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Functionalised liquid rubber materials

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The production of rubber goods is always a tightrope walk between costs and performance. In order to support processors to achieve a maximum of advantages, Kuraray has developed a series of functionalised liquid rubbers with different molecular weights (5,000 – 70,000). Kuraray liquid rubbers (KLR) are designed to have a plasticising effect and vulcanisability with solid rubbers. They consist of isoprene, butadiene, and styrene at the polymer backbone and partly vary at the side chains for interface to polar phases. The unsaturated CC-bond in the backbone provides crosslinkable points. Therefore, they are called reactive or co-curable plasticiser. The KLRs are available as homopolymer type (standard grade), copolymer type and modified type. Their use leads to improvements in a wide range of applications: rubber goods (tyres, belts), adhesives (solution, hotmelt, latex, UV-cured), automotive sealants, construction and other applications (printing plates, coatings). LIR-403 and LIR-410, the polar modified types of KLR, have additional function besides their plasticising effect and vulcanisability. The carboxylated function can improve the adhesion of rubber to metal and the dispersion of fillers in rubber.

1. Introduction

Plasticisers are key components to optimise the processability of rubber compounds. Rubber mixing is still a kind of alchemy and the selection of suitable raw materials is not an easy task. The plasticisers of Kuraray introduced in this article are used to lower the Mooney viscosity in order to improve processability of the compound while preserving its mechanical properties **(fig. 1).** They are able to reduce total material costs because they support the processor in reducing scrap and improving efficiency. The use of plasticisers often provokes a deterioration of the mechanical properties. Another problem is the degradation of the product surface due to migration and bleeding of the plasticiser. Due to their impact on the environment and human health, the use of plasticisers, especially phthalate plasticiser and aromatic oils, has been called into question. Kuraray liquid rubbers (liquid polybutadiene rubber "LBR", liquid polyisoprene rubber "LIR") are plasticisers that are vulcanisable with solid rubbers. Their use can effectively avoid the above-mentioned problems. Kuraray sees therefore a considerable growth potential for KLR. The molecular weight of LIR is aligned on the one hand at the lower limit of rubber materials and on the other hand at the upper limit of oil-like materials with plasticising effect. Therefore, liquid rubber acts as a reactive plasticiser. Crucial factor in rubber compounding is the performance and hardness control. However, supposed to have the same amount of crosslinking agent in a rubber mixture: It is a general experience that the hardness of a rubber compound is kept with higher molecular weight LIR (out of the series of KLR) due to the higher degree of crosslinking. For more soft rubber products it is recommended to use the lower molecular weight KLR because of comparably lower degree of crosslinking **(fig. 2).**

2. Grade line-up

Kuraray liquid rubbers (KLR) are synthesised from isoprene, butadiene and styrene. An overview of the updated grade line-up is depicted in **figure 3.** As explained in a previous paper [1] there are basically three types of polymers:

- the homopolymer type
- the copolymer type (block and random)
- the modified type (hydrogenated, carboxylated, methacrylated, epoxidised).

Recently we introduced KL-352 as a new grade especially for EPDM compounds with high hardness. Furthermore, the epoxidised developing grades KL-610, 613 and 630T have been added to the product line-up.

3. Crosslinking

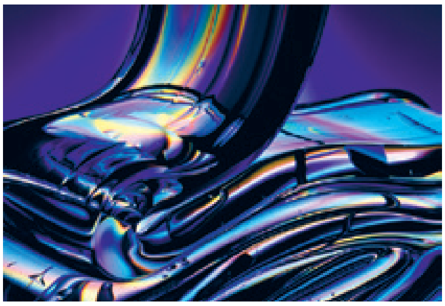
One of the key factors for the durability of the rubber products is imposed by crosslinking or vulcanisation. Crosslinking with KLR can be done with any method that is able to connect unsaturated carbon-carbon bonds. This is e. g. possible with sulphur or peroxides: If carboxyl groups are available, crosslinking can be done by using isocyanates or Bisphenol-A type resins.

