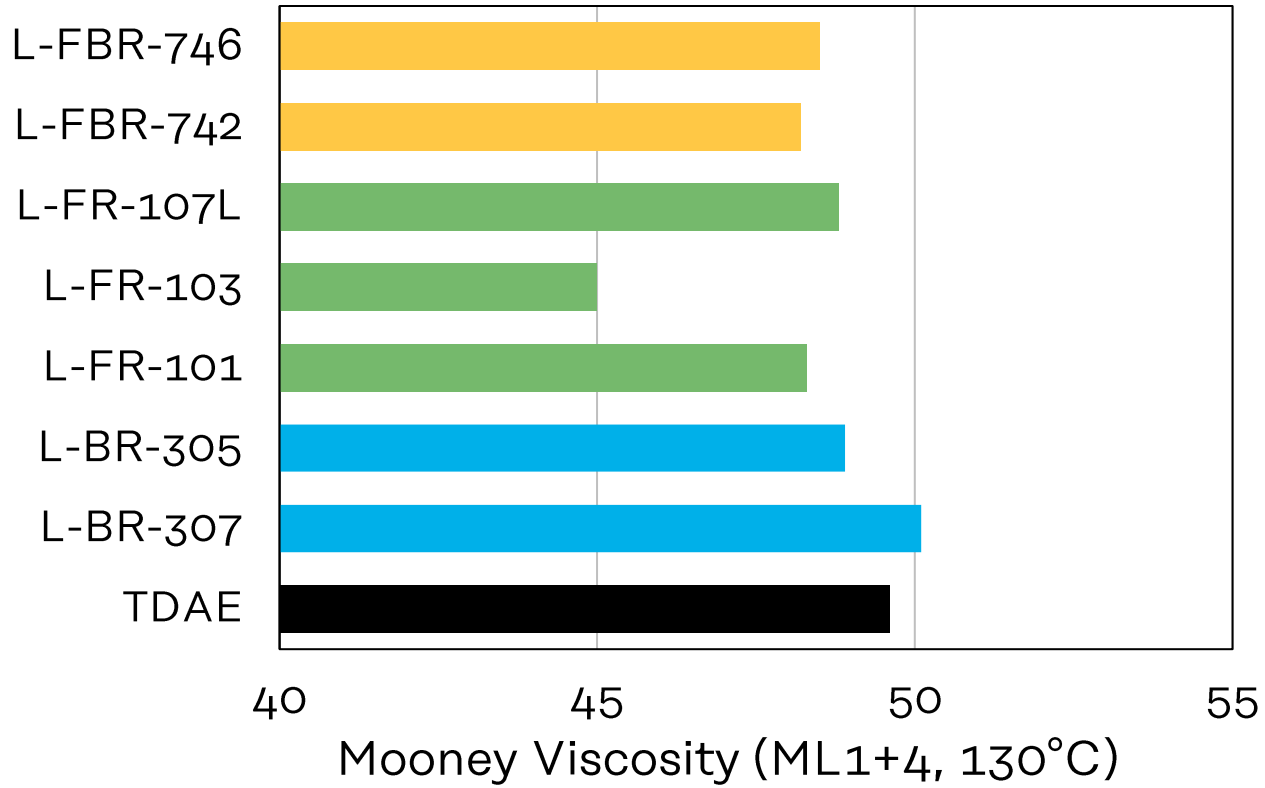
NR/CB Formulation Summary (1)

		TDAE	L-BR-307	L-BR-305	L-FR-101	L-FR-103	L-FR-107L	L-FBR-742	L-FBR746
Mooney Vis., ML1+4 (130°C)		49.6	50.1	48.9	48.3	45.0	48.8	48.2	48.5
Mooney Scorch time (130°C)									
t5	(min.)	18.6	20.4	19.2	18.5	18.1	18.4	19.4	18.1
t35	(min.)	25.7	27.5	26.4	28.4	24.9	25.4	26.0	24.7
Vmin		48.1	47.8	46.7	46.7	43.6	46.5	46.0	46.7
Curelastometer (145°C)									
t10	(min.)	9.59	9.46	9.27	8.97	8.39	8.54	9.22	8.98
t30	(min.)	11.93	12.10	11.81	11.27	10.53	10.85	11.53	11.11
t90	(min.)	22.75	23.19	23.58	22.06	21.42	21.44	22.98	21.85
ML	(N.m)	0.26	0.27	0.26	0.26	0.27	0.28	0.26	0.26
MH	(N.m)	1.34	1.23	1.29	1.23	1.36	1.41	1.28	1.42

NR/CB Formulation Summary (2)

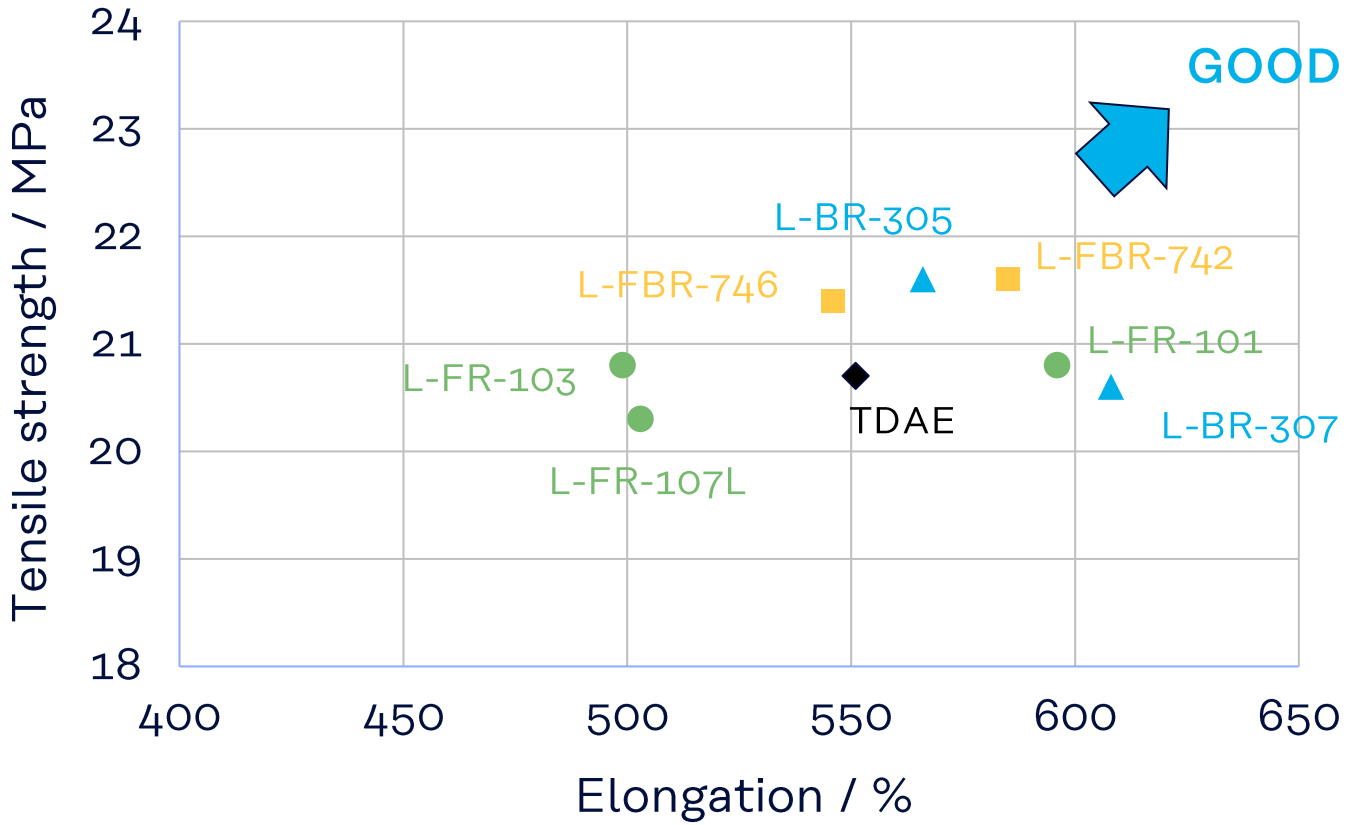
		TDAE	L-BR-307	L-BR-305	L-FR-101	L-FR-103	L-FR-107L	L-FBR-742	L-FBR746
Mechanical Properties									
Hardness	Type A	61	57	59	56	58	58	57	60
EB	(%)	551	608	566	596	499	503	585	546
TB	(MPa)	20.7	20.6	21.6	20.8	20.8	20.3	21.6	21.4
M50	(MPa)	1.19	1.05	1.21	1.05	1.24	1.23	1.12	1.34
M100	(MPa)	2.03	1.75	2.04	1.76	2.23	2.14	1.89	2.35
M200	(MPa)	5.16	4.39	5.24	4.39	5.99	5.70	4.75	5.97
M300	(MPa)	9.4	8.1	9.5	8.1	10.9	10.5	8.8	10.6
Mechanical Properties (100°C x 48H)									
Hardness	Type A	65.8	63.9	65.8	64.2	64.4	64.4	66.0	66.3
EB	(%)	378.1	437.2	399.3	387.5	371.2	358.8	399.4	395.8
TB	(MPa)	18.6	19.2	19.5	18.1	18.7	18.6	19.0	19.7
M50	(MPa)	1.8	1.6	1.8	1.6	1.7	1.7	1.7	1.8
M100	(MPa)	3.5	3.0	3.5	3.1	3.4	3.5	3.3	3.4
M200	(MPa)	8.9	7.6	8.9	8.1	9.0	9.3	8.4	8.7
M300	(MPa)	14.7	12.8	14.7	13.7	14.9	15.4	14.1	14.6
Viscoelasticity (25°C)									
E′	(MPa)	4.75	4.37	4.63	4.32	4.26	4.50	4.68	4.95
tanδ	(-)	0.224	0.243	0.234	0.234	0.194	0.192	0.226	0.211
DIN abrasion	index	100	108	14	86	91	90	96	103
Toluene extraction	(%)	11.97	11.47	8.61	10.60	7.95	7.70	8.28	7.61

Mooney Viscosity



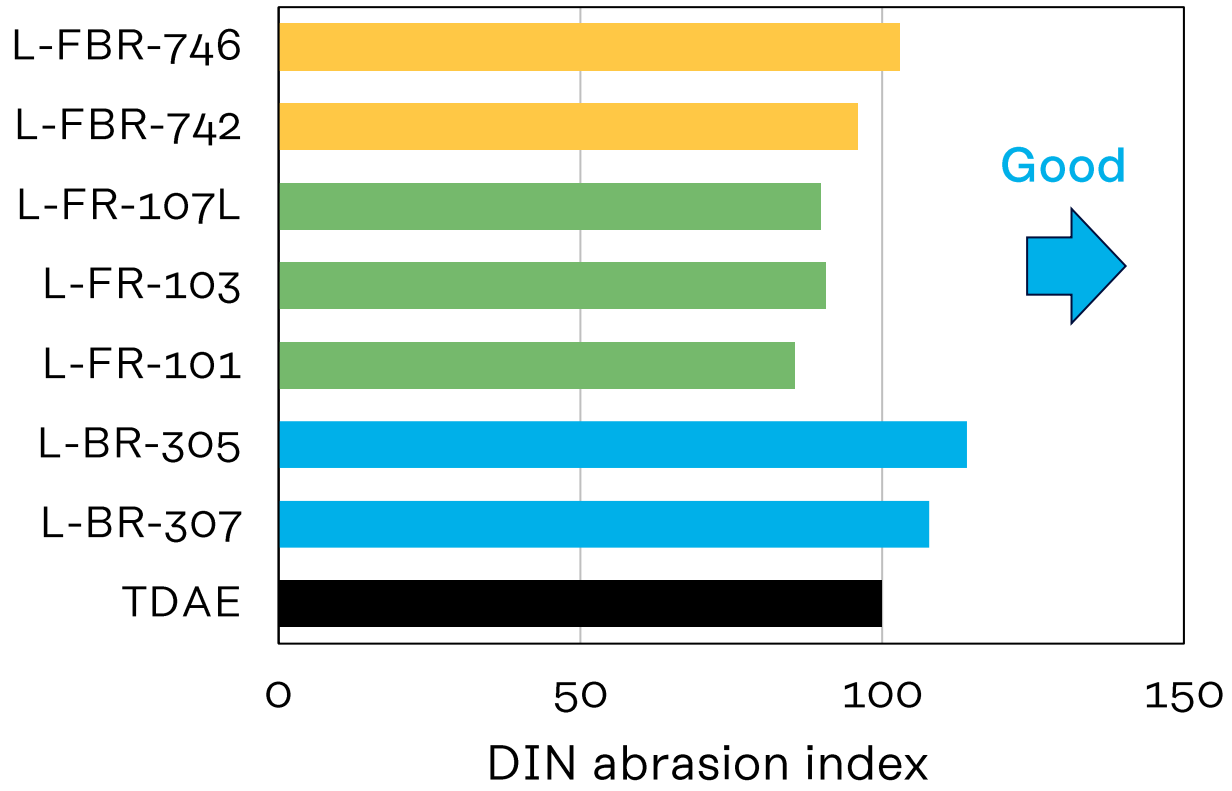
✓ Good plasticizing effect

Tensile Property



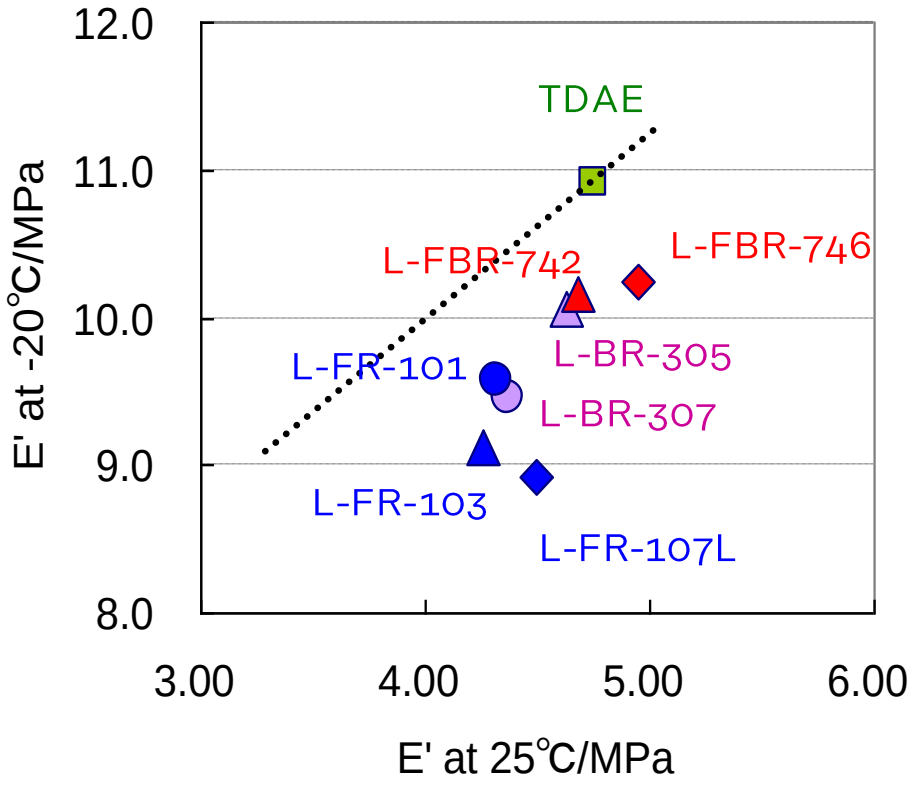
✓ Better tensile property

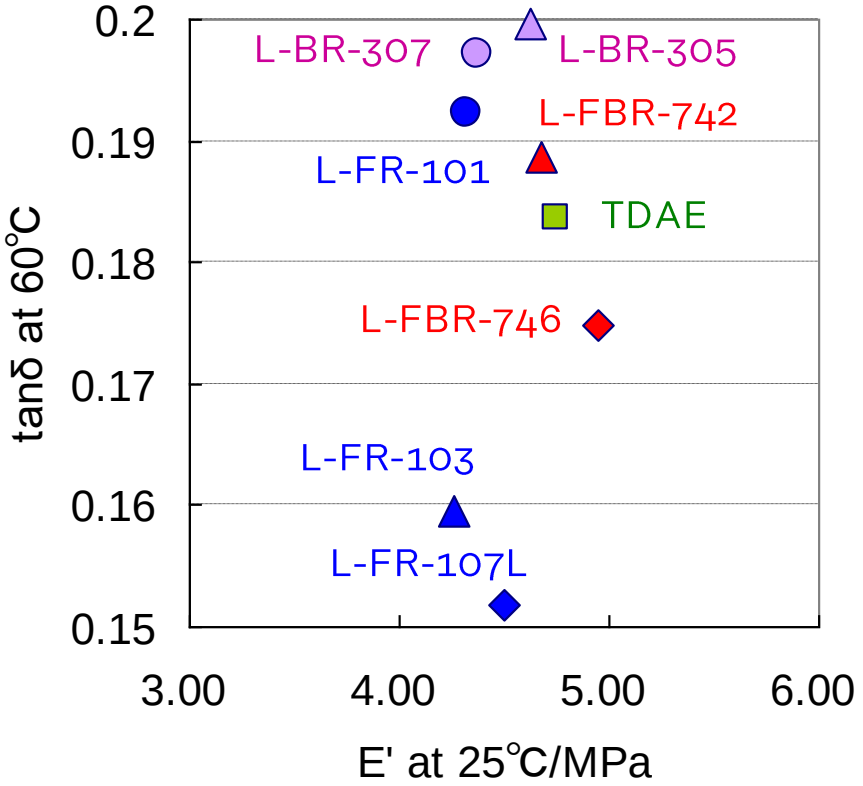
Abrasion Resistance



✓ Similar abrasion resistance

Dynamic Viscoelasticity

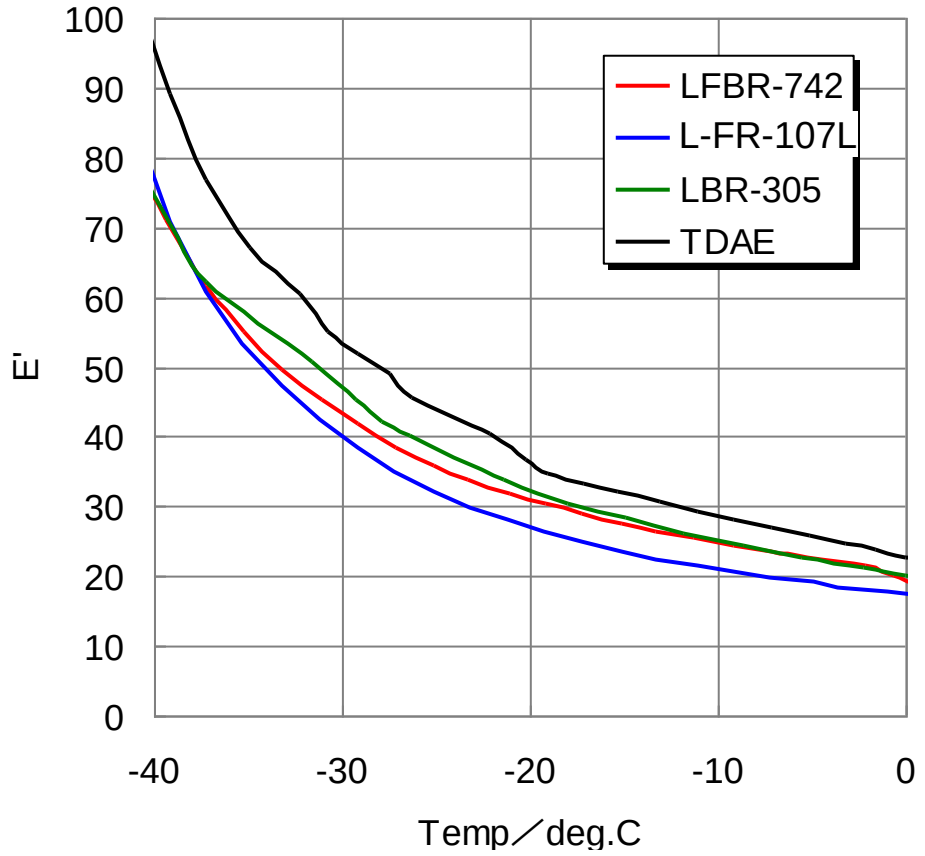


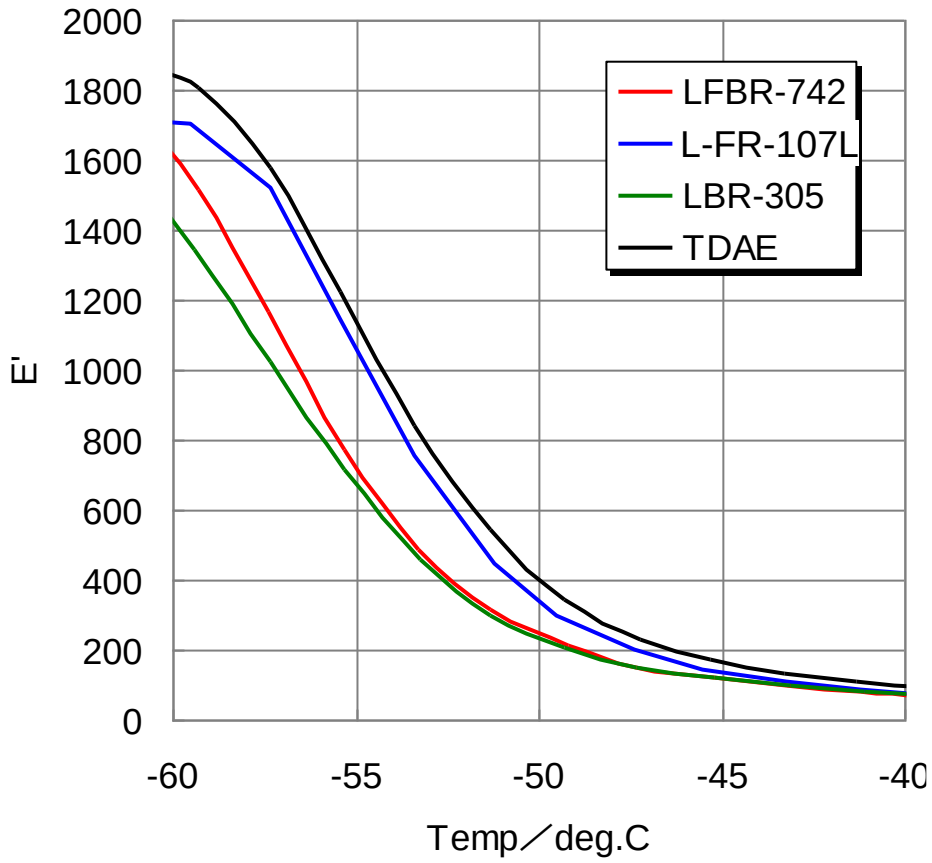


✓L-FBR: same E′ at 25°C, Low E′ at -20°C
✓Excellent softening effect at low temperature

