Technical Insights of KURARAY LIQUID RUBBER

Liquid Farnesene Rubber for Automotive Sealants

Elastomer R&D Department
Elastomer Division

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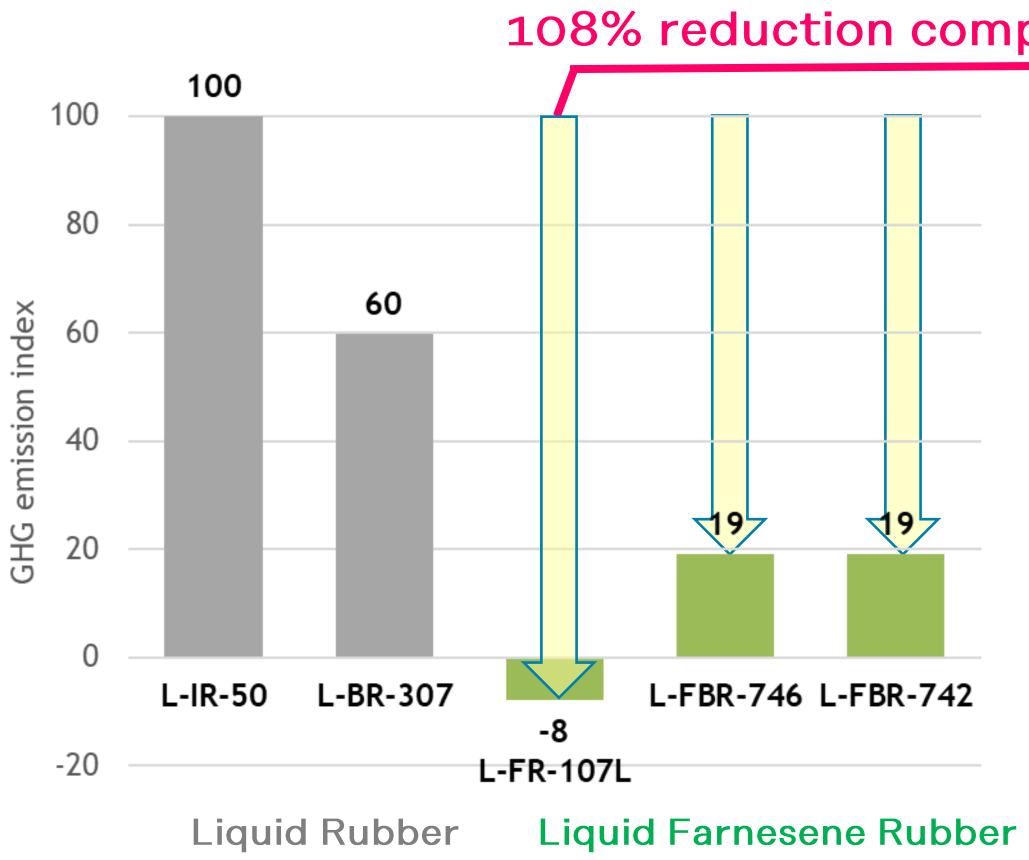
Agenda

- ✓ Liquid Farnesene Rubber (LFR)
- ✓ Transition of curing system in automotive industry
- ✓ Curability of liquid rubbers
- ✓ Advantages of LFR in peroxide formulation

Life Cycle Assessment (LCA) Information of KURARAY LIQUID RUBBER

- Comparison of Greenhouse Gas (GHG) Emissions
- Liquid Farnesene Rubbers are expected to reduce GHG emission.



Method for Calculation:

✓Calculation principles and framework: ISO14040:2006 and ISO14044:2006
✓Lifecycle Inventory database: IDEA (Inventory Database for Environmental Analysis) version 2.3
✓LCIA model: IPCC AR5 100a

System Boundaries:

✓Cradle to gate
✓Biogenic carbon absorption is included.
✓Incineration and transportation to customer sites are not included.

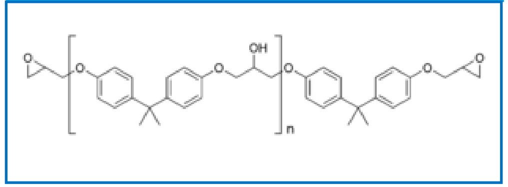
Assumptions and Limitations:

✓LCA for Liquid Farnesene Rubber (L-FR and L-FBR) was conducted based on the production conditions expected by Kuraray at target volumes.
✓This LCA information may be subject to revision as new knowledge and experience becomes available.
✓Kuraray makes no warranties and assumes no liability in connection with any use of this LCA information.

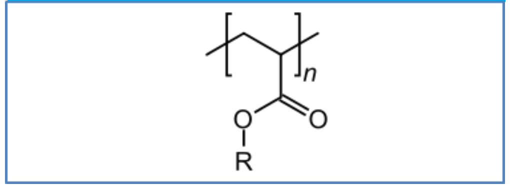
Transition of Curing System in Automotive Industry

