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Liquid rubber (LIR), a crosslinkable plasticiser

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Kuraray liquid rubbers (LIR) are low molecular weight polydienes which consist of isoprene, butadiene, and styrene. The molecular weight of LIR is designed to have plasticising effect and vulcanisability with solid rubbers. Therefore we call our liquid rubbers "reactive plasticiser" or "co-curable plasticiser". There are three types of LIR that is homo polymer type (standard grade), copolymer type, and modified type. LIR can be used for a wide range of applications, rubber goods (tyre, belt), adhesives (solution, hotmelt, latex, UV cure), sealants for automotive or construction and others (printing plate, coating). Modified types of LIR have additional function besides plasticising effect and vulcanisability. LIR-403 and 410, which are carboxylated types, can improve adhesion to metal of rubbers and dispersion of filler in rubbers.

1. Introduction

Plasticisers are one of the key components of the rubber and adhesive industry. Plasticisers are used to lower hardness, improve processability, reduce raw material cost and so on. On the other hand mechanical properties deteriorate with plasticiser content. And plasticisers sometimes cause change in properties with time and stain on contactants due to the volatilisation or bleeding. In addition, recently the use of plasticiser, especially phthalate plasticiser and aromatic oil, tends to be regulated due to environmental and human health issues. Kuraray liquid rubbers (LIR) have a kind of plasticiser with vulcanisability with solid rubbers. Therefore it is very unlikely that LIR causes the above mentioned issues. We expect that LIR has growth potential.

2. Characteristics

Kuraray liquid rubbers (LIR) are low molecular weight polydienes. The molecular weight is designed between solid rubbers and plasticiser as shown in **figure 1.** Therefore LIR has both characteristics of solid rubbers and plasticiser. Namely LIR has plasticising effect and vulcanisability with solid rubbers. We called our liquid rubber a "reactive plasticiser".

Figure 2 shows molecular weight dependency of crosslinking rate in NR/LIR vulcanisates. The molecular weights of the standard grades of LIR, LIR-30 and LIR-50, are designed to be cured with sulfur as mentioned above.

Figure 3 shows the molecular weight distribution of various liquid rubbers. LIR has the narrowest molecular weight distribution of them. Because LIR is synthesised by anionic polymerisation. And the graph shows that LIR doesn't contain low molecular weight part with less than 1,000 which could migrate and evaporate.

Figure 4 shows plasticising effect of LIR-50 compared with process oil. Mooney viscosity reduces with the blend ratio of plasticisers. But there is not so big difference in the plasticising effect between the two. Benzene extractables data of vulcanised NR/LIR-50 blends are shown in **figure 5.** In the case of NR/oil, benzene extractables increase with the blend ratio of oil. On the contrary the benzene extractables from NR/LIR-50 do not increase with the blend ratio of LIR-50. That means LIR-50 can be vulcanised with NR.

3. Grade line-up

There are basically three types, that is homo polymer type, copolymer type (block and random) and modified type (hydrogenated, carboxylated and methacrylated). Kuraray liquid rubbers (LIR) are synthesised from isoprene, butadiene and styrene. And now we have one developing grade, that is vinyl type (LBR-352) **(fig. 6).**

Tab. 1: Properties of vulcanised NR/LIR blends

	1	2	3
Formulation			
NR RSS#3	100	90	100
LIR-50	10	10	
ISAF-HS carbon	90	90	90
ZnO #1	5	5	5
Stearic acid	2	2	2
Sulfur	5	5	5.5
Acceleator CBS[1)]	1.5	1.5	1.65
Antioxidant	1	1	1
Mooney viscosity			
ML (1+4) 100 °C (ME)	150	133	127
t_{90} (140 °C)	13.0	12.0	10.9
Mechanical properties. 50 % modulus	5.7	6.2	5.6
Tensile strength (MPa)	20.6	18.8	21.4
Elongation (%)	150	140	170
Tear strength (kN/m)	26	24	29
Hardness (JIS A)	85	87	85

[1)] N-cyclohexyl-2-benzothiazoyl sulfenamide; Vulcanisation: Press cure at 140 °C for 20 min