✓Lower tanδ than TDAE

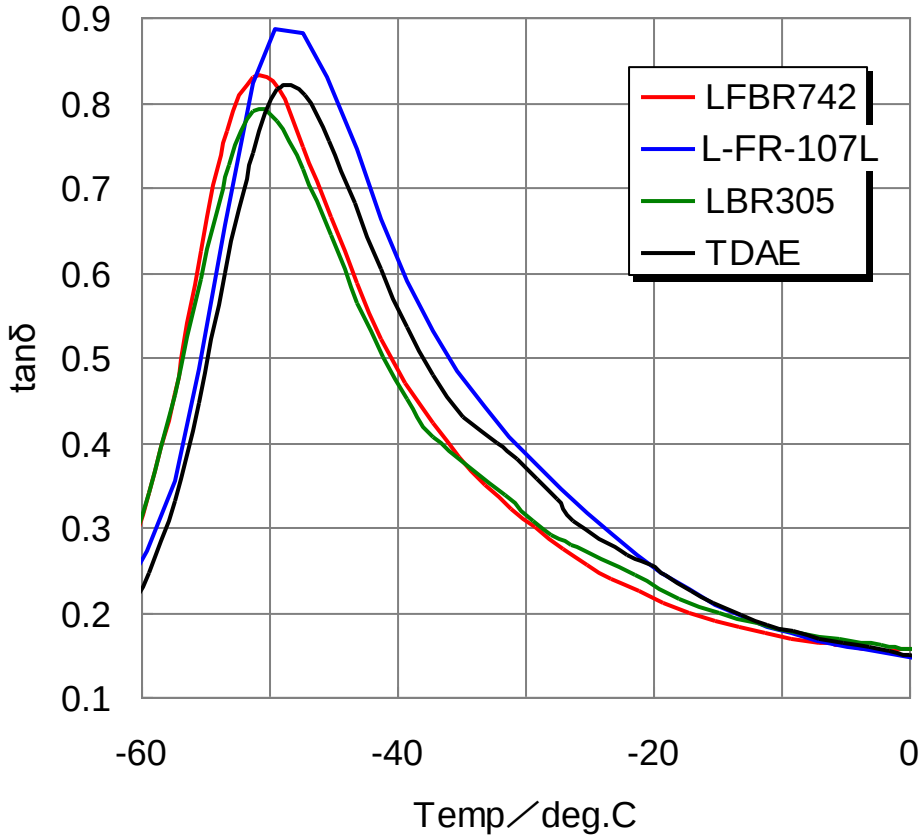
Dynamic Viscoelasticity (Temp. sweep)

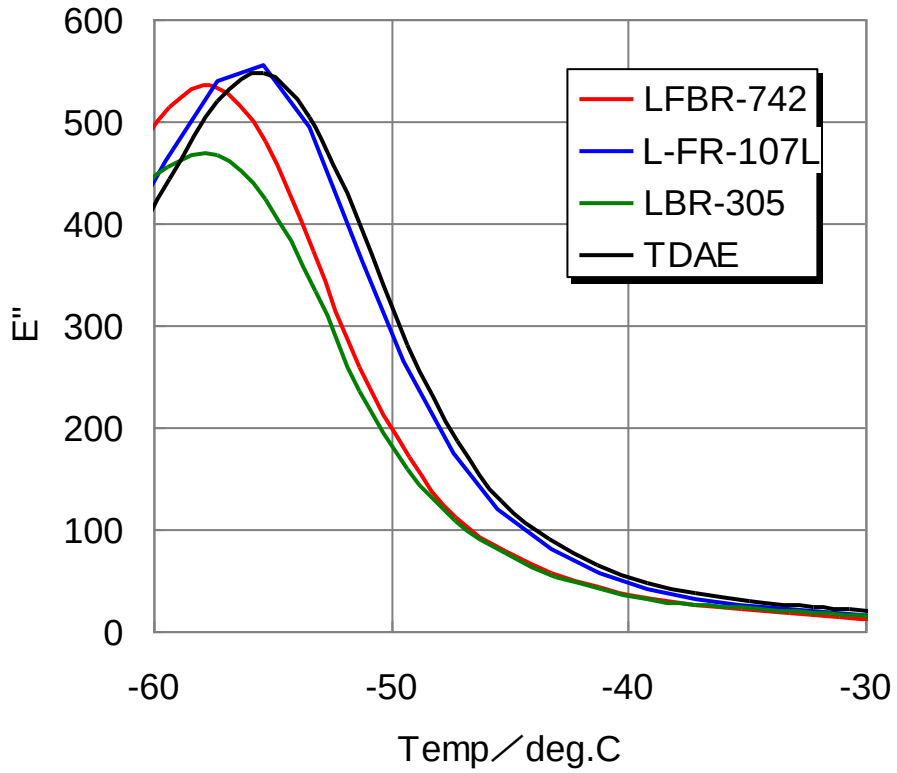




✓Farnesene based polymer show lower E′ at low temperature than TDAE

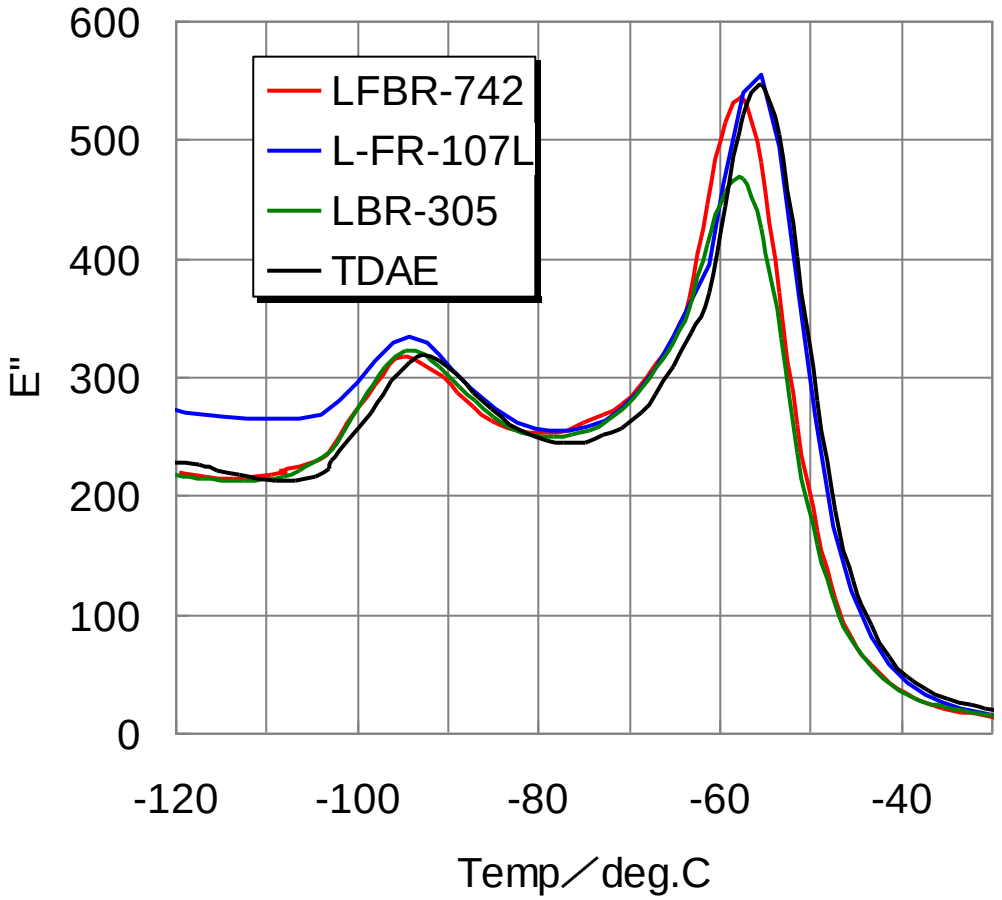
Dynamic Viscoelasticity (Temp. sweep)



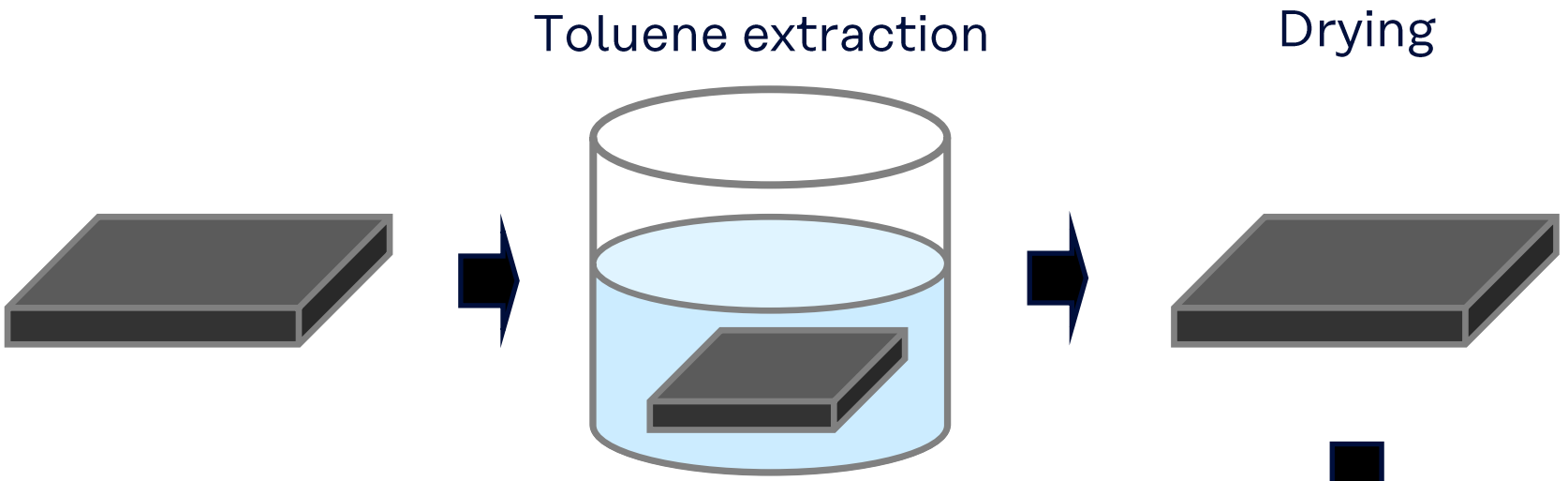


✓Farnesene based polymer show high energy loss at low temperature than LBR

Dynamic Viscoelasticity (Temp. sweep)

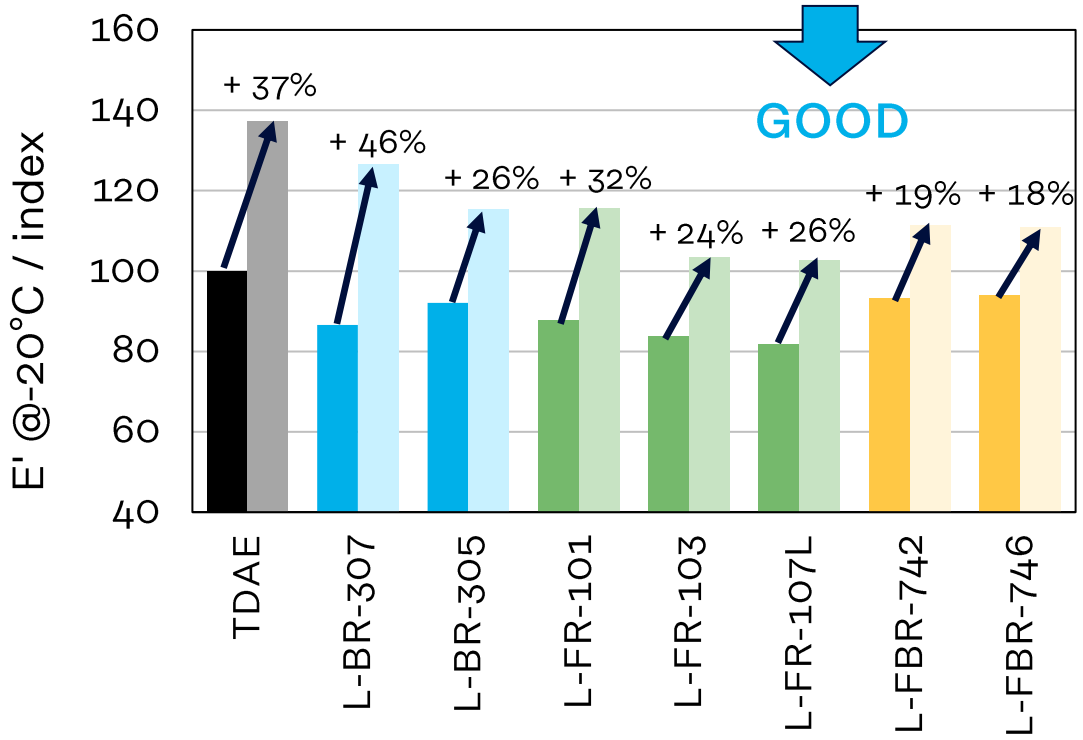


Toluene extraction test

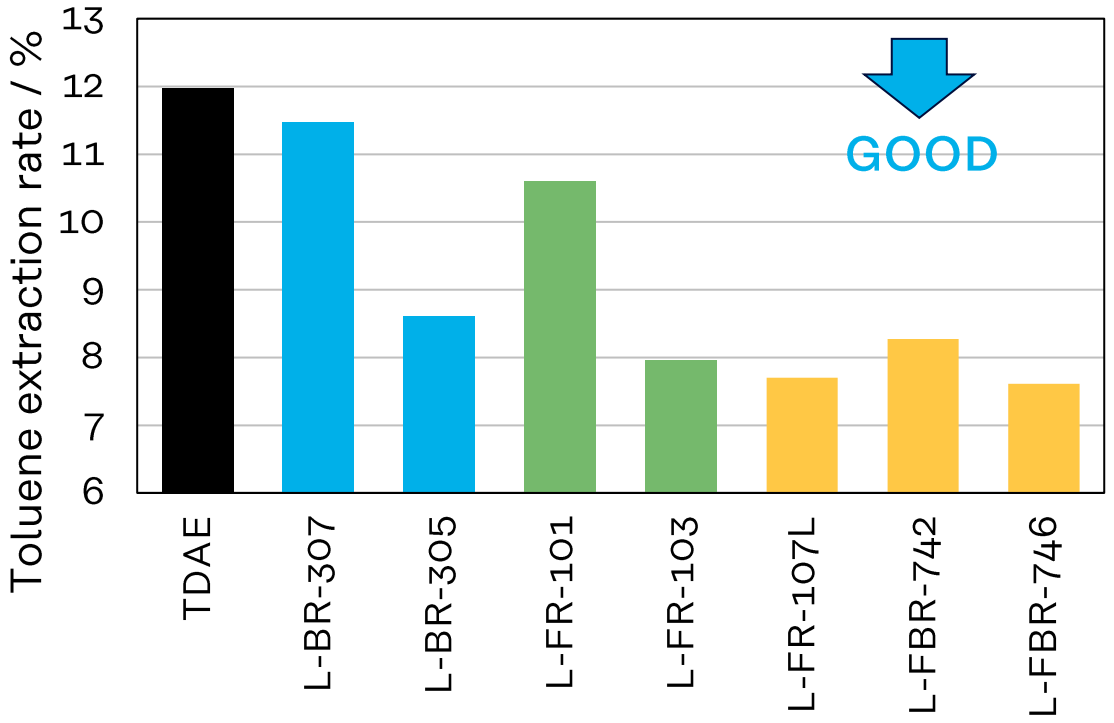


Viscoelasticity
Extraction rate of softener

E′ at -20°C



✓ Good softness at Low temperature
✓ Maintained softness after extraction



✓ Low extraction rate

Summary

	OIL	LBR	LFR	L-FBR
Softness at Low Temperature	+ -	+ +	+ +	+ +
tanδ at -40°C	+ -	- -	+	-
tanδ at 60°C	+ -	- -	+ +	+
Abrasion	+ -	+	-	+ -
Low Migration	+ -	+ +	+ +	+ +

+ +:Excellent, +:Good, + -:Fair, -:Poor, - -:Bad

Features of L-FBR in NR/BR formulation

- Excellent Ice Grip
- Maintaining Softness for a long time
- Good Fuel economy

=> L-FBR can be applied for winter tire tread

Raw materials

Material	Product Name	Manufacturer	Note
Natural Rubber	STR20	Von Bundit Co., Ltd.	
Butadiene Rubber	JSR BR01	JSR Corporation	Cis content: 95% Mooney Vis. @100°C: 45
SBR	JSR 1500	JSR Corporation	St/Bd: 23.5/76.5 (wt/wt) Vinyl content: 15% Tg: -53 °C
Silica	ULTRASIL® 7000GR	Evonik Industries AG	Specific surface area (N2) 175 m^2/g
Carbon black	DIABLACK™ I	Mitsubishi Chemical Corporation	ASTM N220
Silane Coupling Agent	Si-69	Evonik Industries AG	
TDAE	VIVATEC 500	H&R GmbH Co. KGaA	

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Liquid Farnesene Rubber for Winter Tire Tread

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Agenda

1) Introduction of Liquid Rubber
2) Overview of Winter Tire Application
3) Friction Performance on Ice in Winter Tire Tread
    a) NR Based Formulation
    b) BR Based Formulation
4) Summary

Winter Tire Requirement

NR/BR formulation

- **Ice Grip**
- Snow Grip

SBR/NR formulation

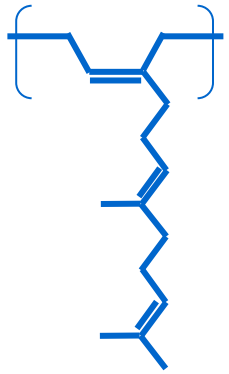
- **Ice Grip**
- Wet Grip
- Handling Stability

+ Others (Wear Resistance, Rolling Resistance, etc.)

NR Based Formulation

Grade List

	Grade	Structure (wt)	Tg (°C)	Mw	Visc. @38°C (Pa.s)
Commercial Grade	L-FR-107L	Far=100	-71	135k	69
	L-FBR-742	Far/Bd=60/40	-78	29k	15
	L-FBR-746	Far/Bd=60/40	-78	88k	520
Development Grade	L-FR-101	Far=100	-73	9k	0.4
	L-FR-103	Far=100	-72	37k	6.5



✓ Less entanglement between molecules because of highly branched structure.
=> High Mw & Low viscosity

Formulation

	Control	Formulation
Natural Rubber	70	70
BR	30	30
Softener		
TDAE	20	10
Liquid Rubber	-	10
Carbon Black (N220)	35	35
Silica	35	35
Silane coupling agent (Si-75)	2.8	2.8
ZnO	3.5	3.5
Stearic acid	2.0	2.0
Anti oxidant 6C [1)]	2.0	2.0
Anti oxidant RD [2)]	1.0	1.0
Wax	1.5	1.5
Sulfur	2.0	2.0
Accelerator NS [3)]	1.0	1.0
Accelerator DPG [4)]	0.5	0.5

1st Stage	Banbury mixer
0′00″	NR, BR (60 °C)
0′20″	CB, Silica, Softener, AO, ZnO, Stearic acid
5′30″	Dump out (150-160 °C)
2nd Stage	Banbury mixer
0′00″	Compound, Sulfur, Accelerators (50 °C)
0′75″	Dump out (95-105°C)

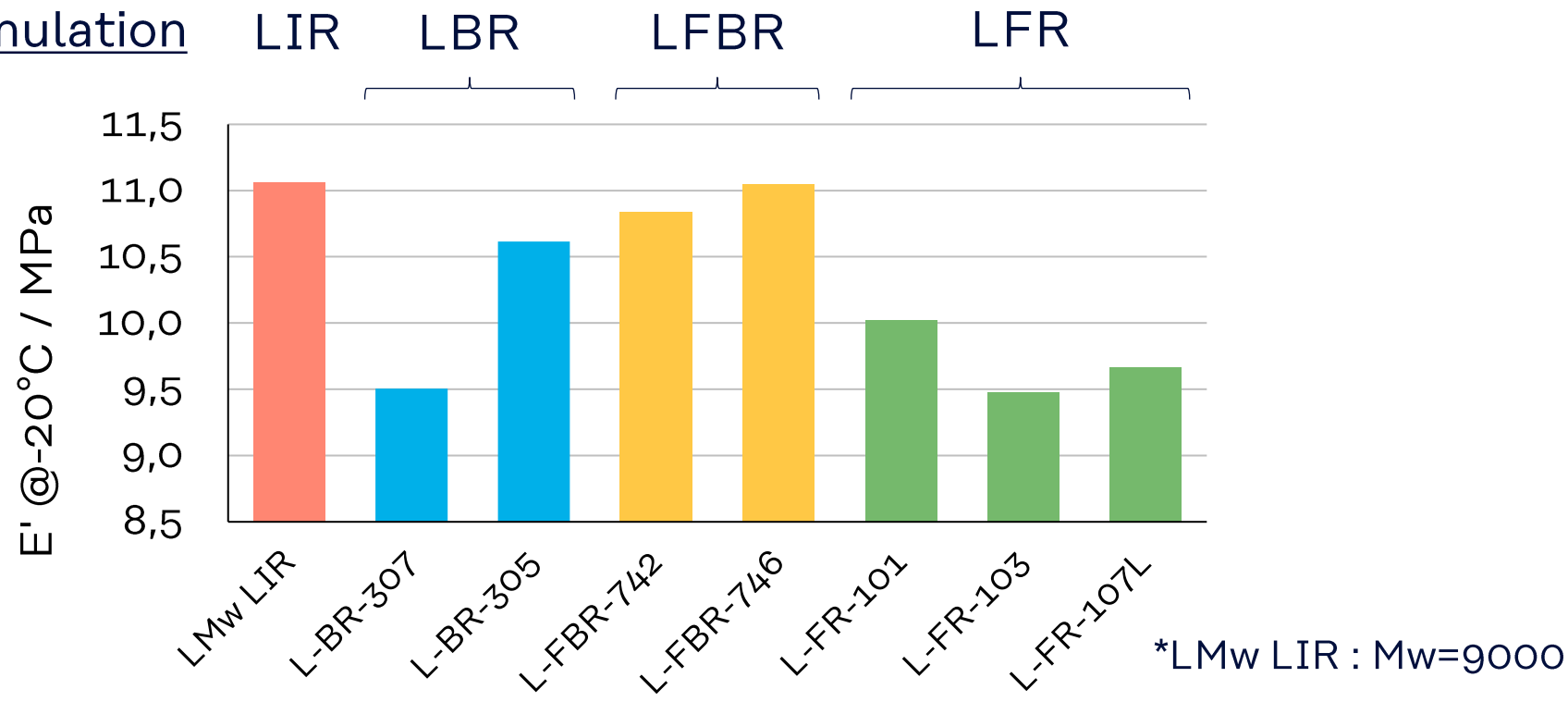
1) N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine
2) Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline
3) N-tert-Butyl-2-benzothiazolesulfenamide
4) 1,3-Diphenylguanidine

