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From excellent damping and barrier properties to gel applications

Two new HSBCs for potential medical use

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Based on a long-term research experience in hydrogenated elastomeric block copolymer plastics and in vinyl-polydiene soft block manufacturing, Kuraray has developed two new materials. Both show superior properties and have high potential for medical applications.

Due to its glass transition temperature T_g near room temperature the new high molecular weight Hybrar grade has high vibration damping properties. It combines oil absorption and good miscibility with polypropylene with oxygen barrier properties. Within this article key parameters of this grade are presented. Moreover, a compounding concept of this material is described. The second new material belongs to the Septon series and is designed for improved gel stability and resilience. Because polyolefinic-based viscoelastic gels are widely used as cushion materials the processing has special needs in flow and dynamics. We will present key properties of this material together with processing instructions and a comparison to other materials.

1. Introduction to Septon and Hybrar

Styrenic thermoplastic elastomers have been produced by Kuraray since the 1990s. They represent the third generation of the company's innovative elastomer developments, and are based on the advanced anionic living polymerisation by Li-based initiator plus additional hydrogenation. Materials of this class therefore are called hydrogenated styrene diene block copolymers (HSBC). The best-known Kuraray material of this kind is sold in the market under the brand name Septon. The brand includes a series of hydrogenated styrene block copolymers (SEP, SEPS, SEBS, SEEPS). The grades exhibit rubber-like properties over a wide temperature range which makes them perfectly suited serving as compound material for automotive and consumer products, as a substitute for vulcanised rubber and PVC, for polymer modification, as impact modifier for PO, PPE, etc., as compatibiliser, in adhesives, hot melts, diapers, sanitary napkins, tapes, etc.

Hybrar is another special thermoplastic elastomer within Kuraray's portfolio. This material is characterised by high vibration damping properties at room temperature. It is available in both hydrogenated and non-hydrogenated grades. In addition to the superior vibration damping properties, hydrogenated grades also exhibit very good miscibility with polypropylene, and may be used to produce blends with high transparency, flexibility and excellent mechanical properties. These benefits result in applications like flexible PVC substitutes, medical tubing, IV bags or high-sophisticated TPE compounds as polymer modifications like vibration damping improved PE, PP, PS, ABS, etc.

2. High molecular weight Hybrar

It is a well-known fact that Hybrar materials can provide excellent kinking properties in medical tubing as well as puncture resistance in multilayer films for IV bags. Recently a new grade, Hybrar KL-7135 has been developed, a high molecular weight styrenic block copolymer having a hydrogenated vinyl-polyisoprene soft block. It provides excellent damping properties, excellent compatibility with polypropylene combined with good heat resistance and weather resistance. Another beneficial feature is its high oil absorbency because of its powder shape and structure. Compared to similar other high molecular weight materials it furthermore exhibits high flowability **(fig. 1).** The grade map shows that nearest to Hybrar KL-7135 in Kuraray's product list is Septon 4055. The full Hybrar line-up plus Septon 4055 is depicted in **table 1** with tensile properties and viscosities.

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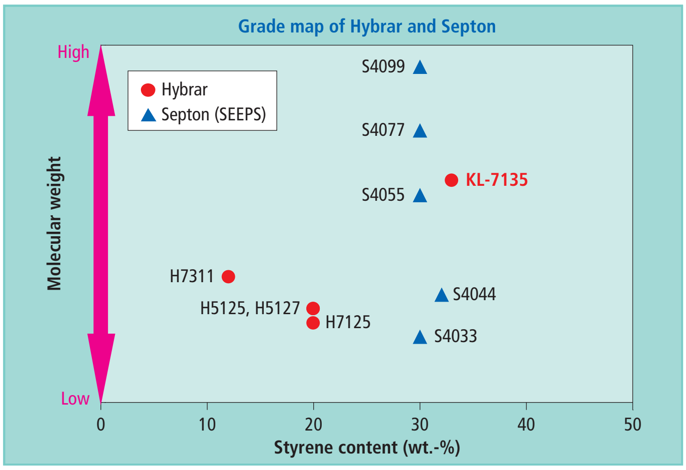


