Styrene Copolymers

Polystyrene and Copolymers Combine Aesthetics with Technical and Sustainable Properties

The aesthetically and mechanically outstanding properties of styrene polymers are extensively enhanced by different blending partners. New developments include weather-resistant grades, laser surface structuring and fiber reinforcement. The newly founded "Styrenics Circular Solutions" industry association recently started a chemical recycling initiative for polystyrene.

The radiator grille of the Peugeot 208 is hot-stamped from Luran S 778 T acrylonitrile styrene acrylic ester (ASA). The material is pre-colored, unpainted and suitable for long-lasting outdoor applications (© Ineos Styrolution)

Styrenic copolymers are typically used for applications with demanding requirements on surface aesthetics, mechanical behavior and processing. Polystyrene (GPPS = general purpose polystyrene, and HIPS = high impact polystyrene) is frequently used for food packaging due to its benign processing behavior, allowing high cycle rates. Modification of polystyrene with co-monomers like acrylonitrile and methyl methacrylate (MMA) leads to polymers with extended usability. Typically, styrene creates brittle and stiff, yet water-clear resins, while acrylonitrile contributes to chemical resistance, strength and improved barrier properties of the styrene-acrylonitrile resin SAN. SAN combines excellent transparency with stress crack resistance against fatty ingredients. Examples for SAN applications therefore are battery housings and pots/jars for cosmetics.

SMMA copolymers also are used in cosmetics and are processed by injection molding. Recently, applications for drinking water contact were developed, such as water filters made out of NAS 30, a transparent, crystal clear SMMA. Modification of polystyrene, SAN and SMMA result in impact resistant plastics. One »

Fig. 1. Water filters such as the Super Filter Kettle from Viomi must meet strict food contact requirements. The company used SAN Luran 368R for this purpose (© Ineos Styrolution)

Single-phase Transparent Stiff and brittle	Multi-phase Transparent Impact resistant	Multi-phase Opaque Impact resistant	Multi-phase blends Opaque Impact/heat resistant
GPPS (standard polystyrene)	SBC (styrene-butadiene block copolymers) Styrolux, K-Resin, brand: Styroflex	HIPS (impact-polystyrene) brand: Styrolution PS	ABS+PC (ABS + polycarbonate) bramd: Novodur Ultra
SAN (styrene-acrylate copolymer) brand: Luran	MABS (methacrylate-acrylnitrile- styrene copolymer) brand: Terlux	ABS (acrylnitrile-butadiene-styrene copolymer) brands: Terluran, Novodur	ASA+PC (ASA + polycarbonate) brand: Luran SC
SMMA (styrene methacrylate copolymer) brand: NAS	MBS (methacrylate-butadiene-styrene blend) brand: Zylar	ASA (acrylate-styrene-acrylate copolymer) brand: Luran S	AABS+PA (ABS + polyamide) brand: Terblend N
			ASA+PA (ASA + polyamide) brand: Terblend S

Table 1. Overview of styrene copolymers (source: Ineos Styrolution)

important example are styrene-butadiene block copolymers (SBC) and MABS (e.g. Terlux). Both polymer classes have one thing in common: a multiple phase morphology yet no light scattering, which is due to the nano dispersion of SBC domains well below the length of visible light, or due to the isorefractive continuous and dispersed phases in MABS.

In addition, such impact modified styrenics can be blended with engineering thermoplastics, such as polycarbonate (PC) or polyamide (PA). Examples for such blends are ABS/PA blend (brand name: Terblend), combining a permanent heat resistance with high toughness at good stiffness. The special haptics of Terblend makes it the material of choice for aesthetic parts in the automotive interior, featuring high thermal and mechanical properties.

Polycarbonate (PC) makes styrenic based polymer blends tougher and increases heat resistance. Examples are automotive interior parts, being exposed to permanently high temperatures. An overview of the variety of styrenic copolymers can be found in **Table 1**.

Developments Trends and Novelties

Styrenic copolymers combine high surface aesthetics with excellent mechanical and thermal properties.

