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Functionalized liquid polyisoprene for rubber modification

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Liquid Isoprene Rubber (LIR) is Kuraray's high-viscosity polymer rubber based on isoprene. LIR grades appear as reactive plasticizer and generate improvements of processability, however, by preventing migration. They are co-vulcanizable with base rubber such as NR, SBR, BR, and EPDM using sulfur or peroxide curing systems (fig. 1). The use of Kuraray Liquid Rubber improves the processability while maintaining the rubber compounds' physical properties – this results in a product with lower processing costs and a longer shelf life.

LIR-403 and LIR-410

LIR-403 and LIR-410 are carboxylated liquid rubber grades which have a reactivity with polar substances **(fig. 2).** These carboxylated grades improve the metal adhesion properties of rubber compounds. LIR-403 and LIR-410 are crosslinkable using metal, epoxy, isocyanate, or amine compounds. They are mainly utilized as adhesion modifier to metals and fibers. The characteristics for improving adhesion to polar material are effective in fields such as hot melt adhesive, sealant, coatings and rubber compounds. LIR-403 and LIR-410 are suitable materials for hoses, conveyor belts, fabrics, automotive parts and tires.

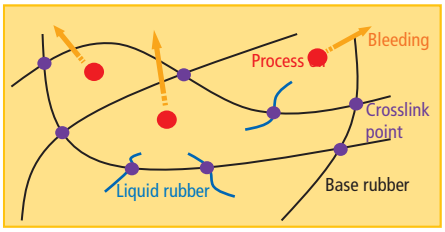
Crosslinking methods

One of the key factors for the durability of rubber goods is imposed by the crosslinking type. Crosslinking with LIR and LBR can be done with any method that is able to connect unsaturated carbon-carbon bonds. **Table 1** shows a range of crosslinking methods processing LIR-403 and LIR-410. The crosslinking temperature of formulation 1 – 4 is above 120 °C. In formulation 5, Bisphenol-A was added and crosslinking was achieved even at room temperature.

Adhesion of rubber to metal: BR-based compound

Table 2 shows some data for the performance of functionalized LIR-403 versus non-functionalized LIR-30. Basically LIR-403 has the same molecular weight range as LIR-30. The result shows the required cohesive failure with LIR-403. Similar results can be obtained with LIR-410.

Fig. 1: Mechanism of liquid rubber: co-vulcanization with base rubber



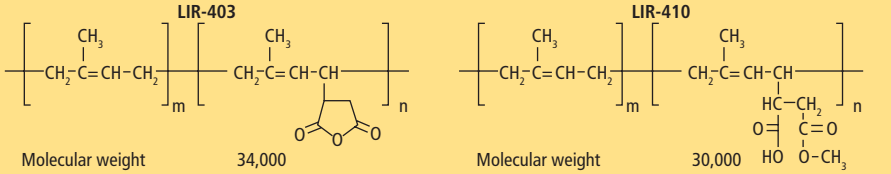
Tab. 1: Adhesion formulation with LIR-403 and LIR-410

Formulation	1	2	3	4	5	6
LIR-403	100	–	100	–	100	
LIR-410	–	100	–	100	–	100
Stearic acid	2	2	2	2	–	–
ZnO	5	5	–	–	–	–
$Ca(OH)_2$	–	–	5	5	–	–
Propylene glycol	3.3	3.3	2.5	2.5	–	–
Bisphenol A Epoxy	–	–	–	–	10	10
Tert-Amine[1)]	–	–	–	–	1	1
Curing Conditions						
25 °C, 1 week	Uncured	Uncured	Uncured	Uncured	Excellent	Uncured
120 °C, 30 min.	Good	Good	Good	Good	Excellent	Excellent
150 °C, 30 min	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
Tested by Kuraray, [1)]Tris(dimethylaminomethyl)phenol						

Tab. 2: BR with LIR-403 and LIR-410 for adhesion to metal

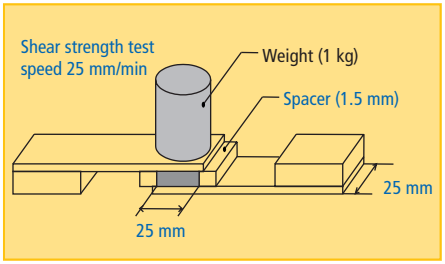
Formulation	1	2
Polybutadiene rubber	40	40
LIR-30	60	–
LIR-403	–	60
Naphthenic process oil	50	50
Activated-$CaCO_3$	200	200
Curing condition	140 °C, 20 min.	140 °C, 15 min.
Shear strength on aluminum and steel		
Max load (N) on aluminum	82	721
Elongation (mm) on aluminum	1.8	4.4
Note (aluminum)	Interfacial fail.	Cohesive fail.
Max load (N) on steel	77	650
Elongation (mm) steel	0.9	4.1
Note (steel)	Interfacial fail.	Cohesive fail.
Tested by Kuraray, active zinc oxide 4 parts, stearic acid 0.5 parts, sulfur 5 parts, Noccelar DM 3 parts, Noccelar DT 2 parts, antioxidant NS-6 1 part		

Fig. 2: Carboxylated grades of LIR



LIR-403		LIR-410	
Molecular weight	34,000	Molecular weight	30,000
Melt viscosity at 38 °C	200 Pa·s	Melt viscosity at 38 °C	430 Pa·s
Glass transition temperature	–60 °C	Glass transition temperature	–59 °C
No. of functional groups	3	No. of functional groups	10

Fig. 3: Shear test scheme



Formulation	1	2	3	4
NR (RSS #1)	100	100	90	90
LIR-403			10	
LIR-410				10
Cobalt naphthenate	3	5	3	3
Physical properties				
Mooney viscosity ML(1 + 4) 100°C	60	61	58	59
Tensile strength (MPa)	28	28	26	26
Elongation (%)	570	590	600	580
Hardness (Shore A)	58	58	58	60
Adhesion properties				
Before heat aging (kg)	210	255	359	343
Surface state of galvanized cord	PS	PS	S	S
After heat aging (kg)	149	154	345	312
Surface state of galvanized cord	I	I	S	S

Tested by Kuraray, other ingredients: GPF Carbon (45), ZnO #1 (5), stearic acid (1), sulfur (2.2), accelerator: N-oxydiethylene-2-benzothiazyl sulfenamide (1), antioxidant: polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (1), surface state: S: substrate failure, PS: partially substrate failure, I: interfacial failure

Tab. 3:
NR with LIR-403 and LIR-410 for adhesion to metal

Adhesion of rubber to metal: NR-based compound

Table 3 shows the adhesion of NR compounds to galvanized cord. The key benefit with addition of LIR-403 (formulation 3) and LIR-410 (formulation 4) is the significantly improved adhesion force. Also, a substrate failure (S) instead of a partially substrate failure (PS) was achieved. The strength forces increase within 50 – 125 % depending on liquid rubber type and conditioning.

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