Fig. 1:
Grade map of Septon and Hybrar

	Grade	Type	Styrene content (wt.-%)	Peak temp. of tan δ (°C)	Glass transition temp. (°C)	Specific gravity	Hardness (Type A)	Tensile property: 100 % Modulus (MPa)	Tensile property: 300 % Modulus (MPa)	Tensile property: Tensile strength (MPa)	Tensile property: Elongation (%)	MFR: 190 °C, 21 N (g/10 min)	MFR: 230 °C, 21 N (g/10 min)	MFR: 230 °C, 98 N (g/10 min)	Solution viscosity: 5 wt.-% (mPa·s)	Solution viscosity: 10 wt.-% (mPa·s)	Solution viscosity: 15 wt.-% (mPa·s)	Solution viscosity: 20 wt.-% (mPa·s)	Solution viscosity: 30 wt.-% (mPa·s)	Physical form
Hydrogenated	Hybrar KL–7135	Vinyl-bond rich SEPS	33	1	–15	0.92	68	2.2	4.1	9.3	550	No flow	No flow	0.02	11	56	350	–	–	Powder
Unhydrogenated	Hybrar 5127	Vinyl-bond rich SIS	20	20	8	0.94	84	2.8	4.7	12.4	730	5	–	–	–	–	–	–	540	Pellet
Unhydrogenated	Hybrar 5125	Vinyl-bond rich SIS	20	– 3	– 13	0.94	60	1.6	2.5	8.8	730	4	–	–	–	–	–	100	650	Pellet
Hydrogenated	Hybrar 7125	Vinyl-bond rich SEPS	20	– 5	– 15	0.90	64	1.7	2.7	7.1	680	0.7	4	–	–	–	–	55	350	Pellet
Hydrogenated	Hybrar 7311	Vinyl-bond rich SEEPS	12	– 17	– 32	0.89	41	0.6	0.9	6.3	1,050	0.5	2	–	–	–	90	240	–	Pellet
Hydrogenated	Septon 4055	SEEPS	30	(– 47) S4033data	– 56	0.91	–	–	–	–	–	No flow	No flow	No flow	90	5,800	–	–	–	Powder
Measurement method			–	–	DSC (temp. increase by 10 °C/min)	ISO 1183	ISO 7619	ISO 37				ISO 1133			Toluene solution 30 °C					–

Tab. 1: Full line-up for Hybrar and for Septon 4055

2.1 Properties of Hybrar KL-7135

2.1.1 Damping properties

From the very beginning Hybrar was developed to introduce damping properties into TPEs. This applies for the new Hybrar KL-7135 grade, too. One useful parameter to evaluate the ability of a material to transfer mechanical impact into heat is the tan δ value, the loss factor. A comparison of tan δ vs. temperature graphs is shown in **figure 2.** In comparing the graphs, the tan δ peak of KL-7135 with Septon 4033 at 1 °C shows high damping effect. In the Hybrar 7000 series KL-7135 has slightly lower tan δ peak because of its higher styrene content.

Because Hybrar KL-7135 has high molecular weight and a crumb structure it can be used together with oil. The compounding of KL-7135 with oil shifts the tan δ peak to lower temperature and broadens the peak.

2.1.2 Thermal stability

Because of thermoplastic processing the heat resistance or polymer degradation curve vs. temperature is used. Obviously, the degeneration by heat is one of the crucial properties in thermoplastic processing of styrenic block copolymers. In tubing and medical film applications Hybrar 7125 is a material that is already widely used. We therefore choose it to make a comparison with the new Hybrar KL-7135 type. **Figure 3** shows the results. Hybrar

		OTR (cc · 20 µm/m² · day · atm)
Hybrar KL–7135	V-SEPS	8,300
Hybrar 7125	V-SEPS	12,000
Septon 2002	SEPS	39,000
Septon 8004	SEBS	37,000
Septon 4033	SEEPS	41,000

Test conditions
measurement method: ASTM D1434 (ISO 15105-1), differential pressure method
gas permeability analyser [GTR-10]: Yanagimoto Mfg. Co., Ltd.
temperature: 35 °C, humidity: 0 % RH, oxygen pressure: 0.25 MPa
specimen: press moulded sheet, 300 µm, (moulding condition: 230 °C, 10 MPa, 2 min)

Reference information (actual measurement value)
PS: 12,000 • PP: 6,000 • HDPE: 5,000 • LDPE: 20,000 • TPU (Hs = 70 A): 31,000
IIR: 9,000 • NR: 77,000 • EPR: 177,000 • Soft PVC (Hs < 85 A): 27,000

