

B. K. Chapman, D. Kilian

High performance styrenic block copolymers

in medical and damping applications

Thermoplastic
Elastomers

TPE

magazine

international

kuraray



P. O. Box 10 41 25
40852 Ratingen/Germany

Volume 4, February 2012

1 | 2012

High performance styrenic block copolymers in medical and damping applications

B. K. Chapman, D. Kilian*

A material class segment of high performance styrenic block copolymers used in clean, soft and particular transparent applications was developed in the early 1990s. As of today these materials are in use for medical and food contact applications, making use of their inherent safety. They are attractive for selected applications in the medical field as they can be processed without plasticizers and are chlorine-free. A recently developed grade of thermoplastic elastomer with high molecular weight has the added benefit of high vibration damping properties due to its glass transition temperature (T_g) near room temperature. Within this presentation we discuss applications and features of the copolymers including various physical properties, e. g. modulus, tensile strength, $\tan \delta$ versus temperature and heat resistance. In addition, sample formulations and compounding concepts of these materials are described.

1. Introduction

Styrenic thermoplastic elastomers have evolved significantly since their introduction in the 1960s. One specialized series has a vinyl rich isoprene midblock which provides damping properties and durable kinking features. In effect, these materials have been designed for damping applications. All other properties have been discovered through extensive material studies at an application laboratory.

Hybrar type block copolymers are characterized by their high vibration damping properties at room temperature [1]. They are available in both hydrogenated and non-hydrogenated grades. In addition, blends of hydrogenated grades with polypropylene ex-

hibit excellent transparency, flexibility and mechanical properties. As a result, this technology creates an attractive replacement of flexible PVC.

Such materials are in use for packaging films, in the medical bag and tubing markets, and as a vibration modifier for a variety of polymer systems including polyolefins, PS, ABS, etc. as shown or discussed in this paper.

2. Characteristics

Styrenic TPEs, i. e., SBC (styrenic block copolymers) based compounds, are widely used in various application areas including auto-

motive, appliances, construction, medical etc., because of their excellent elastic properties, softness, durability, and colorability. Today's market increasingly requires materials that satisfy value added solutions in a variety of processing technologies and end use conditions. Standard grades of styrenic block copolymers are not always best suited to meet these requirements.

In response Kuraray developed Hybrar high performance thermoplastic elastomers. These materials possess the following characteristics [1]:

- High vibration damping properties at room temperature
- High affinity to polyolefins and styrenics
- Foamable
- Curable
- Very good compatibility with polypropylene
- Very good heat and weather resistance
- Rubber-like elasticity.

Table 1 shows the full product line of Hybrar products available to the market today [2]. The following sections will describe some of the ways Hybrar resins can be used advantageously in various applications.

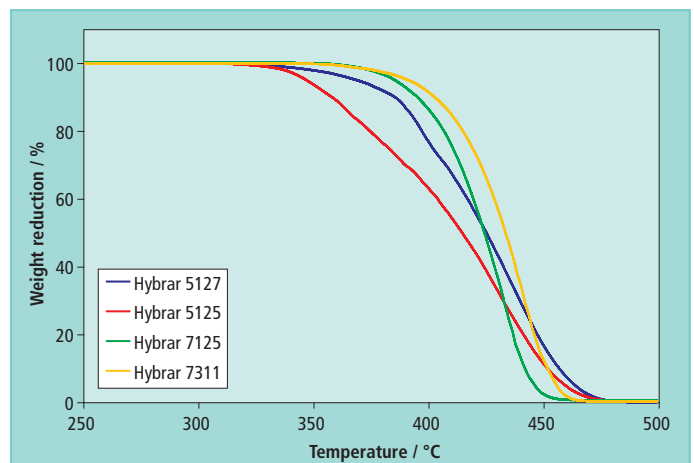
2.1 Heat resistance

Hybrar resins are typically processed by sheet and tube extrusion. As a result, thermal degradation resistance can be of importance due to multiple heat histories associated with various end use product manufacturing. The Hybrar 7000 series has

* Brian K. Chapman, Ph.D.
brian.chapman@kuraray.com
Technical Service and Development Manager
Kuraray America Inc., Pasadena, TX, USA

Dr. Dirk Kilian
Development Manager
Kuraray Europe GmbH,
Frankfurt/Main, Germany

Fig. 1:
Heat resistance of standard Hybrar range



been fully hydrogenated to provide a substantially improved level of thermal degradation resistance [1]. These types are typically used in medical tubing and IV bag products.

