RFP Rubber FIBRES Plastics International
Magazine for the Polymer Industry

S. Kuwahara, M. Gründken,
R. Böhm

Polymer development for sustainable product design

Dr. Gupta Verlag
Volume 9, January 2014
01| 2014

Polymer development for sustainable product design

Advantages of liquid rubber in tire compounds

S. Kuwahara, M. Gründken, R. Böhm

Kuraray has developed a series of liquid rubbers with molecular weights ranging from 5,000 to 70,000. The polymers, which consist of isoprene, butadiene and styrene, can be used by rubber processors to achieve improvements in properties and processing. They are designed to have a plasticizing effect and offer vulcanizability with solid rubbers. These properties allow the materials to act as "reactive plasticizers" or "co-vulcanizable plasticizers". 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). The main application of Kuraray Liquid Rubber (KLR) is in rubber goods, particularly in tire compounds. KLR can be used for various parts of the tire, including tread, carcass, side wall, and bead filler.

1. Introduction

Plasticizers are one of the key components of the rubber and adhesives industry. They are used to lower hardness, improve processability and reduce raw material cost. On the other hand, mechanical properties can deteriorate with increasing 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. KLR are plasticizers that are co-vulcanizable with solid rubbers. Therefore it is very unlikely that KLR will be subject to these bleeding or volatilization issues. As a result, we expect KLR have a growth potential as environmentally friendly plasticizers.

2. Characteristics of Kuraray Liquid Rubber (KLR)

KLR is a low molecular weight polydiene. The molecular weight is designed between a typical solid rubber and plasticizer as shown in **figure 1.** KLR, therefore have characteristics of both rubbers and plasticizers, namely vulcanizability with solid rubbers and excellent plasticizing effects. We call our liquid rubber a "reactive plasticizer" due to these properties. KLR is available in homopolymer (standard grade), copolymer and modified types (hydrogenated, carboxylated, and methacrylated). These polymers consist of isoprene, butadiene and styrene **(fig. 2).**

Shigenao Kuwahara
shigenao.kuwahara@kuraray.eu
Marcel Gründken, Ralph Böhm
Kuraray Europe GmbH, Hattersheim am Main, Germany

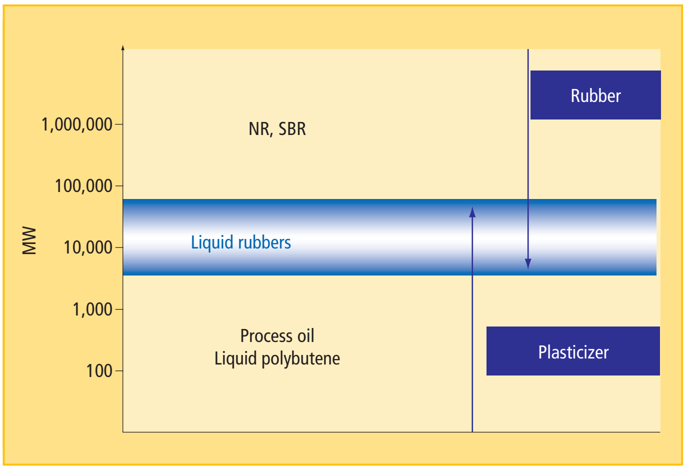
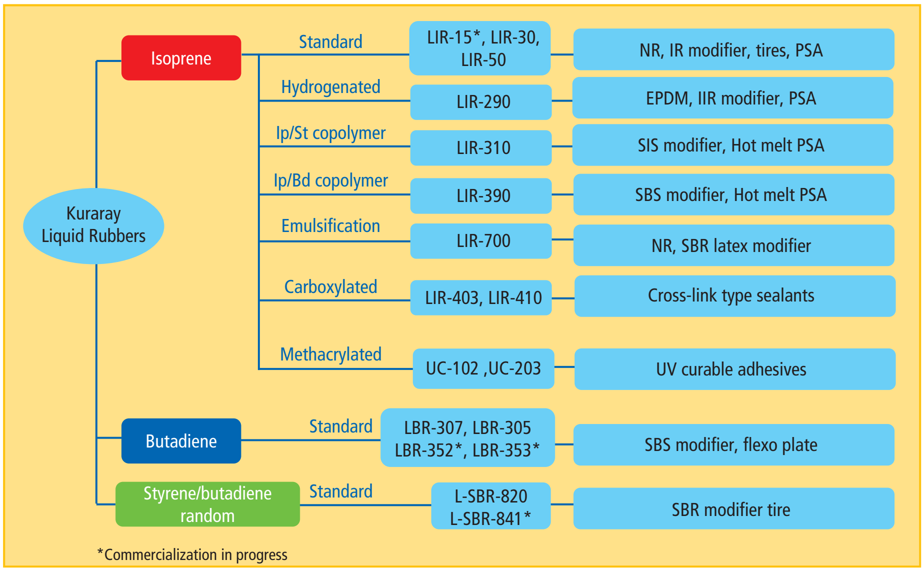


