Styrene Copolymers

Rising Demand for Specialty Polymers

Styrene polymers continue to maintain their position in the global market due to continuous advances and innovations. The sharp surge in demand for specialty copolymers has led to an increase in production capacity by the producers in Asia and the Middle East. The rise of demand will go on.

Developments in processes, products and applications for styrene polymers are being systematically commercialized to exploit the good cost-benefit potential of this class of materials. All suppliers are becoming increasingly reliant for their success on understanding the entire value-creation chain, from polymer raw material through to end-use. Targeted processes and collaboration with leading users in each market segment and region are giving rise to industry-driven developments that are no longer aimed solely at improved or new products and processes, but increasingly target system solutions and collaborative innovations.

To gain a deep understanding of industries, market levels and regional specifics, not only new approaches must be devised but application developers must be hired who combine in-depth product and market knowledge with a broad overview of technology. Among the prominent trends are customized nanostructured surfaces, weight reduction, improvements in application performance and safety, as well as the tailoring of commodity plastics to customers’ needs and their applications.

Examples of such developments are fiber optic systems made from highly transparent styrene polymers, nanostructured surfaces that possess superhydrophobic properties, and highly UV-resistant styrene polymers that are being systematically substituted for high-priced polymers.

Sustainability is gaining traction in all application areas, and is by no means restricted to the use of biodegradable polymers. Goals here include reducing the size of the carbon footprint and/or seeking out the best ecological and economic alternatives to existing solutions. Systematic innovation management is crucial if efficiency of existing resources is to be increased. Integrated innovation processes and open innovation are topics which are gaining importance.

Styrene polymers and especially styrene copolymers enjoyed significant volume growth in the last three years, despite cost pressures (Table 1). This growth mainly came from interpolymer substitution that had already occurred in less technically demanding applications. Packaging, simple injection molded articles for packaging sleeves, toys, small items and the like, together constitute a stable base volume upon which further growth can occur (Fig. 1).
Styrene Acrylonitrile (SAN)

Styrene acrylonitrile (SAN) (Fig. 1) has successfully defended its application areas – in the household sector, in cosmetic packaging and in durable industrial batteries – in recent years. It has done so by virtue of a special property profile comprised of chemical resistance, very good transparency and high rigidity, all of which are essential in nearly every SAN application. Supply and demand in the European market have remained stable in recent years. However, ABS producers in Asia have upped their efforts to serve the European SAN market with imports.

Established uses aside, innovations are spawning more and more new applications. In recent years, Styrolution Group GmbH, Frankfurt, Germany, has succeeded for example in tapping the field of automotive exterior applications by developing customized formulations based on heat-resistant Luran HH-120 (alpha-methyl-styrene-acrylonitrile). This product is used in door pillar trims and other decorative elements because it offers a combination of many factors. Thus, the SPF50 grade possesses very good UV stability, high gloss and exceptional depth of color. This specialty SAN also has other intrinsic advantages, such as increased heat resistance (Vicat softening temperature of 120°C), high chemical resistance and ease of processing. These offer huge benefits for vehicle manufacturers and plastics processors alike and can be expected to translate into above-average growth in this segment. Similar out-performance is expected in other market segments once the product portfolio has been adjusted to meet more stringent user requirements.

Styrene Methyl Methacrylate (SMMA)

Styrenyl methyl methacrylate (SMMA) combines the excellent ease of processing of styrene polymers with the high brilliance and crystal clarity of polymethyl methacrylate (PMMA). It finds widespread application in homeware, such as water filters, water tanks and tumblers, and is also found in optical applications and displays. Crystal clarity, excellent flow in injection molding, low water absorption and high rigidity single out this polymer for thick-walled applications that must meet high aesthetic standards. With NAS (SMMA), Styrolution offers a diversified product portfolio that will be further expanded to include colored variants alongside the transparent grades when the new production site in Ludwigshafen comes on stream. These developments will exploit the market potential of these specialty copolymers while opening up further innovations that will support disproportionately high growth.

Styrene-Butadiene Copolymer (SBC)

Styrolux, an impact-resistant and crystal clear SBC, and Styroflex, an equally transparent thermoplastic elastomer, are produced by Styrolution in world-scale production facilities in Europe and America. SBC polymers are still almost exclusively blended with commodity polystyrene primarily intended for transparent, rigid packaging for foodstuffs and consumer goods. There is hardly any growth potential left for styrene polymers in this market segment in general due to excessive interpolymer competition and price pressure from polypropylene and polyesters, such as polyethylene terephthalate (PET). Within the broad market for transparent packaging, there are still niche areas, such as shrink-wrap film, which still enjoy above-average growth.