The heat resistance of Hybrar as a function of temperature is shown in **figure 1**. Note the increased level of resistance in the hydrogenated 7000 series vs. that seen in the non-hydrogenated 5000 series. This level of stability provides Hybrar resins the ability to be reprocessed many times and warehoused for longer periods of time with much lower risks of yellowing or mechanical failure.

2.2 Damping properties

The damping is defined as the dissipation of energy in a material under load. It varies with the state of the material and its temperature. A useful parameter to determine the damping ability of a material is the loss factor, $\tan \delta$, which measures the ratio of the energy dissipated into heat to that of the energy stored. The peak $\tan \delta$

temperature for most styrenic block copolymers is between -50 and -45 °C. The peak $\tan \delta$ temperatures for all Hybrar grades are between -17 and 20 °C, hence damping properties of these rubbers are good at room temperature [1, 2].

Blends of Hybrar and other polymers also exhibit excellent vibration damping properties. **Table 2** shows the effect of the addition of Hybrar to polystyrene at levels between 10–20 %. The addition of Hybrar increases $\tan \delta$, which therefore increases the damping property of the polystyrene. **Figure 2** shows the vibration damping behavior as struck by a steel ball of pure polystyrene vs. that of an 85 % polystyrene/15 % Hybrar blend [3].

The same effects can be observed for Hybrar/high density polyethylene blends and for Hybrar/polypropylene blends [3]. In combining Hybrar blends with paraffinic oil and typical Septon HSBC styrenic soft compounds, low rebound compounds can be obtained. As a specialty, damping foams can

be produced with Hybrar compounds by using typical foaming and curing technologies. These foams exhibit very low resilience numbers as measured by the percent rebound distance of a metal ball dropped upon the surface of the foam.

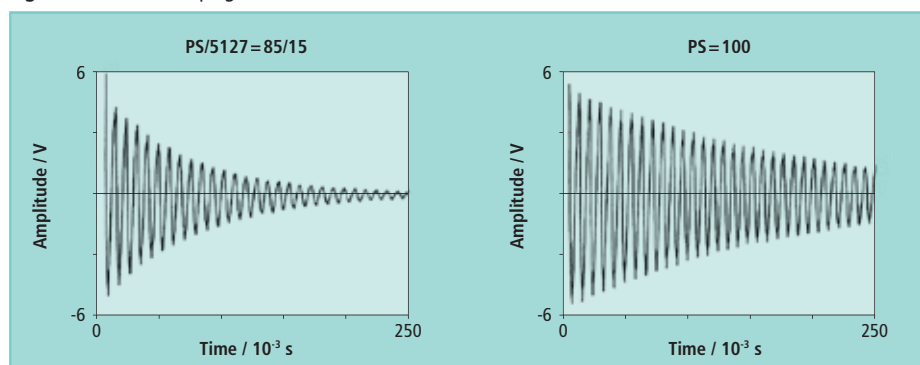
2.3 Flexible, transparent compounds

Especially in medical applications like tubes or IV bags there is a need for flexible, transparent compounds which i. e. can be obtained by blending hydrogenated Hybrar resin with polypropylene. In fact both, PP homopolymer and random copolymer polypropylene can be used to achieve transparency.

Due to high miscibility of polypropylene within the midblock of the Hybrar triblock structure the visible light waves pass through the structure without interference from the polystyrene domains. The application in films or tubes results in optically clear products with low haze and high transmittance. These features meet or surpass levels attained by flexible grades of PVC with the advantage that they do not contain halogens and are fully recyclable.

Additionally, compounds made of Hybrar/PP have high tensile strength and excellent impact strength. Unlike most HSBCs they have a relatively low viscosity and can be used in film, sheet and profile extrusion without the addition of plasticizers. This eliminates any possible leaching in sensitive applications such as medical films and tubing.