Sealant and Adhesive for Automobiles

Epoxy

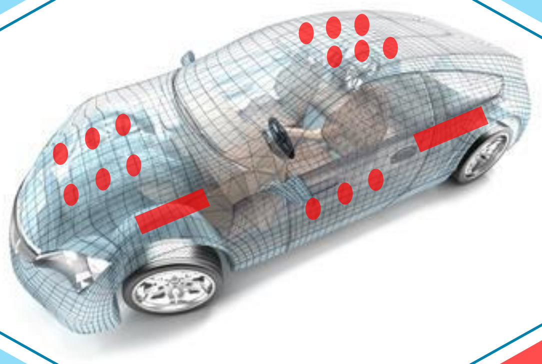


Acrylics



Structural bonding
Hem flange bonding

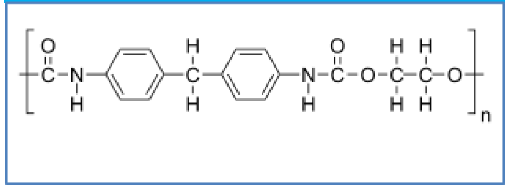
Hem flange bonding
Structural bonding



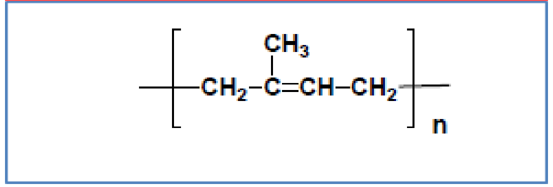
Structural bonding

Anti-flutter
Body sealing
Expandable reinforcement

Polyurethane



Rubber



✓ Flexibility
✓ Elasticity

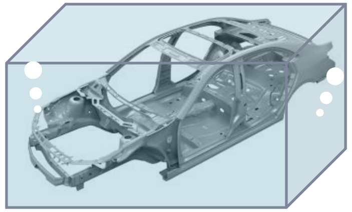
Coating Process

Pre-coating/E-coating

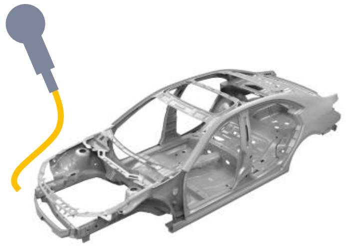
Sealing

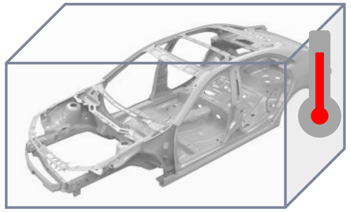
Baking

Process



E-coat bath





Baking oven

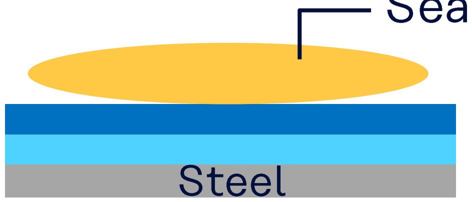
160 – 180 °C, 20 min

Layers

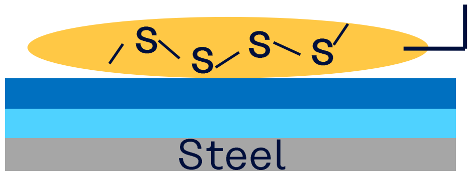
E-coating :
for corrosion resistance

Pre-coating : Zinc phosphate or Zirconium oxide
for corrosion resistance and adhesion to metal

Sealant



Sulfur cure



Hypothesis of Sulfur Curing Issues in Coating Process

Curing agent is switching from sulfur to peroxide (PO) in EU by the following issues.

Environmental issues

Change of the pre-coating

Zinc phosphate

- ✓ Sludge generation
- ✓ Harmful wastewater

↓

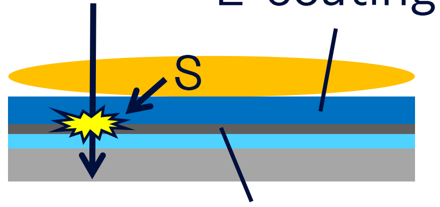
Zirconium oxide

REACH Regulation

REACH allows only 4 or 5 vulcanization accelerators instead of past 20 accelerators

Technical issues

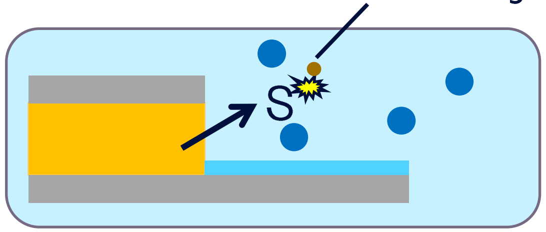
Sulfur spoils the bismuth-rich layer*1



✓ Insufficient corrosion resistance

◆ In case sealant is applied before e-coating...