Table 1 shows a collection of useful recipes with LIR-403 and LIR-410. Crosslinking temperature of formulation 1 – 4 is above120 °C. In formulation 5 and 6 Bisphenol-A was added and crosslinking was achieved even at room temperature. Because of their carboxylation these formulations show good adhesion to metals and textiles. The chemical structure is depicted in **figure 4.**

4. Automotive sealants

Recent trends in car production show an increased use of specialised adhesives (up to

Fig. 1: Liquid rubber in polarised light



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15 kg per vehicle) [2]. One fraction of these is used in NVH applications (Noise Vibration Harshness), for example in anti-flutter (hard), acoustic damping (soft), but also in anti-corrosion coatings (medium).

Table 2 shows various formulations for elastic anti-corrosion sealants or coating applications. Within the application scope of KLR these applications have a share equivalent to that of the adhesives. The chemical structures of the raw materials are shown in **figure 5**. The aim here is to ensure a good low temperature flexibility, a feature that is required by the OEMs. Key factor here is the low T_g of the formulations. They can be used for adhesion both to metals and textiles.

The share of anti-flutter, anti-vibration and acoustic damping applications with KLR is increasing, especially in the production of middle and luxury class cars. Cosmetic sealants formerly accomplished with PVC are today executed with KLR rubber compounds. These applications are usually highly filled with inorganic filler. Here, the plasticising effect of liquid rubber acting as a processing additive is appreciated. Because of the strong polar character of the inorganic component, the functionalised rubbers LIR-403 and LIR-410 provide better dispersion compared to aliphatic type additives like process oil or non-functionalised KLR. For a demonstration formulation see **table 4.**

5. Adhesion to metal

Special grades of KLR are also able to promote adhesion to metal. For the test-

Fig. 2: Molecular weight distribution of rubber and plasticisers

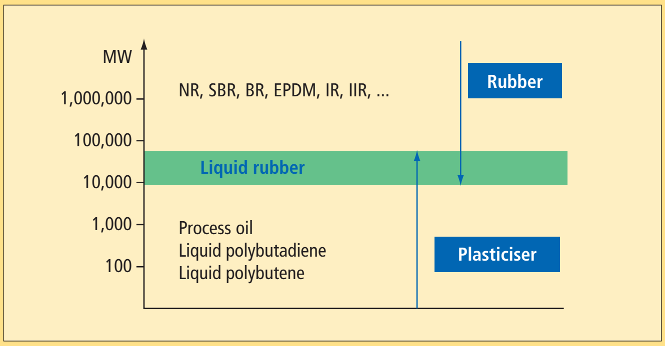


Fig. 3: Grade line-up of Kuraray Liquid Rubbers

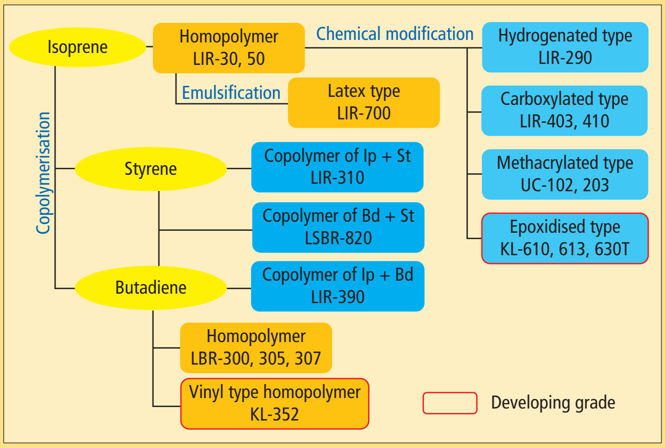
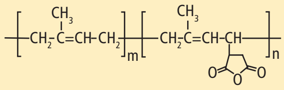
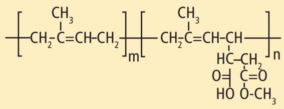