Fig. 2: Vibration damping effect



Tab. 1: Hybrar product line

	Hybrar grade	Type (vinyl-bond rich)	Styrene content / wt%	Peak temperature of $\tan \delta$ / °C	Glass transition temperature / °C	Specific gravity	Hardness / Type A	Tensile properties				MFR			Solution viscosity					Physical form
								100 % modulus / MPa	300 % modulus / MPa	Tensile strength / MPa	Elongation / %	190 °C, 21 N / g/10 min	230 °C, 21 N / g/10 min	230 °C, 98 N / g/10 min	5 wt% / mPa·s	10 wt% / mPa·s	15 wt% / mPa·s	20 wt% / mPa·s	30 wt% / mPa·s	
Hydrogenated	KL-7135	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	5127	SIS	20	20	8	0.94	84	2.8	4.7	12.4	730	5	-	-	-	-	-	-	540	Pellet
Unhydrogenated	5125	SIS	20	-3	-13	0.94	60	1.6	2.5	8.8	730	4	-	-	-	-	-	100	650	Pellet
Hydrogenated	7125	SEPS	20	-5	-15	0.90	64	1.7	2.7	7.1	680	0.7	4	-	-	-	-	55	350	Pellet
Hydrogenated	7311	SEEPS	12	-17	-32	0.89	41	0.6	0.9	6.3	1,050	0.5	2	-	-	-	90	240	-	Pellet
Measurement method					DSC*	ISO 1183	ISO 7619	ISO 37				ISO 1133			Toluene solution 30 °C					

* Temperature increase by 10 °C/min

3. Applications

From the given explanations these resins obviously provide a potential in a wide variety of possible applications covering damping and transparent areas. As stated earlier, the addition of Hybrar can significantly improve the vibration damping properties of compounds. This is especially useful in applications like athletic equipment grips, audio speaker cones and boxes, tool grips, shoe soles, automotive sound damping, athletic impact equipment, and as a damping modifier for various thermoplastics and rubbers.

Hydrogenated versions of these resins can be blended with polypropylene to obtain products with good transparency and easy processability. They are a good choice for processors looking for alternative non-halogen containing TPEs. Some of these applications include food wrap, toys, and medical film and tubing.

Medical and food packaging applications often require resins with relatively good oxygen barrier properties. For these application fields the high molecular weight grade of Hybrar shows a marked improvement vs. other grades of HSBCs including SEEPS, SEBS and SEPS as well as other grades of Hybrar [2]. In addition to oxygen, moisture permeability is of great interest in these applications as well as benefits of water vapor transmittance with KL-7135 vs. other HSBCs as described earlier [2].

The use of Hybrar in medical tubing applications provides the improvement of kinking

properties which are substantial. Generally the softness of Hybrar in PP/Hybrar blends provides for a better kinking resistance. For qualitative investigation Kuraray defined its own method similar to others mentioned elsewhere [3]. Resistance against kinking is easily checked by forming a loop and parallel pulling at both ends for lowering the diameter. The lowest possible diameter measured in mm just before kinking is defined as kinking resistance in mm. This experiment is defined for ambient temperatures 20 °C, 50 % RH and record of inner and outer diameter (fig. 3).

In using Hybrar blends or compounds for tubing the reopening of the tube after us-

ing a flow stopper clamb is another characteristic that is commonly checked. For this basically the time period for reopening after 24 h application of closed clamb is measured. While reopening usually a characteristic sound can be detected. The two stages – begin and end of reopening – are exemplary displayed in figure 4.