Summary of Properties

			LMw LIR	L-BR-307	L-FR-101	L-FR-107	L-FBR-742	L-FBR-746
Mooney Viscosity, ML1+4 (130°C)			47	50	48	49	48	49
Mooney Scorch time (130°C)								
t5		(min.)	19.2	20.4	18.5	18.4	19.4	18.1
t90		(min.)	26.2	27.5	24.8	25.4	26.0	24.7
Vmin			45.4	47.8	46.7	46.5	46.0	46.7
Curelastometer (145°C)								
t10		(min.)	9.1	9.5	9.0	8.5	9.2	9.0
t30		(min.)	11.5	12.1	11.3	10.9	11.5	11.1
t90		(min.)	22.5	23.2	22.1	21.4	23.0	21.9
ML		(N.m)	0.3	0.3	0.3	0.3	0.3	0.3
MH		(N.m)	1.2	1.2	1.2	1.4	1.3	1.4
Mechanical properties								
Hs		Type A	57	57	56	58	57	60
EB		(%)	570	610	600	500	590	550
TB		(MPa)	20.4	20.6	20.8	20.3	21.6	21.4
M50		(MPa)	1.1	1.1	1.1	1.2	1.1	1.3
M100		(MPa)	1.9	1.8	1.8	2.1	1.9	2.4
M200		(MPa)	4.8	4.4	4.4	5.7	4.8	6.0
M300		(MPa)	8.9	8.1	8.1	10.5	8.8	10.6
Viscoelasticity(10%-2%、 Preload, Temp sweep -30〜+70°C)								
E′	-20°C	(MPa)	11.1	9.5	10.0	9.7	10.8	11.0
	25°C	(MPa)	4.3	4.4	4.3	4.5	4.7	5.0
tanδ	-20°C	(-)	0.46	0.44	0.45	0.43	0.43	0.42
	25°C	(-)	0.24	0.24	0.23	0.19	0.23	0.21
DIN abrasion		(mm3)	102	86	109	104	97	91

E′ at -20 deg. C

NR/BR/CB/Si formulation

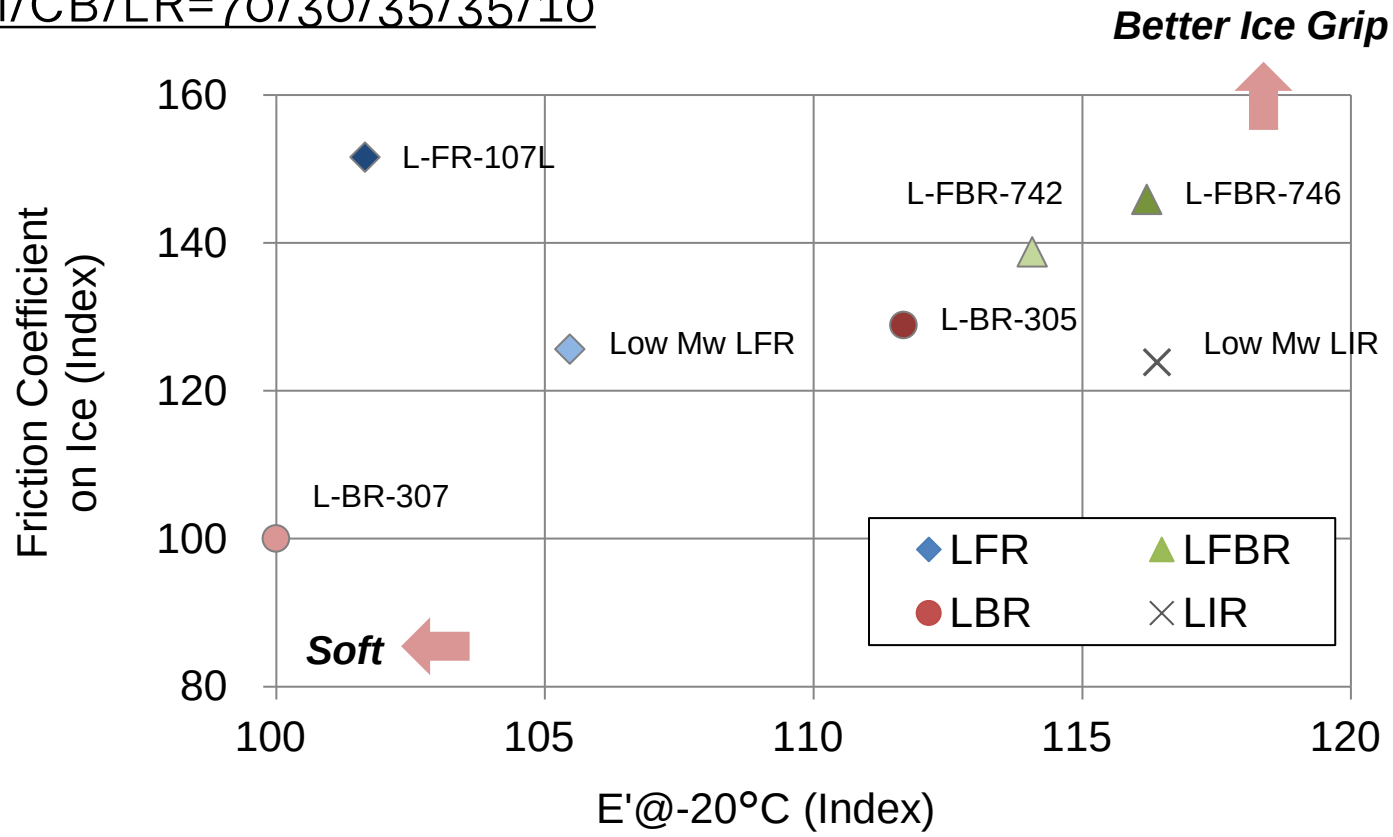


*LMw LIR : Mw=9000

- LFR showed similar E′ to L-BR-307
  ⇒ Similar ice grip ?
  ⇒ Checked friction performance of rubber compound.

Friction Test Results

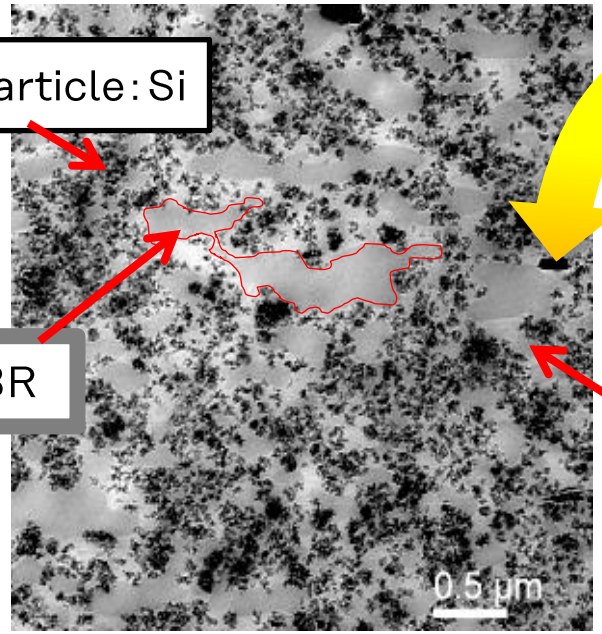
NR/BR/Si/CB/LR=70/30/35/35/10



- ✓ Especially LFR and L-FBR showed good ice grip
- ✓ E′ have little correlation with actual ice grip

Hypothesis

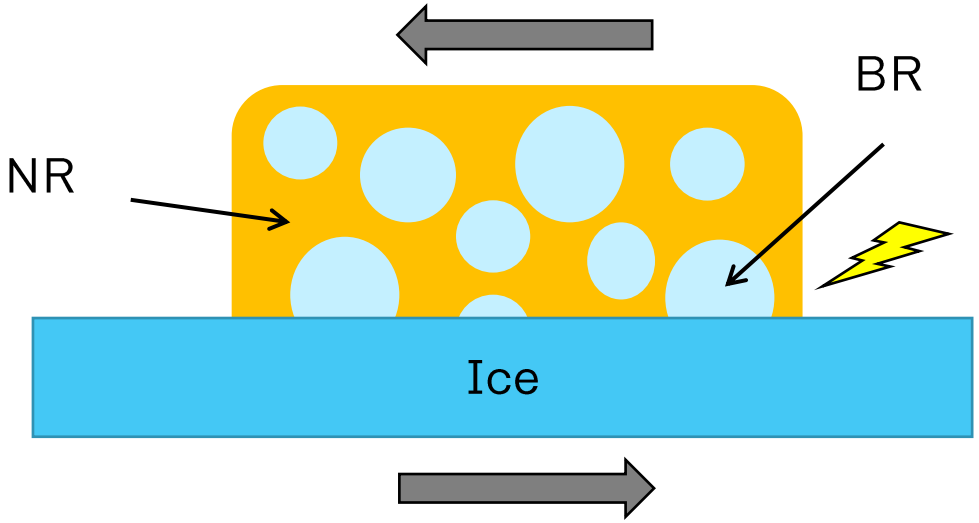
NR/BR/Si (TEM)



Where to locate?
Compatibility?

Liquid Rubber

White : NR



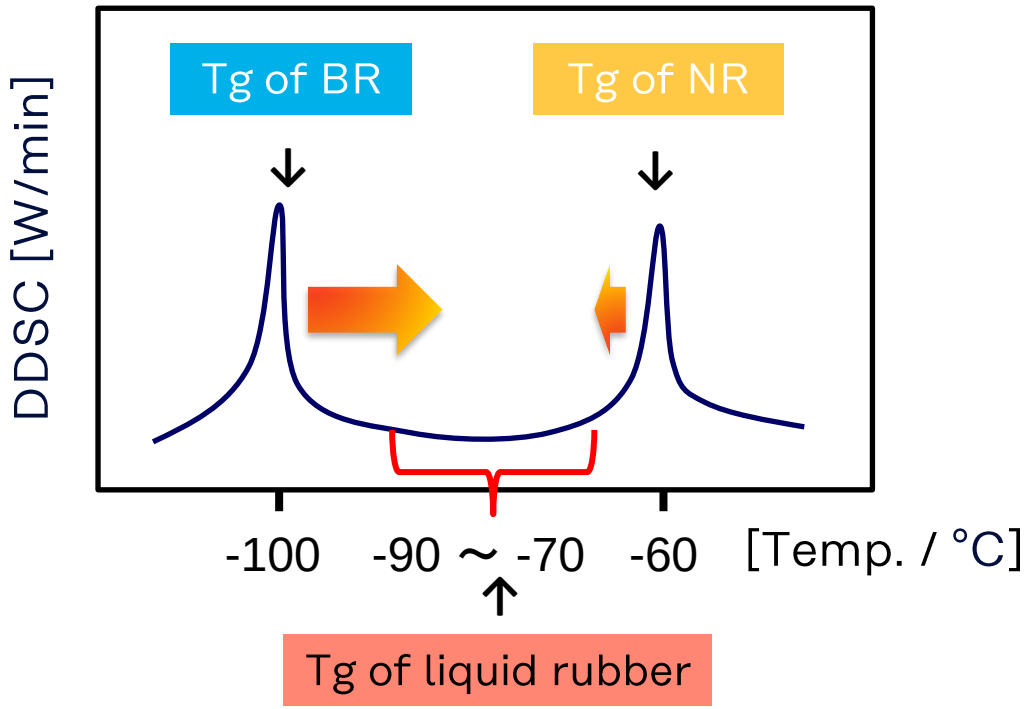
Different LR shows different distribution to NR and BR

Contact area : NR>BR
⇒ Increased friction coefficient by softening NR phase

Determination of distribution ratio of liquid rubber by DSC

- Calculated distribution ratio from Tg sift.

Formulation	phr
Butadiene Rubber	50
Natural Rubber	50
Liquid Rubber	20

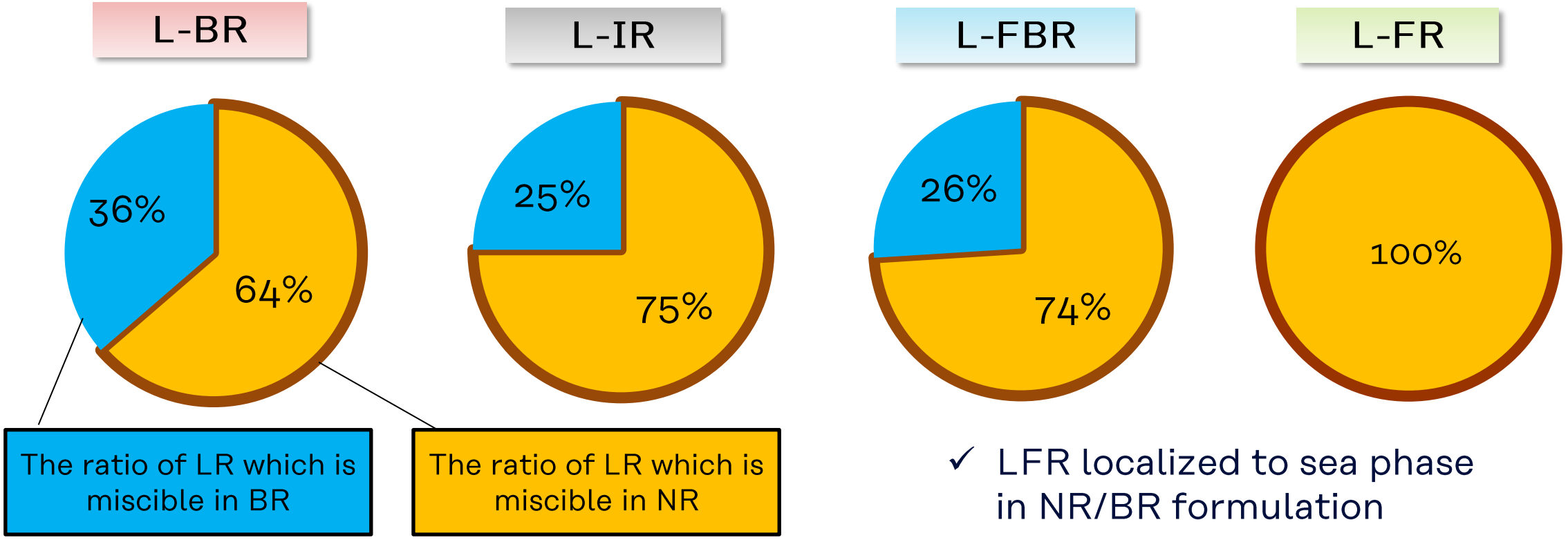


Method

Distribution Ratio by DSC

NR/BR/LR = 50/50/20

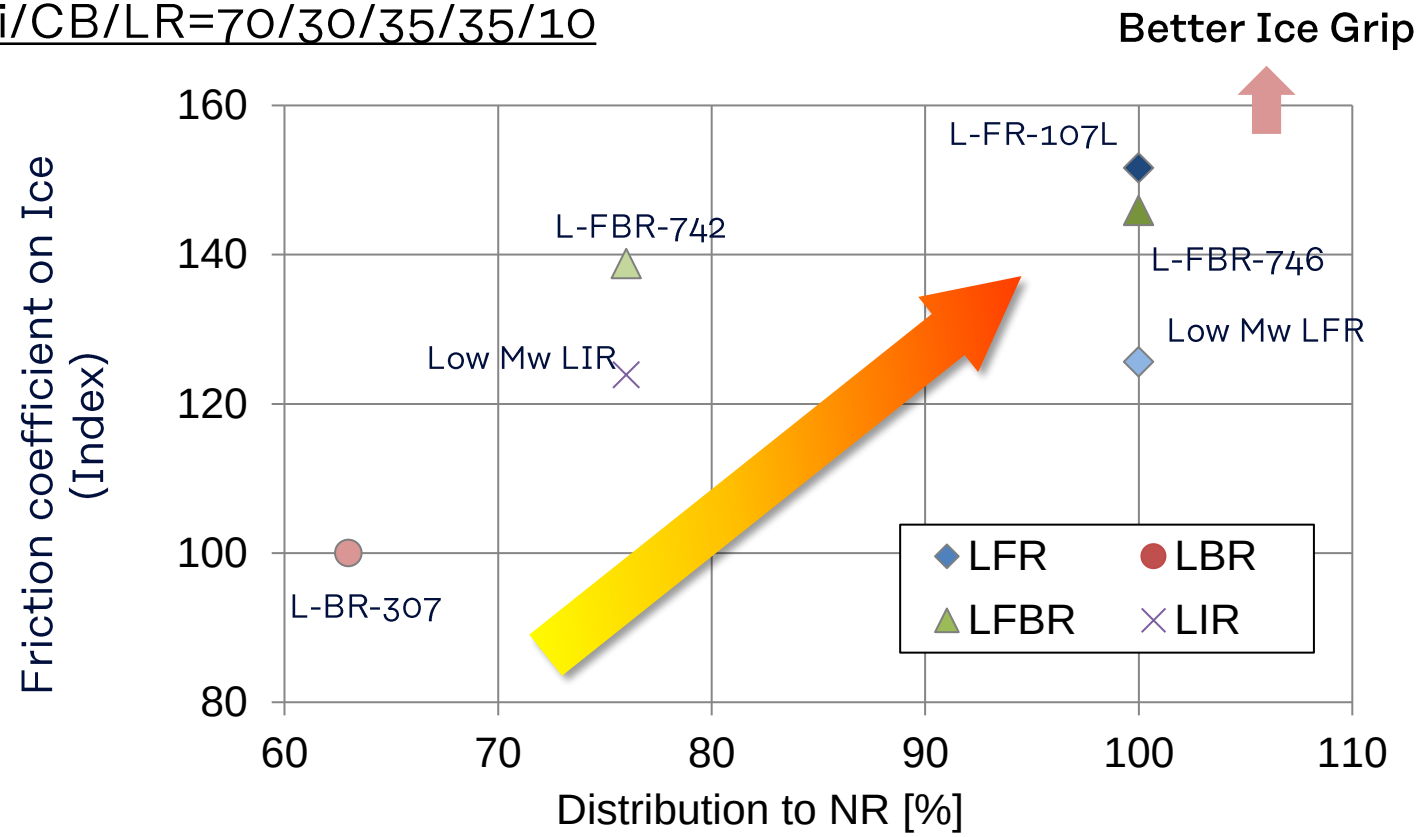
All Liquid rubbers have same range Mw (8000-10000).



✓ LFR localized to sea phase in NR/BR formulation

Friction & Distribution Ratio

NR/BR/Si/CB/LR=70/30/35/35/10



- ✓ Higher distribution ratio to sea phase shows higher ice grip.
- ✓ L-FR&L-FBR can effectively improve ice grip

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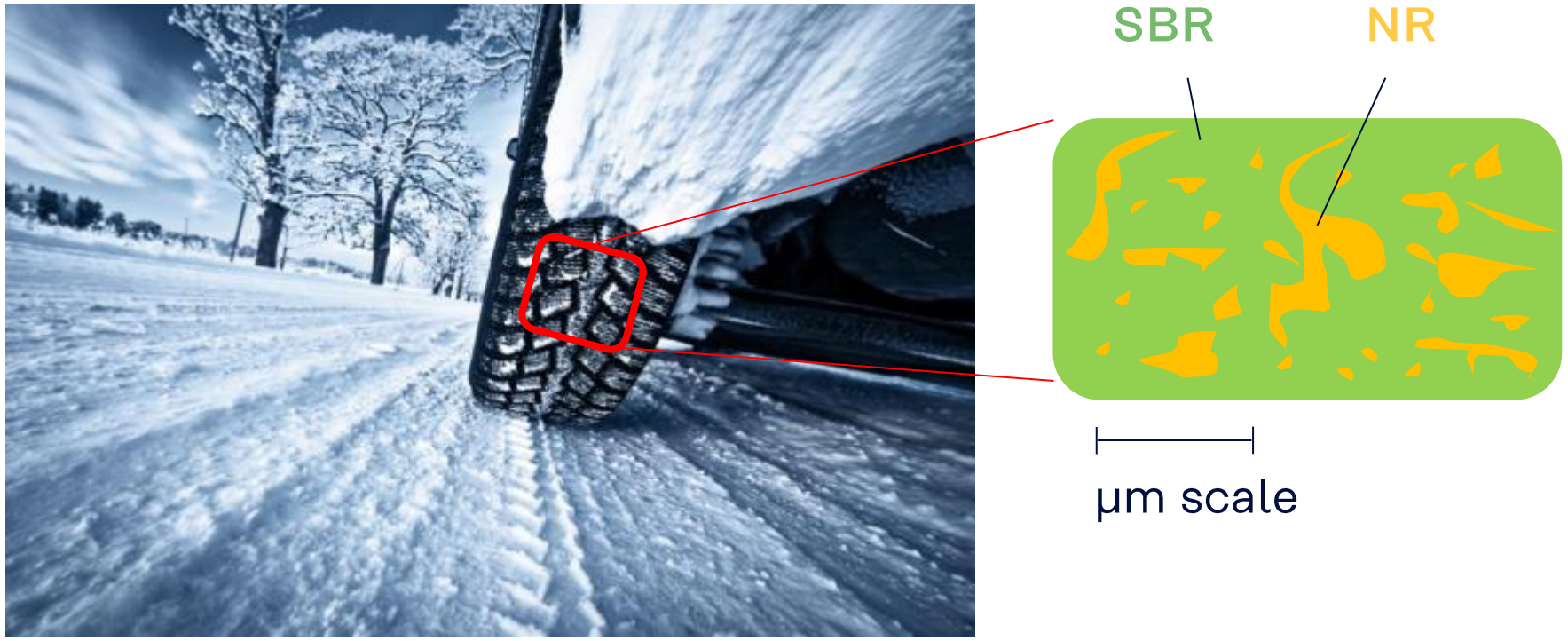
SBR Based Formulation

Ice Grip Improvement



- Contact area : SBR > NR
- Softness of sea phase improves friction coefficient on ice based on the experience of NR/BR .

