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New styrene block copolymer with low oxygen transmission rate

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Oxygen transmission rates of HSBCs and other TPEs still show a big gap to those of vulcanized rubber (e. g. butyl rubber). Kuraray took this opportunity and successfully developed a new material. The first product introduced in this paper is a new high molecular weight and vinyl-rich HSBC. Its structure provides a good morphology with optimized barrier performance. The second product is a new masterbatch with outstanding oxygen transmission rates.

HSBC with enhanced barrier performance

Hybrar is a series of styrenic block copolymers (SBCs and HSBCs), which consists of styrene-based hard blocks and vinyl-rich (hydrogenated) diene soft blocks. HSBCs exhibit rubber elasticity since the hard block acts as a crosslinking point below the glass transition temperature of polystyrene and the soft block provides elasticity. Hydrogenation provides excellent heat and weather resistance. Major applications of HSBCs are thermoplastic compounds, adhesives and polymer modification. The compounds are used for automotive and consumer products, or as replacing materials for vulcanized rubber and PVC as a soft molding material. Hot melt adhesives consisting of HSBCs are used for diapers, sanitary napkins, and tapes. HSBCs can be furthermore added to polymers as impact modifier or compatibilizer.

In the area of flexible materials, barrier properties are often characterized either by their "low barrier" or "high barrier" performance. These terms are not comprehensively defined and vary from case to case. In flexible food packaging for example only very few polymers are categorized as high or ultra-high barrier materials. Even EVOH is usually not market as an ultra-high barrier material compared to SiO_2 or aluminum. Gas and water barrier properties usually depend on the morphology and chemical structure. In all soft-elastic materials the focus is significantly shifted to higher transmission rates. However, lowest oxygen transmission rates can be found in thermoset rubber and more specific in butyl rubber (IIR). Standard TPEs show up to ten times higher transmission rates. Kuraray has developed a new HSBC material that significantly reduces the oxygen transmission. The values of the final compound are in fact lower than those of butyl rubber and polyolefins.

Hybrar KL-7135 is a new development grade HSBC with a specifically designed macro- and microstructure for lower oxygen transmission rates. In contrast to Septon, Hybrar includes vinyl-rich soft segments. These were originally designed to optimize shock absorption. Due to its densely packed morphology, this chemical structure also provides lower oxygen transmission values. The commercially available Hybrar 7125 already shows OTR values of 12,000 which is up to four times lower compared to conventional HSBC. OTR values have been determined according to ISO15105-1 (differential pressure method, 35 °C). In the new product, the molecular

Fig. 1: Oxygen transmission rate (OTR) of Hybrar KL-7135 and Septon 4055

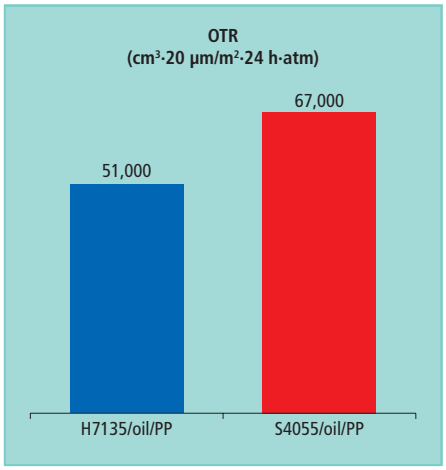
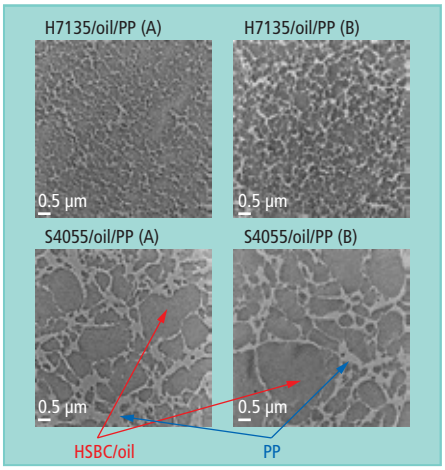


Fig. 2: Morphology/TEM photographs of Hybrar KL-7135 and Septon 4055



Tab. 1: Physical properties of Hybrar KL-7135 and two Septon grades

Properties	Hybrar KL-7135	Septon 4055 (Reference)	Septon 4033 (Reference)
Molecular weight	High	High	Low
Styrene content / wt%	33	30	30
Density / g/cm³	0.92	0.91	0.91
Hardness / Shore A	68	-	76
Tensile strength / MPa	9.3	-	35.3
100 % modulus / MPa	2.2	-	2.2
Elongation / %	550	-	500
10 % toluene solution viscosity (mPa·s)	56	5,800	50
MFR (230/10) g/10 min	0.02	-	< 0.1

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weight is further optimized resulting in an OTR of 8,300. **Table 1** gives an overview of the performance of Hybrar KL-7135 in comparison to two Septon grades. Septon 4055 has a similar molecular weight and styrene content. Septon 4033 has a much lower molecular weight but shows similar mechanical and rheological properties. Usually high molecular weight means better mechanical durability, but worsened processability. Due to the microstructure (vinyl content), Hybrar combines mechanical durability with a good processability.