SAN has been selected by the manufacturer Viomi Appliance Technology for its L1 Viomi filter kettle. The company had identified Luran 368R as the material of choice for the clear and transparent wall of its filter kettle. This SAN grade offers high mechanical strength, brilliant color and is compliant with Food and Drug Administration (FDA) and European Union (EU) food contact regulations. Luran 368N provides outstanding surface quality, excellent transparency and food contact compliance, enabling the creation of products that are aesthetically pleasant, durable and safe for daily household use (**Fig. 1**).

The specific properties of styrenic copolymers were recently utilized for new surface modifications within a development cooperation between Ineos Styrolution Group GmbH, Frankfurt, Germany, and Reichle Technologiezentrum GmbH, Bissingen/Teck, Germany. Styrenic copolymers allow new and accurately laser-imprinted surfaces, intended for automotive interior applications. More details were recently presented (see ***Kunststoffe*** *international* 6–7/2019, p. 18).

A continuous trend are new process improvements and product developments, especially for additive manufac-

Fig. 2. Crystal clear and good processing due to easy-flowing melt predestine styrene-butadiene copolymers for use in medical drip chambers (© Ineos Styrolution)

turing. Especially the selective laser sintering (SLS) is making great progress towards mass customization. By developing blends consisting of amorphous and partly crystalline materials, both requirements – broad temperature range for laser printing and high dimensional stability – can be successfully combined [1].

Weather resistant copolymers (acrylonitrile-styrene-acrylate, ASA) are frequently used for automotive exterior applications. The unique value proposition of ASA lies in the combination of high weather stability with a very good toughness/stiffness ratio, excellent processability and very good surface aesthetics.

One example is the Peugeot 208 front grille, using ASA Luran S778T in combination with hot stamping technology and decoration film provided by Leonhard Kurz Stiftung & Co. KG, Fürth, Germany. The material features a high polarity and hence a high surface tension, resulting in excellent film adhesion at superior weather resistance. ABS Novodur P2MC is used for the galvanized frame due to its highly speck-free surface, in combination with excellent metal adhesion and high dimensional stability (**Title figure**).

Styrene-Butadiene Copolymers and Other Styrene Copolymer Specialties

Styrene-butadiene block copolymers (SBC) is another specialty amongst the styrenic copolymers, produced via anionic polymerization. This special polymer technology allows the generation of exactly defined polymer molecules and polymer morphologies. By in-depth understanding of the underlying structure-property relationship, e.g. it was possible to further extend the property range of SBCs. Styrolux 4G60, a newly developed SBC grade for medical applications, combines excellent processing behavior with low density, high transparency, flexibility and heat resistance. Due to its outstanding bonding behavior with PVC and other polymers it is a material of choice for parts of infusion sets (**Fig. 2**).

Styrene copolymers are well miscible with other polymers, such as engineering plastics. SAN, but also ABS and ASA are compatible among one another. This broad miscibility range offers the generation of new property combinations by blending. PC and PA for example can boost impact strength and heat resistance in blends with ABS and ASA.

The ABS/PC specialty Novodur Ultra 4255 is such an example, being developed for demanding automotive interior parts like door and seat trim, glove boxes and consoles. Major features of this material are high impact strength and »

Service

References & Digital Version

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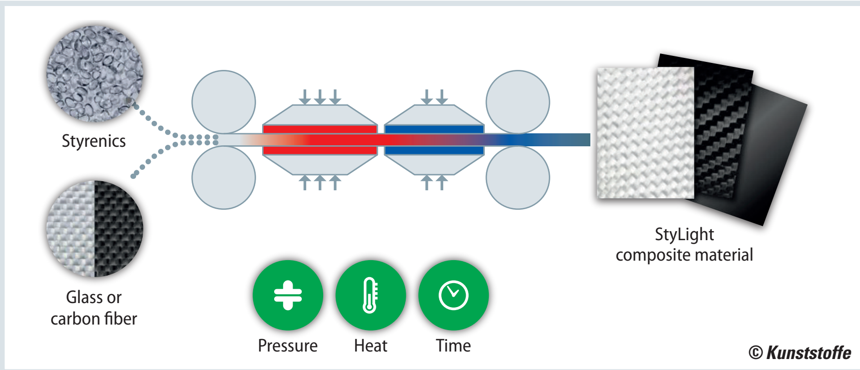

Fig. 3. The StyLight process in a 2-stage press: pre-impregnated thermoplastic semi-finished products as styrenics offer very good mechanical properties with glossy surfaces (© Ineos Styrolution)

heat resistance, combined with low emission (VOC) and high flowability.