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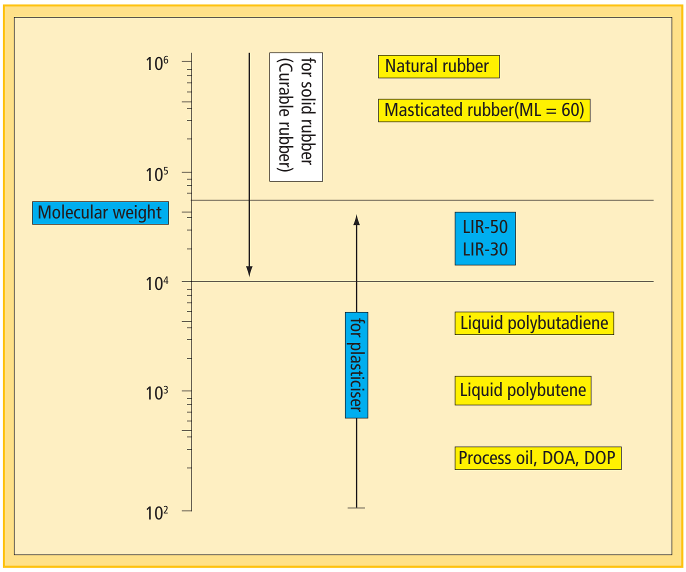