Tab. 2: Oxygen barrier properties as OTR values measured for Hybrar KL-7135 and reference materials

Fig. 2: Temperature dependence of tan δ

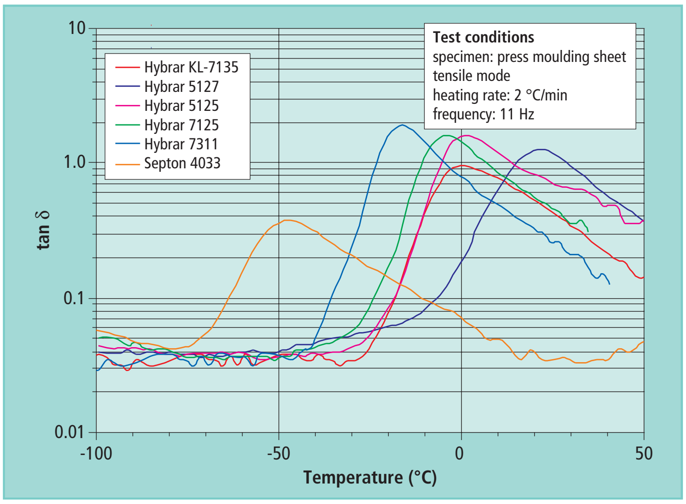
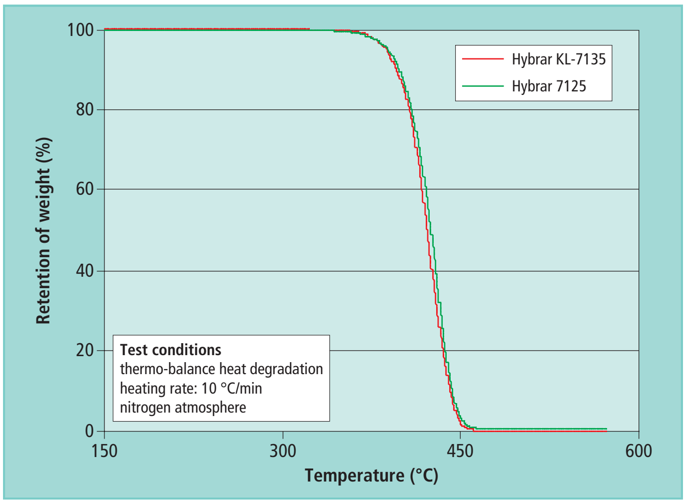


Fig. 3: Heat resistance of Hybrar KL-7135 and Hybrar 7125



KL-7135 shows almost same thermal stability as the other hydrogenated Hybrar grade 7125.

2.1.3 Barrier properties

The use of some Hybrar grades in food packaging and similar applications indicate the necessity for an investigation on barrier properties. The data in **table 2** show a sharp difference between the new Hybrar KL-7135 compared to other HSBC like SEPS, SEBS, SEEPS in Kuraray's product portfolio. Regarding the neat materials Hybrar KL-7135 shows much better oxygen barrier properties than conventional HSBCs. Data for blendable polymers such as PP or LDPE are given in the foot note for reference.

Beside the transition of oxygen and other non-polar gases the moisture permeability is of great interest. Many products need to be kept away from water but must allow some moisture control. The data in **table 3** may be useful for compounders because they demonstrate the potential of high molecular weight Hybrar KL- 7135 to improve compound properties. Here Hybrar KL-7135 shows better moisture barrier properties than conventional HSBCs.

2.1.4 Formulation and physical properties

We evaluated the physical properties by comparing extruded compounds of identical formulation by exchanging Hybrar KL-7135 with Septon 4055. For compatibility and preview in different applications we chose two types of PP, a random and a homo type. The results are given in **table 4.** Conditions and details on materials are given in below the table.