Sample preparation

Samples were premixed and components are added in three steps: Septon and Hybrar (100 parts), oil (100 parts), PP (40 parts) and AO (0.1 wt%). The temperature was kept below 60 °C to avoid fish eyes and to ensure reasonable blending. After pre-mixing, the dry-blends were compounded on a co-rotating twin screw compounder (D: 47 mm, L/D: 42). In the final step, the compounds were injection-molded to 2 mm thin walled sheets.

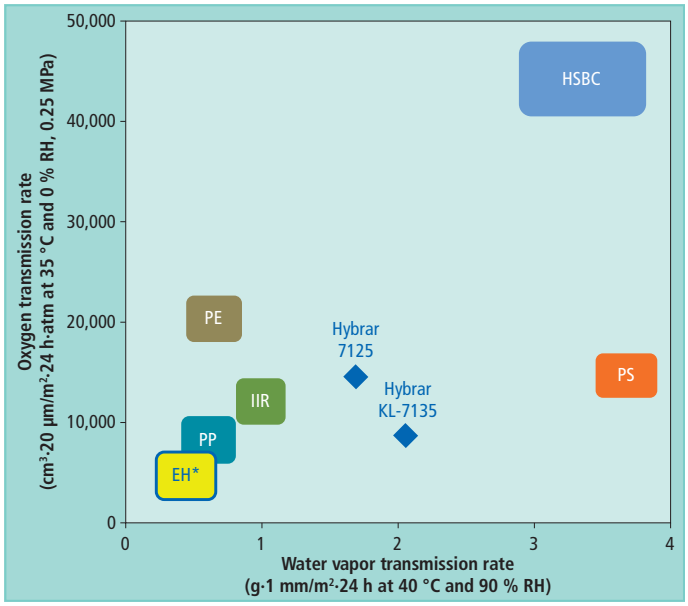

Fig. 3: Map of several soft-elastic barrier materials

Tab. 2: Performance of Hybrar KL-7135 vs. Septon 4055

Properties	H7135/oil/PP (100/100/40)	S4055/oil/PP (100/100/40)
MFR (230/2.16) / g/10min	3.4	0.2
Compression set @ 70°C / %	38	39
Hardness / Shore A	59	61
Tensile strength / MPa	5.1	7.7
100 % Modulus / MPa	1.4	2.5
Elongation / %	620	710
Haze / %	28	74
Resilience / %	43	52

Tab. 3: Blends of polypropylene and EH504H

Properties	EH504H	EH504H/PP (94/6)	EH504H/PP (88/12)	EH504H/PP (75/25)	Reference compound
Hardness (initial) / Shore A	40	56	74	89	72
Hardness (after 15 s) / Shore A	20	39	58	82	65
100 % modulus / MPa	-	1.0	1.7	4.4	1.9
Tensile strength / MPa	-	5.0	7.4	10.0	13.2
Elongation / %	-	690	730	500	900
MFR (230/2.16) / g/10min	-	0.2	0.2	1.6	1.2
MFR (230/5) / g/10min	20	-	-	-	-
Compression set @ 70 °C/22 h / %	-	43	41	49	45
OTR (cm^3·20µm/m^2·24 h·atm)	-	4,270	4,140	3,730	38,970

Characteristics

Septon 4055 shows excellent values in compression set and in tensile properties **(tab. 2).** Hybrar KL-7135 has a similar mechanical performance plus the big advantage of better processability. The medium MFR of 3.4 g/10 min (230/2.16) illustrates a good flowability that makes this compound suitable for blow molding and injection molding applications. Viscosity can be adjusted by modifying the content of PP and processing oil. Additionally, the Hybrar-based compound shows a 60 % lower haze than the Septon-based compound.

Hybrar KL-7135 based compounds show a significantly lower OTR than Septon 4055 compounds **(fig. 1).** The vinyl-rich structure and the fine morphology contribute to the significant characteristics of OTR. TEM photographs of both compounds **(fig. 2)** show a fine dispersion of the HSBC, the PP, and the oil.

New prototype EH504H

EH504H is a new HSBC alloy with low OTR. Compounds were produced based on EH504H with different amounts of polypropylene on a co-rotating twin screw extruder (D: 47 mm, L/D: 43). After compounding, thin sheets were injection-molded. The analysis of oxygen transmission shows a synergistic effect of the blends. 6 wt% of polypropylene added result in an OTR of less than 4,300.

EH504H shows a good ratio of barrier properties, softness, and soft-elasticity compared to conventional TPE and thermoset rubber materials **(fig. 3).** Target applications include soft components in medical devices and the beverage industry.