One beneficiary thereof is the advanced 2-component concept by which shrink-wrap films and sleeves are made from Styrolux T and Styrolux S. This concept allows processors to customize the film’s mechanical and shrinkage properties. New quality standards in terms of defects have been set for premium products in this demanding market segment and have led to excellent printability.

Food packaging continues to be an application for SBC polymers in multi-layer composite films with other polymers, some of which provide functional tasks, such as gas barrier properties. The role of the SBC polymers is to contribute mechanical strength, elasticity and optical clarity. Compounding SBC polymers with other styrene polymers, as well as with polyolefins, can produce equally significant improvements in film properties, such as greater puncture resistance, improved stress cracking resistance and elastic recovery. Unlike film unmodified with SBC, there is scope here for either reducing the thickness without com-
The medical industry, too, is beginning to appreciate the core properties of SBC polymers. These include transparency and toughness, elasticity, and outstanding neutral behavior when sterilized with high-energy radiation. Ease of shaping by almost all processing methods and simple bonding to other materials round out this list.

The focus of novel styrene polymers is on improved products rather than on wholly new polymers. For the user, this often means a better-customized drop-in solution that obviates the need for extensive modification to the processing technology. One example of targeted control over the structure/property design is the polymerization of styrene and butadiene by controlled pathways (Fig. 2).

Styroflex 2G66 is an SBC that is ideal for combining sustainability with improved product properties [1]. Its special tensile/elongation properties have proved suitable for creating packaging applications that feature a combination of improved strength and reduced film thickness. Styroflex is melt-processable without the need for further plasticizers. Its structure renders it eminently suitable for compatibilizing immiscible polymers, a property that opens up new possibilities for the use of post-consumer recycled materials. SBC makes an important contribution to sustainability. At the same time, the material’s extreme toughness greatly improves the elongation at break and the stress-crack resistance of thermoplastics such as acrylonitrile butadiene styrene (ABS) and high impact polystyrene.

This material has been used by Microspec Corp., Peterborough, New Hampshire, USA, to make the tube systems Multi-Lumen (Fig. 3). The tubing contains multiple holes of different diameter that allow different medications to be delivered at optimal flow rates in a single application.

Methacrylate Butadiene Styrene (MBS)

New applications are continually emerging for crystal-clear, impact-resistant polymers based on methacrylate butadiene styrene (MBS) in high-growth market segments, e.g. transparent housing parts for domestic vacuum cleaners and transparent displays and panels for gym equipment. Applications of MBS materials in medical technology and in quality packaging of consumer goods are well established, but not yet exhausted.
Since MBS is a comparatively small specialty polymer in volume terms, there are relatively few suppliers. The Styrolution Group GmbH produces MBS resins (type: Zylar) in the USA and will soon open up two locations in Europe. In general, these polymers feature a special block architecture created by combining the SMMA polymers and SBC polymers in a single compounding step. Precision matching of the refractive indices of the two components imbues the multiphase MBS polymers with high optical clarity, outstanding ratio of rigidity to toughness, and very good flowability for demanding injection molded parts. The Zylar product line ranges from high-strength brands that possess sufficient scratch resistance for display and point-of-sales applications to very tough, softer products for dialyzer housing materials in medical technology.

Injection molding uses aside, the properties of MBS support the production of hollow blow molded articles, as illustrated by the cleaning-fluid canisters supplied by Dienes Packaging GmbH, Kaiserslautern, Germany (Fig. 4). These are a highly transparent variant of the established PE canisters.

**Acrylonitrile Butadiene Styrene (ABS)**

Styrene polymers have customizable surface properties. ABS is suitable for the electroplating of metallic surfaces of the kind widely employed in bathrooms or in the automotive sector (Fig. 5). Electroplated auto parts are an area that imposes multiple and sometimes conflicting requirements on products. Novodur Ultra 4140PG is a specialty ABS polymer for automotive front-grills, trim and metallized emblems. It has much greater heat resistance than ABS and has high impact strength, but does not suffer from the familiar disadvantages of ABS blends, most of which contain polycarbonate, such as high melt viscosity at 200°C and a resultant higher processing temperature relative to styrene polymers.

**Methyl Methacrylate Acrylonitrile Butadiene Styrene (MABS)**

Polymers based on methyl methacrylate acrylonitrile butadiene styrene (MABS) also rank as specialties within the styrene copolymer family. As their property profile bears a close resemblance to that of acrylonitrile butadiene styrene (ABS), especially its mechanical properties, and as some application segments are therefore similar, they overlap with the transparent MBS polymers described above. The transparent ABS polymers, which Styrolution, for example, sells under the trade name Terlux, outperform MBS materials in two important properties: resistance to heat and resistance to chemicals, especially greases and oils. MABS has firmly established itself among the preferred materials for numerous medical applications, such as connectors, filter and dialy-
ABS is highly versatile and offers important property advantages over other materials in a wide variety of applications and industries. The material is also found in those applications and industries which are boosted by strong, lasting trends, such as demographic change, urbanization, and mobility.