Typical Properties

	Structure	St cont. (wt%)	Tg (°C)	Melt Vis. @38°C (Pa.s)
L-FR-101	Far	-	-73	0.4
LBR-307	Bd	-	-94	1.3
LIR-A	Ip	-	-63	3.0
L-SBR-B	St/Bd	10	-74	1.2
L-SBR-C	St/Bd	23	-75	7.3
L-FSBR-232*	Far/St/Bd	23	-65	5.9

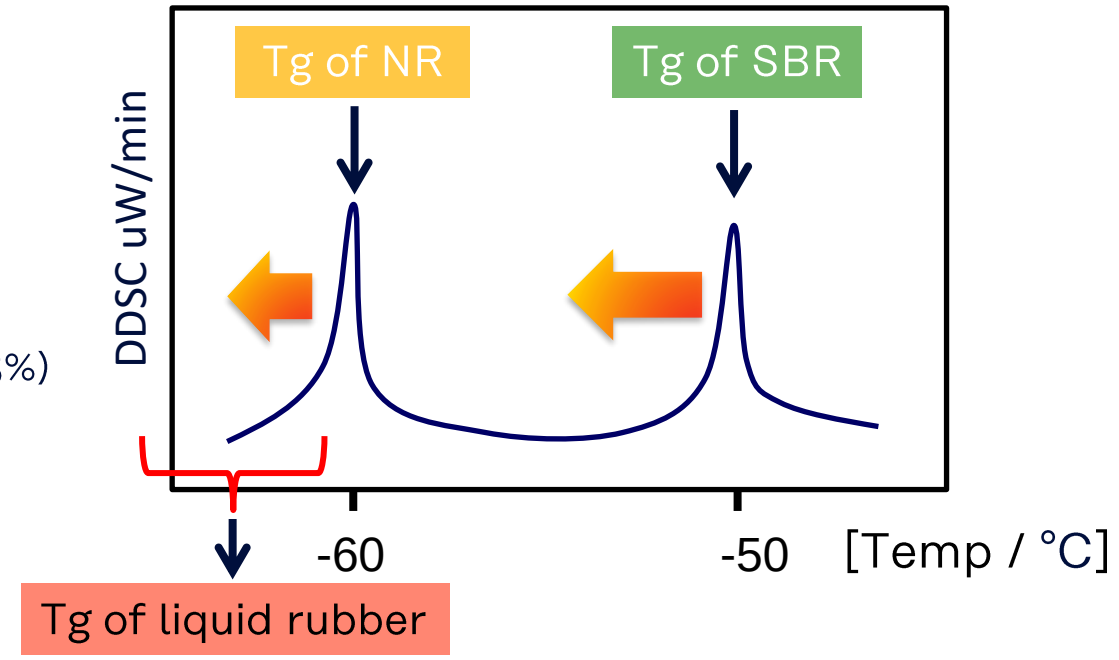
*Development Grade

Distribution Ratio by DSC

- Calculated distribution ratio from Tg sift.

Formulation	phr
Styrene Butadiene Rubber[1)]	50
Natural Rubber	50
Liquid Rubber	20

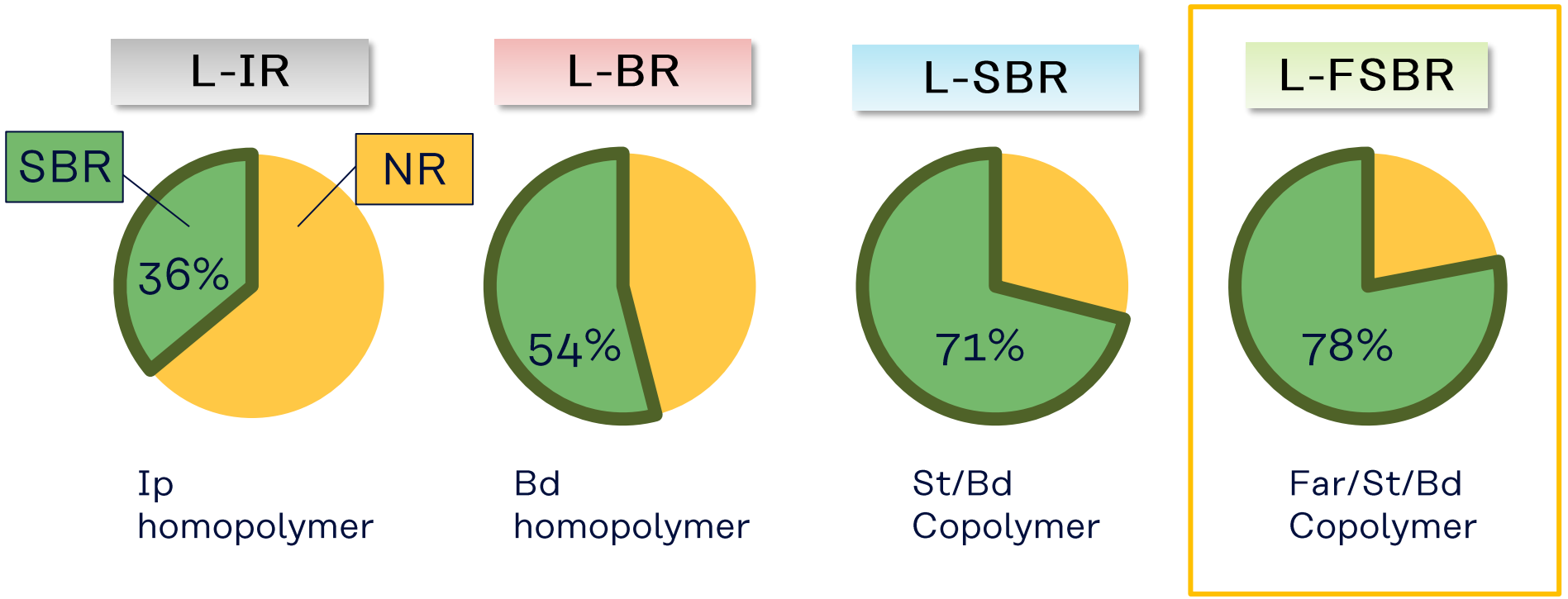
1) Emulsion SBR (St/Bd=23/77wt%, Bd vinyl=15%)



Method

Distribution Ratio by DSC

SBR/NR/LR=50/50/20



✓ LFSBR-232 shows good compatibility to SBR.

Formulation

	Control	Formulation
Natural Rubber	30	30
E-SBR1500 (Emulsion SBR)	70	70
Softener		
TDAE	10	10
Liquid Rubber	-	20
Carbon Black (N220)	10	10
Silica	70	70
Silane coupling agent (Si-75)	5.6	5.6
ZnO	3.5	3.5
Stearic acid	2.0	2.0
Anti oxidant 6C [1)]	2.0	2.0
Wax	1.0	1.0
Sulfur	1.5	1.5
Accelerator TBT-N [2)]	1.0	1.0
Accelerator D [3)]	0.65	0.65
Accelerator CZ [4)]	0.45	0.45

1st Stage	Banbury mixer
0′00″	NR, E-SBR (60 °C)
0′20″	CB, Silica, Softener, AO, ZnO, Stearic acid
5′30″	Dump out (150-160 °C)
2nd Stage	Banbury mixer
0′00″	1st mixed compound(80°C)
4′30″	Dump out (150-160°C)
3rd Stage	Banbury mixer
0′00″	Compound, Sulfur, Accelerators (50 °C)
0′75″	Dump out (95-105°C)

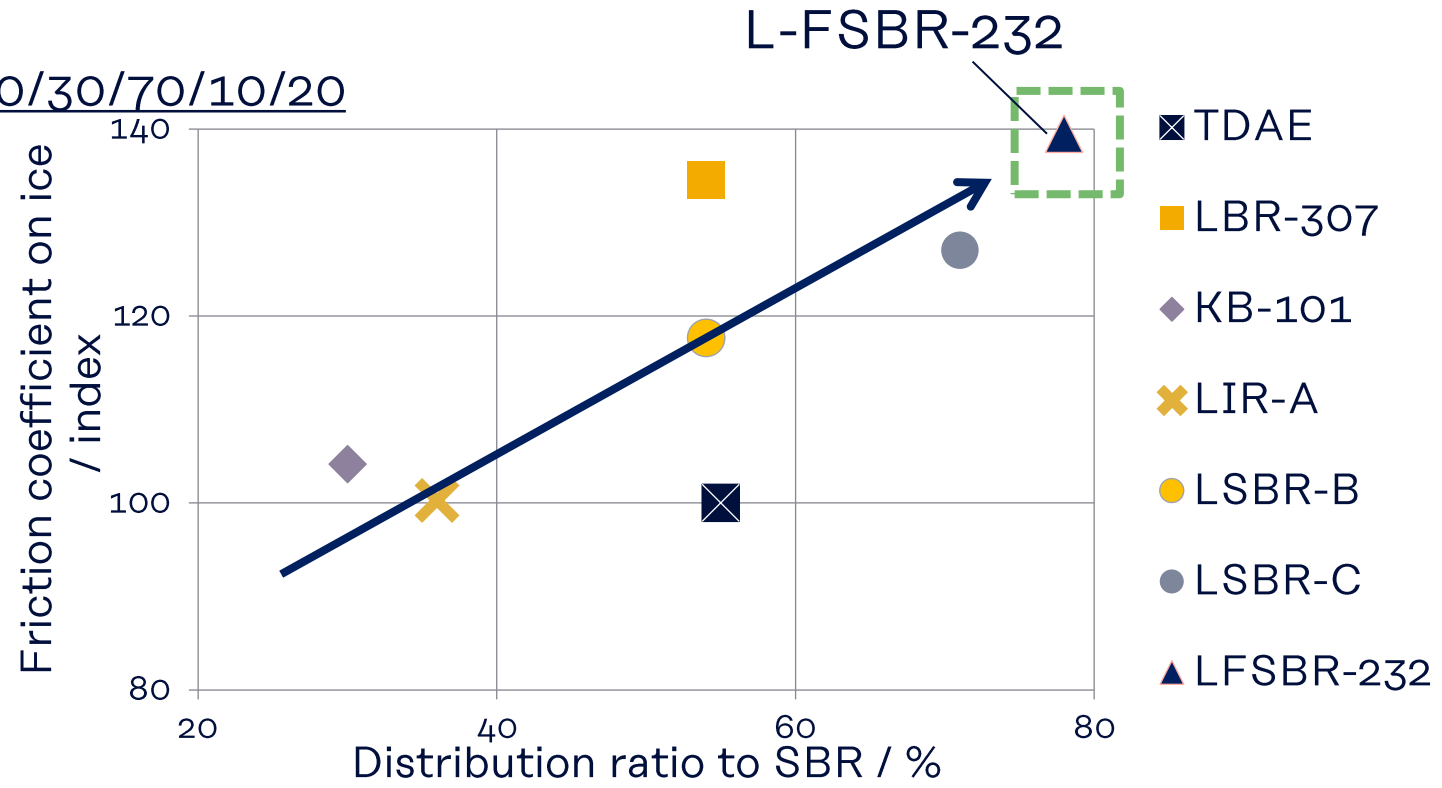
1) N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine
2) Bis(dibutylthiocarbamoyl)Disulfide
3) 1,3-Diphenylguanidine
4) N-Cyclohexyl-2-benzothiazolylsulfenamide

Summary of Properties

			TDAE	LIR-A	L-BR-307	L-FR-101	L-SBR-B	L-SBR-C	L-FSBR-232
Mooney Viscosity, ML1+4 (130°C)			36.8	36.2	34.9	36.4	36.9	37.9	39.4
Curelastometer (160°C)									
t90		(min.)	18.2	17.9	19.3	19.2	16.9	18.3	17.5
Mechanical properties									
Hs		Type A	63	59	59	60	62	60	60
EB		(%)	600	650	670	650	650	630	630
TB		(MPa)	20.9	19.2	19.8	18.7	19.7	20.1	20.2
M100		(MPa)	1.97	1.60	1.65	1.56	1.66	1.73	1.66
M300		(MPa)	8.95	7.00	7.36	6.82	7.50	8.13	7.83
Viscoelasticity(10%-2%、Preload, Temp sweep -30～+70°C)									
E′	-20°C	(MPa)	19.3	15.2	13.7	14.2	14.9	17.7	18.0
	0°C	(MPa)	11.16	9.00	8.80	8.91	9.42	10.43	10.45
	25°C	(MPa)	8.15	6.48	6.48	6.49	6.87	7.60	7.49
	60°C	(MPa)	6.17	4.71	4.86	4.85	5.11	5.37	5.38
tanδ	-20°C	(-)	0.64	0.57	0.52	0.55	0.55	0.57	0.57
	0°C	(-)	0.38	0.37	0.37	0.36	0.37	0.38	0.38
	25°C	(-)	0.30	0.32	0.32	0.31	0.32	0.33	0.32
	60°C	(-)	0.23	0.26	0.25	0.25	0.25	0.27	0.27
Friction coefficient on ice		index	100	100	135	104	118	127	140
DIN abrasion		(mm^3)	114	130	92	163	109	105	125

Distribution Ratio & Friction on Ice

SBR/NR/Si/CB/LR=70/30/70/10/20



- ✓ Distribution of LR shows good correlation with friction coefficient on ice.
- ✓ Especially LFSBR-232 shows good friction.
- ✓ LFSBR-232 can improve friction on ice very well.

Summary

NR Base Formulation

- Friction coefficient on ice shows good correlation with distribution ratio of Liquid Rubber.
- High distribution to NR improves friction coefficient on ice.
- LFR&LFBR can improve friction on ice very well.

SBR Based Formulation

- Farnesene can control compatibility with SBR.
- High distribution to SBR improve friction coefficient on ice.
- LFSBR-232 can improve friction on ice very well.

APPENDIX

Raw materials

Material	Product Name	Manufacturer	Note
Natural Rubber	STR20	Von Bundit Co., Ltd.	
Butadiene Rubber	JSR BR01	JSR Corporation	Cis content: 95% Mooney Vis. @100°C: 45
SBR	JSR 1500	JSR Corporation	St/Bd: 23.5/76.5 (wt/wt) Vinyl content: 15% Tg: -53 °C
Silica	ULTRASIL® 7000GR	Evonik Industries AG	Specific surface area (N2) 175 m^2/g
Carbon black	DIABLACK™ I	Mitsubishi Chemical Corporation	ASTM N220
Silane Coupling Agent	Si-75	Evonik Industries AG	
TDAE	VIVATEC 500	H&R GmbH Co. KGaA	

DMA Measuring Conditions

EPLEXOR® 500N (GABO)

Frequency	10 Hz
Static strain	10 %
Dynamic strain	2 %

Conditions for RTM measurement

Road Surface	Ice
Temperature	-3°C
Initial circumferential speed	30 km/h
Load	50N
Slip ratio	0 to 40%

The peak top value was regarded as the ice μ value.

Technical Insight of KURARAY LIQUID RUBBER

Liquid Farnesene Rubber Comparison with resins

Elastomer R&D Department
Elastomer Division

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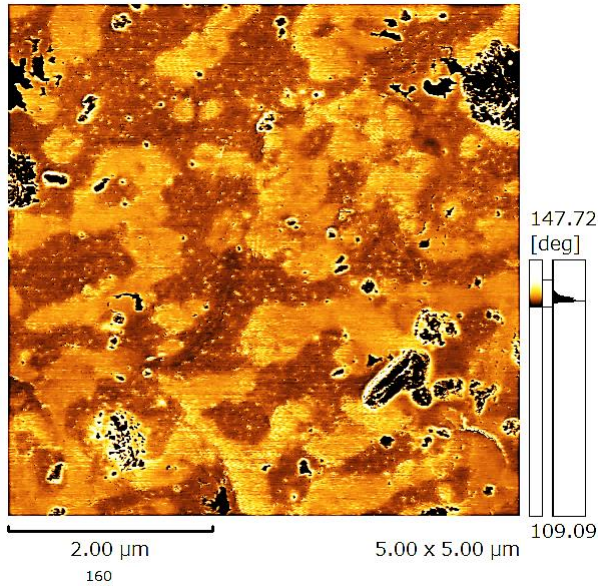
Agenda

1) Introduction of Liquid Rubber
2) Friction Performance in Winter Tire Tread
3) Summary

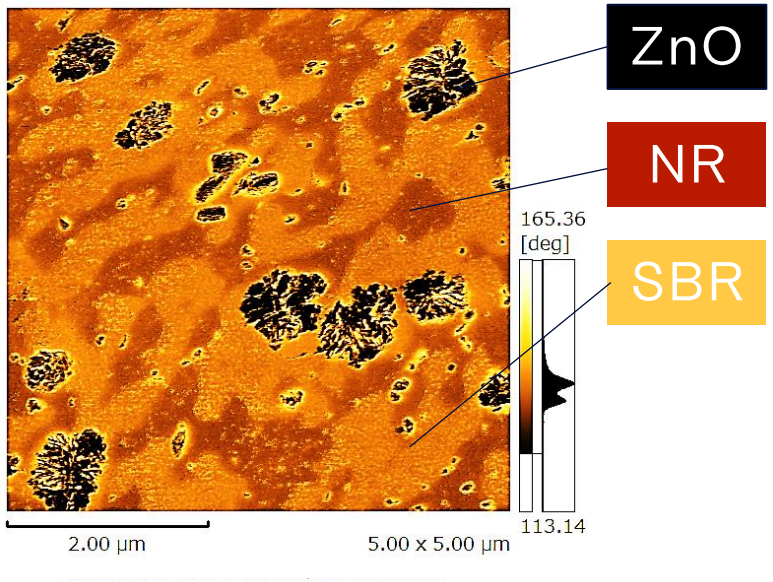
L-FSBR-232

Grade	Structure	Mw	St cont. (wt%)	Tg (°C)	Melt Vis. @38°C (Pa.s)
L-FSBR-232	Far/St/Bd	9,000	23	-65	5.9

NR/SBR=50/50



NR/SBR/L-FSBR-232=50/50/20



AFM: Vulcanized rubber, cross section

- High compatibility to SBR
- Improve friction in low temp.

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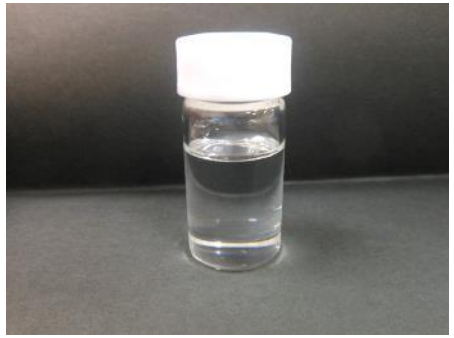
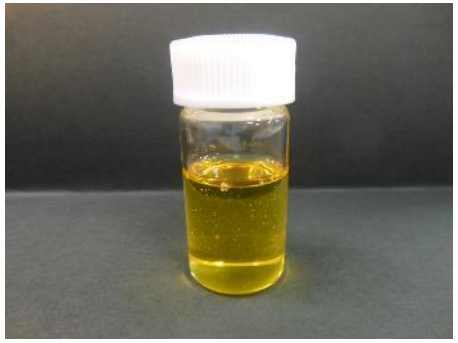
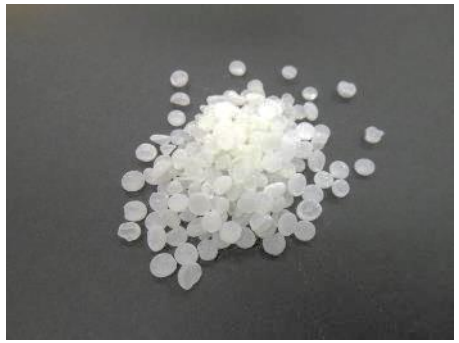
Samples



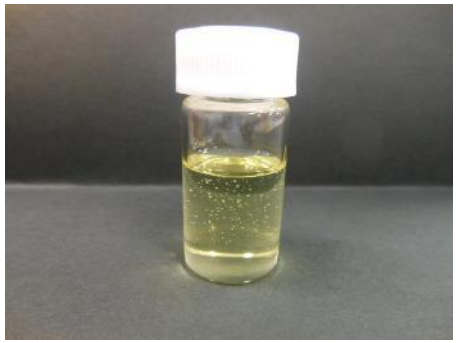
L-FSBR-232



Resin A



Resin B



Resin C

	Structure	Tg (°C)
L-FSBR-232*)	Far/St/Bd (St cont. 23wt%)	-65
Liquid resin A	Terpene-hydrocarbon resin	-36
Solid resin B	Aromatic-Terpene-hydrocarbon resin	78
Liquid resin C	Aliphatic resin	-36

*)Development Grade

Resin A,B,C : Product from resin manufacturer

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Formulation

	Control	Formulation
Natural Rubber	30	30
E-SBR1500 (Emulsion SBR)	70	70
Softener		
TDAE	10	10
Resin	20	-
Liquid Rubber	-	20
Carbon Black (N220)	10	10
Silica	80	80
Silane coupling agent (Si-75)	6.4	6.4
ZnO	3.5	3.5
Stearic acid	2.0	2.0
Anti oxidant 6C [1)]	2.0	2.0
Wax	1.0	1.0
Sulfur	1.5	1.5
Accelerator TBT-N [2)]	1.0	1.0
Accelerator D [3)]	0.65	0.65
Accelerator CZ [4)]	0.45	0.45

1st Stage	Banbury mixer
0′00″	NR, E-SBR (60 °C)
0′20″	CB, Silica, Softener, AO, ZnO, Stearic acid
5′30″	Dump out (150-160 °C)
2nd Stage	Banbury mixer
0′00″	1st mixed compound(80°C)
4′30″	Dump out (150-160°C)
3rd Stage	Banbury mixer
0′00″	Compound, S, Accelerators (50 °C)
0′75″	Dump out (95-105°C)

1) N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine
2) Bis(dibutylthiocarbamoyl)Disulfide
3) 1,3-Diphenylguanidine
4) N-Cyclohexyl-2-benzothiazolylsulfenamide