Fig. 1: Molecular weight of Kuraray liquid rubber

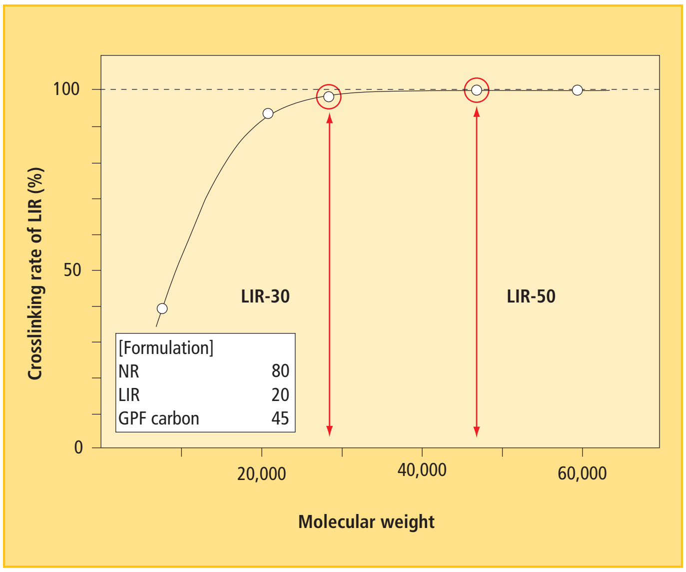


Fig. 2: Molecular weight dependency of crosslinking rate of polyisoprene

Fig. 3: Molecular weight distribution of various liquid rubbers

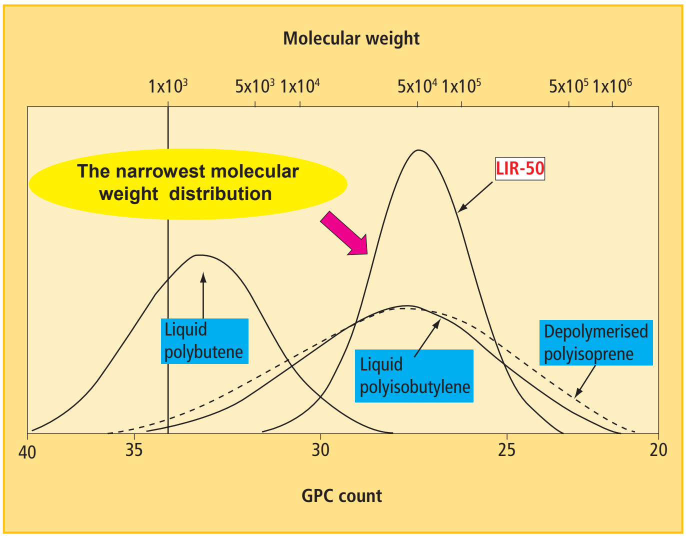


Fig. 4: Plasticising effect of LIR-50

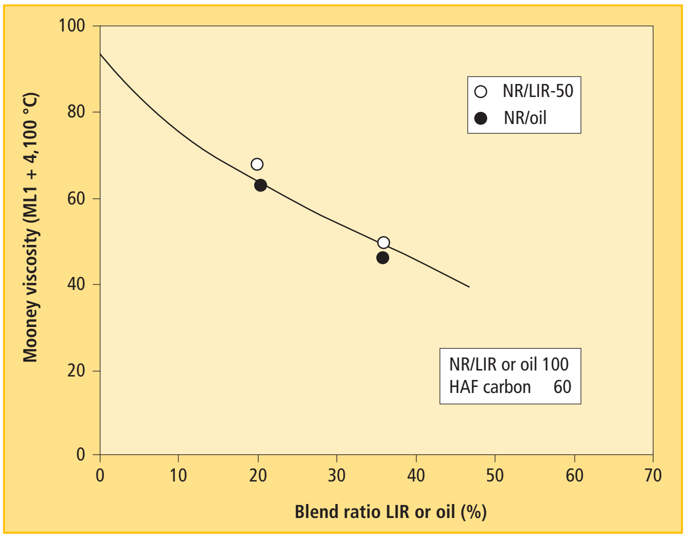


Fig. 5: Benzene extractables of NR/LIR-50 vulcanisates

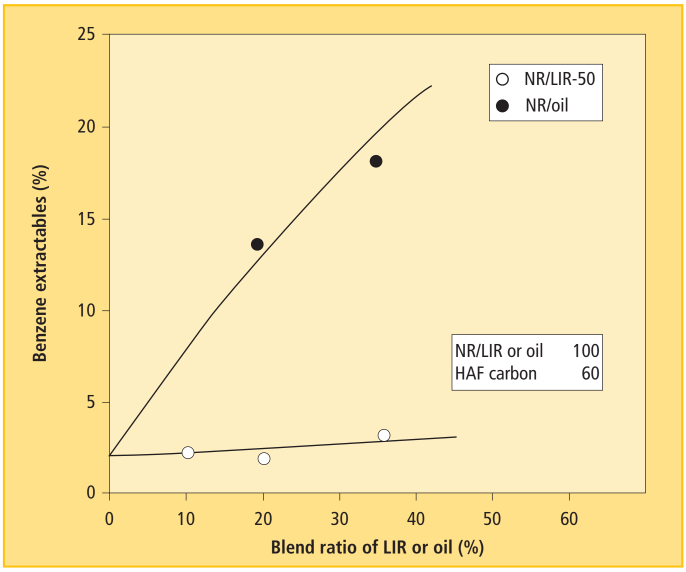
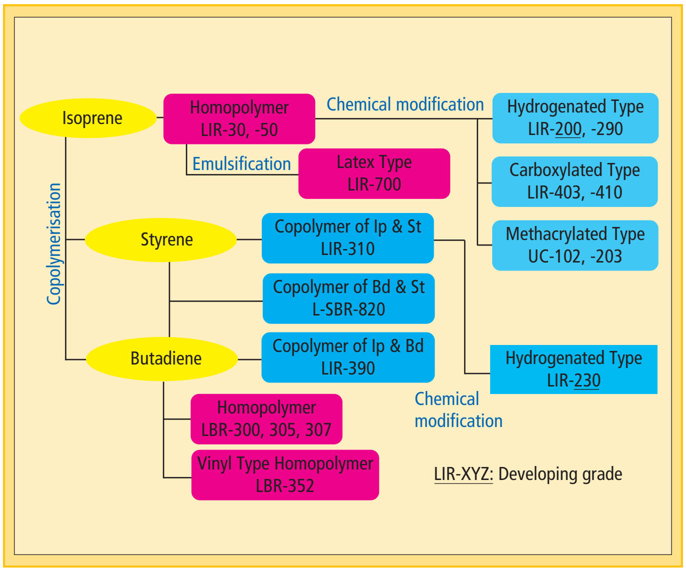


Fig. 6: Grade line-up of Kuraray liquid rubbers



4. Application

Kuraray liquid rubbers (LIR) can be used for a wide range of applications as shown in **figure 7.** The main application of LIR is rubber good, especially tyre compounds. LIR can be used for various tyre compounds, that is tread, carcass, side wall and bead filler compounds. Beside rubber goods, LIR can be used for adhesives, sealants, printing plate and so on.