These demonstration compounds show high flowability in about one order of magnitude. The high molecular weight in combination with high flow results in a very good compression set (see higher temperatures in CPD 3 vs. CPD 4). In addition we note an improved compression set in comparison to other Hybrar grades. The OTR values for

Tab. 3: Water vapour transmission rate of Hybrar KL-7135

		Water vapour transmission rate (g·1 mm/m²·24 h)
Hybrar KL-7135	V-SEPS	1.93
Hybrar 7125	V-SEPS	1.43
Septon 2004	SEPS	2.97
Septon 8004	SEBS	3.37
Septon 4033	SEEPS	3.06

Test conditions
measurement method: ASTM E96-94; temperature: 40 ± 0.5 °C; humidity: 90 ± 2 % RH
specimen: press moulded sheet, thickness 1 mm, (moulding condition: 230 °C, 10 MPa)

Reference information (actual measurement value)
PS: 3.60 • LDPE: 0.34 • PP: 0.45 (30 °C) [1] • IIR: 0.77 (37.5 °C) [1]

Tab. 4: Physical properties of KL-7135 based compounds

CPD no.			1		2		3		4	
Formulation										
Hybrar KL-7135		parts by weight	100		–		100		–	
Septon 4055			–		100		–		100	
Process oil			100		100		100		100	
Random-polypropylene	(MFR = 7 g/10 min)		40		40		–		–	
Homo-polypropylene	(MFR = 15 g/10 min)						40		40	
Antioxidant		wt.-%	0.1		0.1		0.1		0.1	
Physical properties										
MFR	(230 °C, 21 N)	g/10 min	3.4		0.2		4.0		0.02	
	(230 °C, 49 N)	g/10 min	83		8.0		87		5.0	
Compression set	(70 °C, 22 h)	%	38		39		35		40	
(Small test specimen)	(100 °C, 22 h)	%	49		48		43		47	
∅ 13 ± 0.5 mm	(120 °C, 22 h)	%	51		50		48		54	
OTR (ISO 15105-1)		cc · 20 µm/m² · day · atm	51,000		67,000		No data		No data	
(Injection moulding)			MD	TD	MD	TD	MD	TD	MD	TD
Hardness	(Type A)		59		61		67		75	
100 % Modulus		MPa	1.4	1.1	2.5	1.6	2.2	1.3	3.4	1.9
Tensile strength		MPa	5.1	9.9	7.7	20	7.7	8.5	5.6	15
Elongation		%	620	990	710	920	630	830	490	820
Optical properties	Haze	%	28		74		31		83	
Resilience	(ISO 4662) 24 °C, humidity 33 %	%	43		52		44		53	

Test conditions
process oil: Dianaprocess PW-90, viscosity (at 40 °C) = 95.54 mm²/s, Idemitsu Kosan Co., Ltd • Random-polypropylene: F327, film grade, MFR = 7 g/10 min, Prime Polymer Co., Ltd
homo-polypropylene: J106G, injection grade, MFR = 15 g/10 min, Prime Polymer Co., Ltd • antioxidant: Irganox 1010, Ciba • preblend conditions: Super Mixer (100 L), (1) HSBC 150 rpm 3 min + (2) oil 300 rpm 5 min + (3) PP, AO 300 rpm 2 min • mixing condition: twin screw extruder (φ 47 mm, L/D = 42), KL-7135 CPD; 180 °C, S4055 CPD; 200 °C
preparation of C-set test piece: a) making 110 x 2 mm sheet by injection moulding at 200 °C • b) cutting the above-mentioned moulded sheet to round shape (13 mm ∅) • c) put three round shape sheets into the hole of the mould for compression set test, • d) press moulding at 160 °C and 1 MPa for 2 min
preparation of test sheet for mechanical properties evaluation: 55 t injection moulding machine (cylinder 200 °C, mould 40 °C), size of sheet: 110 x 110 x 2 mm

CPD 1 and CPD 2 show the improvement of the barrier properties by about 25 %. Moreover, we observe that the optical properties are improved for about 3 times in comparing CPD 1/3 vs. CPD 2/4. In addition Hybrar KL-7135 has better damping properties as can be seen in the resilience measurements in accordance to ISO 4662.

Further investigation on the mixing properties of new Hybrar KL-7135 have been performed in taking TEM pictures **(fig. 4).** These pictures give evidence for the improved homogenity of the texture in the phase separation of HSBC/oil and PP where PP is the matrix and HSBC/oil the domain islands. In **figure 4** we see the morphology of a Hybrar KL-7135 based compound which has excellent compatibility with polypropylene. The new KL-7135 leads to compounds with a well-dispersed microstructure.