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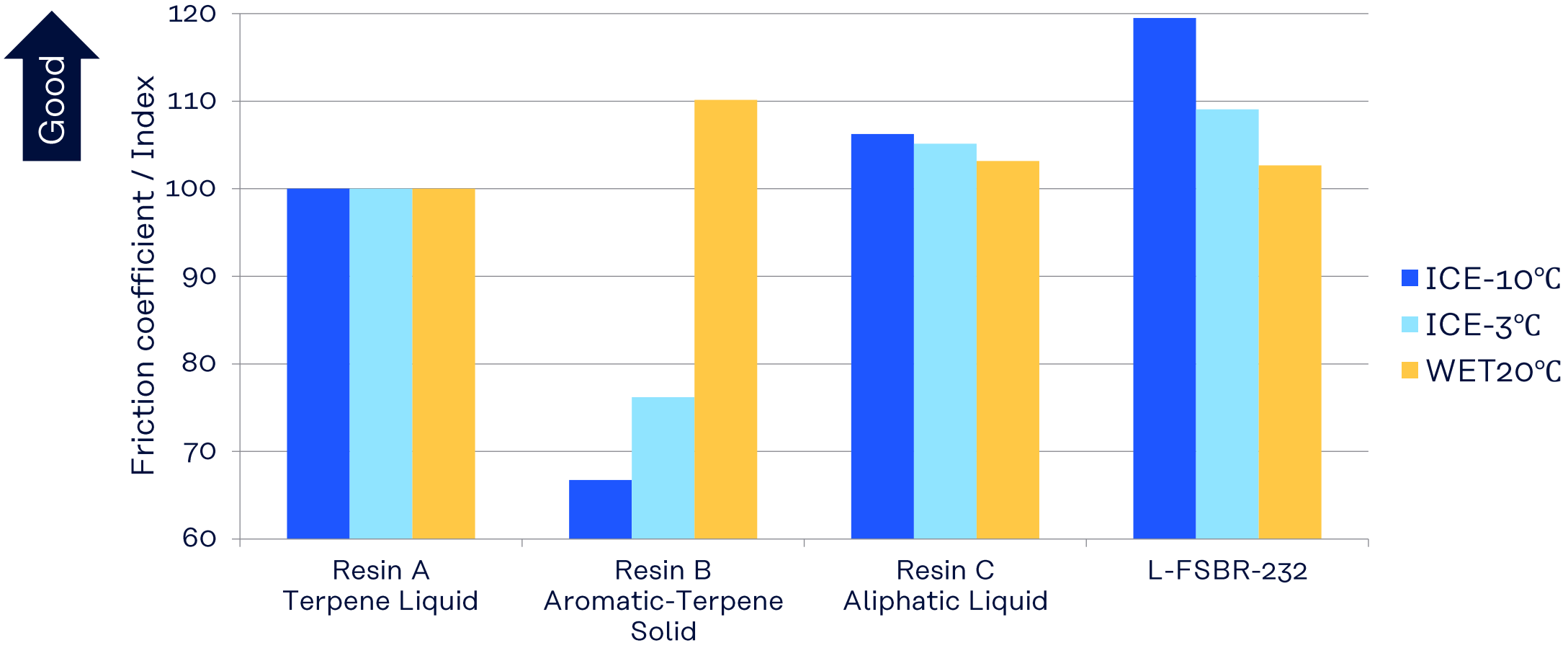
Summary of Properties

			Resin A	Resin B	Resin C	L-FSBR-232
Structure			Terpene Liquid	Aromatic-terpene Solid	Aliphatic Liquid	Liquid rubber
Mooney Viscosity (130°C) ML1+4			33.6	38.7	33.6	33.1
Curelastometer t90 @160°C		(min.)	18.6	14.8	15.2	16.3
Mechanical properties						
Hs		Type A	61	65	60	59
EB		(%)	670	670	710	730
TB		(MPa)	18.8	20.5	19.6	18.2
M100		(MPa)	1.64	1.89	1.56	1.47
M300		(MPa)	7.09	7.94	6.55	6.02
Viscoelasticity(10%-2%、Preload, Temp sweep -30～+70°C)						
E′	-20°C	(MPa)	18.2	45.2	20.2	15.7
	0°C	(MPa)	10.3	12.9	10.7	9.2
	60°C	(MPa)	5.3	5.8	5.6	4.5
tanδ	-20°C	(-)	0.73	0.91	0.72	0.60
	0°C	(-)	0.43	0.56	0.43	0.41
	60°C	(-)	0.26	0.28	0.27	0.29
tanδ peak temperature		(°C)	-31.7	-24.8	-33.7	-38.7
Friction coefficient						
Ice	-10°C		100	66	105	120
Ice	-3°C		100	76	105	109
Wet	20°C		100	111	104	103

Friction on Ice & Wet



- L-FSBR-232 shows good friction on ice.
- L-FSBR-232 shows good friction on wet as well as resin.

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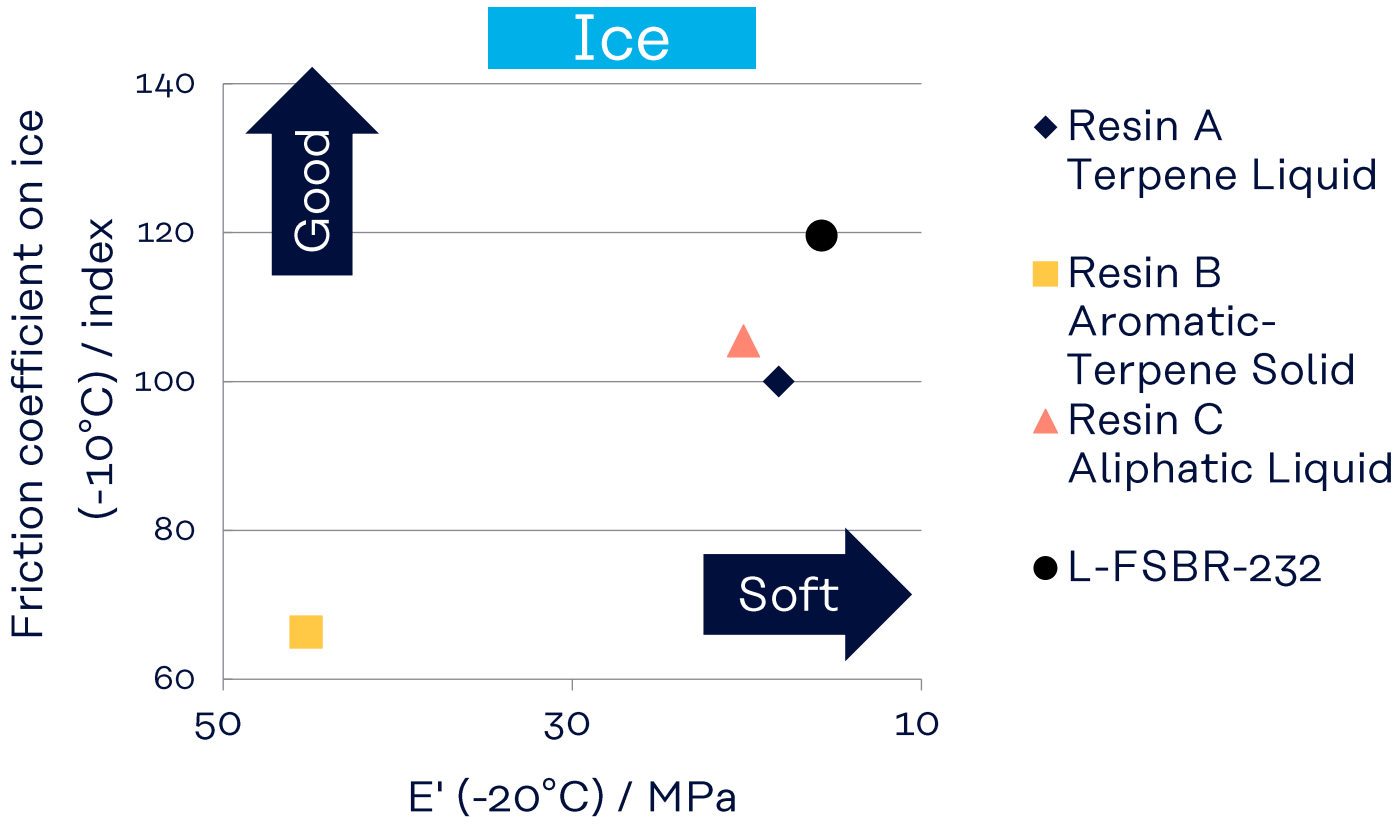
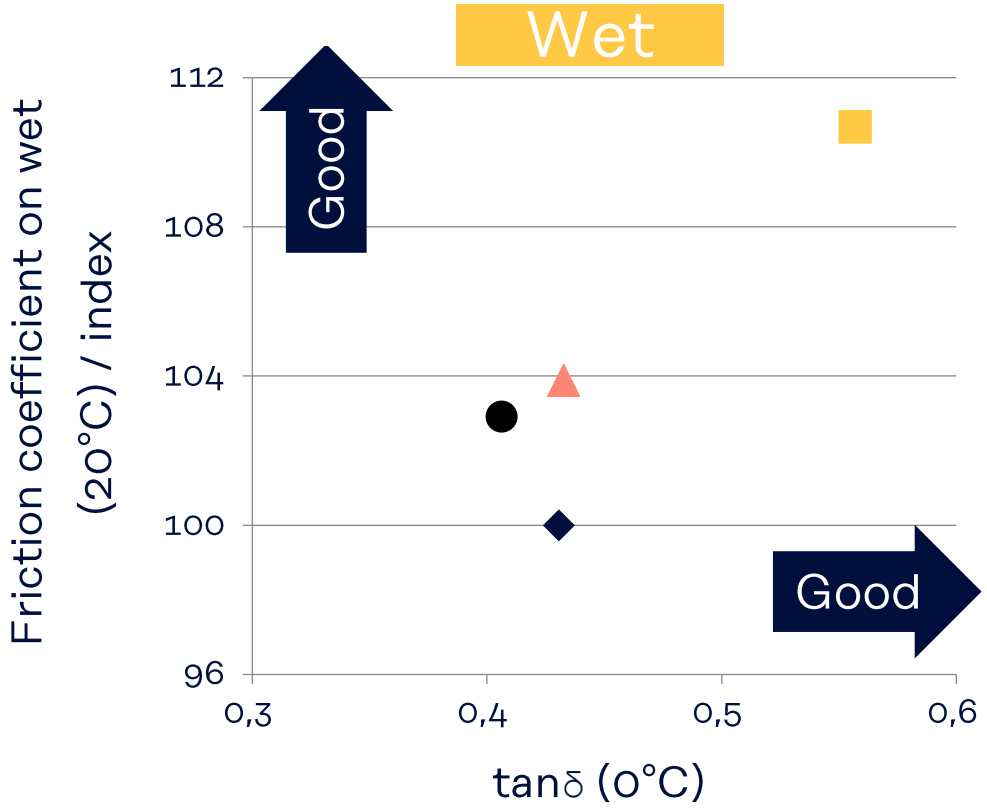
Friction & Viscoelasticity





- Friction on ice shows correlation with E′(-20°C)
- Shows better friction on wet as well as liquid resin

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Summary

- L-FSBR-232 can improve friction on **Wet & Ice**.

	Liquid resin	Solid resin	L-FSBR-232
Wet (20°C)	Good	Very good	Good
Ice (-10°C)	Good	Poor	Very good
Ice (-3°C)	Good	Poor	Very good

APPENDIX

Raw materials

Material	Product Name	Manufacturer	Note
Natural Rubber	STR20	Von Bundit Co., Ltd.	
Butadiene Rubber	JSR BR01	JSR Corporation	Cis content: 95% Mooney Vis. @100°C: 45
SBR	JSR 1500	JSR Corporation	St/Bd: 23.5/76.5 (wt/wt) Vinyl content: 15% Tg: -53 °C
Silica	ULTRASIL® 7000GR	Evonik Industries AG	Specific surface area (N2) 175 m^2/g
Carbon black	DIABLACK™ I	Mitsubishi Chemical Corporation	ASTM N220
Silane Coupling Agent	Si-75	Evonik Industries AG	
TDAE	VIVATEC 500	H&R GmbH Co. KGaA	

Raw materials

Material	Product Name	Manufacturer	Structure	Tg (°C)
Liquid rubber	L-FSBR-232*)	Kuraray	Far/St/Bd St cont. 23wt%	-65
Liquid resin A	Dimaron	YASUHARA CHEMICAL CO., LTD.	Terpene–hydrocarbon resin	-36
Solid resin B	YS RESIN TO125	YASUHARA CHEMICAL CO., LTD.	Aromatic-Terpene-hydrocarbon resin	78
Liquid resin C	Wingtack 10	Total Cray Valley	Aliphatic resin	-36

*)Development Grade

DMA Measuring Conditions

EPLEXOR® 500N (GABO)

Frequency	10 Hz
Static strain	0.5 %
Dynamic strain	0.1 %

Conditions for RTM measurement

Road Surface	Safety walk (for wet), Ice
Temperature	-10, -3, 20 ℃
Initial circumferential speed	30 km/h
Load	50N
Slip ratio	0 to 40%

The peak top value was regarded as the ice μ value.

Technical Insight of KURARAY LIQUID RUBBER

DMA results of L-FSBR-232

Elastomer R&D Department
Elastomer Division

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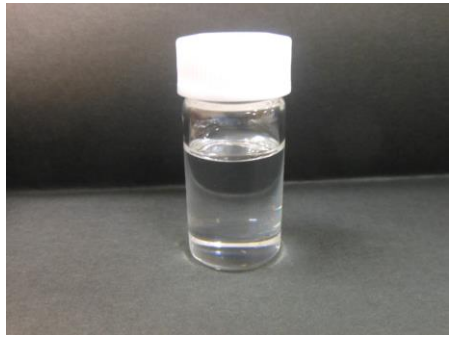
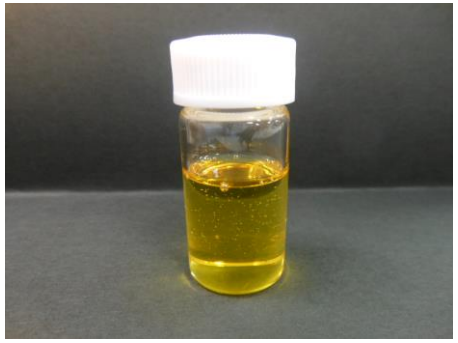
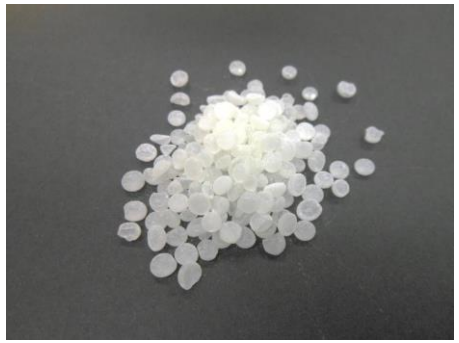
Samples



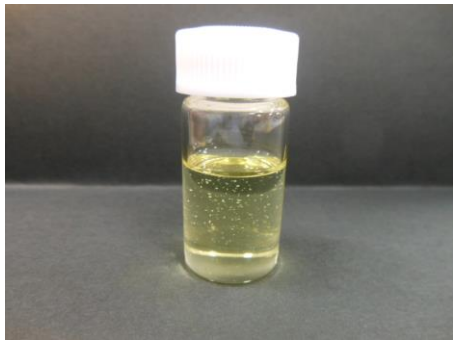
L-FSBR-232



Resin A



Resin B



Resin C

	Structure	Tg (°C)
LFSBR-232*)	Far/St/Bd (St cont. 23wt%)	-65
Liquid resin A	Terpene-hydrocarbon resin	-36
Solid resin B	Aromatic-Terpene-hydrocarbon resin	78
Liquid resin C	Aliphatic resin	-36

*)Development Grade

Resin A,B,C : Product of resin manufacturer

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DMA Measuring Conditions

EPLEXOR 500N (GABO)

Frequency	10 Hz
Static strain	0.5 %
Dynamic strain	0.1 %

Formulation

	Control	Formulation
Natural Rubber	30	30
E-SBR1500 (Emulsion SBR)	70	70
Softener		
TDAE	10	10
Resin	20	-
Liquid Rubber	-	20
Carbon Black (N220)	10	10
Silica	80	80
Silane coupling agent (Si-75)	6.4	6.4
ZnO	3.5	3.5
Stearic acid	2.0	2.0
Anti oxidant 6C [1)]	2.0	2.0
Wax	1.0	1.0
Sulfur	1.5	1.5
Accelerator TBT-N [2)]	1.0	1.0
Accelerator D [3)]	0.65	0.65
Accelerator CZ [4)]	0.45	0.45

Reference curve A : NR/CB=100/40

Reference curve B : E-SBR/CB=100/50

1) N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine
2) Bis(dibutylthiocarbamoyl)Disulfide
3) 1,3-Diphenylguanidine
4) N-Cyclohexyl-2-benzothiazolylsulfenamide

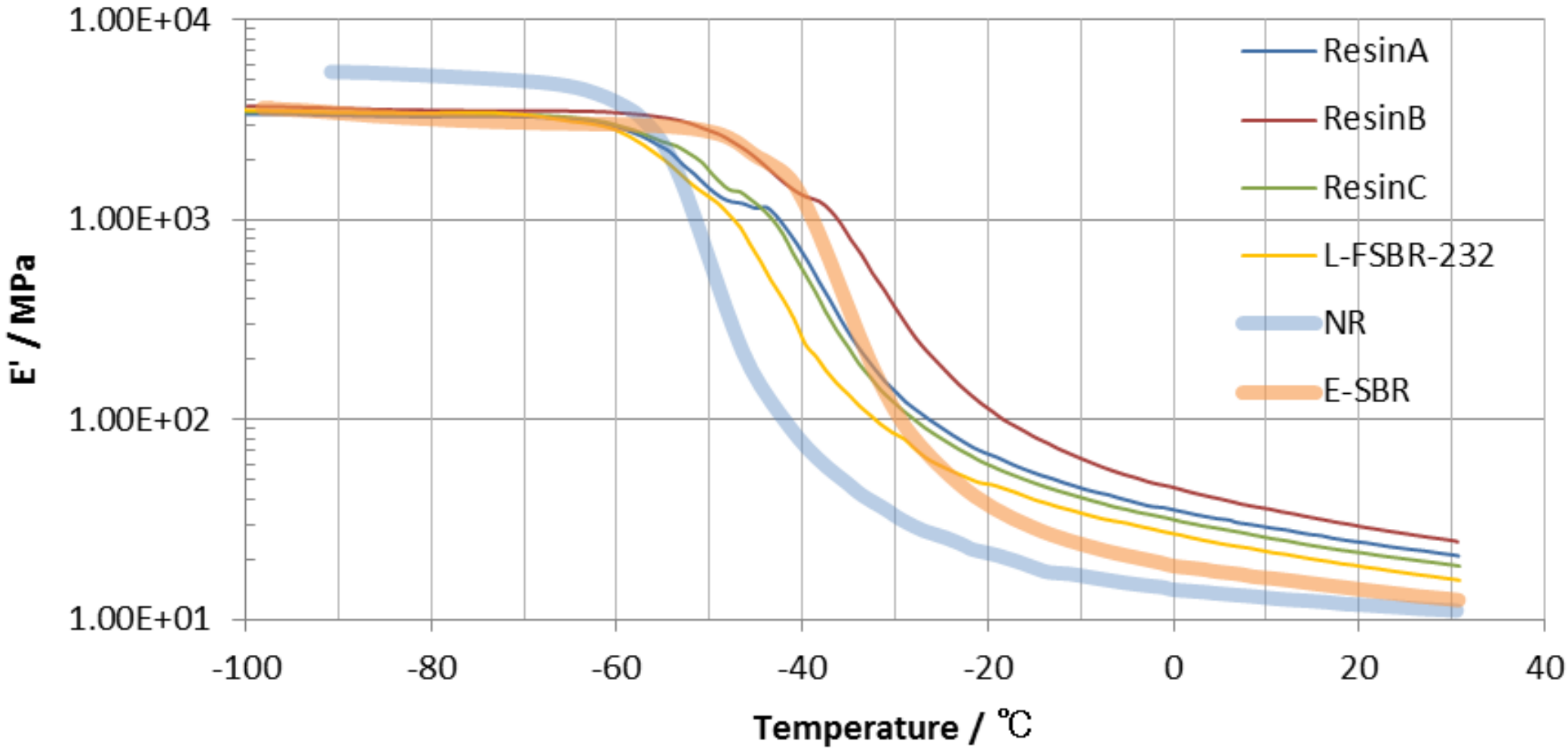
Mixing conditions

1st Stage	Banbury mixer
0′00″	NR, E-SBR (60 °C)
0′20″	CB, Silica, Softener, AO, ZnO, Stearic acid
5′30″	Dump out (150-160 °C)
2nd Stage	Banbury mixer
0′00″	1st mixed compound(80°C)
4′30″	Dump out (150-160°C)
3rd Stage	Banbury mixer
0′00″	Compound, S, Accelerators (50 °C)
0′75″	Dump out (95-105°C)

Comments

- L-FSBR-232 moves E′ and tanδ to low temperature side.
- L-FSBR-232 moves E″ of SBR to low temperature side because of good miscibility to SBR.