Blends of PC and ASA are frequently used in exterior truck applications. High UV resistance in combination with high heat resistance and impact strength allow unpainted exterior applications.

Weather Resistant Surfaces, In-Mold Coating and Composites

Luran S KR 2864 C shows an outstanding chemical resistance. It was selected for a windscreen A pillar body trim, using the new ColorForm technology developed by Krauss Maffei Group GmbH, Munich, Germany. The ColorForm technology is a liquid in-mold painting of the thermoplastic body material. The paint is injected directly between the mold and the part surface. No second processing step is required. The ColorForm process streamlines painting and hardening into one.

The very good surface aesthetics of the final solutions allow for new designs while improving productivity and sustainability. Customers receive completely refined components, high-gloss and surface-textured products directly generated from the tool and completed without separate process step. Luran S KR 2864C used with the ColorForm technology is extremely scratch-resistant because of a polyurea coating, ensuring longer-lasting quality and sustainability.

Both, ABS/polyamide and weather resistant ASA+polyamide blends combine excellent melt flow with special surface haptics. They hence are the material of choice for application with high aesthetic requirements. By blending with specific fillers, such as minerals and glass fibers, the heat resistance can be improved to meet requirements of interior automotive application. A recent development example of a of an aesthetically and haptically sophisticated ASA+PA blend is Terblend S SG-02EF with outstanding haptics, flow and high heat properties.

StyLight SAN composites are an example for a new class of functionalized organic/inorganic hybrid materials for high end applications. They have outstanding strength and stiffness, low density compared to traditional materials and hence qualify for lightweight applications (**Fig. 3**). These composite materials are based on a chemically modified matrix and only fatigue after up to approx. 1,000,000 load cycling cycles, with periodic application of force and relief (**Fig. 4**).

Conventional thermoplastic composites based on carbon or glass fibers have so far mostly been used in structural components that require very high mechanical resistance to replace metal or thermoset composites. StyLight SAN composites outperform many currently available thermoplastic composite products in terms of stiffness and strength.

While the fiber fabric plays a key role in the mechanical properties of the material, the polymer matrix has a major influence on the aesthetics of the component surface. SAN-based composite materials therefore offer excellent aesthetics compared to commercially available composite thermoplastics based on semi-crystalline materials. Directly from the mold, they exhibit very little unevenness on the otherwise gloss surfaces. The high polarity of the styrene copolymer matrix makes it easier to print or decorate with films.

Sustainability and Circular Economy

The industry association Styrenic Circular Solutions (SCS) was founded in Brussels, Belgium, mid 2017 and represents companies involved in the styrenic polymers value chain. SCS´s mission is to drive the whole value chain towards circular economy. A specific focus is chemical recycling of polystyrene. The association demonstrates the industry's responsibility to reuse waste as a new raw material for plastics. The aim is to recycle at the same quality level as virgin material, in line with the circular-flow economy. Chemical recycling is a process that enables the recycled polymer to achieve a level of quality previously unattained by other methods (**Fig. 5**).

