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Effects of crosslinkable plasticizers

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Avoiding migration and reduction of mineral oil usage are up to date topics in rubber formulation development, not only regarding to tire production. As reported earlier [1] a series of liquid rubbers with molecular weights ranging from 5,000 to 70,000 have been developed by Kuraray. These polymers, which consist of isoprene, butadiene and styrene, can be used by rubber processors to achieve improvements in properties and processing. These liquid rubbers are designed to have a plasticizing effect and offer vulcanizability with solid rubbers. These properties allow these materials to act as "reactive plasticizers" or as "co-curable plasticizers". The rubbers are available as homopolymer (standard grade), co-polymer and modified types.

Liquid rubbers can be used for a wide range of applications including rubber goods (tires, belts), adhesives (solution, hot melt, latex, UV curable), automotive/construction sealants and others (printing plate, coating). Modified liquid rubbers can offer additional functionality. Carboxylated types, for instance, can improve rubber adhesion to metal and improve the dispersion of fillers in rubber compounds.

1. Introduction

The usage of plasticizers is one of the key tools in the rubber and adhesives industry. On the one hand plasticizers are used to lower hardness, improve processability and reduce raw material cost. On the other hand, mechanical properties deteriorate with plasticizer content. In addition, plasticizers often cause changes in properties with time and staining due to volatilization or bleeding. Phthalate plasticizers and aromatic oils are or possibly will be regulated due to environmental and human health issues.

Kuraray liquid rubbers (KLR) are plasticizers which are co-vulcanizable with solid rubbers. Therefore it is very unlikely that they will be subject to these bleeding or volatilization issues. As a result, we expect KLR have a growth potential as environmentally friendly plasticizers. The characteristics,

Tab. 2: Typical properties of KLR Effect of molecular weight and chemical structure.

KLR grade	Structure	Mn	Melt viscosity at 38 °C (Pa-s)	T _g (°C)
LIR-50	Poly-IP	54,000	500	-63
LIR-30	Poly-IP	28,000	70	-63
KL-15	Poly-IP	20,000	15	-62
LBR-300	Poly-BD	44,000	225	-95
LBR-305	Poly-BD	26,000	40	-95
LBR-307	Poly-BD	8,000	1.5	-95
L-SBR-820	SBR	8,300	350	-14

Tab. 3: Formulation, mixing and vulcanization conditions

Formulation	phr	Mixing conditions
Natural rubber (RSS#3)	100	Stage 1: Banbury mixer
Oil or liquid rubber	6	0.00 min NR (85 °C)
Carbon black (N330)	50	0.30 min CB, oil/liquid rubber, AO
ZnO	3	1.30 min ZnO, stearic acid
Stearic acid	2	7.00 min Dump out
Sulfur	2	Stage 2: roll mill
Accelerator NS ¹⁾	1.5	0.00 min Compound (55–60 °C)
Antioxidant 6C ²⁾	1	1.00 min Sulfur, accelerator
		7.00 min Sheetting
		Vulcanization condition
		145 °C for 20 min

¹⁾ N-tert-Butyl-2-benzothiazolesulfenamide

²⁾ N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine

grade line-up and scheme of applications have been reported earlier [2] and are summarized briefly in **table 1**.

2. KLR as natural rubber modifier

Typical properties of KLR are shown in **table 2**. These polymers were mixed with natural rubber, carbon black and vulcanizing agents in a Banbury mixer and laboratory roll mill as seen in the formulation in **table 3**.

Properties of vulcanized and non-vulcanized compounds are summarized in **table 4**. The plasticizing effect of aromatic oil is better than naphthenic oil in natural rubber

Tab. 1: Applications of KLR

Category	Application
Rubber goods	Tires, belts, hoses, foot wear, rolls
Adhesives	Solution, hot melt, latex, UV curable types
Sealants	Automotive, construction, electronics
Others	Printing plates, coatings, lubricants

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formulations (entries 2, 3). Low molecular weight KLR showed a similar level of plasticizing effect in comparison to aromatic oil (entries 4, 5, 7, 9), and all KLR formulations maintained tensile strength, elongation and hardness compared with process oil formulations.

As the tire rotates under the weight of vehicle, it experiences cycles of deformation and recovery repeatedly, and it loses energy as heat. This phenomenon is called hysteresis loss and is the main cause of en-

ergy loss associated with rolling resistance. The tire is also deformed during braking and sliding on the rough road surface and accordingly loses energy. This hysteresis loss relates to frictional force between the tire and road surface. Hysteresis loss is attributed to the viscoelastic characteristics of the rubber composition. The loss factor ($\tan \delta$) at -20, 0, 25 and 60 °C have been used to indicate ice, wet, dry traction and rolling resistance properties respectively when the measurement is carried out at 10 Hz condition (fig. 1).