Fig. 4: Carboxylated grades of LIR for adhesives

Grade	Chemical structure	Melt viscosity at 38 °C (Pa·s)	Molecular weight[1] (g/mol)	Number of functional groups (per chain)
LIR-403		200	34,000	3
LIR-410		430	30,000	10

[1] Average molecular weight (calculated vs. standard polystyrene)

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 resin	–	–	–	–	10	10
tert-Amine [*)]	–	–	–	–	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

[*)] Tris(dimethylaminomethyl) phenol
LIR-403 and LIR-410 can be cured with metal oxide, metal hydroxide and epoxy resin

Tab. 2: Formulations with LIR-50 and LIR-390 for anti-corrosion coatings

	Foamed		**Non-foamed**	
Formulation [1)]	1	2	3	4
LIR-390	100	–	100	–
LIR-50	–	60	–	60
BR	–	40	–	40
Naphthenic process oil	200	200	100	100
Activated $CaCO_3$	200	200	100	100
Heavy $CaCO_3$	400	400	200	200
Blowing agent (DPT)	1	1	–	–
Blowing promoter	1	1	–	–
Heat resistance [2)]				
190 °C, 30 min	Good	Good	–	–
210 °C, 30 min	Good	No good	–	–
Shear strength (MPa) [3)]	–	–	0.58	0.42

[1)] Active zinc oxide: 4 parts; stearic acid: 0.5 parts; sulphur: 5 parts; accelerator (dibenzothiazolyl disulfide): 3 parts; accelerator (o-tolyl biguanide): 2 parts; antioxidant (NS-6): 1 part; curing conditions: 150 °C, 30 min
[2)] Hardening measurement
[3)] Adhesion for oil coated iron plate (adhesion area: 20 x 50 mm, shear speed: 300 mm/min)

ing method we set up a simple experiment depicted in **figure 6.** The rubber mixture in the test is being filled into the small cavity (25 x 25 x 1,5 mm). After curing is accomplished, the excessive part of the material is cut with a sharp knife before pulling test.

Table 4 shows some data for the performance of functionalised LIR-403 versus non-functionalised LIR-30. Basically LIR-403 is of same molecular weight as LIR-30. The result shows the required cohesive failure with LIR-403. Similar results can be obtained with LIR-410.

6. Electronic and other applications

Another set of KLRs are the so-called UC-grades **(tab. 5);** their structure is shown in **figure 7.** Beside the reactivity of carboxyl groups it is their in-built polarity that rein-

Tab. 3: Formulations with LIR-403 and LIR-410 for automotive sealants

Formulation	**1**	**2**	**3**	**4**
LIR-403	100	100	–	–
LIR-410	–	–	100	100
Naphthenic process oil	50	30	50	50
Light $CaCO_3$	150	–	150	–
Activated $CaCO_3$	–	125	–	150
Bisphenol-A epoxy resin	2	2	4	4
tert-Amine [1)]	1	1	2	1
Mechanical properties [2)]				
Modulus 100 % (MPa)	0.17	0.05	0.35	0.39
Tensile strength (MPa)	0.22	0.02	1.22	1.09
Elongation (%)	340	760	380	260

[1)] Tris(dimethylaminomethyl) phenol
[2)] Curing condition: 25 °C, 30 days, test piece size: 10 x 50 x 2 mm, test speed: 50 mm/min

Tab. 4: LIR-403 and LIR-410 for adhesion to metal

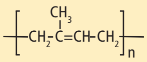
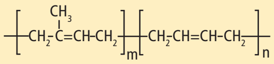
Formulation [*)]	**1**	**2**
BR	40	40
LIR-30	60	–
LIR-403	–	60
Naphthenic process oil	50	50
Activated $CaCO_3$	200	200
Curing condition	140 °C, 20 min	140 °C, 15 min
Aluminium plate		
Max load (N)	82	721
Elongation (mm)	1.8	4.4
Note	Interfacial failure	Cohesive failure
Steel plate		
Max load (N)	77	650
Elongation (mm)	0.9	4.1
Note	Interfacial failure	Cohesive failure