Sulfur poisons the bismuth catalyst*2



✓ Need more catalysts

*1: improves corrosion resistance

*2: Catalyst for E-coating

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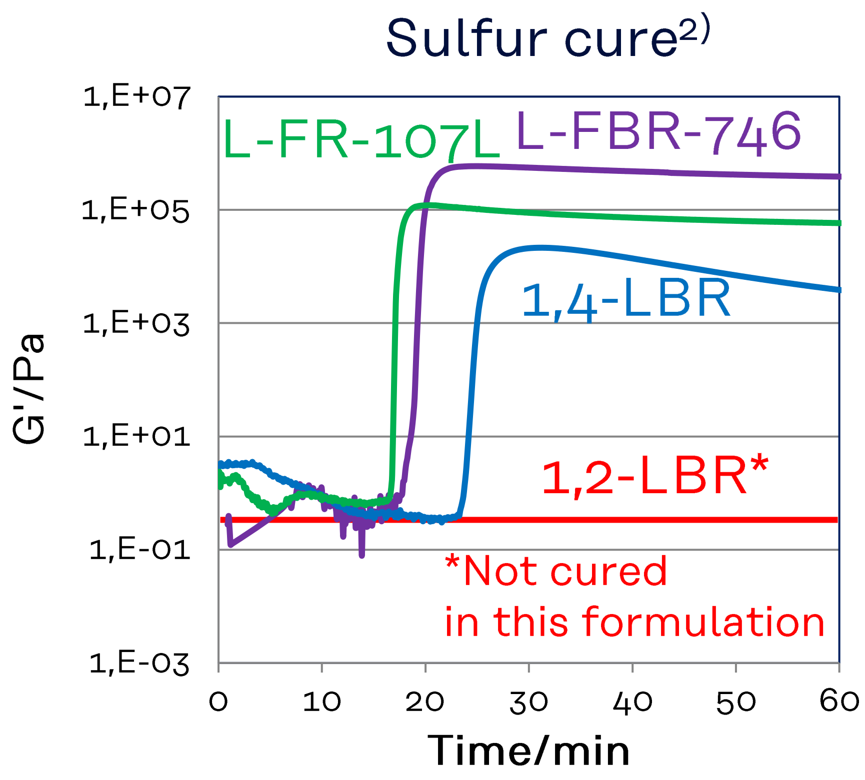
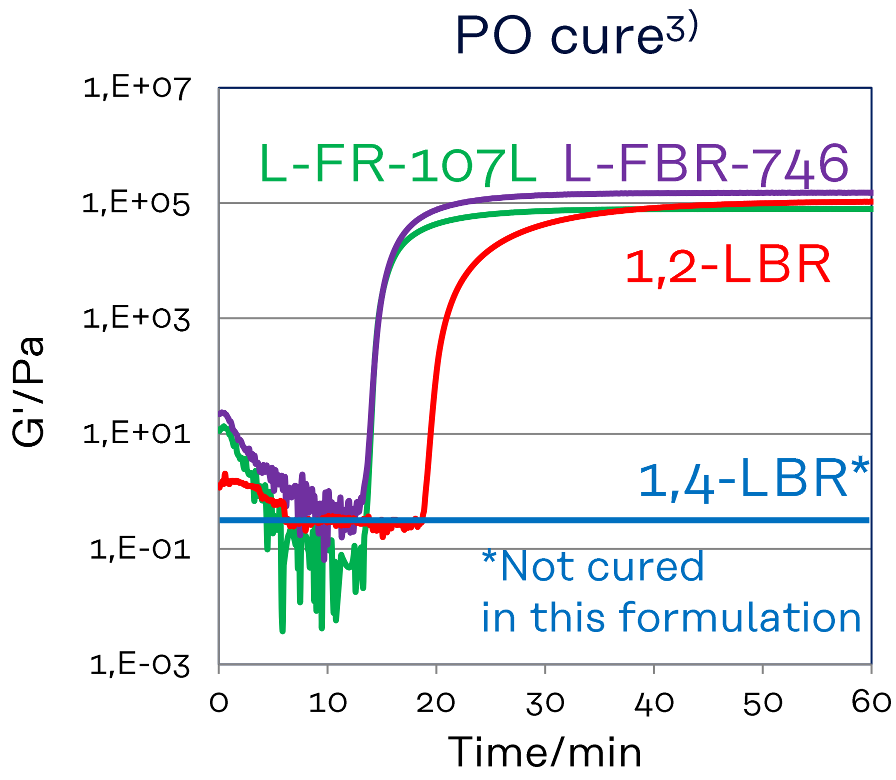
Curability of Liquid Rubbers

Curability of Liquid rubbers changes when curing agent is changed.