$\tan \delta$ and storage modulus (E') were measured with a high torque dynamic mechanical analysis unit, Eplexor (Gabo Qualimeter Testanlagen GmbH) under conditions of static strain of 2 % and dynamic strain of 0.2 %, and normalized to the naphthenic oil formulation (fig. 2). The $\tan \delta$ of the LBR-307 and L-SBR-820 formulations were much higher than that of naphthenic oil. These liquid polymers therefore are expected to improve traction control in dry, wet and wintry conditions although they do not contribute to the improvement of the rolling resistance. The E'

Fig. 1: Relationship between $\tan \delta$ and tire performance

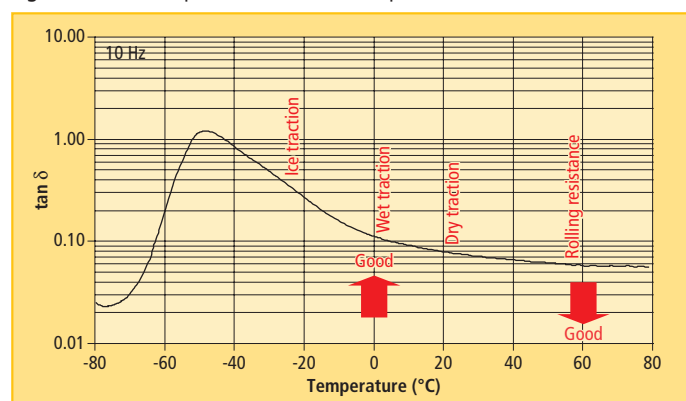


Fig. 2: Normalized $\tan \delta$ of NR/KLR formulations

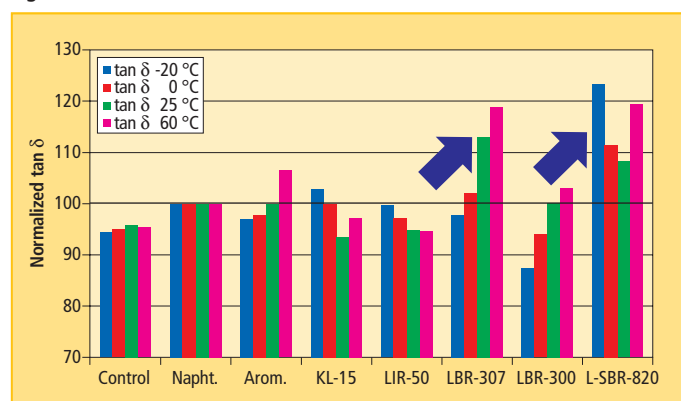


Fig. 3: Normalized E' of NR/KLR formulations

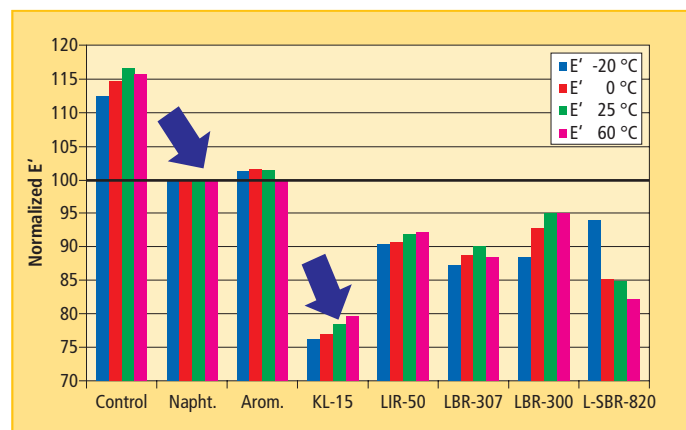
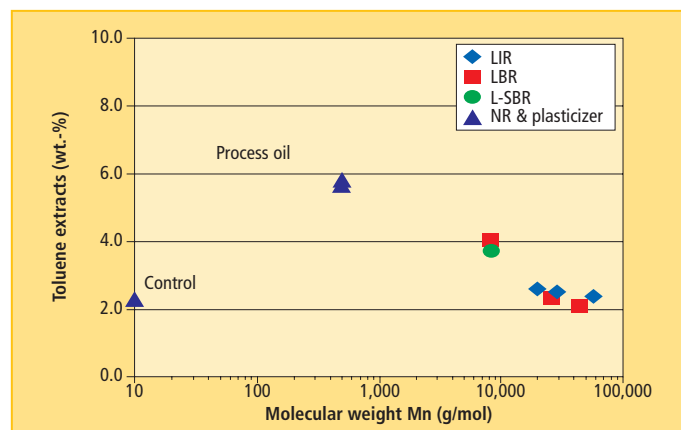