During the chemical recycling of plastic waste, the macromolecules are

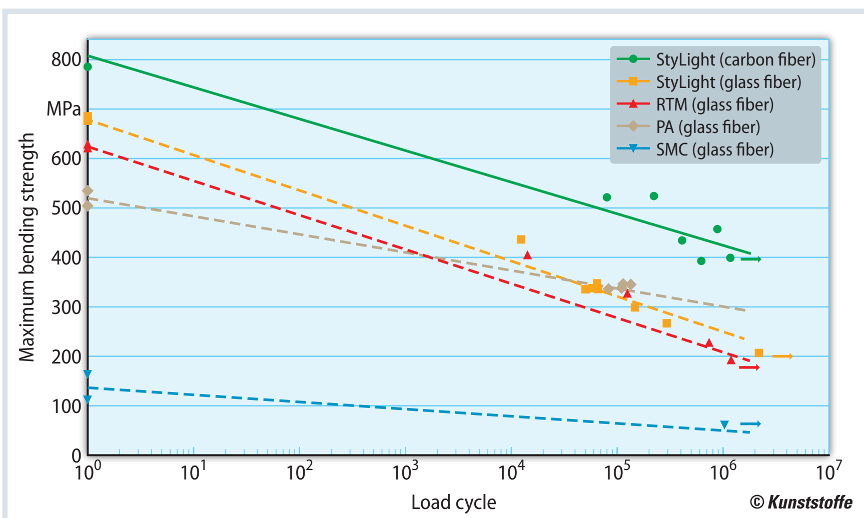

Fig. 4. Maximum bending strength according to ISO 14125 depending on load cycle at 23 °C and 50 % relative humidity. Styrenics show the best fatigue behavior (© Ineos Styrolution)

split into monomers (**Fig. 6**). These can then be used again for polymer synthesis. It is important to mention here that there are only a few plastics that can be broken down into their monomers using this method and then recovered from the monomers in a controlled manner and in their original quality. Polystyrene is the best-known example of a mass plastic that can be recycled using this method.

In order to investigate this behavior in-depth, the interdisciplinary R&D consortium ResolVe was founded, financially supported by BMBF, the German ministry for education and research. The project, steered by Ineos Styrolution R&D, aims for a commercial use of polystyrene post consumer waste as raw material for chemical recycling. The ResolVe PS de-polymerization process is subdivided into several phases. In a first step, a sorted, PS enriched feedstock is made from post consumer waste, which is subjected to thermal de-polymerization in a second step. Styrene and further decomposition products are separated, and purified styrene is again used for polymerization to

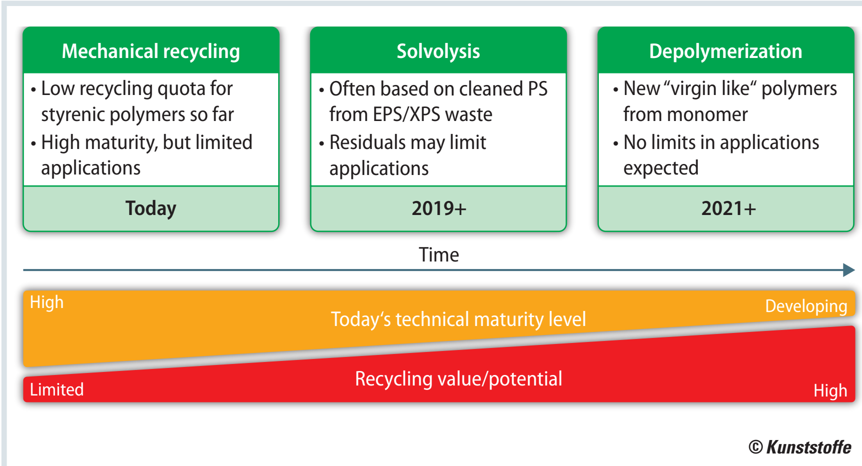

Fig. 5. Various reprocessing processes with self-assessment by industry. Chemical recycling to increase the recycling rate of PS (© Ineos Styrolution)

PS. This process can provide the recycled feedstock for other styrenic polymers as well, e.g. for ASA, ABS, or SBC. The by-products can be used either directly or as an additive, e.g. in a steam cracker.

Polystyrene shows comparatively good-natured behavior during thermal decomposition into monomers. Neither with the large polyolefins nor with PVC is it possible to split the polymers highly selectively into monomers by thermal treatment after the useful phase (post consumer). This is possible with polystyrene due to the particularly low "Ceiling Temperature" Tc of around 380 °C, above which polystyrene degrades to styrene. »