Crosslinked

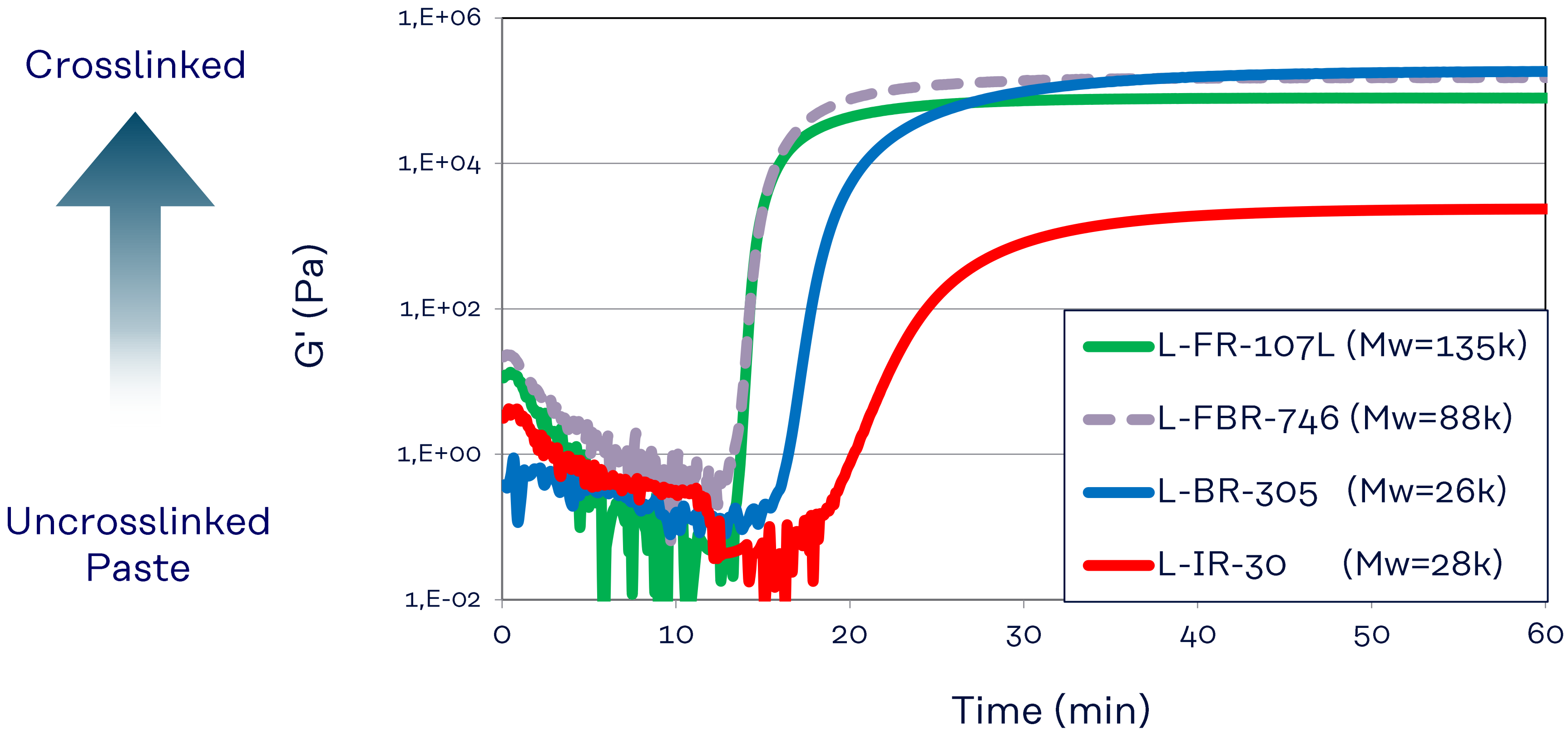
Uncrosslinked Paste





✓ **LFR/LFBR show fast crosslink with both sulfur and PO.**

Crosslink speed in a peroxide formulation



<u>Formulation</u>
Liquid Rubber 100, PO 1

<u>DMA method</u>
Frequency: 10 Hz
Strain: 0.05~5%
Temp: 165 °C

	Melt Vis. @38°C (Pa.s)
L-FR-107L	69
L-FBR-746	520
L-BR-305	40
L-IR-30	70

✓ Crosslink speed of L-FR-107L and L-FBR-746 is much faster than LIR or LBR.

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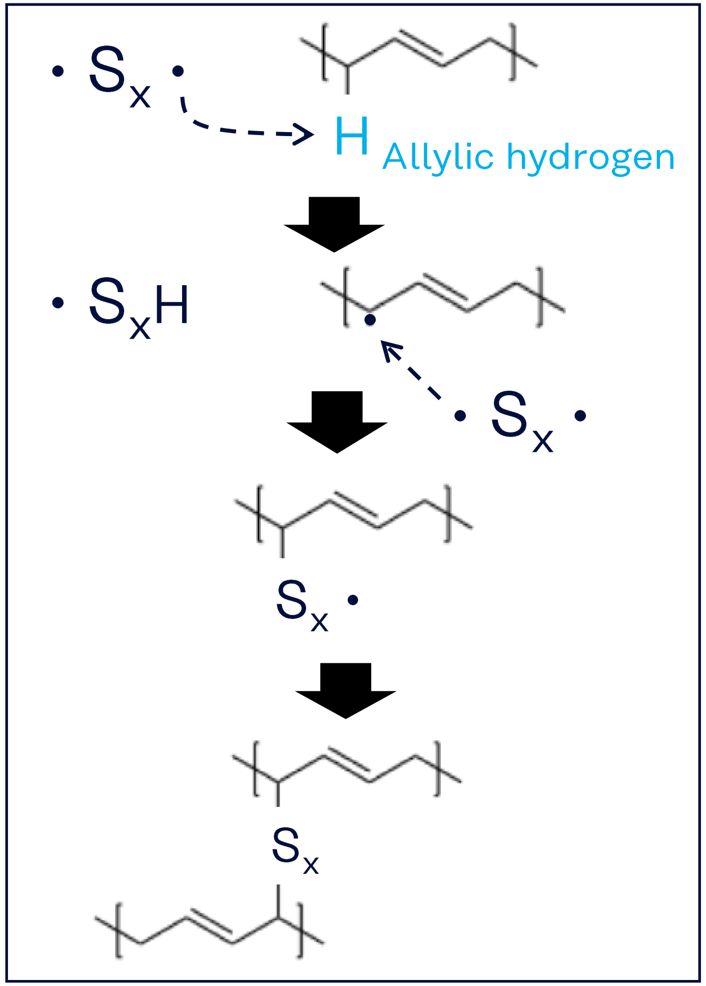
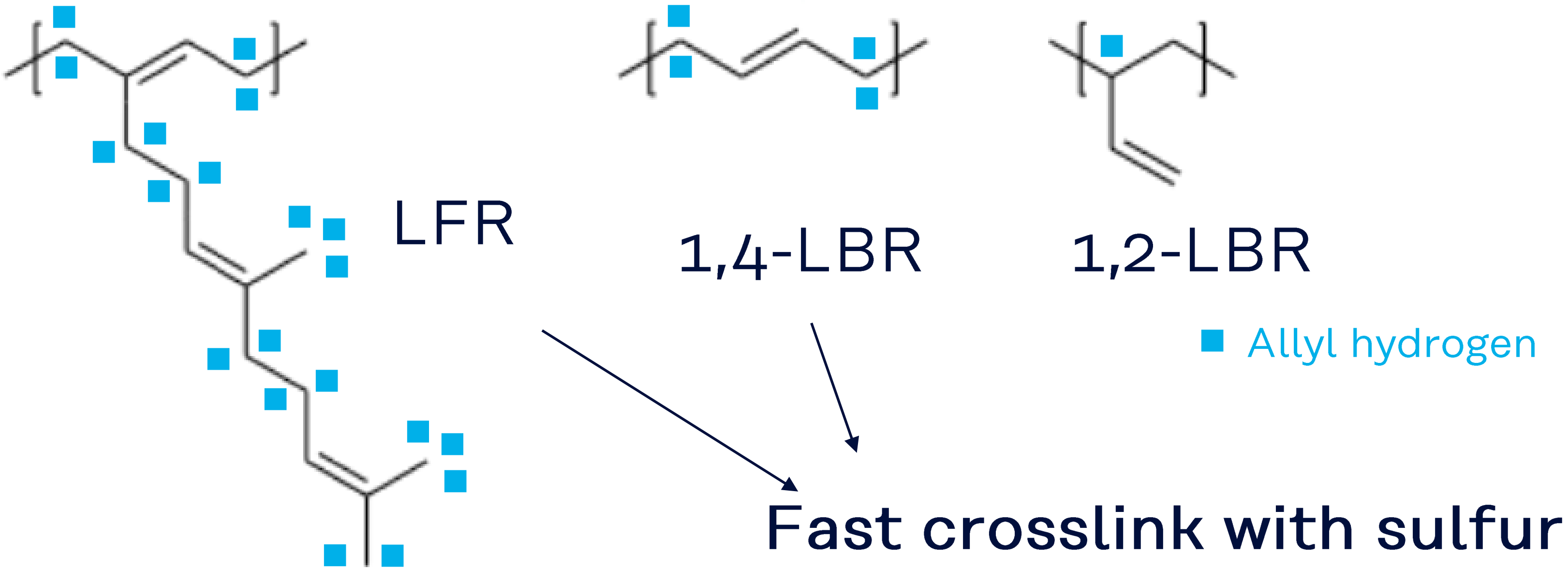
Mechanism of Sulfur Crosslink (hypothesis)