Fig. 4: Toluene extraction test



Tab. 4: Properties of natural rubber based compounds

Entry	1	2	3	4	5	6	7	8	9	10
Plasticizer	None	Naphthenic oil	Aromatic oil	KL-15	LIR-30	LIR-50	LBR-307	LBR-305	LBR-300	L-SBR-820
Mooney viscosity, ML_{1+4} (100 °C)	80	69	64	65	65	66	64	65	67	66
Mooney scorch time, 125 °C, T_5 (min)	22.0	24.4	26.3	25.1	24.9	23.2	25.8	25.9	25.2	25.4
Curelastometer, 145 °C, T_{90} (min)	9.3	10.1	11.2	9.7	9.5	9.5	10.3	10.6	9.6	9.8
Mechanical properties										
M300 (MPa)	23.1	20.2	20.4	21.2	21.6	21.9	20.6	20.2	21.8	20.0
Tensile strength (MPa)	30.5	29.4	30.8	30.1	29.1	30.3	30.5	28.3	30.6	29.8
Elongation (%)	410	430	440	410	405	410	430	410	415	440
Hardness (JIS type A)	75	73	73	72	74	74	72	71	73	74

of KLR formulations were much lower than the process oil formulations, especially when KL-15 was added (fig. 3). Accordingly, KLR can soften vulcanized natural rubber compositions better than process oil.

These phenomena are considered to arise from the following: KLR aggregates on the surface of carbon black and inhibits the reinforcement effect by bonding between carbon black and natural rubber resulting in a reduction of E'. The hysteresis loss (tan δ) of LBR-307 and L-SBR-820 formulations was increased especially on the interface between carbon black and rubber since partially vulcanized low molecular weight rubber was present there and the mobility of rubber molecules was increased. Figure 4 shows the results of a toluene extraction test for each vulcanized composition. Extracts of high molecular weight KLR formulations were almost the same as the control since they were co-vulcanized with natural rubber. Process oils were extracted completely, and LBR-307 and L-SBR-820 were only partially extracted.

The extraction test also indicated another advantage of KLR. KLR can maintain the flexibility of vulcanized compositions for long periods because it does not bleed out. This is unlike the behavior of process oil. These properties are suitable for winter tires in which high traction and long term flexibility are required rather than all season tires which prioritize fuel economy.

3. Benefits of KLR in tire manufacturing

Beside the positive impact in tire performance the benefits of KLR for the manufacturing process have been investigated [6] by simple modeling formulation and recording of mechanical data depicted in table 5.

At the mixing the reduction of mixing stages from 4 to 3 was properly realized by exchange of 4 phr LIR-50 as replacement of the rubber matrix. This also results in the shortening of mixing time and electric power savings at last.

In figure 5 we show the effects at the calendering step. A smooth surface was found

compared to rough together with a restraining mill shrinkage. At NR/BR mixtures with 4 phr replacement of NR by LIR-50 the mill shrinkage was improved more than 15 %, whereas at NR/SBR mixtures this effect improves by over 10 % (tab. 6).

At the extruding step the LIR-50 rich formulation achieved a high extrusion rate and good appearance, by maintaining accuracy of size. This especially supports the produc-

tion of tires and other rubber goods with an adequate and stable tackiness. All test formulations showed the retaining of original mechanical properties as the base for this study.

