2 Basic Structure/Property Relationships of Styrenic Polymers

2.1 Introduction

The term styrenics (or styrenic polymers) is used to describe a family of major plastic products that use styrene as the key building block. Due to their amorphous structure, styrene polymers can be easily processed over a wide temperature range well above their softening point, the so-called ‘glass transition temperature’ (T\textsubscript{g}). Other than partly crystalline polymers such as polyethylene (PE) or polypropylene (PP), polyamides (PA), polyesters, styrenic polymers (except syndio- and iso-tactic polystyrene) do not show a distinct melting point and, hence, no thermal energy for melting of polymeric crystals (melt enthalpy) is required during processing. That means faster processing under the same conditions, but also high dimensional stability and largely constant mechanical properties up to the T\textsubscript{g}. Styrenics show a comparably slow change of melt viscosity with temperature. This benign rheological behaviour is beneficial for processing as well.

Examples of styrene polymers are [1]:

- Polystyrene (PS) is being used as crystal clear, stiff, but brittle homopolymer ‘general purpose polystyrene’ (GPPS) or as impact modified, stiff but opaque ‘(high) impact polystyrene’ (HIPS).

- Expandable polystyrene (EPS): is a foam based on GPPS beads containing pentane, which are expanded under heat. EPS is lightweight, strong, and offers excellent thermal insulation, making it ideal for use in the packaging and construction industries.

- Styrene - acrylonitrile copolymer (SAN): is a transparent, stiff and thermoplastic polymer material with enhanced stress cracking resistance. SAN is based on the monomers styrene and acrylonitrile.

- Styrene – methyl methacrylate copolymer (SMMA): is a transparent and brittle polymer with enhanced scratch resistance compared to that of polystyrene (GPPS). It is often used in blends with styrene-butadiene copolymers (SBC) for clear and tough goods, which need enhanced scratch resistance.
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- Acrylonitrile-butadiene-styrene copolymer (ABS): is an opaque, ductile and stiff thermoplastic polymer with a broad processing window, which is strong and durable even at low temperatures, with good resistance to heat and chemicals.

- Methylmethacrylate-acrylonitrile-butadiene-styrene copolymers (MABS): are transparent, ABS-like materials with improved resistance against fats and oils compared to acrylonitrile-free styrenic polymers.

- Acrylonitrile-styrene-acrylate copolymer (ASA): is a product similar to ABS, but with excellent weatherability because of the use of butyl acrylate rubber containing no double bonds compared to butadiene rubber. It is widely used for automotive exterior parts (mirror housings, grilles, and so on) and for other outdoor applications in the area of sports/leisure and durable electrical and electronics (E&E) housings.

- Blends: polystyrene blends homogeneously with polyphenylene (PPE) ether to yield high temperature resistant, stiff and tough materials (polyphenylene ether (PPE/HIPS). ABS and ASA blend well with polycarbonate (PC) and PA to yield PC/ABS, PC/ASA, PA/ABS and PA/ASA blends combining the excellent thermal properties of the engineering thermoplastics PC and PA with those of ABS and ASA.

Other examples are [1]:

- Unsaturated polyester resins: are durable, resinous polymers derived from styrene and used mainly in the construction, boat building, automotive and electrical industries.

- Styrene-butadiene copolymers (SBC): are transparent, stiff and tough polystyrenes manufactured by a specific anionic process. SBC are widely used in food packaging (beakers, multi-layer co-extruded and thermoformed ‘modified atmosphere packaging’ or shrink sleeves). They are different from styrene-butadiene rubber (SB) made by similar technologies, which have rubber-like properties. They also need to be differentiated from (crosslinked) styrene-butadiene latexes, which are used, for example, as paper sizing dispersions.

- Syndiotactic polystyrene: a material being produced by a specific catalytic polymerisation process to yield a semi-crystalline, high temperature-resistant material.

- Other copolymers: styrene-maleic anhydride (SMA) copolymers, as well as styrene/N-phenyl maleimide copolymers display high heat resistance and are often used as blend components in high heat ABS and high heat ASA.

An overview of the different major classes of styrene polymers is shown in Figure 2.1.
Styrenic polymers offer many industries a wide variety of benefits, including [1]:

- Lightweight, water resistant and excellent thermal insulation.
- Rigid, with a high strength-to-weight ratio that offers energy-savings benefits in transportation and an excellent cost performance.
- Can be shatterproof and transparent if required.
- Good electrical insulation.
- Easy to process and produce in a range of attractive colours.
- Easy to recycle.

Manufacturers use styrene-based resins to produce a wide variety of everyday goods ranging from computer and printer housings to yoghurt cups, extruded polystyrene (XPS) foam boards for insulation, kitchen appliances, toys, consumer electronics, automobile parts, and durable lightweight packaging of all kinds.
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Styrene polymers are present in a variety of highly demanding applications. Their unique selling point is to combine cost efficiency, high performance and easy processing and, thus, make it the material of choice for use in electronic equipment, high-end domestic appliances and state-of-the-art packaging.