Sulfur addition to 1,4-LBR



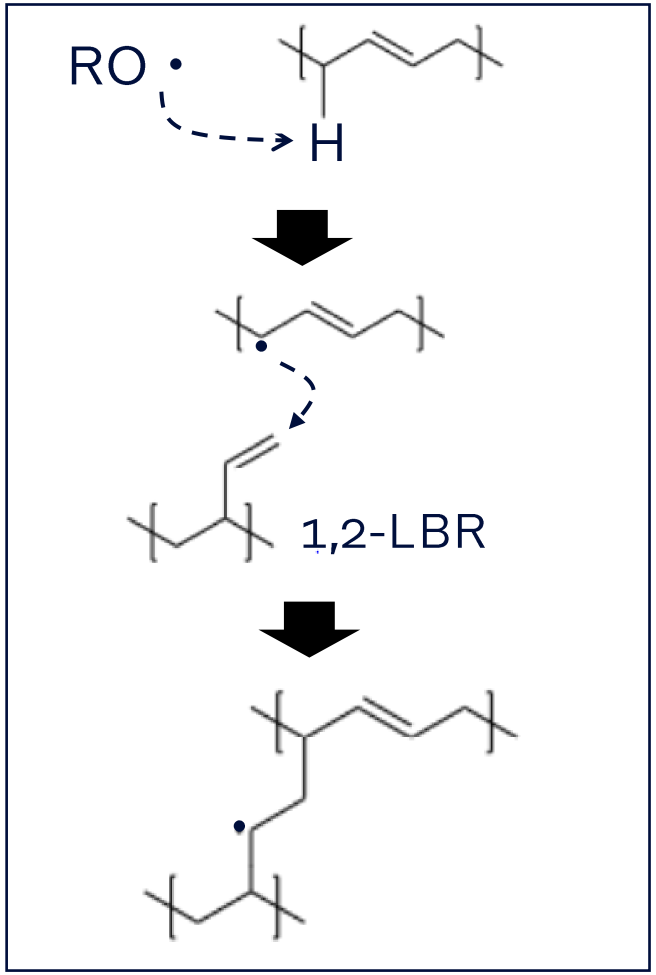
Crosslink speed may correlate with the number of allylic hydrogen, which can be attacked by sulfur radicals.

1,4-LBR and LFR have much allylic hydrogen.