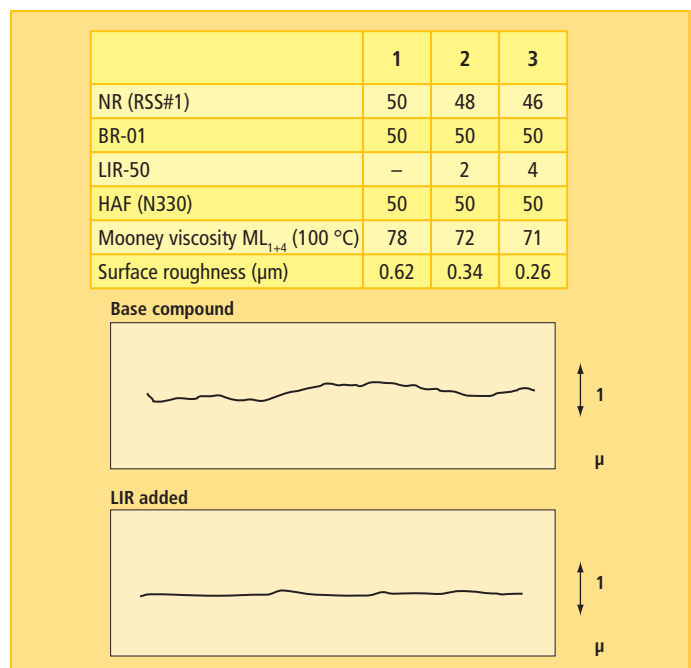
A progress in uniformity is contributing to many aspects in tires. The potential benefits of LIR-50 in tire parts are summarized in figure 6. Processability of high hardness compounds for bead fillers is improved and

Tab. 5: Effect of LIR-50 in mixing Reduction of mixing time and stages

	1	2	3
NR (RSS#1)	100	98	96
LIR-50	–	2	4
ISAF-HS (N285)	45	45	45
Number of mixing stages	4	2	2
Mixing time (min)	4	4	3
Electric power consumption (KW)			
Stage 1	5.2	5.2	5.2
Stage 2	6.2	–	–
Stage 3	6.3	–	–
Last stage	6.3	6.6	6.3
Mooney viscosity (ML ₁₊₄ , 100 °C)	76	75	75

Mixing		
Equipment	BR type Banbury mixer	
Procedures		
	NR	NR/LIR-50
1 Mastication	1 min	1 min
2 Mixing 2/3 of CB	1 min	All CB 2 or 3 min
3 Mixing 1/3 of CB	1 min	
4 Remill	1 min	

Fig. 5: Effect of LIR-50 in calendering on the surface roughness



this supports tire building. A smooth and sometimes even shiny surface improves not only the look of the sidewalls, the adequate tackiness control and restrain of the mill

shrinkage are trigger at the carcass construction. Improved high extrudability and shaping of the tread part are fact in modern tire making.

	1	2	3	4	5	6
NR (RSS#1)	50	48	46	70	68	66
BR-01	50	50	50	–	–	–
SBR (1502)	–	–	–	30	30	30
LIR-50	0	2	4	0	2	4
HAF (N330)	50	50	50	50	50	50
Mill shrinkage (%)						
0 min	32.6	27.1	27.1	22.4	21.0	19.9
5 min	36.5	31.3	30.1	25.7	24.0	22.7
10 min	37.3	32.6	30.3	25.9	24.3	22.7
30 min	37.3	32.6	30.6	26.0	24.3	23.0
60 min	37.3	32.6	30.7	26.0	24.5	23.0
180 min	37.3	32.6	30.9	26.0	24.5	23.0
300 min	37.3	32.6	30.9	26.2	24.6	23.2

Tab. 6: Effect of LIR-50 Improvement of the mill shrinkage

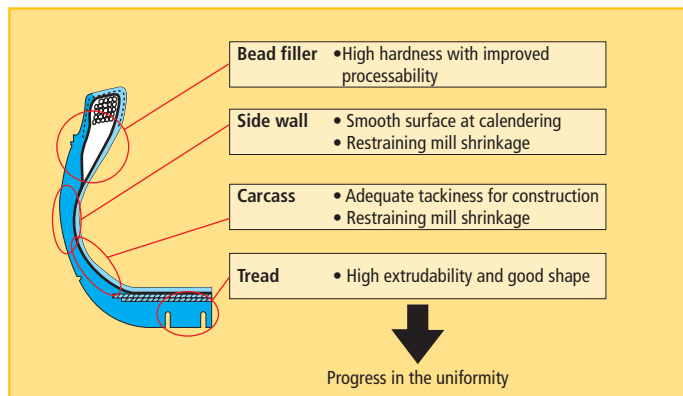


Fig. 6: Effect of KLR in tire parts

4. Summary

Kuraray liquid rubber (KLR) improves the processability without deteriorating the mechanical properties. In case of tire tread applications, KLR can reduce E' and increase tan δ. It softens rubber compounds and improves the grip properties. Furthermore, KLR can help rubber compounds to maintain softness for a long period of time since it does not bleed out due to co-vulcanization with the base rubber. Progress in uniformity can be achieved by partial replacement of KLR in NR matrix that improves mixing, processing, surface, extrudability, restrain of mill shrinkage, and saves energy.

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