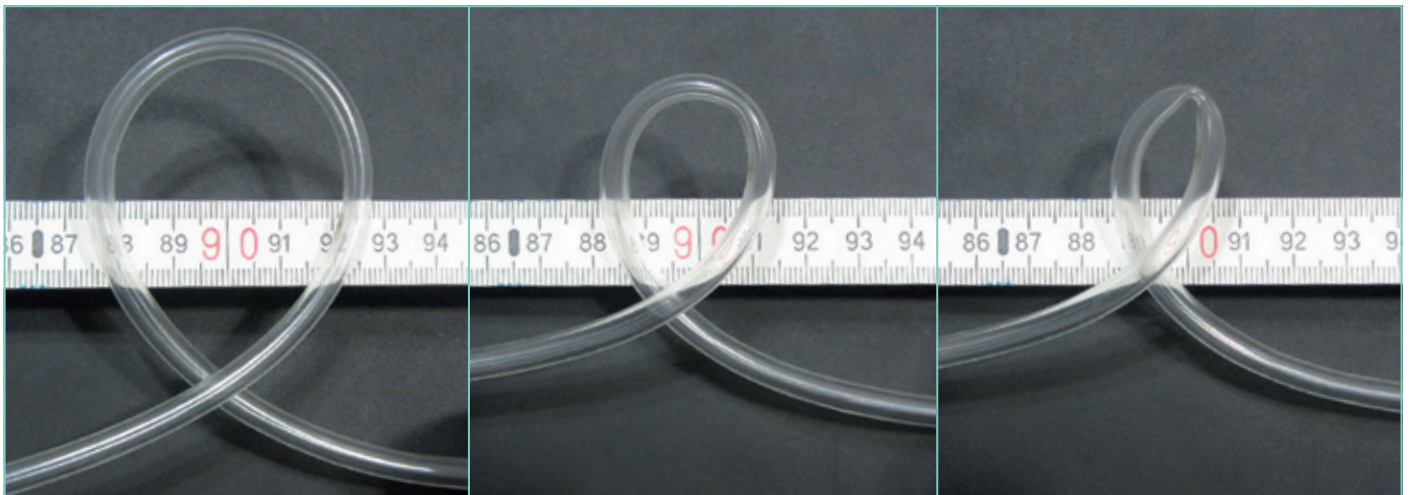
4. Processing

As mentioned earlier, Hybrar has a much lower viscosity than other standard HSBCs which typically need a plasticizer in order to be processed via molding or extrusion. This lower viscosity enables dry blends with ole-

Tab. 2: Effects of blending polystyrene with Hybrar

Formulation	1	2	3	4
Polystyrene	80	85	90	100
Hybrar 5127	20	15	10	0
Damping properties				
Tan δ at 0 °C	0.049	0.047	0.044	0.033
25 °C	0.115	0.075	0.051	0.035
40 °C	0.094	0.063	0.045	0.037
Loss factor	0.068	0.040	0.023	0.016
Mechanical properties				
Tensile modulus / MPa	1,863	2,157	2,255	2,647
Tensile strength / MPa	43	47	57	49
Elongation / %	17	21	18	13
Flexural modulus / MPa	1,667	2,059	2,255	2,647
Flexural strength / MPa	22	28	34	74
Hardness / Shore D	74	74	80	83
Mixing condition: Twin screw extruder @ 200 °C; Molding condition: Injection molding, cylinder @ 200 °C, Mold @ 60 °C; Evaluation of damping properties: Tan δ measured with Rheovibron (Dynamic Viscoelastometer, Orientec) @ 110 Hz Loss factor (degree of damping): Measured by resonance method with a cantilever beam				

Fig. 3: Kinking resistance test



fins to be easily extruded on film lines, tubing lines or in profile extrusion. In addition the material can easily be injection-molded.

The material is not hygroscopic, therefore does not require any predrying prior to processing. Most grades come in pellet form and can easily fed into extruders or molders. The high level of miscibility with polypropylene allows processors to skip preblending steps and use less intensive screw designs to get well blended compounds.

Processing conditions for these resins are similar to those of most HSBCs. Extrusion temperatures generally are between 190 – 240 °C. The hydrogenated grades are more apt to handle higher temperatures and multiple heat histories.

5. Conclusion

In this paper we presented a soft TPE material which originally was designed for

shock absorbing and sound damping applications, e. g. in athletic sports goods, or automotive parts. Later on it was found that the material is also good in soft PVC replacement, food packaging, and medical film or tubing applications. We showed the vast application potential based on the compatibility of the Hybrar microstructure to i. e. styrenic and polyolefinic matrices. In addition, we demonstrated that special Hybrar compounds provide for very good clearness, transparency, and durability as well as kinking and impact resistance.

6. References

- [1] Hybrar brochure, Kuraray Co. Ltd., 1st ed. 2008, 3E
- [2] TPE Magazine (4) 2010, 220 – 225
- [3] [http://:www.septon.info](http://www.septon.info)
- [4] I. e. USP 3865776, USP 6846535

Fig. 4: Tube directly after clamb application and after reopening of the tube