Mechanism of PO crosslink

Radical addition to 1,2-LBR

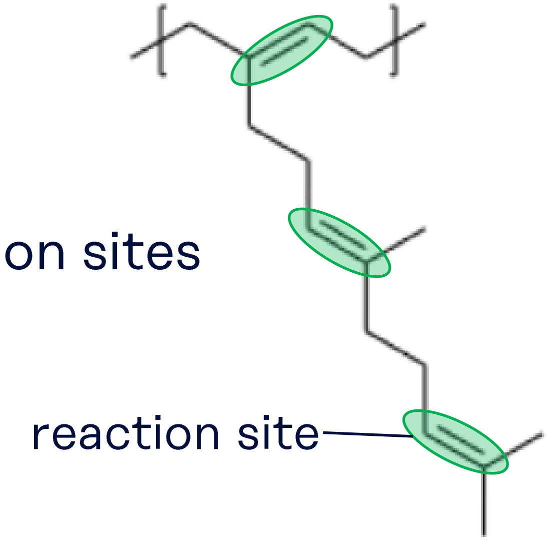


1,2-LBR

- ✓ Less steric hindrance
- ✓ Addition reaction (Good crosslinking efficiency)

LFR

- ✓ Less steric hindrance
- ✓ Highly reactive due to much reaction sites
- ✓ Networking because of High Mw



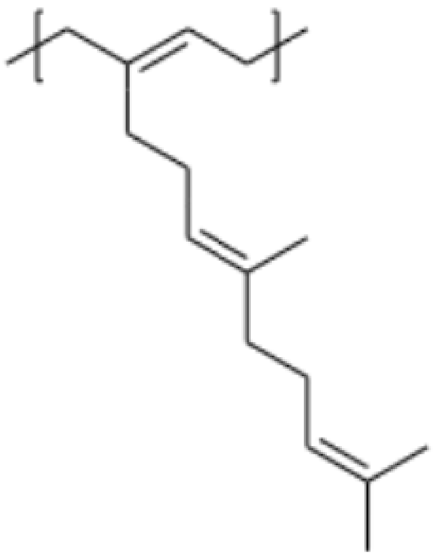
✓ LFR shows fast crosslink with PO as 1,2-LBR.

Summary for curability of Liquid Rubbers

Curability of Liquid rubbers changes when curing agent is changed.

	Sulfur	PO
1,4-LBR	Fast	Slow
1,2-LBR	Slow	Fast
LFR/LFBR	Fast	Fast

LFR



✓ Allylic hydrogen
✓ Less steric hindrance
✓ Highly reactive
✓ Networking

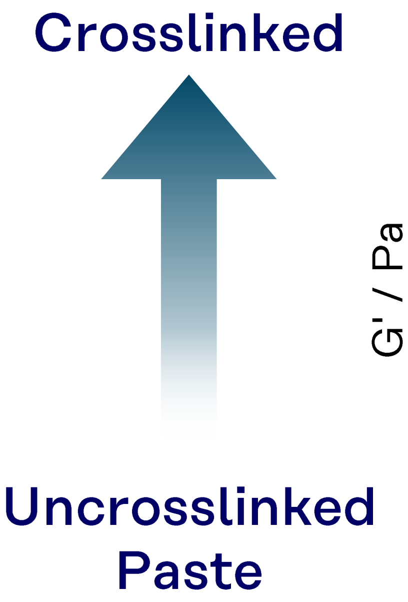
✓ LFR/LFBR exhibit fast curing with both sulfur and PO curing.

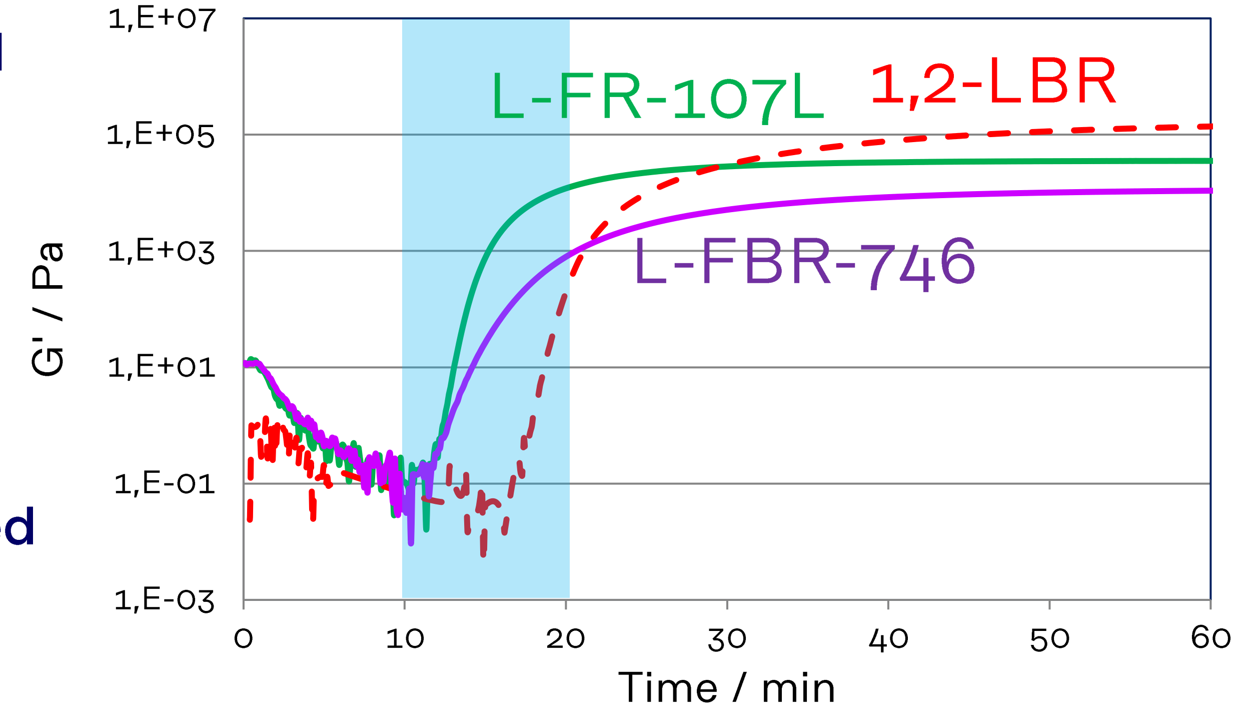
Advantages of LFR in peroxide formulation