Results of E′



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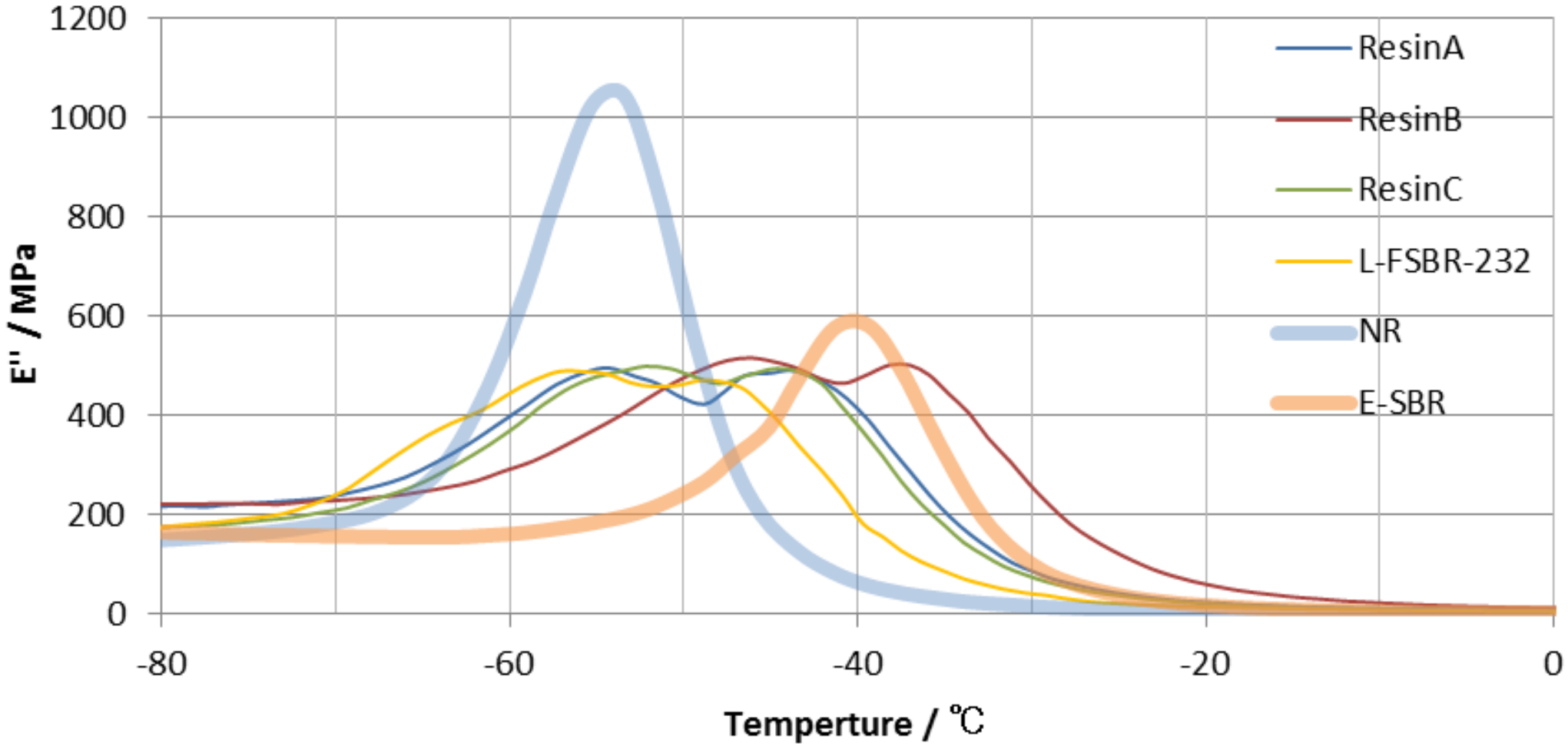
Results of E''



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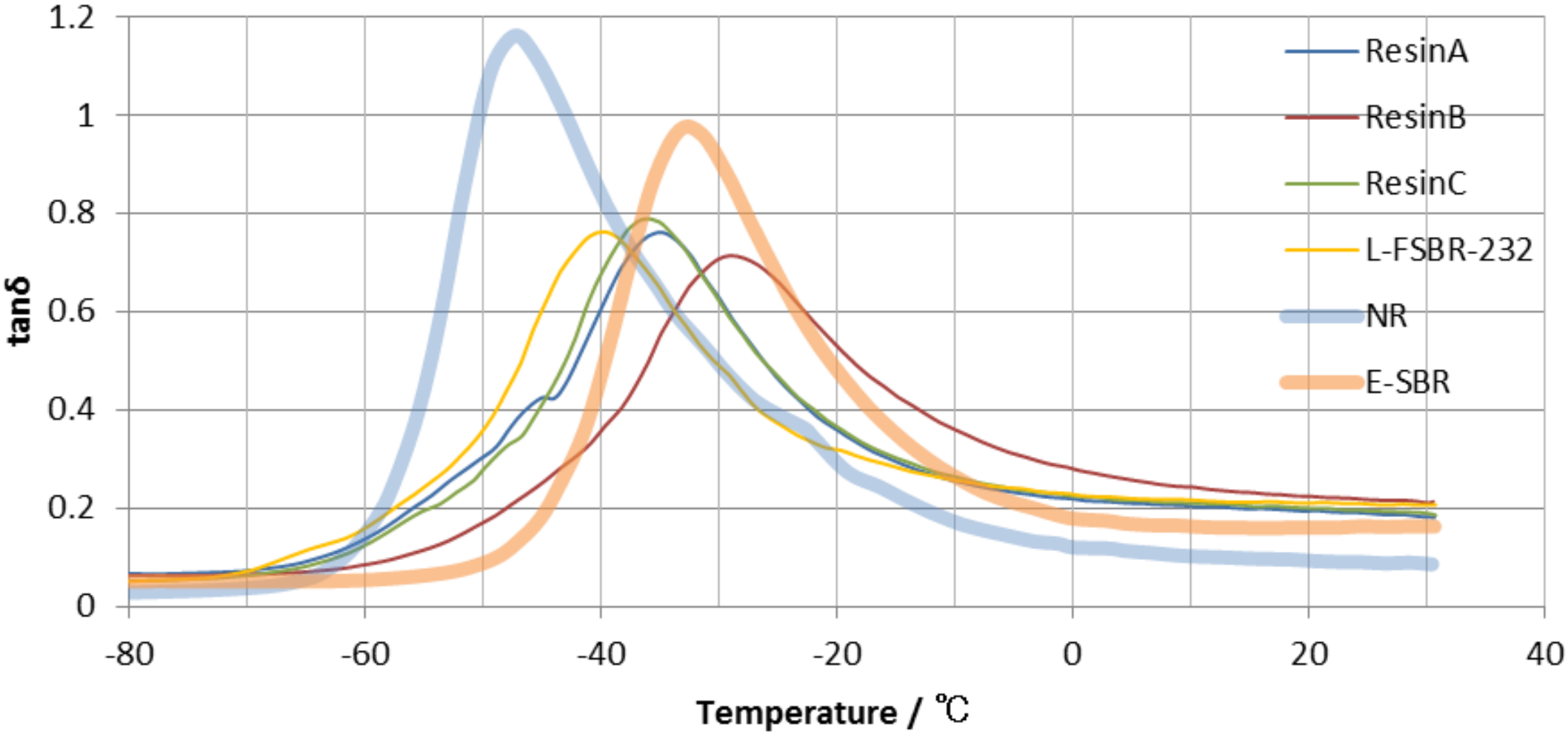
Results of tanδ

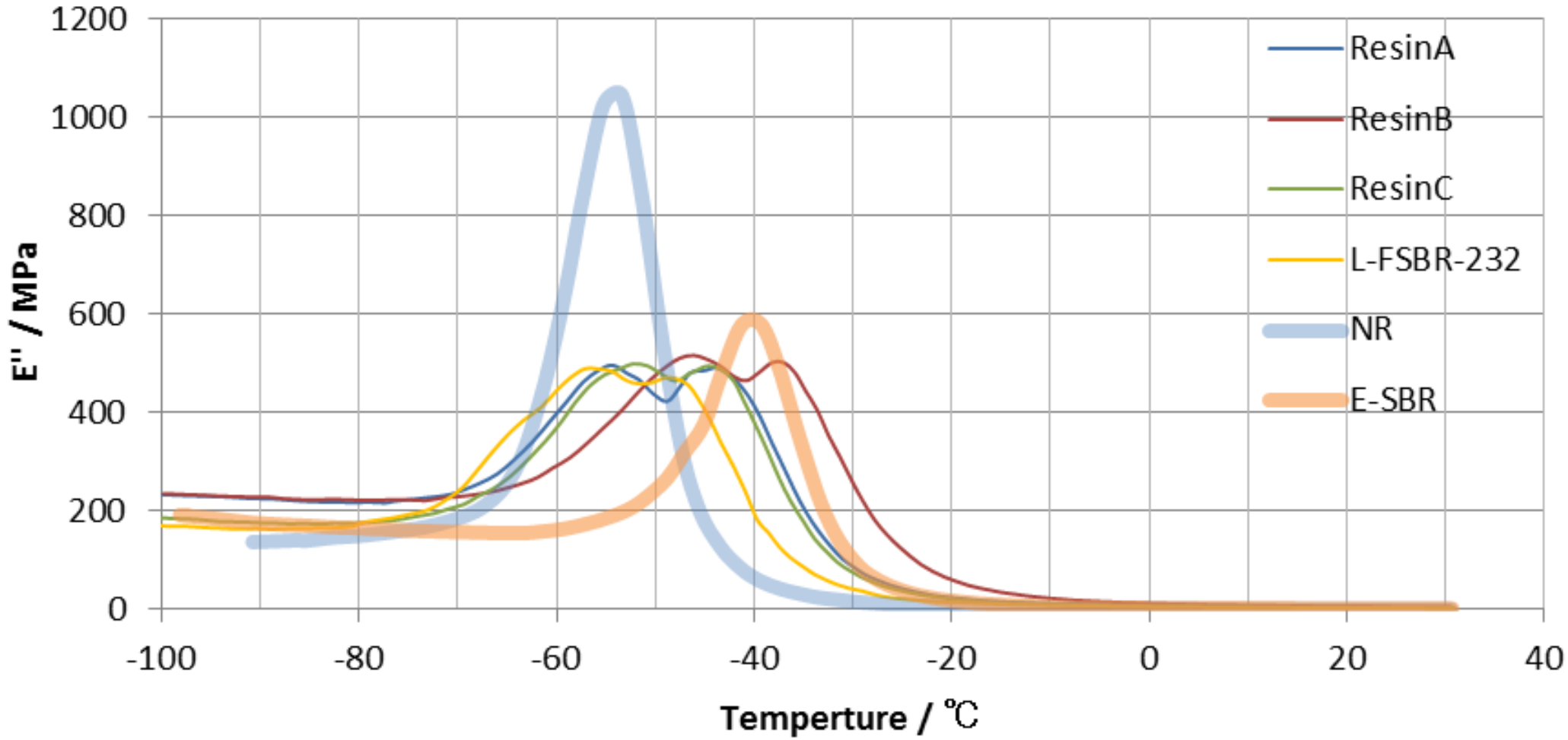


APPENDIX

Raw materials

Material	Grade	Manufacturer	Note
Natural Rubber	STR20	Von Bundit Co., Ltd.	
Butadiene Rubber	JSR BR01	JSR Corporation	Cis content: 95% Mooney Vis. @100°C: 45
SBR	JSR 1500	JSR Corporation	St/Bd: 23.5/76.5 (wt/wt) Vinyl content: 15% Tg: -53 °C
Silica	ULTRASIL® 7000GR	Evonik Industries AG	Specific surface area (N2) 175 m^2/g
Carbon black	DIABLACK™ I	Mitsubishi Chemical Corporation	ASTM N220
Silane Coupling Agent	Si-75	Evonik Industries AG	
TDAE	VIVATEC 500	H&R GmbH Co. KGaA	

Results of E''



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Technical Insight of KURARAY LIQUID RUBBER

LFR & LFBR grades for winter tire (SBR formulation)

Elastomer R&D Department
Elastomer Division

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Contents

- Liquid Farnesene Rubber properties
- Grip performance in SBR formulation
    - Wet grip
    - Ice grip
- Rolling resistance in SBR formulation

Background

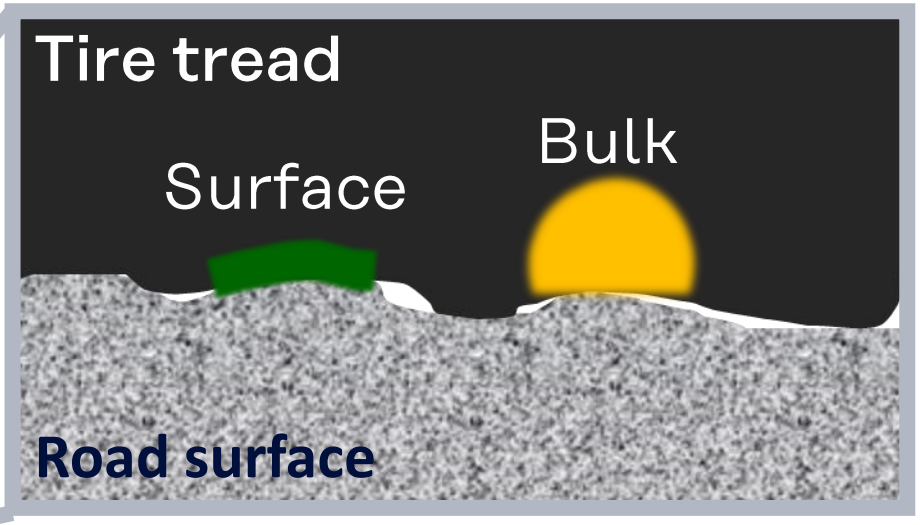
- ☐ Important properties of winter tire
- ✓ Wet grip
- ✓ Ice grip
- ✓ Rolling resistance

LFR & LFBR improves these properties.

Contents

- Liquid Farnesene Rubber properties
- Grip performance in SBR formulation
    - Wet grip
    - Ice grip
- Rolling resistance in SBR formulation

Background



Grip = Adhesion + Hysteresis

In general, tanδ at 0°C is regarded as a wet grip indicator.

However actual wet grip is improved by multiple factors.

Effect of Liquid Rubbers to Adhesion factor was evaluated.

Typical Properties

Grade	Structure (wt)	Tg (°C)	Mw	Visc. @38°C (Pa.s)
L-FR-107L	Far=100	-71	135k	69
L-FBR-742	Far/Bd=60/40	-78	29k	15
L-FBR-746	Far/Bd=60/40	-78	88k	520
L-BR-307	Bd=100	-94	9k	1.3

Formulation

	Control	Formulation
Natural Rubber	30	30
E-SBR1500 (Emulsion SBR)	70	70
Softener		
TDAE	10	10
Resin	20	-
Liquid Rubber	-	20
Carbon Black (N220)	10	10
Silica	80	80
Silane coupling agent (Si-75)	6.4	6.4
ZnO	3.5	3.5
Stearic acid	2.0	2.0
Anti oxidant 6C [1)]	2.0	2.0
Wax	1.0	1.0
Sulfur	1.5	1.5
Accelerator TBT-N [2)]	1.0	1.0
Accelerator D [3)]	0.65	0.65
Accelerator CZ [4)]	0.45	0.45

1st Stage	Banbury mixer
0′00″	NR, E-SBR (60 °C)
0′20″	CB, Silica, Softener, AO, ZnO, Stearic acid
5′30″	Dump out (150-160 °C)
2nd Stage	Banbury mixer
0′00″	1st mixed compound(80°C)
4′30″	Dump out (150-160°C)
3rd Stage	Banbury mixer
0′00″	Compound, S, Accelerators (50 °C)
0′75″	Dump out (95-105°C)

1) N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine
2) Bis(dibutylthiocarbamoyl)Disulfide
3) 1,3-Diphenylguanidine
4) N-Cyclohexyl-2-benzothiazolylsulfenamide

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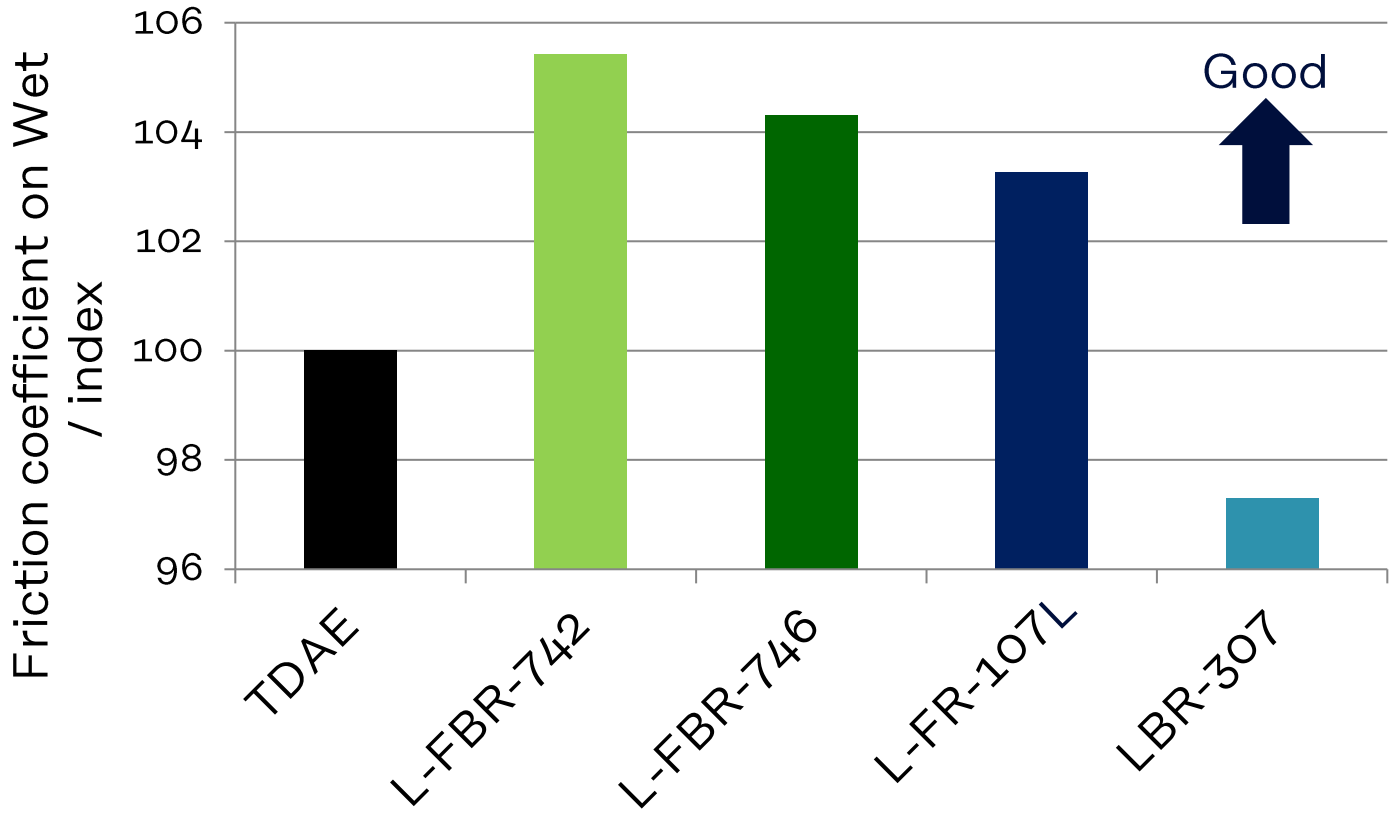
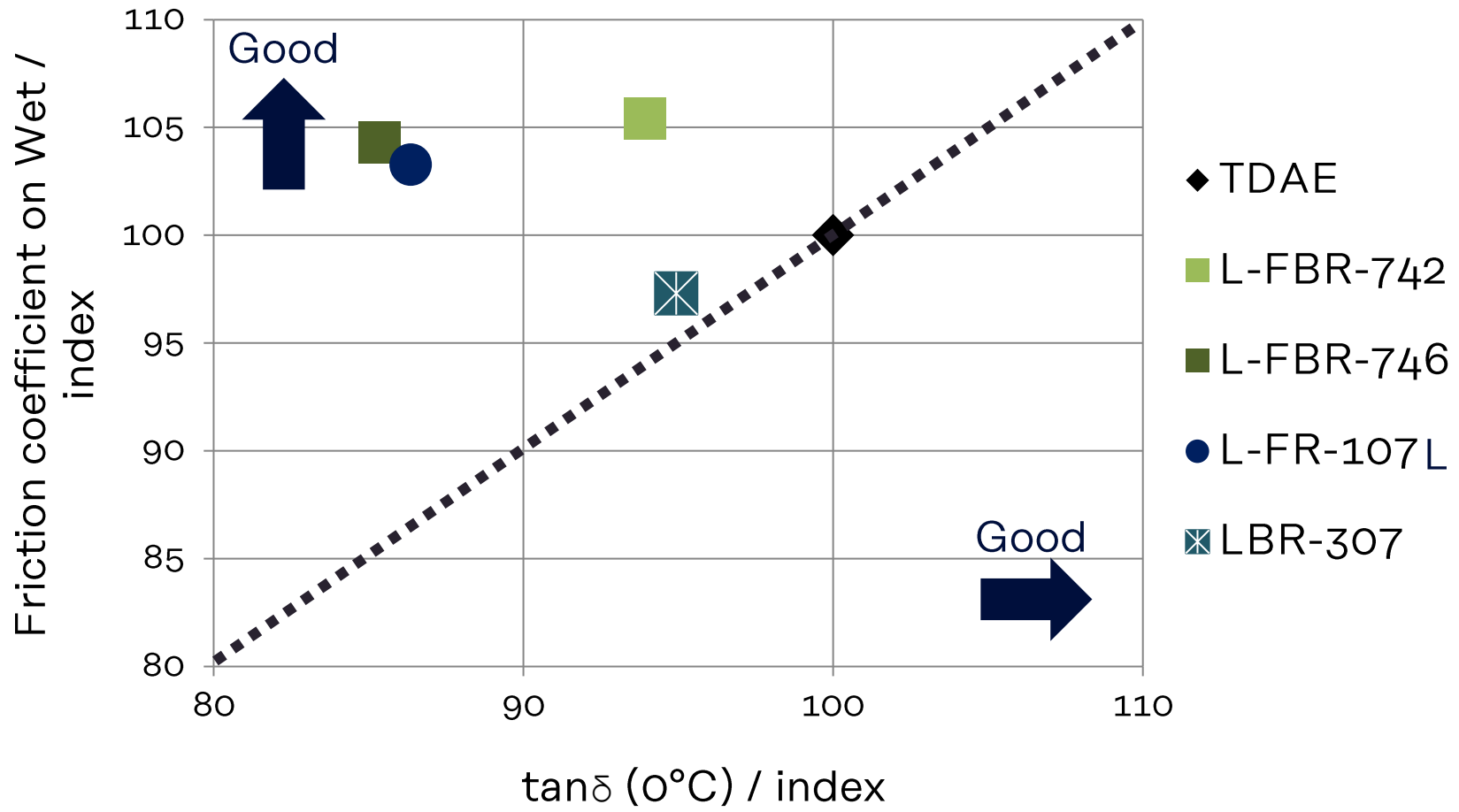
Friction coefficient on Wet



L-FR & L-FBR show excellent friction on Wet.

We checked relation between friction & tanδ (0°C) .

Friction on Wet vs tan δ (0°C)



L-FR & L-FBR show good friction on Wet even at low tanδ (0°C).