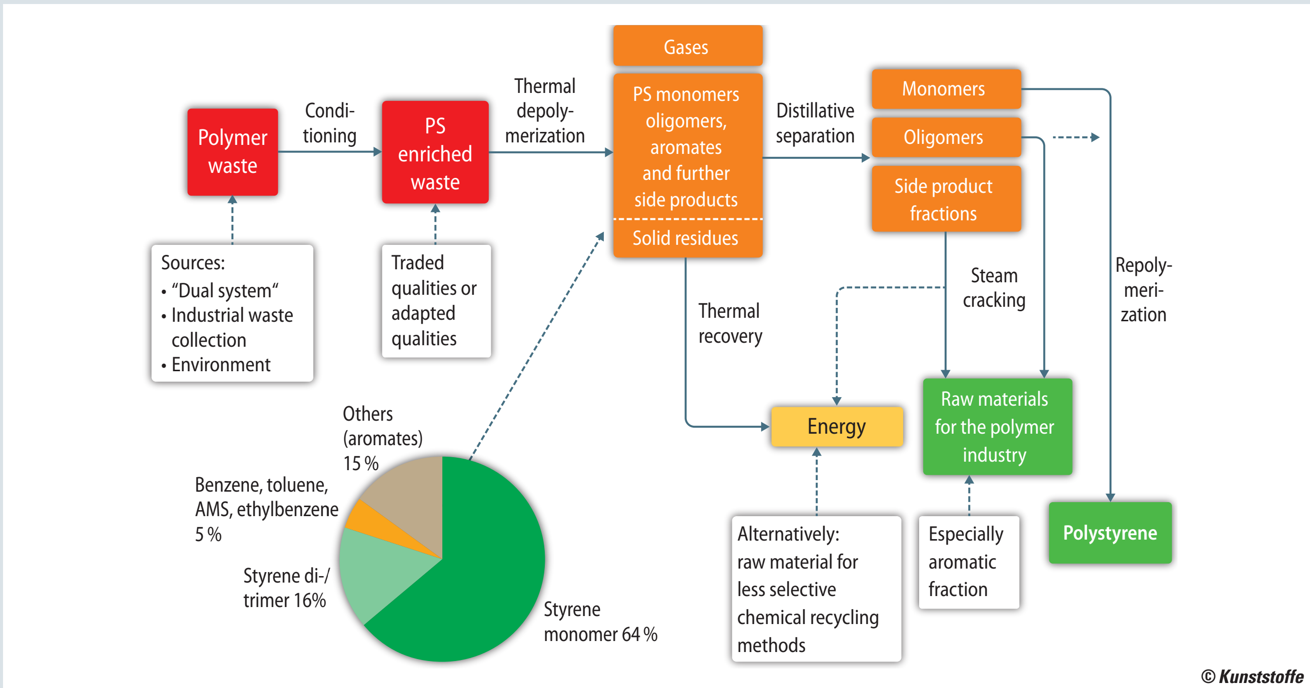

Fig. 6. Diagrams for the depolymerization of polystyrene. Compared to other polymers, the polymer is relatively easy to break down into monomers by thermal cleavage (source: Ineos Styrolution)

At Tc, the thermodynamic equilibrium of polymer and monomer is on the side of the monomer. Chemical recycling aims for "virgin quality" PS, while mechanical recycling often compromises on the quality, with consequences for the use of recycled materials for food or medical applications. It is expected to position chemically recycled Polystyrene in exactly these applications, amongst many others.

In near future it will be decisive to turn these promising results into commercial scale, with polystyrene as the unique "made-for-recycling" product. This will happen only in close cooperation of all major stakeholders along the value chain, starting with collecting, sorting and recycling and ending with the manufacturing of sustainable products for the consumer. SCS is pursuing this target in Europe, and it is important to mention that many other initiatives were started to leverage this "unique value" of Polystyrene. But not only in Europe, also in North America, partners are joining forces. Citeo, Total, Saint-Gobain and Syndifrais are committed to bring recycled polystyrene to the market until 2020 [2]. In North America, the "closed loop consortium" amongst Pyrowave, Revital Polymers and Ineos Styrolution was founded with the aim to establish polystyrene based circular solutions [3]. SCS and US-based Agilyx recently announced the next step in their collaboration on building de-polymerization capacities for European polystyrene post-consumer waste [4]. American Styrenics (AmSty) and Agilyx started a joint venture on polystyrene recycling via de-polymerization in the USA [5].

Ineos Styrolution recently reported the first demonstration of successful styrene-polymerization from de-polymerized, used PS in their Global R&D laboratories. The same company recently announced a collaboration with the large recycler Indaver N.V., Mechelen, Belgium, on de-polymerization of PS. ■

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