- ◆ Low temperature curability
- ◆ Damping sealant

PO Curing at Lower Temperature

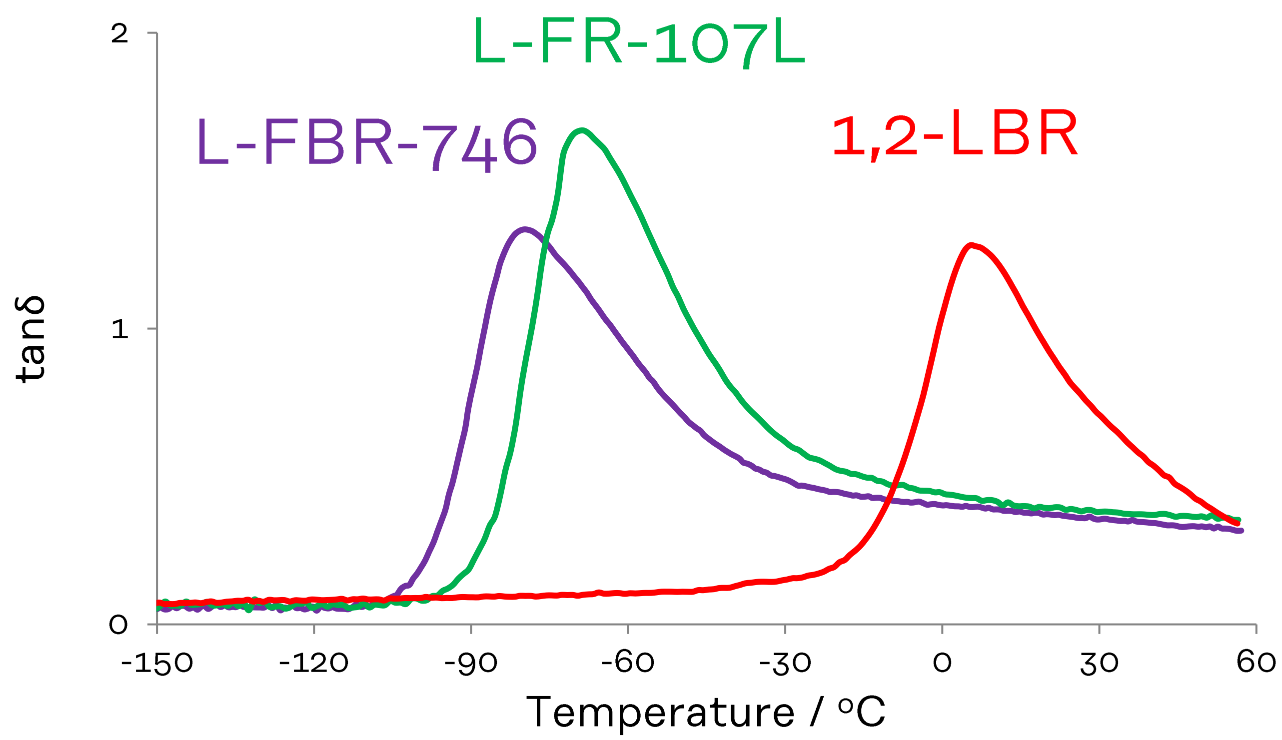
Baking conditions for incumbent process : 160 – 180 °C for 20 min.
With LFR, baking temperature can be lowered, which will contribute to energy saving of production.





Measured at 140°C[4)]

Viscoelasticity of PO Curable LRs



Liquid rubber	PO curing speed	Peak top temp. of tanδ/°C
1,2-LBR	Fast	5
L-FR-107L	Fast	-68
L-FBR-746	Fast	-80
1,4-LBR	Slow	-90

Formulation: LR 100, Dicumyl peroxide 3, CaCO3 85, Antioxidant 2
Cure conditions: 160 °C, 30 min., 10 MPa
DMA: strain 0.15 %, 10 Hz, in the tension mode

✓ LFR/LFBR are the only LRs which can be cured with PO and show low temperature property.

Blend of LRs with High and Low Tg

PO curable sealant formulation which shows high tanδ over wide temperature range can be created using LFR combined with L-SBR.

Liquid Rubber	Structure	Tg / °C
L-SBR-820 (High Tg LR)	Styrene/Butadiene	-14
L-FR-107-L (Low Tg LR)	Farnesene	-70

Formulation		wt%
L-FR-107L		50
L-SBR-820		50
Curing agent	Dicumyl peroxide	3
Filler	$CaCO_3$	85
Antioxidant	Nocrack NS-6	2
Curing conditions	160 °C, 30 min,10 MPa	