Fig. 1: Molecular weight of liquid rubber

Fig. 2: Grade line of KLR



3. Effect in NR/carbon black compounds

Typical properties of KLR are shown in **table 1.** The polymers were mixed with natural rubber, carbon black and vulcanizing agents with a Banbury mixer and laboratory roll mill in two formulations (NR/CB/plasticizer = 100/50/10 and 100/50/6).

Mooney viscosity values are shown in **figure 3.** The plasticizing effect of KLR was equivalent to TDAE in natural rubber formulations. Furthermore, low molecular weight KLR showed a better level of plasticizing effect in comparison to TDAE and all KLR formulations maintained tensile strength and elongation with TDAE formulations.

Properties of DIN abrasion are shown in **figure 3.** LBR formulations showed a better level of wear resistance compared with TDAE.

3.1 Performance in tires

Tire labeling has been introduced in the EU in November 2012, and has also been adopted by countries outside Europe such as Japan and South Korea. Key indicators are fuel efficiency, noise and break safety. Scientists connected these properties with physical detectable properties such as tan δ and storage modulus E'. As the tire rotates under the weight of the vehicle, it experiences repeated cycles of deformation and recovery, and it dissipates energy as heat. This phenomenon, called hysteresis loss and is the main cause of energy loss associated with rolling resistance. On the other hand, the tire is also deformed during braking and sliding on the rough road surface, and accordingly dissipates 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 tangents (tan δ) 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. 4).**

Storage modulus (E') is measured with a high torque dynamic mechanical analysis unit, Eplexor (Gabo Qualimeter Testanlagen GmbH) under conditions of static strain of 0.5 % and dynamic strain of 0.1 % **(fig. 5).** The E' of the LBR was much lower than that of TDAE because LBR has the lower T_g. Therefore, LBR is expected to keep softness of vulcanized natural rubber compositions at lower temperature and improve ice traction control.

Liquid rubber	Structure	M_n	Melt viscosity at 38 °C / Pa·s	Glass transition temperature / °C
LIR-30	IR	28,000	70	–63
LIR-50	IR	54,000	500	–63
LBR-300*	BR	44,000	225	–95
LBR-305	BR	26,000	40	–95
LBR-307	BR	8,000	1.5	–95
L-SBR-820	SBR	8,300	350	–14
L-SBR-841*	SBR	10,000	130 / 60 °C	–6
*Commercialization in progress				

Tab. 1: Typical properties of KLR

Fig. 3: General properties (NR)