In the case of adhesives, LIR is used as a tackifier and a plasticiser.

4.1 Application of LIR-50 for NR

Typical properties of LIR-50 are shown in **figure 8.** LIR-50 is isoprene homo-polymer, so that it has good miscibility with natural rubber (NR) and works well as a reactive plasticiser for NR. The properties of vulcan-

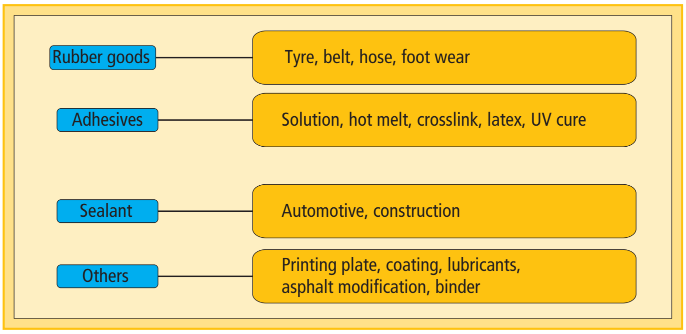
Tab. 2: Properties of NR/LIR-403 or 410 vulcanisates

Formulation	**1**	**2**	**3**	**4**
NR RSS#1	100	100	90	90
LIR-403	–	–	10	–
LIR-410	–	–	–	10
GPF carbon	45	45	45	45
ZnO #1	5	5	5	5
Stearic acid	1	1	1	1
Sulfur	2.2	2.2	2.2	2.2
Accelerator MSA[1)]	1	1	1	1
Antioxidant	1	1	1	1
Cobalt naphthenate	3	5	3	3
Mooney viscosity ML (1+4) 100 °C (ME)	60	61	58	59
Mechanical properties [145 °C, 20 min]				
100 % Modulus (MPa)	2.3	2.4	2.4	2.5
Tensile strength (MPa)	28.0	27.8	25.8	25.6
Elongation (%)	570	590	600	580
Tear strength (kN/m)	52	48	54	46
Hardness (JIS A)	58	58	58	60
Adhesion properties [145 °C, 50 min]				
to zinc plated steal cord (kg)	210	225	359	343
Feature of cord surface after drawing[2)]	B	B	A	A
Hardness (JIS A)	55	54	56	58
Heat resistance [140 °C, 50 min]				
Adhesion of zinc plated steal cord (kg)	149 (71 %)	154 (68 %)	345 (96 %)	312 (91 %)
Feature of cord surface after drawing[2)]	C	C	A	A
Hardness (JIS A)	54 (– 1)	55 (+ 1)	56 (+/– 0)	59 (+ 1)

[1)] N-oxidiethylene-2-benzothiazyl sulfenamid

[2)] A: much rubber remains; B: a little rubber remains; C: no rubber remains

Fig. 7: Applications of Kuraray liquid rubbers

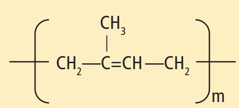


Tab. 3: Properties of NR/LIR-410/Silica vulcanisate

	1	**2**
Formulation		
IR-10	100	90
LIR-410	–	10
Nipsil VN3	45	45
ZnO #1	5	5
Stearic acid	3	3
Sulfur	2	2
Accelerator MBTS[1)]	1	1
Accelerator DOTG[2)]	0.3	0.3
Activator DHA[3)]	3	3
Antioxidant	1	1
Mooney viscosity ML (1+4) 100 °C (ME)	99	81
Mechanical properties		
300 % Modulus (MPa)	3.1	6.3
Tensile strength (MPa)	26.8	30.0
Elongation (%)	800	720
Tear strength (kN/m)	77	87
Hardness (JIS A)	60	66