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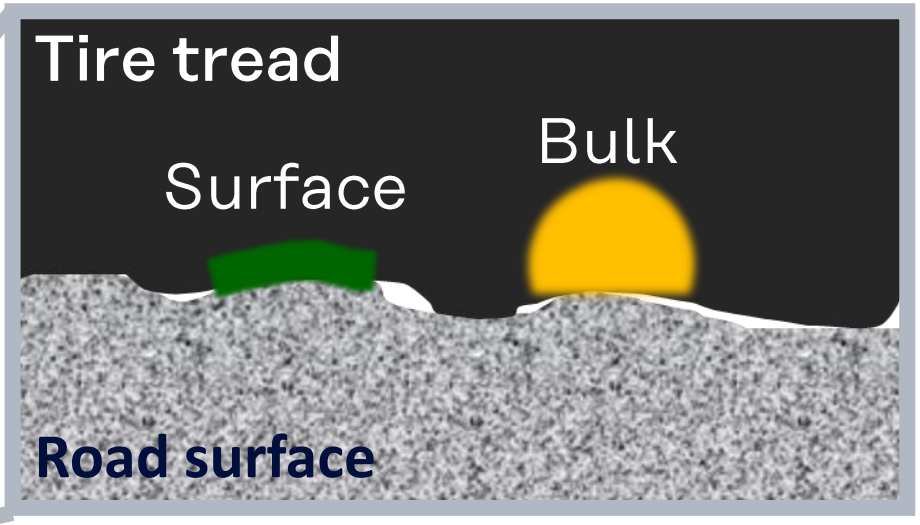
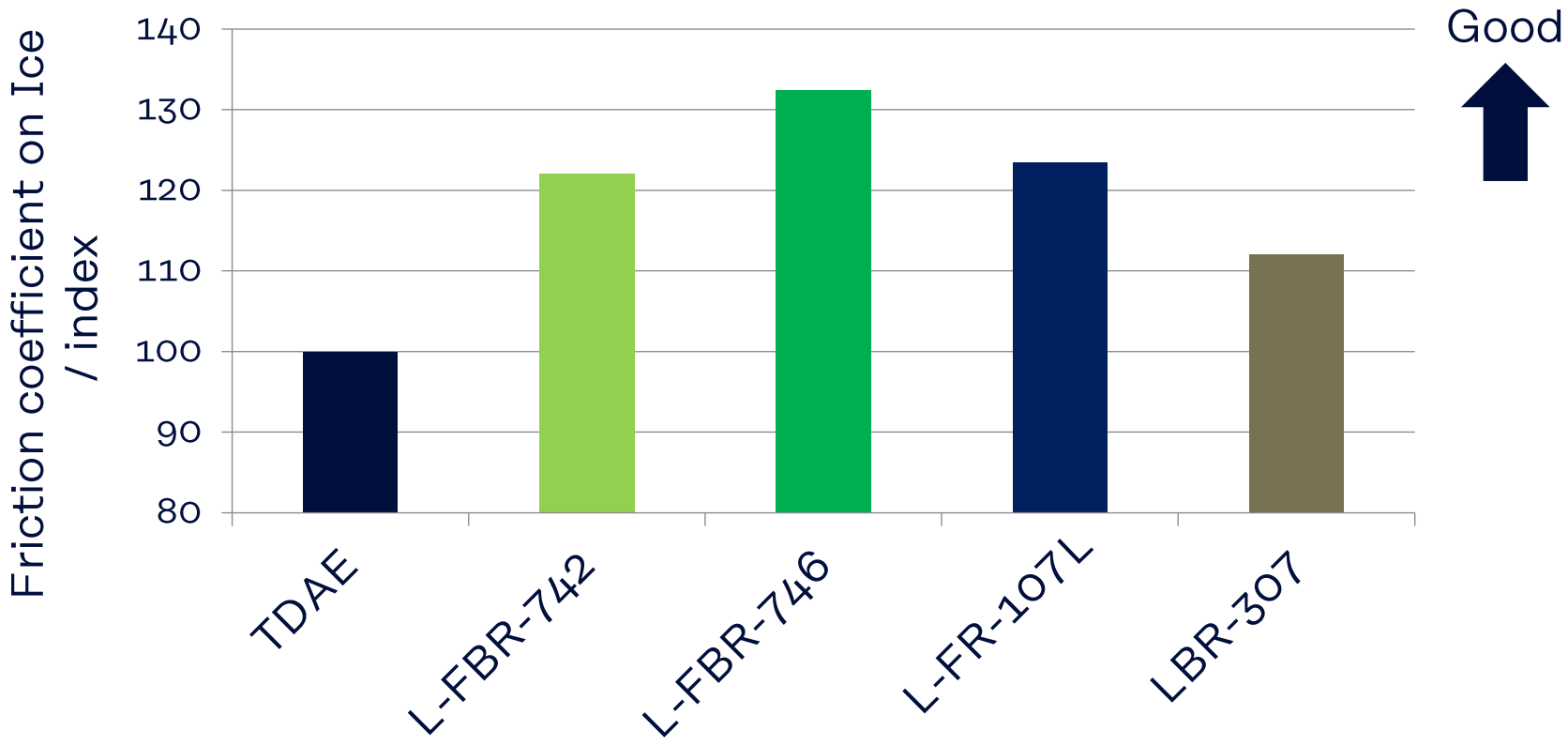
Hypothesis



Grip = Adhesion + Hysteresis

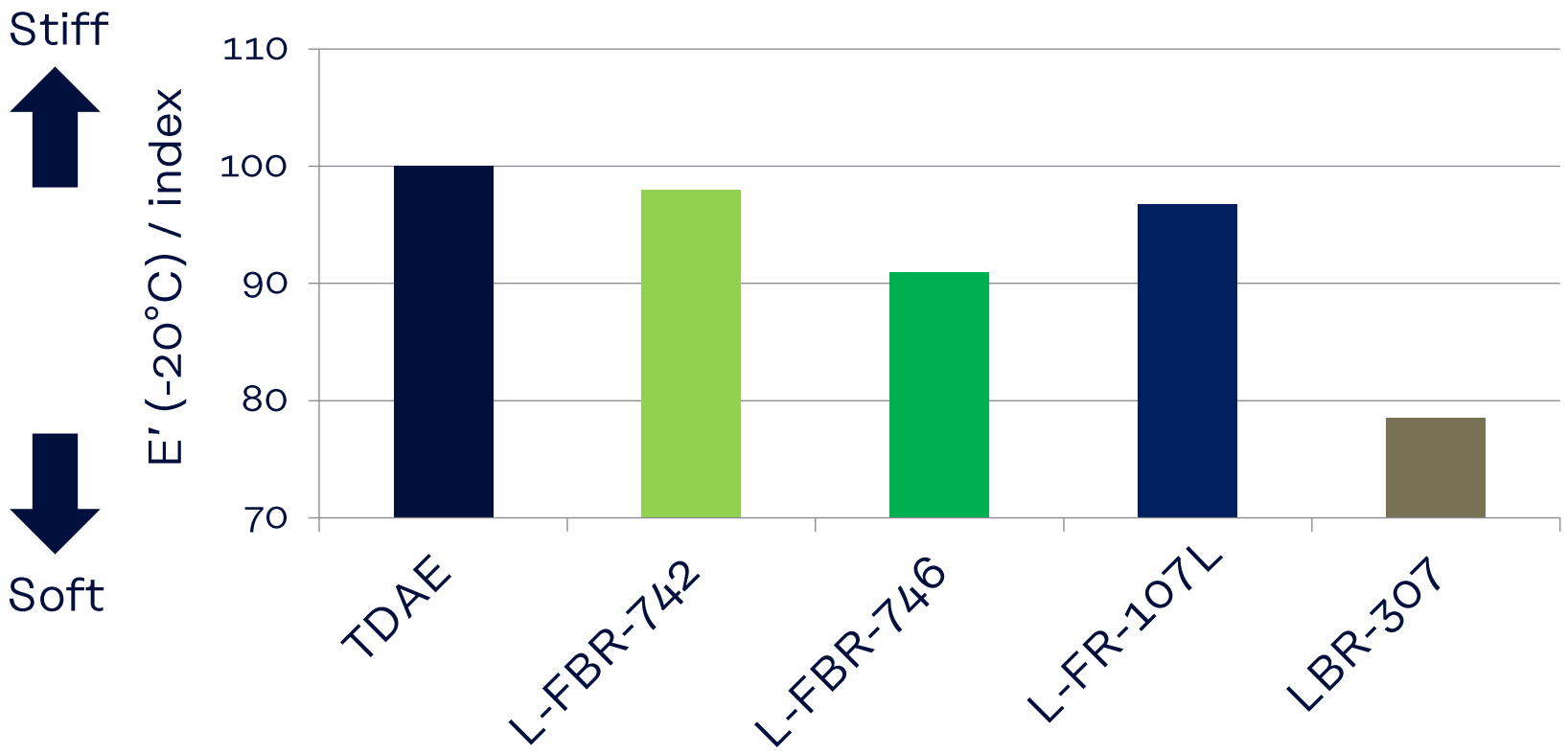
Farnesene structure contribute to the Adhesion factor.

Friction on Ice (-3°C)



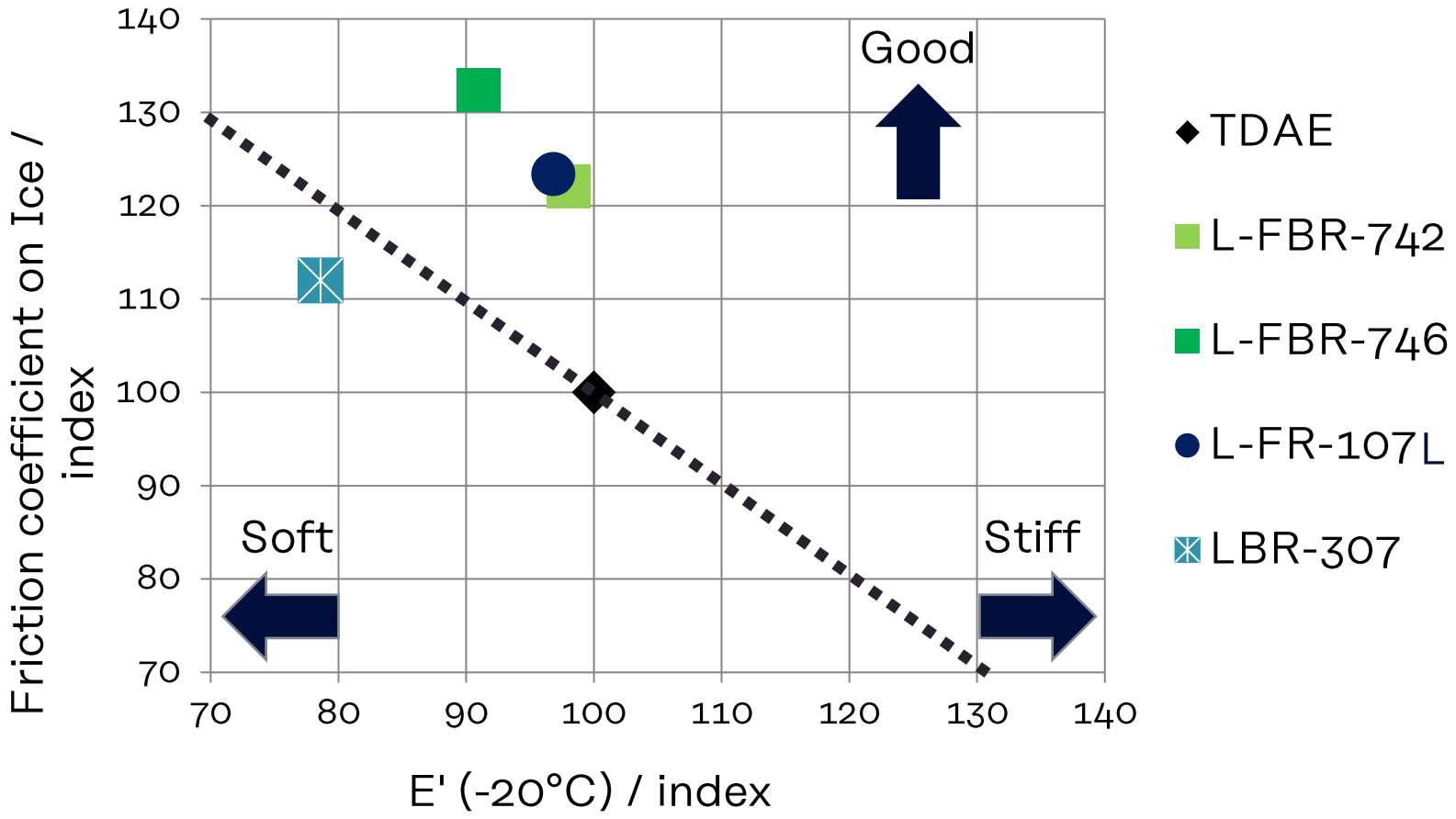
L-FR & L-FBR show excellent friction on Ice.

E′ at low temperature



L-FR & L-FBR shows slightly lower E′.
We also checked relation between friction & E′.

Friction on Ice vs. E′ (-20°C)



L-FR & L-FBR shows excellent friction maintaining E′ at low temperature.

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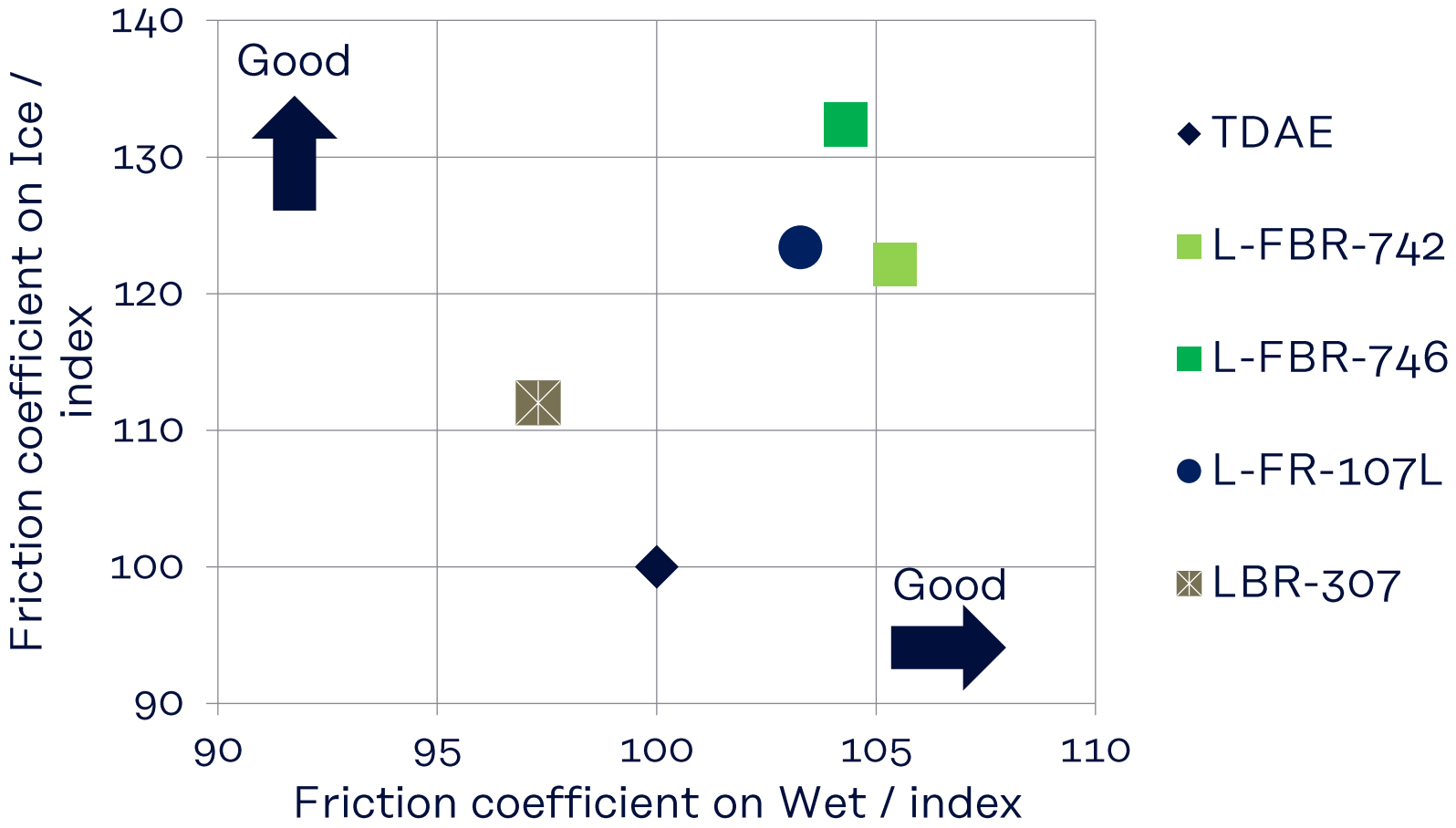
Friction on Wet & Ice



L-FBR-746 shows the best friction balance.

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Grip performance results

L-FR & L-FBR

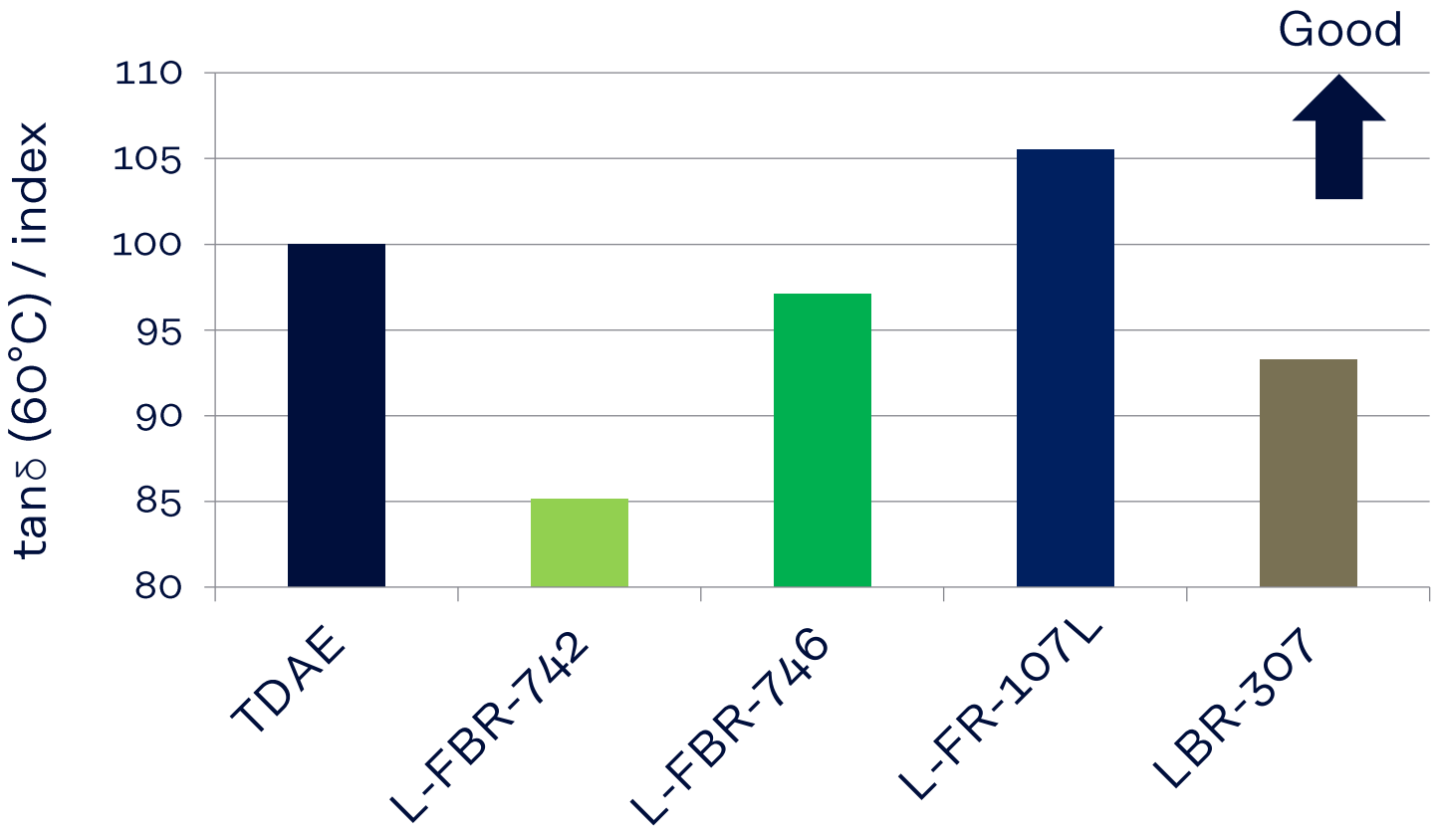
- Excellent friction on Wet even low tanδ (0deg. C)
- Excellent friction on Ice maintaining E′ (-20 deg. C)

L-FBR-746 shows best friction balance.