Surface properties are a particularly prominent feature of ABS applications. Product design is increasingly becoming the channel for product differentiation. A good example here is the exclusive interior designs used by various auto manufacturers and auto models aimed at differentiating themselves more clearly. ABS offers plenty of scope here by virtue of its existing properties and its potential for further development. For one thing, components made from ABS polymers yield highly aesthetic surfaces which are perceived by consumers as being of particularly high quality. For another, ABS surfaces are ideal for further functionalization, e.g., by coating, galvanizing, hot embossing or printing. Specialty ABS grades that confer various significant advantages on surfaces and meet key requirements, such as increased heat resistance and impact resistance, are already available and are continually being jointly developed with users.

**Acrylonitrile Styrene Acrylate (ASA)**

Acrylonitrile styrene acrylate (ASA) picks up where ABS left off in terms of mechanical properties and mechanics. However, its outstanding resistance to UV radiation and chemicals makes it a superior, long-lasting alternative, particularly for uncoated exterior applications. The market for ASA, too, is showing signs of product standardization in the form of base grades that are available in standard black or natural color. However, the best surface quality and customized part appearance are achieved with precolored products in which basic type, pigments and additives are matched to each other – the vast bulk of business, especially in Europe, is conducted in this way. This helps preserve the specialty nature of this product class.

Product and application development tends to focus on UV resistance, which is a key property of this product class. Thus, the new generation of UV-protected ASA grades from Styrolution, namely Luran S SPF30, is frequently still being used for demanding automotive projects, such as radiator grills and mirror housings – three years after its introduction.

The construction sector offers great potential for ASA in extrusion, e.g., for terrace flooring, wall coverings and window profiles, but can also impose extreme requirements on durability and color fastness, with the result that the market is grateful for any improvement in UV resistance. In addition to the above-mentioned ASA material, Styrolution has rounded out its range of low-gloss grades for extrusion. A specialty variant of the standard grade with the abbreviation Q440 is available globally and yields a durable surface with a gloss <10% (60°) on co-extruded ABS or PVC substrates.

A combination of high-gloss surfaces and low density has been achieved by using Luran S in conjunction with the Mu-Cell process. The latter, further developed by KraussMaffei Technologies GmbH, Munich, Germany, yields parts which have high-quality optics and can made them with a low shot weight. The physical blowing agent added during injection molding generates a fine foam structure and lowers the density of the finished part by about 10%. As a result of the improved processing properties arising from using a suitable blowing agent to lower the melt viscosity, the manufac-
tured panel has a reduced wall thickness and is some 30% lighter overall than the same part produced by conventional process technology (Fig. 6).

There are other techniques available for imparting new properties to conventional polymers. Work here is focusing not so much on the chemical structure or composition of the polymer, as on tailoring the process technology to the end use. This applies especially to the design of surface properties. Nanostructured surfaces for generating super-hydrophobia, i.e. water-repellent or self-cleaning surfaces, are the trend to watch out for here (Fig. 7). An EU consortium project has shown that for example with laser nano-structuring styrene polymers can yield superhydrophobic surfaces [3].

ASA+PC blends play only a minor role in the market but, through their combination of enhanced color fastness and outstanding mechanical properties, represent a good solution for many automotive applications, such as truck exterior parts. These must offer a combination of ruggedness and, in the case of large parts, aesthetic quality at a cost-effective price, i.e. as far as possible uncoated or, if coated, with a clear topcoat only. Similarly, dust-repellent, highly heat-resistant grades are used for demanding applications in the roof console in the interior. New impetus for developments in this product class is expected to come from electronics, due to the simultaneous demand for ruggedness, aesthetics and inherent flame retardance combined with empirically high cost pressures in this industry segment.

**Blends with Polyamide (PA)**

By skilfully combining the amorphous styrene polymers with semi-crystalline polymers, it is possible to tailor individual property profiles that combine the positives of both. ABS+PA is the best known product class here, mostly for its excellent flowability and impact resistance. A relatively new blend member is ASA+PA. Terblend S NM-31 from Styrolution, for example, combines the dimensional stability of ASA with the good melt flow properties of PA6, yielding a readily processable blend that possesses good chemical resistance, impact resistance and good color fastness. The product is an attractive candidate for a variety of automotive interior applications in which a high-quality surface finish and ruggedness are needed, especially in the cases of bright colors and no coating, and for which conventional ABS+PA blends cannot provide the necessary color stability (Title figure).

Aside from automotive interiors, this material is increasingly being used in electronics (e.g. for garden tools) and even in the construction industry, where the unique combination of toughness, ease of processing and longevity in a single product make it a cost-effective substitute for existing complex multi-component systems.