[*)] Activated zinc oxide: 4 parts; stearic acid: 0.5 parts; Noccelar DM: 3 parts; Noccelar DT: 2 parts; antioxidant (NS-6): 1 part

Tab. 5: Characteristics of the UC-grades

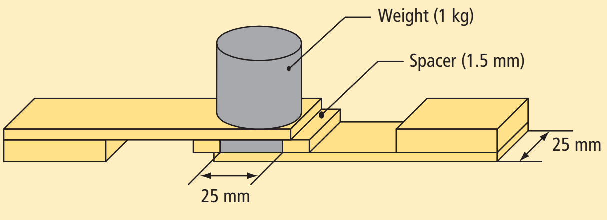
Items	**UC-203**	**UC-102**
Molecular weight	36,000	19,000
Methacryloyl group	3 units/chain	2 units/chain
Methacrylate equivalent (g/eq)	6,700	5,900
Melt viscosity (Pa·s 38 °C)	160	30
Appearance	Transparent and slightly yellow	Transparent and slightly yellow

Fig. 5: KLR types for anti-corrosion coatings

Grade	**Chemical structure**	**Melt viscosity at 38 °C (Pa·s)**	**Molecular weight**[1] **(g/mol)**	**T_g (°C)**
LIR-50	 $\left[-CH_2-\overset{CH_3}{\overset{\vert}{C}}=CH-CH_2-\right]_n$	500	54,000	-63
LIR-30		70	28,000	-63
LIR-390	 $\left[-CH_2-\overset{CH_3}{\overset{\vert}{C}}=CH-CH_2-\right]_m\left[-CH_2-CH=CH-CH_2-\right]_n$	400	48,000	-95

[1] Average molecular weight (calculated vs. standard polystyrene)

Fig. 6: Shear test scheme



Test speed : 25 mm/min

Fig. 7: Chemical structure of the UC-series

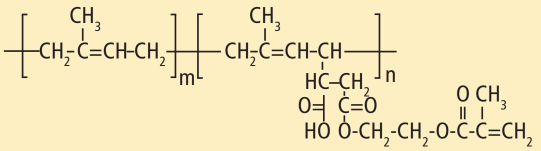
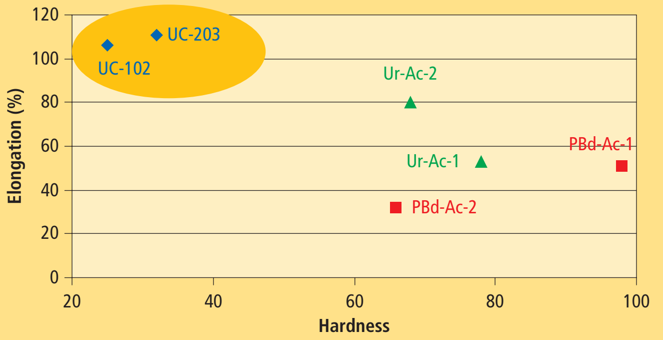


Fig. 8: Elongation and hardness map for model mixture (polymer/Darocure 1173 – 100:3)



forces the dispersing effect. These materials are able to mix even with acrylic monomer and/or oligomer and can be cured with UV- or electron-beam irradiation.

We also see potential for KLR in electronic applications as potting materials. These applications require a low viscosity and high durability in combination with high temperature resistance (heat ageing). In this range of applications the higher molecular weight UC-types provide better sealing compared to common acrylic or urethane based products.

