SBS are found in a wide variety of applications and are processed by various methods (photos: BASF)

Styrene-Butadiene-Block Copolymers. By using living anionic polymerization of rigid styrene and flexible butadiene blocks, it is possible to design SB block copolymers with customized properties. The spectrum of properties ranges from soft and elastic for soft-touch applications, to flexible for film and rigid as well as impact-resistant for transparent injection molded parts. Most applications are currently found in the packaging sector.

Designer Products Based on a Modular Approach

20 years of Styrolux in Antwerp, Belgium, and 15 years of Styroflex.

The SB block copolymer Styrolux was first produced on a commercial scale about 30 years ago in Ludwigshafen, Germany. In 1990, barely ten years later, a second production facility was built in Antwerp. In 2004, an additional production facility was added in in Altamira, Mexico. Today, BASF has a production capacity of 110,000 t/a.

A special variant of this product family, the thermoplastic elastomer (TPE) Styroflex, was launched at the K show in Düsseldorf, Germany, only 15 years ago.

Modules for a Wide Range of Properties

A particular characteristic of the SB block copolymers is the intentional creation of block structures through living anionic polymerization to yield a sequence of hard styrene blocks and soft butadiene or butadiene-rich blocks in clear distinction from the elastomers produced from styrene and butadiene (the SBR synthet-
ic rubbers) using the radical technology and high-impact polystyrene (HIPS) with grafted, cross-linked polybutadiene particles. The “living” nature of this polymerization with Li alkyls as chain starters was discovered and defined in 1956 by Szwarc. The block structure is achieved through sequential addition and complete reaction of the monomers. The reactive chain ends can be terminated by protonization or through addition of multi-functional coupling agents to yield star polymers. This yields very monomer-poor styrene copolymers that are found to be very rugged thermoplastics.

The creation of statistical SB blocks or block sequences requires the addition of specific additives, so-called randomizers, under closely defined conditions, since otherwise anionic copolymerization of styrene and butadiene occurs with preferential incorporation of butadiene into the chain [1].

The driving force for phase separation and the formation of nanoscale structures is the incompatibility of the polystyrene (PS) and polybutadiene (PB) blocks. The high transparency and mechanical strength of this product class result from this morphology. The hard-soft-hard (i.e. PS-PB-PS) block sequence alone has gained technological significance, since it is responsible for the strength of the material. Good overviews of the production and uses of SBS block copolymers and their blends with other plastics can be found in the literature references [2] and [3]. The CEH Report [4] analyzes the worldwide market for this product group.

With the symmetrical SBS block copolymers, the phase volume ratio decides whether the thermoplastic or the elastomeric character predominates (Fig. 1).

High Butadiene Content Yields Thermoplastic Elastomers

If the soft, elastic component forms the continuous phase, classic thermoplastic elastomers (TPE) result. These include, in addition to SBS, the SIS- (styrene-iso-prene-styrene) and the hydrated, more weather-resistant SEBS (styrene-ethylene-butylene-styrene) as well as the SEPS (styrene-ethylene-propylene-styrene) copolymers that were first marketed by Shell in the mid-1960s under the trade name Kraton [5, 6].

The primary characteristics of this product class include, among others, the good elastic recovery (resilience) and the low Shore hardness — lowered preferentially through addition of white oil — making soft touch applications possible for instance.

Except for polyolefins, however, these classic styrenic TPEs exhibit only unsatisfactory compatibility with other plastics. Their low polarity makes printing problematic, and the sometimes very high order-disorder temperature (ODT) causes inhomogeneities in the melt, making film extrusion and stable processing difficult [7].

Developed originally as an alternative to flexible PVC, Styroflex can, in the meantime, be found in many applications, for instance, in stretch and cling films for transparent meat packaging or as the soft touch component on baby toys and razors.

High-impact Products with Increasing Styrene Content

SBS block copolymers with a 70 to 80 % polystyrene hard phase (HS-SBS) belong to the class of tough-rigid, transparent thermoplastics. In addition to the transparency and mechanical strength inherent to SB block copolymers, good compatibility with general-purpose polystyrene (GPPS) along with high ductility and an elongation at break frequently exceeding 300 % are particular characteristics of these materials. The latter are attributable to the deformation mechanism under shear, which is distinctly different from the “crazing” found in HIPS.

Thanks to its considerably more polar soft phase, the Styroflex 2G 66 introduced by BASF in 1995 no longer exhibited these drawbacks. Above 145°C (ODT), it yields a homogeneous melt, making it easier to process and, in addition, is extremely resistant against thermo-oxidative degradation. This TPE can be printed readily and offers good adhesion and part compatibility with a number of transparent and opaque plastics. This permits its use in two-component injection molding and as an adhesion promoter in multi-layer films, and sealing wax formulations and as a compatibilizer in plastic blends. Furthermore, as an impact modifier, it improves the application characteristics of HIPS (high-impact polystyrene) and ABS (acrylonitrile-butadiene-styrene copolymer) [3].
leads to a broad molar mass distribution as a consequence of the statistical frequency distribution. The average of three to five branches per polymer chain improves processing and reduces the orientation dependence of mechanical properties.