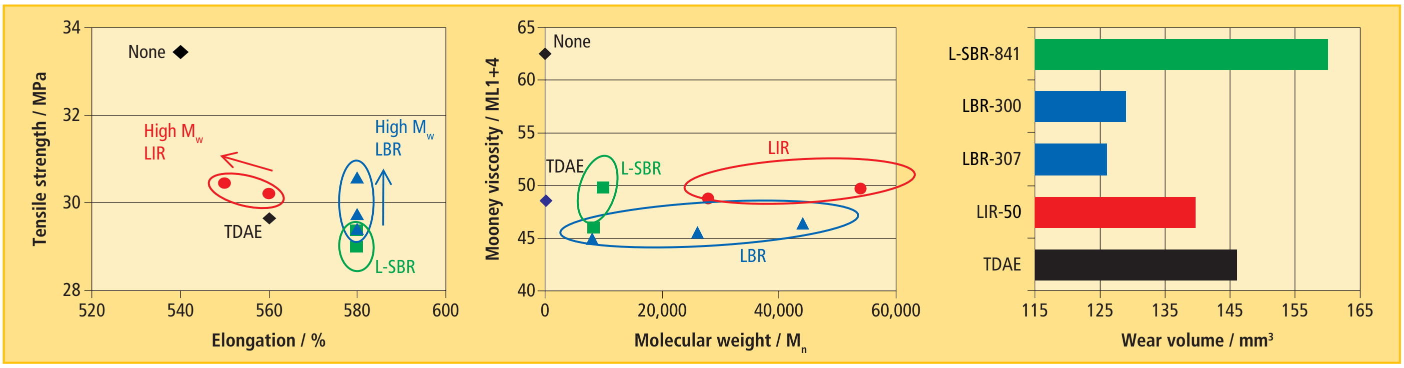


Fig. 4: Viscoelastic characteristics

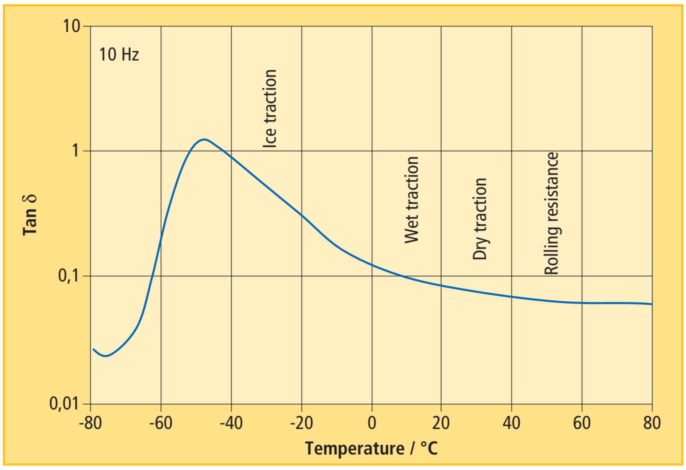


Fig. 5: Storage modulus E'

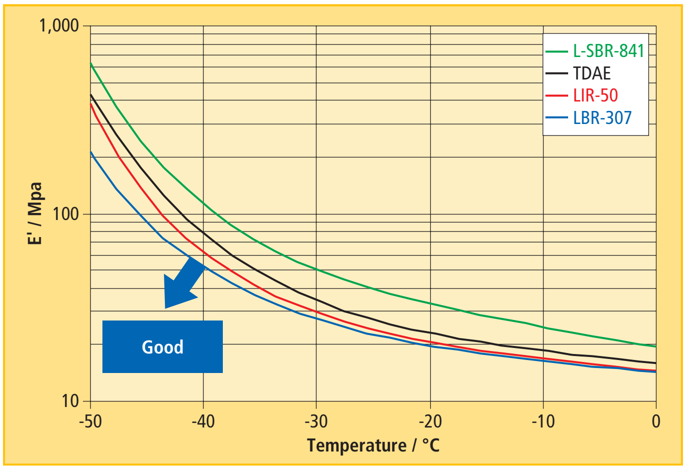


Figure 6 shows the results of a toluene extraction test for each vulcanized composition in the formulation (NR/CB/plasticizer = 100/50/6). Extracts of high molecular weight KLR formulations were almost the same as the control since they were co-vulcanized with natural rubber. On the other hand, process oils were extracted completely. 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.