[1)] 2,2'-Dibenzothiazyldisulfid · [2)] Di-o-tolylguanidin · [3)] Activator DHA

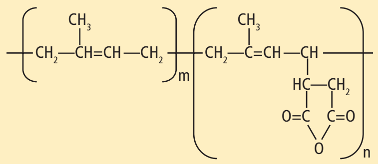
Fig. 8: Typical properties of LIR-30 and LIR-50



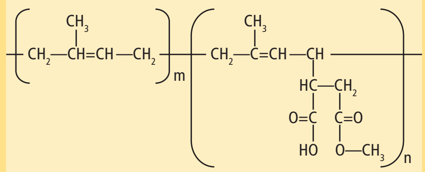
	LIR-30	**LIR-50**
Molecular weight	28,000	54,000
Melt viscosity (at 38 °C)	70 Pa·s	500 Pa·s
T_g	– 63 °C	
Microstructure	Vinyl content ~ 10 %	

ised NR/LIR-50 are shown in **table 1.** The results show that LIR-50 can reduce Mooney viscosity without loss of hardness.

Fig. 9: Typical properties of LIR-403 and LIR-410



LIR-403



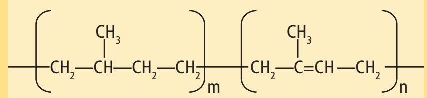
LIR-410

	LIR-403	LIR-410
Molecular weight	34,000	30,000
Melt viscosity (at 38 °C)	200 Pa·s	430 Pa·s
T_g	– 60 °C	– 59 °C
Number of functional groups in a molecule	3	10

4.2 Application of LIR-403 and 410 for NR (adhesion to metal)

Typical properties of LIR-403 and 410 are shown in **figure 9.** LIR-403 and LIR-410 are carboxylated grades. Carboxyl groups generally have reactivity or affinity with polar substances, so that these grades are expected to show additional function beside plasticising effect and vulcanisability. **Table 2** shows properties of NR/LIR-403 and NR/LIR-410 vulcanisates. The results show that both grades can improve adhesion properties to zinc plated steal cord beside functions of reactive plasticiser. And the adhesion properties are stable even after heat ageing.

Fig. 10: Typical properties of EPDM/LIR-290 vulcanisates



	LIR-290
Molecular weight	31,000
Melt viscosity (at 38 °C)	1,200 Pa·s
T_g	– 59 °C
Microstructure	Vinyl content ~ 10 % Hydrogenation rate = 90 % (Iodine value 40 g/100 g)

4.3 Application of LIR-410 for NR (silica dispersion)

As shown in **table 3,** LIR-410 works as a plasticiser and NR/LIR-410/silica vulcanisate

Formulation (Tab. 5)	
EPDM	100
LBR-352, LBR-307 and/or LIR-290	20
FEF carbon	100
Paraffin oil	10
ZnO	5
Stearic acid	1
Sulfur	6
Accelerator CBS-80[1)]	2.3
Accelerator TMTD-80[2)]	0.6
Accelerator ZDBC-80[3)]	1.3

1) N-cyclohexyl-2-benzothiazyl sulfenamide
2) Tetramethylthiuram disulfide
3) Zinc di-n-buthyl dithiocarbamate
(all: polymer-bound, dispersion agent)

Mixing condition: Roll mixing 8 inch., Roll Temperature: 55 ± 5 °C
Curing condition: 150 °C