2.2 Polystyrene

The chemical structure of polystyrene (PS) or general purpose polystyrene, (GPPS) is a polyethylene backbone with laterally attached phenyl rings, which are responsible for the high $T_g$ (100 °C) and high refractive index ($n_{D}^{25} = 1.590$). Stiffness, brilliance, gloss and hardness are the main characteristics of GPPS. Thus, it is used in applications such as transparent food packaging, beakers, shower cabinets, lamp covers, and so on [2].

To overcome the brittleness of GPPS, the material is modified by the incorporation of butadiene-based rubber. The resulting material is called impact polystyrene or high-impact polystyrene (HIPS). It consists of a polystyrene matrix with embedded polybutadiene rubber particles of a typically cellular or core/shell type morphology.

Due to light scattering at rubber particles with different refractive indexes, HIPS is opaque. With reduced particle size, it is possible to create a translucent, in thin layers a near-transparent, material.

2.3 Acrylonitrile-butadiene-styrene and Styrene Copolymers [1]

ABS is positioned between the commodity and the engineering plastics in terms of its properties. Significant product performance improvements in recent years as well as reinforcement with glass fibres allowed the use of ABS to downgrade from more expensive engineering plastics or even metals.

The combination of three building blocks styrene, acrylonitrile and butadiene provides a unique combination of properties as shown in Figure 2.2.

Product differentiation through design is becoming more and more important in a wide array of sectors. Designers like ABS grades that can be easily coloured, that show high-quality surface finish and gloss. The comparably good scratch and abrasion resistance of ABS ensures that products retain their decorative appearance, even after prolonged use.
During last 20 years, the ABS market has become clearly differentiated: for cost saving reasons, a major portion of ABS converters tend towards using natural coloured ABS. Converters (injection moulders) perform the colouring process more and more on-line, using coloured masterbatches and additional dosing and mixing devices, by pre-mixing of highly coloured ABS and feeding this dry blend in a conventional way into the injection moulding machine. Extrusion manufacturers often start from natural coloured ABS as well, using colour compounders to provide coloured masterbatches which allow them to switch colours fast, to produce small lots and to deliver products just-in-time. On the other hand, white pre-coloured ABS is often used in the so-called ‘white goods’ industry, for example, domestic appliances such as parts for washing machines, dishwashers and refrigerators. Other pre-coloured ABS is often used as a specialty, for parts with highest requirements on lot-to-lot colour consistency or for products with special requirements for mechanical properties.

It is obvious that the use of natural coloured material not only saves the cost of colouring, but also reduces logistic efforts and complexity in warehousing, in pre-drying prior to melt processing and in the capital cost involved. A prerequisite for a successful, high-quality colour are ABS grades which fulfil the following requirements:

- Light and consistent colour of natural resin.
- Low pigment effect on mechanical properties.
• Ease in processing.
• High gloss.
• Global manufacturing specifications and supply.

ABS grades such as Terluran® fulfil these high requirements and, thus, offer a significant cost-saving potential. On the other hand, pre-coloured ABS polymers such as Novodur® provide combinations of specific properties, and are thus used to serve the ‘specialty’ ABS market.

Another example for ABS in high-end applications are super-stiff, temperature resistant and dimensionally stable technical parts, which were formerly produced with high-tech thermoplastics or even metals. Glass fibre (GF)-reinforced grades offer a variety of substitution potential as they feature an outstanding performance/price ratio, and thus are the material of choice when it comes to reducing the costs in the mass-production of technical parts, as shown in Figure 2.3.

**Figure 2.3** Glass-fibre reinforced ABS in high-end applications
2.4 Styrene/Butadiene Block Copolymers

Styrene-butadiene block co-polymers combine the toughness of HIPS with the transparency of GPPS. A special manufacturing process is required, which allows production of exactly defined molecular structures, being predominantly composed of styrene (typically between 65 and 85%), with polybutadiene dispersed in a controlled way, yielding a high impact resin with high transparency.

SBC block co-polymers such as Styrolux® are the ideal materials for various articles from the sanitary, cosmetics, household, office equipment and toy sectors, because of its crystal-clear transparency, appealing surface gloss, good breaking strength as well as excellent flow properties.

Thin films made of Styrolux® and Styroflex® help to increase the shelf-life, attractiveness and freshness of food products such as vegetables and ready-made salads. In addition to transparency, the requirements here primarily include puncture resistance, printability, high resistance to shrinkage as well as high permeability to water vapour and gases.

SBC block co-polymers can be found in growing market segments, previously dominated by other plastics. One example is shrink sleeves made from Styrolux®, or Clearen® (manufacturer: Denka), featuring a combination of high transparency, benign shrink behaviour and easy printability.

2.5 Other Styrenic Polymers

Although there are more different styrenic polymers, as mentioned previously, this book is focussing on some of the major classes of styrenic polymers only, in order to facilitate the understanding of the structure/property relationships. However, many of the insights gained in Chapters 3-5 can be transferred to other styrenic polymers as well. For the discussion of foams, based mainly on GPPS, such as EPS or XPS, see Gausepohl and Gellert [3].

References


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