2.2 Applications

Considering the features of KL-7135 based compounds – excellent compression set, high vibration damping properties, high flowability, good transparency, good oxygen and moisture barrier properties – we are convinced that these compounds can be used as a replacement of vulcanised rubber, IIR, and PVC. We see a focused application area in the medical field with emphasis on films and tubing. In general, compounds made with Hybrar KL-7135 can be utilised also in other medical devices (e. g. stoppers for infusion devices, medical plugs, medical bags, plugs for vacuum blood collection tubes, syringe gaskets, etc.). The material should not be used in any devices or materials intended for implantation in the human body.

But also applications in the construction field (various anti-vibration parts, sealant for window profiles, flooring parts), electrical appliances, acoustic parts (covers of exterior parts, cable covering, gaskets), power tools (grips, vibration absorption material, damping material), sports goods (grips, shoes, cushioning material), automotive parts (weather-strip, grommet, instrument panel covers, damping material), plugs (cap liners, wine closures, packaging) are possible.

In some damping applications the materials development may be beneficial for flooring parts, construction parts, consumer goods and automotive parts, exemplary. This is valid also for foamed (crosslinked, non-crosslinked), shoes and cushioning parts.

Other application areas include various hot melt sealants, adhesives, sealing materials for automotive parts, electric parts, construction parts and machinery parts. Especially the barrier properties point towards applications in frame-sealing and junction box potting for photovoltaic.

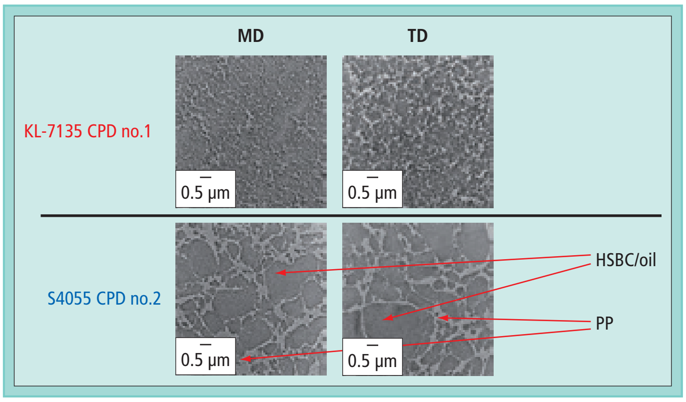


Fig. 4: Morphology of KL-7135 based compounds Formulation: HSBC/process oil/F327 random PP = 100/100/40

Grades		Septon J series KL–J3341	Septon 4055
Styrene content	wt.-%	40	30
Density	–	0.93	0.91
MFR (230 °C-21 N)	g/10 min	No flow	No flow
Melt viscosity*) 5 wt.-%	mPa·s	25	90
Shape		Powder	Powder

*) Toluene solution 30 °C

Tab. 5: Technical data of Septon KL-J3341 compared to Septon 4055

3. Septon J for gel applications

In daily life we enjoy the comfort of gels with super soft characteristics. The advantage of stability and soft cushioning is also attributed to applications with medical background. For example artificial limbs or prostheses can be made with a skin-like feeling. In the wound care of burns there is a need to cover the wound without pressure. These are only some of the fields where we see an increasing demand for gel applications.

We introduce here a new developing grade, Septon KL-J3341, which is suitable for soft gel compounds. In **table 5** we show a comparison of Septon KL-J3341 vs. conventional Septon 4055 with regard to some typical properties. KL-J3341 has higher styrene content and lower melt viscosity than Septon 4055 which is mainly used as a base polymer for HSBC compounds. Septon KL-J3341 is available in powder form and therefore it can easily absorb process oil to produce low hardness compounds.

To investigate the performance of the new material, it has been processed into gel compounds under various formulations. We chose two strategies: First a comparison of both materials at the same formulation and in a second step a comparison of the two materials at the same hardness level.

3.1 Properties of Septon J series (KL-J3341) base compounds

Table 6 shows various properties of low hardness compounds based on Septon J series (KL-J3341) and Septon 4055.

3.1.1 Hardness

As shown in **table 6,** both formulations 1 and 2 based on KL-J3341 show lower hardness than the Septon 4055 based compound. Additionally they show good resilience properties and a soft-touch feeling like soft PVC.

3.1.2 Flowability

Figure 5a shows the frequency dependency of complex viscosity of formulation 1, and **figure 5b** the shear rate dependency of melt viscosity of formulation 2. In both formulations, the Septon J series based low hardness compounds have lower melt viscosity than the compounds based on Septon 4055. As can be seen from the graph in **figure 5a**, the Septon J series based compounds show very low viscosity and excellent processability at low shear rate.