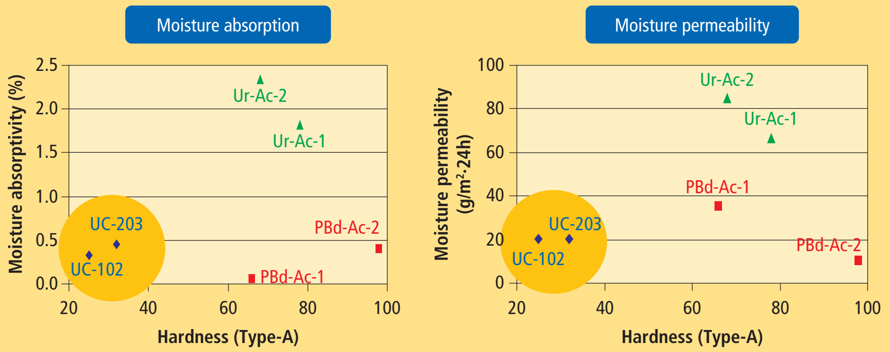
A basic benefit for electronic applications is the very low shrink ratio of KLRs. Some values are depicted in **table 6.** In **figure 8** we show an elongation and hardness map of two UC-types compared to different urethane and acrylic products. This diagram helps formulation designers to choose the appropriate material; it can be customised by addition of acrylic monomer and/or oligomer if necessary. In contrast to common harder rubber sealants the very soft sealant mixtures are in use for G-shock protection of electronic equipment.

Tab. 6: Comparison of the physical properties for model mixture (polymer/Darocure 1173 – 100:3)

Grades	**Mn** (g/mol)	**Viscosity** (Pa·s 38 °C)	**T_g** (°C:DSC)	**Shrinkage ratio** (%)	**Tensile strength** (MPa)	**Tensile elongation** (%)	**Hardness** (Type-A)
UC-203	36,000	160	–60	0.5	0.4	111	32
UC-102	19,000	30	–61	1.2	0.3	106	25
UC-105	19,000	70	–58	1.5	0.7	29	61
PBd acrylate-1	1,000~5,000	700	–15	3.4	10.9	51	98
PBd acrylate-2	1,000~5,000	3	–72	2.6	1.1	32	66
Urethane acrylate-1	5,000~1,000	50	–30	2.2	2.5	53	78
Urethane acrylate-2	5,000~1,000	110	–36	1.5	2.1	80	68

Formulation: Polymer (oligomer)/Darocure 1173 – 100:3, lamp: high pressure mercury lamp
Curing conditions: light intensity 64 mW/cm²; conveyor speed 1m/min = 670 mJ/cm²; irradiation times: 4
Hardness: Type A (ASTM D 2240)

Fig. 9: Moisture absorption and moisture permeability for model mixture (Polymer/Darocure 1173 – 100:3)



(Test piece): 25 x 25 x 1 mm
(Conditions): 60 °C, 90 % RH, 90 h

(Method): Dish method (JIS Z 0208)
(Thickness): 0.5 mm
(Conditions): 40 °C, 90 % RH

In electronic applications the performance of the sealant in regard to the low moisture absorbance (swelling) and low moisture permeability (anti-corrosion) is fairly important. In our experimental comparison we used a model mixture of polymer and Darocure 1173 at ratio 100:3 **(fig. 9).** The resulting data show the ability to provide very good properties for even soft material. This data can also support the formulation designer.

7. Summary

In this article we presented the extended grade map of functionalised curable liquid rubber materials in the KLR (Kuraray Liquid Rubber) portfolio. In the technical descriptions we focused mainly on applications in automotive sealants, an area where we identified a high growth potential. We provided application data and formulations. In addition we showed potentials and advantages for the dispersion of fillers, the adhesion to metal and in corrosion protection as well as in anti-flutter and vibration damping applications. We also described some applications as sealing materials for electronic parts.

8. References

[1] RFP Rubber Fibres Plastics, vol. 4, 3, 2009, p. 152 – 156.

[2] Weigel, Gudrun: Epoxidharzklebstoffe zum Verbinden von Metallen können Schweißen ersetzen. konstruktionspraxis.de, 5 Mar 2008.