Contents

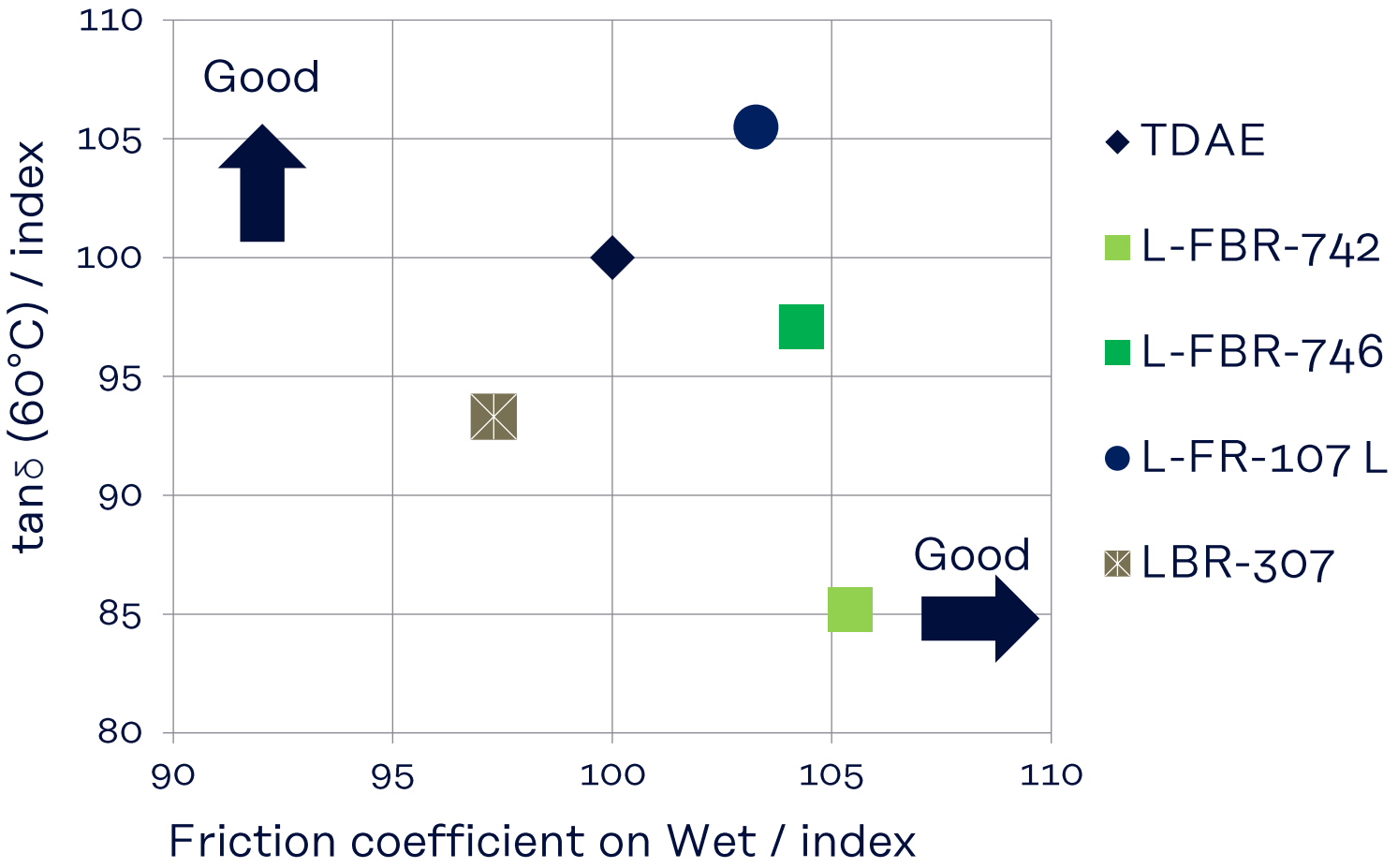
- Liquid Farnesene Rubber properties
- Grip performance in SBR formulation
    - Wet grip
    - Ice grip
- Rolling resistance in SBR formulation

Tanδ at 60°C



L-FR-107 shows excellent RR.

Friction on Wet vs. tanδ (60°C)



L-FR-107L shows the best balance.

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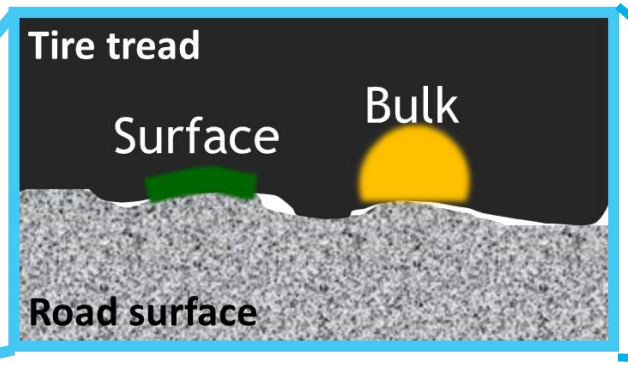
Summary

- L-FBR-746 improves friction on Wet and Ice.
- L-FR-107L improves friction on Wet/Ice as well as RR .
- Farnesene structure contributes to adhesion factor for grip performance.
- When liquid rubber is formulated, friction coefficient data is suitable to confirm grip performance.

Friction on Wet



Grip = Adhesion + Hysteresis

Friction on Ice

Summary of Properties

		unit	TDAE	L-FBR-742	L-FBR-746	L-FR-107L	LBR-307
Mooney Viscosity (130°C)							
ML1+4			33	32	32	36	33
Curelastometer (160°C)							
t90		(min.)	14.0	14.5	13.8	14.3	19.1
Mechanical properties							
Hs		Type A	60	60	63	64	58
EB		(%)	690	670	635	630	740
TB(MPa)		(MPa)	19.9	18.1	19.5	19.8	17.8
M100		(MPa)	1.7	1.6	1.8	2.0	1.5
M300		(MPa)	6.9	6.3	7.4	7.6	6.1
Viscoelasticity (10% to 2%, Preload, Temp. sweep -50 to +70 °C)							
	-20°C	(MPa)	16.5	16.2	15.0	16.0	13.0
E′	0°C	(MPa)	9.4	10.2	9.9	10.3	8.4
	60°C	(MPa)	5.0	5.3	5.6	5.9	4.4
	-20°C		0.67	0.53	0.52	0.55	0.55
tanδ	0°C		0.41	0.38	0.35	0.35	0.40
	60°C		0.25	0.30	0.26	0.24	0.27
Friction coefficient							
Wet	20°C		100	105	104	103	97
Ice	-3°C		100	122	132	123	112

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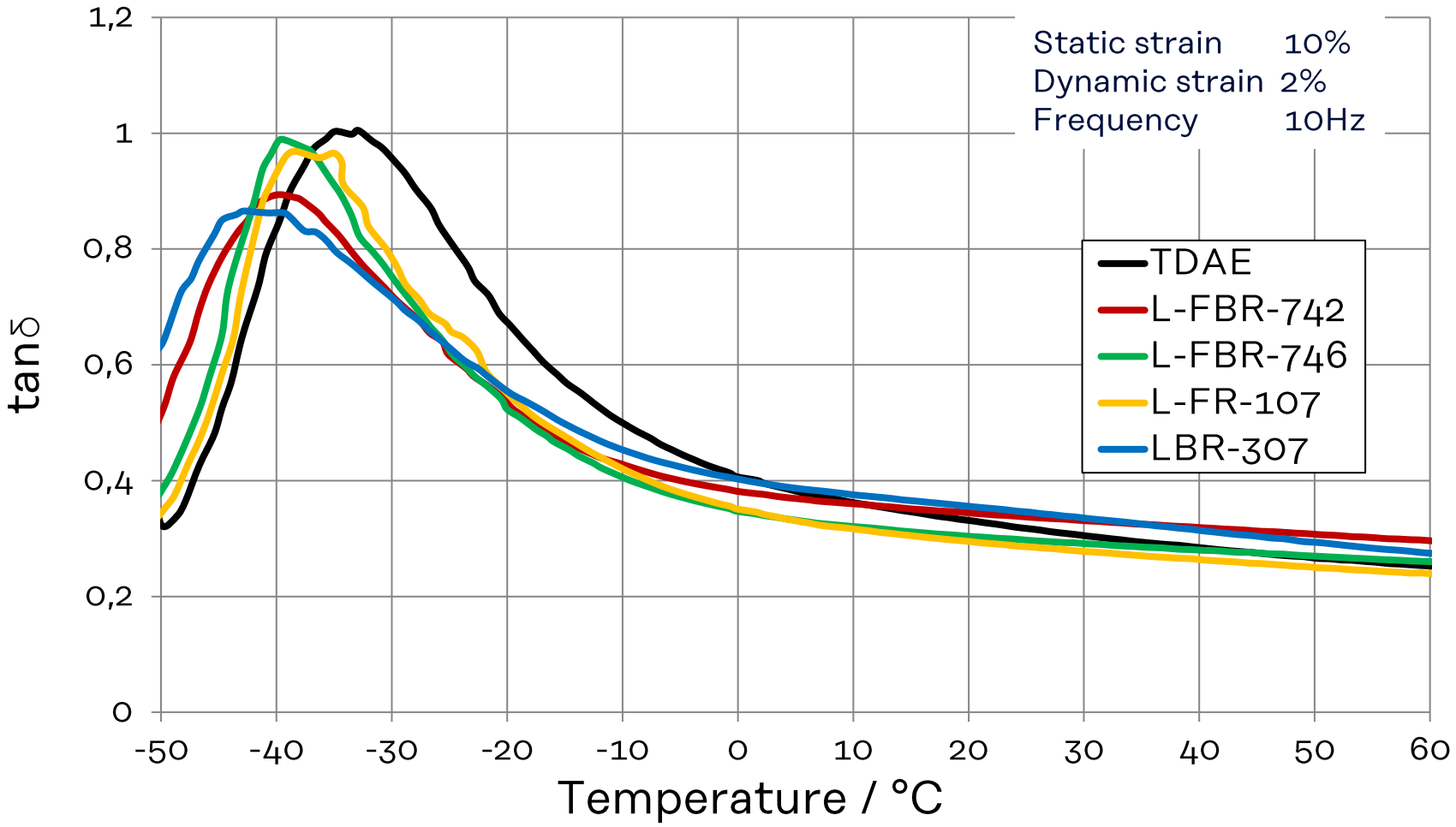
APPENDIX

DMA results (tanδ)



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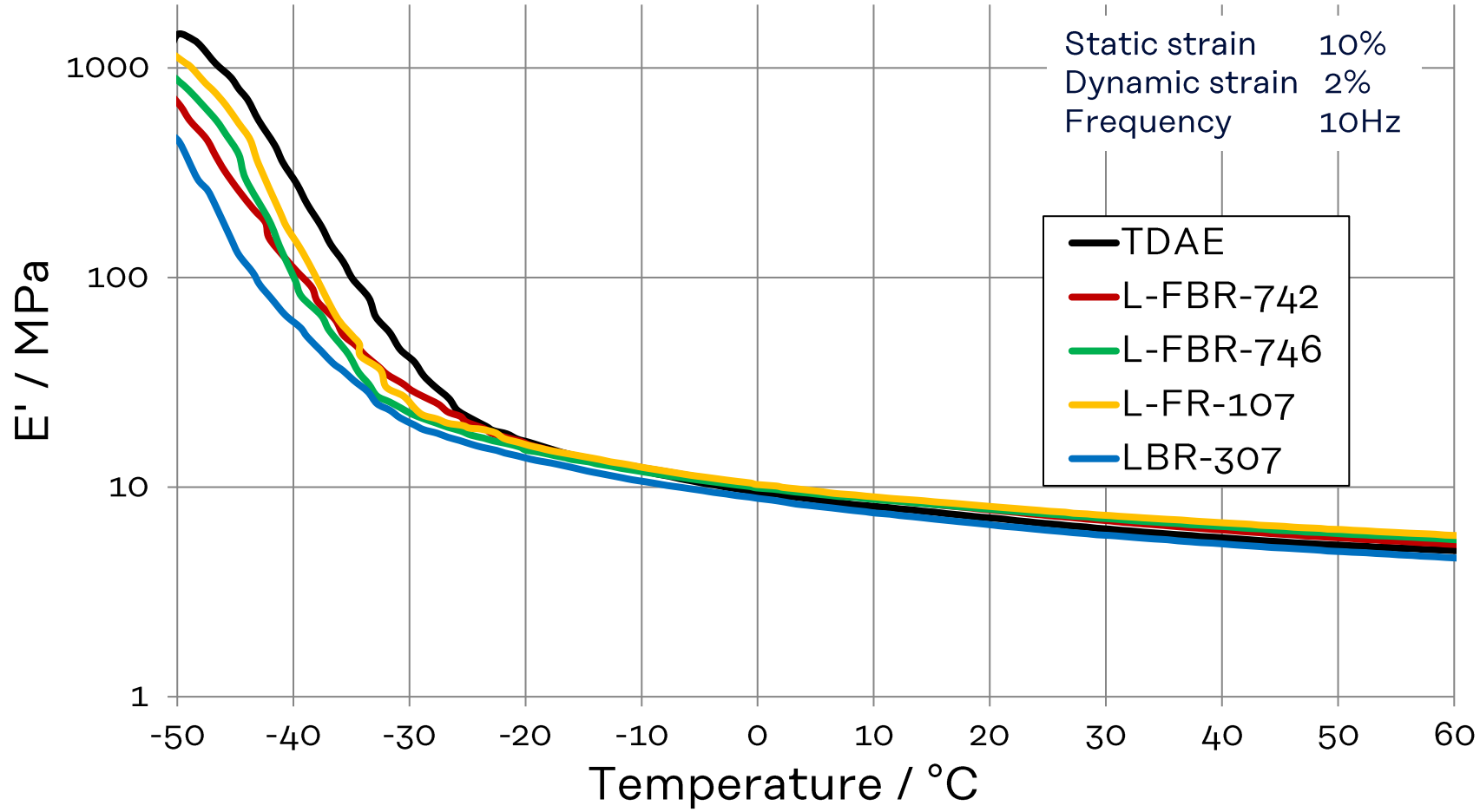
DMA results (E')



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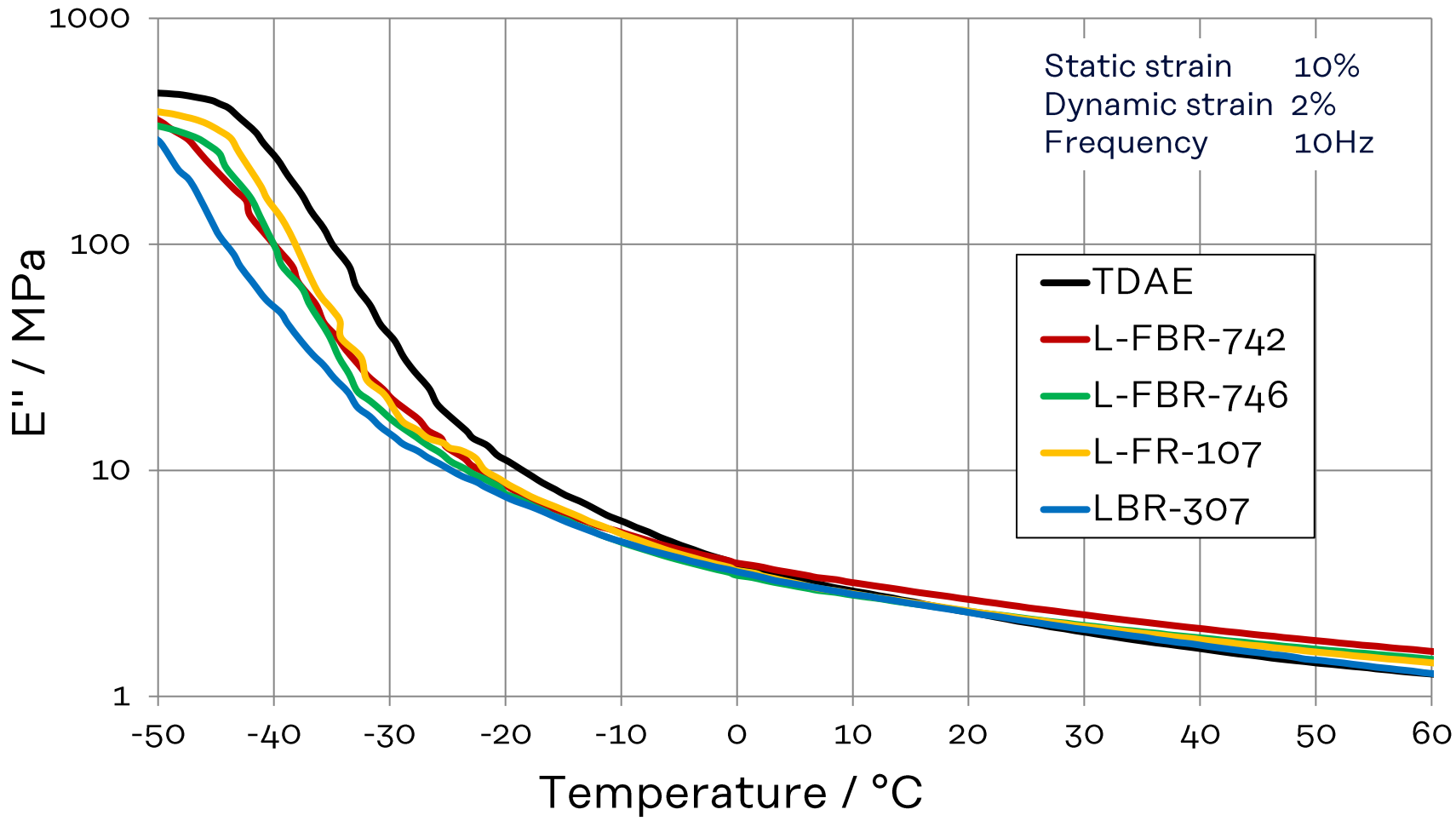
DMA results (E'')



Raw materials

Material	Product Name	Manufacturer	Note
Natural Rubber	STR20	Von Bundit Co., Ltd.	
SBR	JSR 1500	JSR Corporation	St/Bd: 23.5/76.5 (wt/wt) Vinyl content: 15% Tg: -53 °C
Silica	ULTRASIL® 7000GR	Evonik Industries AG	Specific surface area (N2) 175 m^2/g
Carbon black	DIABLACK™ I	Mitsubishi Chemical Corporation	ASTM N220
Silane Coupling Agent	Si-75	Evonik Industries AG	
TDAE	VIVATEC 500	H&R GmbH Co. KGaA	

Conditions for RTM measurement

Road Surface	Safety walk (for wet), Ice
Temperature	-3, 20 °C
Initial circumferential speed	30 km/h
Load	50N
Slip ratio	0 to 40%

The peak top value was regarded as the ice μ value.

Technical Insight of KURARAY LIQUID RUBBER

Distribution to base rubber Evaluation method

Elastomer R&D Department
Elastomer Division

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Evaluation by DSC

Fox Equation

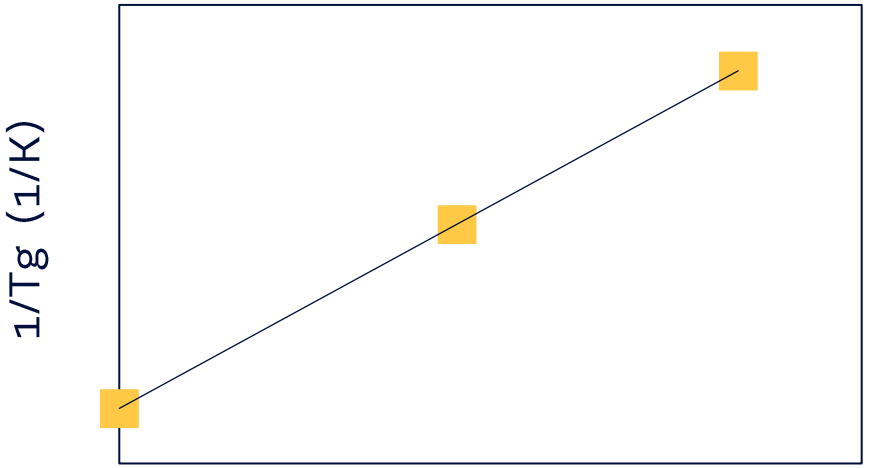
$$\frac{1}{T_g} = \frac{1-x}{T_{g1}} + \frac{x}{T_{g2}} \cdots (1)$$

$$\frac{1}{T_g} = \frac{T_{g1} - Tg_2}{T_{g1}T_{g2}} \times x + \frac{1}{T_{g1}} \cdots (2)$$

Tg_1: Tg of Base Rubber / Kelvin

Tg_2: Tg of Softener / Kelvin

x: Weight fraction of softener



Slope: $\frac{T_{g1} - Tg_2}{T_{g1}T_{g2}}$ Intercept: $\frac{1}{T_{g1}}$

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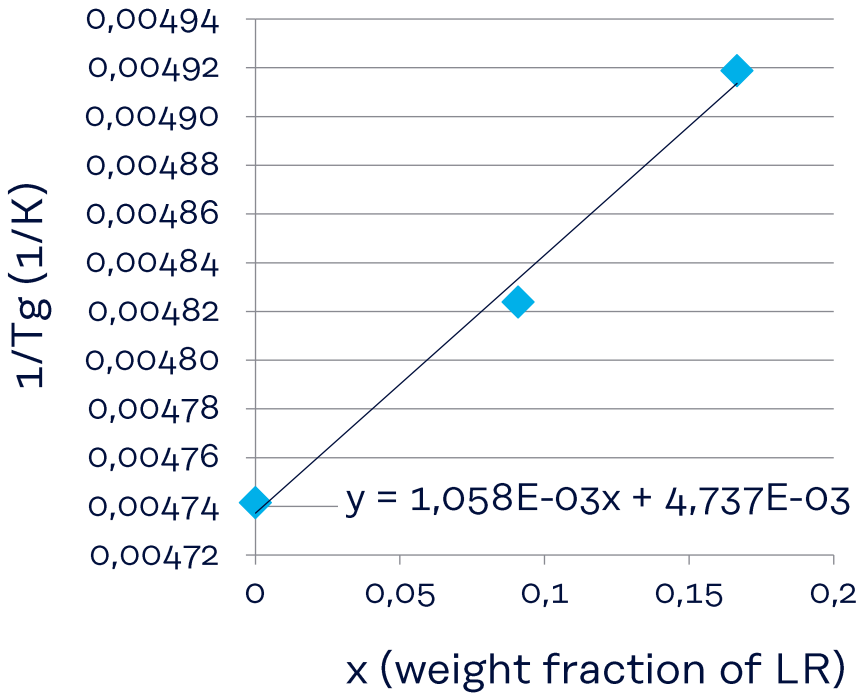
Making standard curve

Measure Tg shift of Base Rubber and LR to create standard curve.

NR ＋LR 10, 20phr

Formulation			
NR	100	100	100
LBR-300	0	10	20
total	100	110	120
x (wt fraction of LR)	0	0.091	0.167
Tg (°C)	-62.6	-66.2	-70.2
1/Tg (1/K)	0.00474	0.00482	0.00492



Calculation

Measure Tg shift of the rubber compound,
and the weight fraction of LR were calculated.

+LR 20phr

Formulation	
NR	50
BR	50
LBR-300	20
total	120

$$\frac{1}{T_g} = \frac{T_{g1} - T_{g2}}{T_{g1}T_{g2}} \times \boldsymbol{x} + \frac{1}{T_{g1}} \quad \cdots (2)$$

$$\boldsymbol{x} = \left(\frac{1}{T_g} - \frac{1}{T_{g1}}\right) \div \frac{Tg_1 - Tg_2}{Tg_1 Tg_2} \quad \cdots (3)$$

Measured value

Intercept from standard curve

Slope from standard curve

Distribution ratio ⟶

	Peak of NR	Peak of BR
Measured Tg (°C)	-71.3	-102
1/Tg (K^{-1})	0.0049	0.0058
x	19.69	11.57

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