3.1.3 Compression set

As shown in **table 6,** Septon J series based compounds show almost equivalent compression set below 70 °C. The compounds can achieve both good flowability and excellent compression set, far beyond conventional HSBCs.

3.1.4 Resilience

Table 6 also demonstrates that the Septon J series based compounds exhibit low rebound resilience compared to the Septon 4055 based compounds. **Figure 6** shows the relationship between hardness and rebound resilience. Septon J series (KL-J3341) based low hardness compounds usually show lower rebound resilience in a wide range of hardness, compared to conventional Septon based compounds.

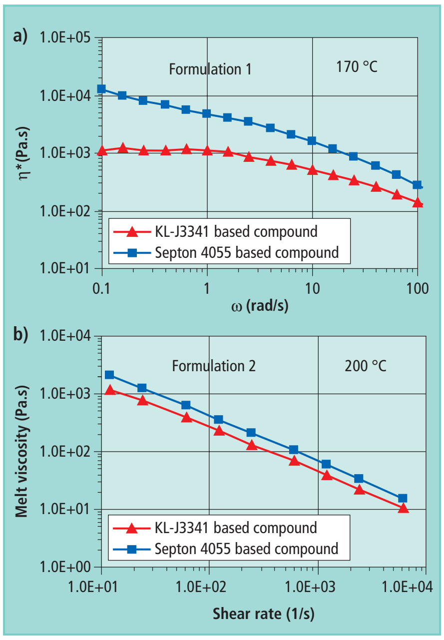
Figure 7 shows the dynamic viscoelastic behaviour of low hardness compounds based on the Septon J series (KL-J3341). It has the tan δ peak at – 50 °C and the other tan δ peak at 30 °C. Consequently, it exhibits excellent low temperature properties as well as low resilience/damping properties.

3.2 High potential for gel and soft-touch applications

Table 7 shows the performance comparison among the Septon J series based low hardness compound, conventional HSBC based compound and other low hardness materials (gel-like materials). The KL-J3341 based compounds show light weight, good compression set, high strength, good tear strength while retaining good low-temperature characteristics. In addition these materials result in very soft-feeling and flexible compounds with good flowability. Furthermore, they show excellent shock absorbing and damping properties, not achievable by conventional Septon based compounds.

Considering these characteristics, the Septon J series based low hardness compounds are well suited for applications in household

Fig. 5. a) Frequency dependency of complex viscosity
b) Shear rate dependency of melt viscosity



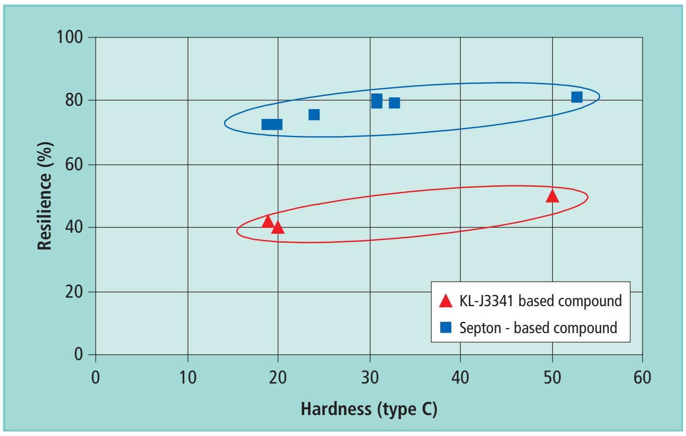


Fig. 6: Relationship between hardness and resilience

	Unit	Formulation 1		Formulation 2		Test method
		KL–J3341 base	S4055 base	KL–J3341 base	S4055 base	
Hardness						
Type A		0	0	14	21	JIS K 6253
Type B		8	15	43	54	JIS K 7312
Transparency						JIS K 7105
Haze (2 mm)	%	9	11	47	67	
Tensile properties						JIS K 6251
Tensile strength	MPa	1.6	>1.7	3.3	5.3	
Elongation	%	1,300	>1,500	830	1,100	
Compression set						JIS K 6262
40 °C	%	9	10	11	15	(22 h)
70 °C	%	59	51	28	27	
100 °C	%	100	99	61	52	
Resilience						
(Lupke method)	%	–	–	45	70	JIS K 6255
(Ball drop)	%	36	71	–	–	Kuraray method
MFR						JIS K 7210
160 °C - 21.2 N	g/10 min	34	3	–	–	
200 °C - 21.2 N	g/10 min	–	–	3	0.3	