BASF also followed this structure concept with the Styrolux brands introduced in the early 1980s. In this case, a primary development objective was to further increase the “toughness efficiency” of these products in mixtures with GPPS (Fig. 2). Here, the expression “toughness efficiency” stands for the ability of SBS block copolymers to retain a good, useful toughness even when mixed with relatively high amounts of GPPS. The Styrolux brands with very high toughness efficiency thus permit economical production of transparent packaging.

With intentional synthesis of mixed, so-called “smeared” block transitions containing styrene and butadiene regions, the BASF researchers achieved their objective without having to incorporate more butadiene into the polymer chains. In a further development step, these smeared transitions were replaced through the intentional incorporation of defined statistical SB blocks in Styrolux 3G 55.

In addition to the hard PS blocks and the highly elastic PB blocks, the mixed blocks create their own semi-hard and pronounced ductile phase (also called an “interphase”) that improves the toughness efficiency of products in SBS/PS blends enormously.

The Styrolux grades are characterized by high transparency, surface gloss as well as a good ratio of toughness to stiffness. Mixed primarily with GPPS, they are extruded into film and thermo-formed to yield a variety of parts, but also find use in injection molding. Among the newest grades is the extremely transparent Styrolux 3G 46, which can be found in high-quality display packages, for instance.

**Focus on Memory Effect**

While essentially the basic structure-property relationships were examined in the past two decades, today’s research in the field of SBS block copolymers produced using anionic technology is focused increasingly on the synthesis of “memory” materials and mixtures of different SBS block structure types. The latter occasionally exhibit unexpected synergistic effects, expanding the property spectrum of this product group further.

In 2007, BASF first presented a product optimized for production of shrink film in the form of Styrolux HS 70. Modeling of the shrink curve, very high final shrinkage of over 70 % at temperatures near 80°C and little natural shrinkage at temperatures below 40°C was achieved through intentional tuning of different glass-transition temperatures. BASF researchers made an additional advance with the two-component Styrolux T/S, which allows film producers to achieve the properties desired in their product by mixing the two components T and S themselves. Styrolux T/S films have the same optimized shrinkage behavior found in film produced from the HS 70 grade (Figs. 3 and 4). With an even further improved toughness-stiffness ratio in combination with exceptional transparency and brilliance, these materials differ distinctly from transparent polypropylene and in this regard achieve the level characteristic of polyesters. The density advantage of up to 30 % compared

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*Fig. 2. The long PS block in the asymmetric SBS block structure ensures that the polymer is quite compatible with the low-cost GPPS; coupling of long and short segments to form star-shaped structures with good toughness was already achieved in the early Styrolux grades, also in mixtures with large amounts of GPPS*

*Fig. 3. The Styrolux T/S system can be custom-formulated directly at customers thanks to the newly developed individual components Styrolux T and Styrolux S; film producers and packagers benefit from the uniform shrinkage behavior as well as the high final shrinkage of films made from Styrolux T/S*

*Fig. 4. Films made of Styrolux T/S are very well-suited for shrink-labeling of complex bottle shapes by means of sleeves (left), but also when using the ROSO method, which uses a wrap-around adhesive-bonded label (right)*
to PET-G that is so important for the economics of SBS remains unchanged.

The stretch hoods made of the TPE Styroflex 2G 66 used to protect goods effectively during loading and unloading as well as handling in warehouses are another example of a memory product. Films made of pure Styroflex in multi-layer structures with polyethylene are also encountered in this application. Thanks to their good elastic recovery, films with Styroflex layers conform closely to the package goods even after being stretched by 220%. Here, the high tear strength and good puncture resistance of the elastic TPE are beneficial, above all when packaging sharp-edged items (Fig. 5).

Impact Modifier, Adhesion Promoter and Slip Preventer in One

Another example from the logistics sector is a new application where Styroflex 2G 66 is used as an impact modifier for a two-layer HIPS film (Fig. 6). It protects the lightweight polystyrene foam core of a plastic pallet against damage. Addition of even small amounts of the highly elastic TPE can raise the basic toughness of HIPS considerably. This converts the general-purpose plastic into a mechanically very strong material in a very economical way. Moreover, addition of Styroflex also improves adhesion of the film to the foam and creates a non-slip surface.

Outlook

Development of SBS block copolymer applications and markets targeted at growth segments is accompanying the product innovations.

While the classic segments – transparent food packaging, flexible film and injection molded items – still represent the primary areas for sale of SBS polymers, special applications such as the above-mentioned shrink and stretch films, impact modification of other thermoplastics or elastomers and the compatibilizing effect in blends are gaining in importance.

Even though the principles of anionic polymerization of styrene and butadiene, and the SBS block copolymers based on this technology have long been known, dedicated and intense research and market development efforts together with customers continue to expand the potential of these products.

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