4. Effect in SBR/silica compounds

KLR were mixed with SBR, silica and vulcanizing agents with a Banbury mixer and laboratory roll mill in the formulation (SBR/silica/plasticizer = 100/50/10).

Properties of Mooney viscosity are shown in **figure 7.** The plasticizing effect of KLR was almost equivalent to TDAE in SBR formulations. Especially, LBR showed an excellent level of plasticizing effect and LBR-307 formulations showed better elongation compared with TDAE formulations. Properties of DIN abrasion are shown in **figure 7.** LBR showed a better level of wear resistance compared with TDAE as well as natural rubber and carbon black composition.

4.1 Performance in tires

The tan δ and E' were measured with the same analysis unit, Eplexor under conditions of static strain of 10 % and dynamic strain of 5 % **(fig. 8).** The tan δ of the L-SBR at 0 °C was much higher than that of TDAE but L-SBR also increased tan δ at 60 °C slightly because L-SBR has the higher T_g. From these results, L-SBR is expected to improve wet grip although it deteriorates rolling resistance a little.

5. Summary

With polymer development for sustainable product design we managed to combine benefits from unique technology of liquid polymers as reactive plasticizers. This results in our unique polymer structure with high plasticizing effect. The effect of co-vulcanizability at higher level of molecular weight compared with standard oils like TDAE provides low migration property over all grades and supports better environmental protection with longer life durability.

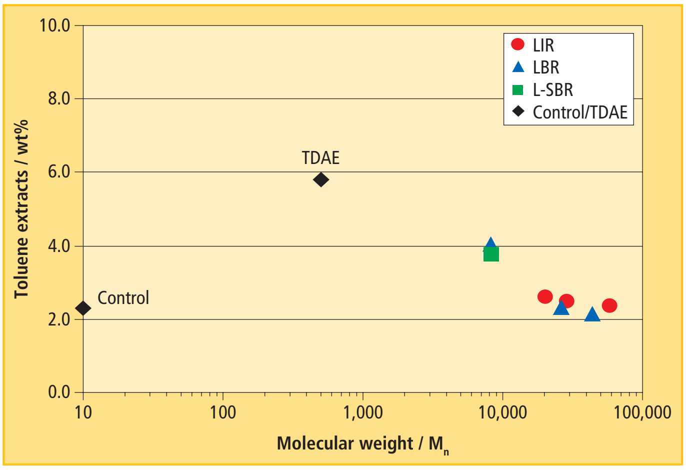


Fig. 6:
Toluene extraction test

Fig. 8: Analysis of viscoelasticity

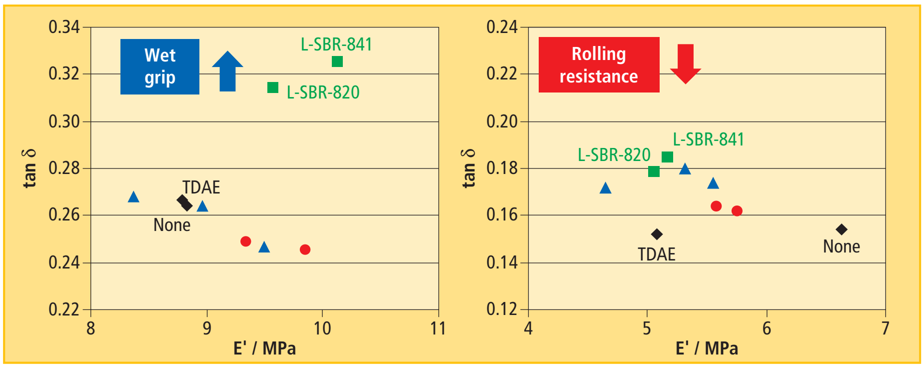


Fig. 7: General properties (SBR)