Formulation 1: HSBC/paraffin oil (PW-32, K.V.(@40 °C) = 30.98 mm²/s) = 100/400
Formulation 2: HSBC/paraffin oil (PW-32, K.V.(@40 °C) = 30.98mm²/s)/h-PP=100/200/15

Tab. 6: Properties of the Septon J series (KL-J3341) based low hardness compounds goods, medical and nursing supplies, sporting goods, industrial parts, electrical and electronic parts, and we are expecting it to be used for value-added and high-performance applications.

Besides the applications mentioned above the Septon J series has big potential for high-performance applications where long-lasting stability and compression set are key requirements. This is the case for cushions for artificial limbs, cushions for beds, soft toys, gel dampers and grips, etc. **Figures 8** and **9** show samples that demonstrate the exceptional high clarity and softness of the material.

Tab. 7: Comparison of Septon J series (KL-J3341) and various soft materials

	Septon J series (KL–J3341) based compound	Conventional low molecular weight HSBC based compound	Conventional high molecular weight HSBC based compound	Silicone gel	Urethane gel
Flowability	○	**O**	X	XX	XX
Compression set	○	XX	○	**O**	**O**
Shock absorption · damping	○	X	X	**O**	○
Tensile strength	○	X	**O**	△	△
Tear strength	○	XX	**O**	XX	△
Light weight	**O**	**O**	**O**	○	△
Low odour	**O**	**O**	**O**	○	X
Recyclability	**O**	**O**	**O**	XX	XX
Legend: poor XX<X<△<○<**O** good					

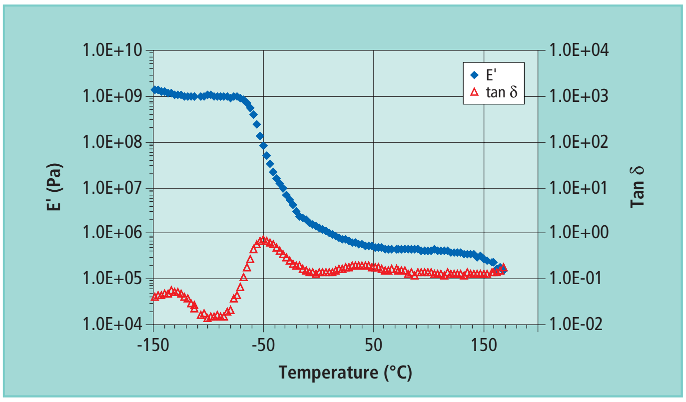


Fig. 7: Dynamic viscoelastic behaviour of soft compounds based on Septon J series (formulation 2)

4. Summary – Septon J and Hybrar KL-7135

In this article we gave an overview on features and benefits of two new Kuraray materials. Firstly, the new polymer Hybrar KL-7135 was presented. Compounds made with this polymer show excellent compression set because of the high molecular weight. Therefore this polymer is a base material of choice for various soft compounds. As this product comes in powder form, it can easily absorb oil in a premix process. Because of its excellent damping properties, transparency, flowability, oxygen and moisture barrier properties this materials stands out from other HSBCs or from conventional high molecular weight styrenic block copolymer like SEBS. In addition KL-7135 is foamable and can be vulcanised.

Secondly, with the Septon J series (KL-J3341) a new HSBC type with properties especially adapted to applications in gel compounds was presented. It was found that Septon KL-J3341 based gel compounds show an optimised balance between flowability and compression set as well as low resilience. In addition it was shown that these gel compounds have a set of advanced features compared to standard material Septon 4055. The advantages in particular result from a lower melt viscosity into better processability at the final mould. The lower resilience provides better damping properties in the set, and the lower compression modulus is very useful to achieve optimal cushioning properties.

5. References

[1] Polymer Handbook. J. Brandrup et al. (eds.), 4th ed. Wiley, 2005

Fig. 8: Demo. sample of a flexible and easy-to-fit knee support

Fig. 9: Demo. sample of a shoe insole serving as heel piece to reduce impact on heels