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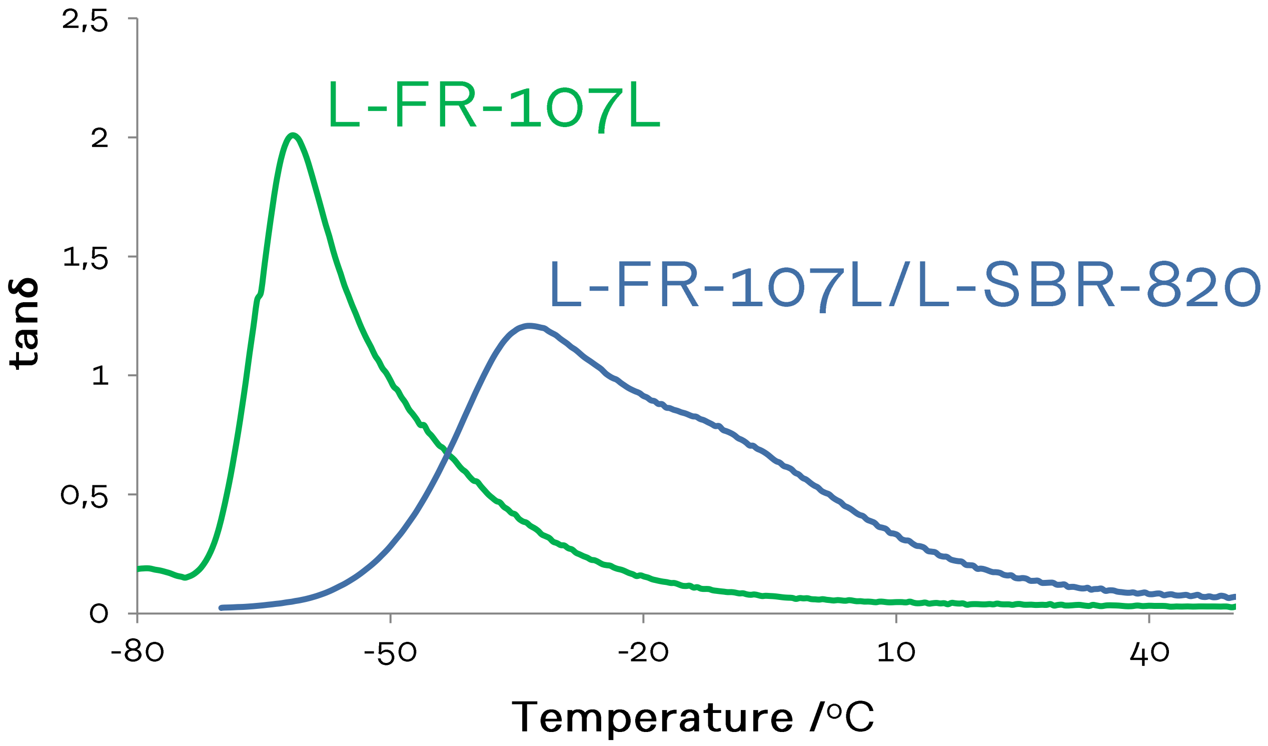
Blend of LRs with high and low Tg



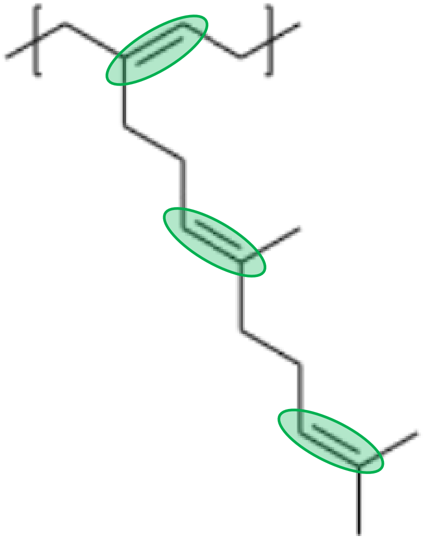
- ✓ Maintain high tan δ over wide temperature range (from -50 to +20 °C)

- ✓ Show damping property over wide temperature rage.

Formulation: LR 100, Dicumyl peroxide 3, $CaCO_3$ 85, Antioxidant 2
Cure conditions: 160 °C, 30 min., 10 MPa
DMA: strain 0.1-1 %, 1 Hz, in the shearing mode

Summary

LFR



LFR = Low viscosity, Low temperature curability
LFBR = Low Tg

LFR&LFBR

- ✓ High reactivity
- ✓ Curable with both sulfur and PO
- ✓ Show damping property over wide temperature range combined with high Tg LR

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
TDAE	VIVATEC 500	H&R GmbH Co. KGaA	

Measuring Conditions of DMA

1) Formulation : Liquid rubber 100, ZnO 2, SA 1, AO 1, S 3, DM 1.5, DT 0.5
   DMA : Frequency: 10 Hz, Strain: 5.0%, Temp: 125℃

2) Formulation : Liquid rubber 100, sulfur 3, ZnO 3.5, Stearic acid 2, Accelerator 1.2 Antioxidant 1
   DMA : Frequency 10Hz, Strain 5%, Temp 165℃

3) Formulation : Liquid rubber 100, PO*[a] 1
   DMA : Frequency 10Hz, Strain 5%, Temp 165℃

4) Formulation : Liquid rubber 100, PO*[b] 1
   DMA: Frequency 10Hz, Strain 5%, Temp 140℃

*a : Dicumyl peroxide

*b : 1,1-Di(t-butylperoxy)cyclohexane

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Liquid Butadiene Rubbers for DMA

	Polymer	Mw	Vinyl content(%)	Melt viscosity at 38°C (Pa.s)	Tg(°C)
1,4-LBR	LBR-305[*1]	27,000	Low	40	-94
	LBR-307[*2]	9,000	Low	1.5	-94
1,2-LBR	1,2-polybutadiene	5,000	High	183	-24

*1: used for "sulfur cure" on slide 11
*2: used for "PO cure" on slide 11

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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.

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