Tab. 4: Properties of EPDM/LIR-290 vulcanisates

	1	2	3	4	5	6	7
EPDM	100	95	90	85	80	100	100
LIR-290	–	5	10	15	20	–	–
Naphthenic oil	–	–	–	–	–	10	20
HAF carbon	50	50	50	50	50	50	50
ZnO #1	5	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1	1
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Accelerator CBS	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Accelerator DPTT[1)]	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Processability	+/– 0	+ 2	+ 2	+ 2	+ 2	+ 2	+ 2
Surface smoothness	+/– 0	+ 1	+ 4	+5	+ 5	+ 1	+ 1
Green tack	+/– 0	+/– 0	+ 1	+ 2	+ 4	+/– 0	+ 3
Mooney viscosity ML (1+4) 100 °C (ME)	82	70	62	53	45	57	43
Curelastometer 150 °C t_{10} (min)	3.6	3.4	4.0	4.2	4.0	4.2	4.8
t_{90} (min)	11.6	12.6	13.6	13.4	14.0	13.3	14.0
Modulus 100 % (MPa)	5.6	5.4	5.3	4.9	4.6	4.1	3.1
Modulus 300 % (MPa)	20.2	19.6	18.5	17.7	17.1	15.2	11.7
Tensile strength (MPa)	22.8	23.3	21.2	20.8	20.4	21.5	18.3
Elongation (%)	340	360	350	340	350	370	420
Tear strength (kN/m)	35.3	34.3	39.2	36.3	35.3	37.2	33.3
Hardness (JIS A)	76	76	76	75	74	71	66
Extraction by benzene at r. t. for 2 days (%)	2.8	2.9	3.0	3.1	3.3	8.6	13.7

1) Dipentamethylen-thiuramtetrasulfid

Tab. 5: Properties of EPDM/LBR-352 vulcanisates

	LBR-352	LBR-307	LIR-290
Properties			
Mooney viscosity ML(1 + 4) 100 °C (ME)	60	57	62
Mooney scorch 125 °C			
Vm	67.3	66.1	67.8
t_5 (min)	7	6.3	7.3
t Δ 30	1.46	0.9	2.8
Curelastometer 150 °C			
t_{10} (min)	1.6	1.2	1.8
t_{90} (min)	4	2.6	10.2
Mechanical properties			
Modulus 100 % (MPa)	10.1	8.6	10.9
Tensile strength (MPa)	14	10.8	14.2
Tensile elongation (%)	290	310	260
Hardness (Type A)	90	87	85
Tear strength (N/mm)	40	39.5	39.5
Heat resistance (100 °C, 168 h)			
Tensile strength (MPa)	15.5	11.1	13.9
Tensile elongation (%)	260	250	220
Hardness (Type A)	91	90	84
Retention TB (%)	10.7	2.8	– 2.1
Retention EB (%)	– 10	– 19	– 15
Δ HS	1	3	– 1
Compression set (%)			
(70 °C, 22 h)	21.5	29	42.1
(70 °C, 96 h)	38.2	46.2	63.2

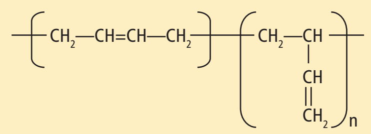
has higher hardness and better tensile and tear strength than NR/silica vulcanisate. The results support LIR-410 can improve silica dispersion.

4.4 Application of LIR-290 for EPDM

Typical properties of LIR-290 are shown in **figure 10.** LIR-290 is partially hydrogenated low molecular weight polyisoprene. 10 % of double bonds are remained to keep the crosslinkability. LIR-290 is designed for saturated rubbers like EPDM and IIR.

Table 4 shows properties of EPDM/LIR-290 vulcanisates. In this case LIR-290 can show advantages against process oil as well as LIR-50 in NR/LIR-50 vulcanisates.

Fig. 11: Typical properties of LBR-352



	LBR-352
Molecular weight	9,000
Melt viscosity (at 38 °C)	6 Pa·s
T_g	– 60 °C
Microstructure	Vinyl content = 56 %

4.5 Application of LBR-352 for EPDM

LBR-352 is low molecular weight polybutadiene with high vinyl content. This polymer is a developing grade which is suitable for high hardness EPDM compounds. Typical properties of LBR-352 are shown in **figure 11.**

As shown in **table 5,** EPDM/LBR-352 vulcanisate shows higher hardness and better compression set than other vulcanisates.

5. Summary

- LIR works as a “reactive plasticiser”, that is “co-curable plasticiser”.
- LIR shows plasticising effect equal to process oil, but loss of mechanical properties is a little.
- LIR can be used for a wide range of applications, that is rubber goods, adhesives, sealants, coating and so on.
- LIR can be used for various rubbers, because LIR has good compatibility with them.
- Carboxylated LIR can improve adhesion properties of rubber to polar material like metal and dispersion of silica in rubber in addition to functions as a reactive plasticiser.