Acrylonitrile Butadiene Styrene: Recycling Successes and Challenges

Right Combination of Mechanical and Esthetic Properties

Acrylonitrile butadiene styrene (ABS) is a material for esthetically and mechanically demanding applications in the automotive industry, electronic housings, household appliances, and medical technology. The importance of ABS products with high proportions of post-consumer recyclate is increasing enormously. The trend here is toward high-quality recyclate brands replacing virgin material in many applications.

Among engineering thermoplastics, acrylonitrile butadiene styrene (ABS) plays a significant role. The polymer is characterized by high chemical resistance and impact strength along with high surface quality and heat resistance. As an amorphous material, ABS is very easy to process. ABS plastics are produced by polymerizing styrene and acrylonitrile, followed by blending with a butadiene-based rubber. This so-called emulsion ABS accounts for about 90 % of the ABS produced worldwide. The remaining 10 % are so-called bulk ABS products, in which the polymerization of styrene and acrylonitrile takes place in the presence of butadiene polymers. As a rule, the styrene content is between about 50 and 60 % and the acrylonitrile content of the matrix is in the range of about 20 to about 30 %. ABS has very good miscibility with other plastics such as polyamide (PA), polymethyl methacrylate (PMMA), thermoplastic polyurethane (TPU), and polycarbonate (PC). Technically relevant blends are ABS/PA and ABS/PC, whose properties can be varied over wide ranges by targeted selection of blend composition and morphology. These blends offer high-quality properties at favorable prices.

ABS is particularly in demand for electrical and household appliances.

The main areas of use for ABS plastics are kitchen and household appliances and electrical and electronic applications such as housings for computers, printers, and games consoles. These application areas dominate the growth in global demand for ABS. The worldwide market volume reached 10 million t/a in 2021 for the first time (**Fig. 1**), according to market research company IHS. The main reason for this is the continuing unbroken demand for kitchen appliances and diverse electronic devices of high-quality appearance, especially in the emerging economies. Other important areas of application are heat-resistant, low-emission components for the automotive interiors, toys, the leisure sector, and extruded, thermoformed parts and water pipes. According to IHS, the global market for ABS is expected to grow by about 5 % per annum over the next few years.

Focus is on China

Northeast Asia is still the largest market for ABS and also the largest export region for ABS plastics. This is not expected to change in the next five years. In North America, the experts at IHS expect the ABS market to grow by about 1.7 % per year until 2026. For Western Europe, about 1.6 % growth is predicted over the next five years. Consistently, most capacity expansions and new plants are planned in China (**Fig. 2**). Ineos agreed to set up a 50:50 joint venture with Sinopec around the end of July 2022. This is expected to build a production capacity of up to 1.2 million t of ABS to meet growing demand in China. A 600,000 t/a ABS plant in Ningbo, China, currently being built by Ineos and scheduled to come on stream by the end of 2023, will be part of the joint venture.

China remains the main importer of ABS plastics, despite the capacity expansions. However, the additional capacity in China is likely to lead to changes in the international flow of goods. Currently, the largest ABS producers are Chi Mei Corporation, LG Group, and Ineos Styrolution.

While there were some signs of delays in new capacity during the first year of the 2020 pandemic – including Versalis announcing the postponement of an HIPS conversion to bulk ABS – plans in the main markets remain ambitious. This is true, even assuming that not all announced additional capacities are actually built on a one-to-one basis, as previously predicted.

The disruptions to supply chains caused by the pandemic have impacted almost all markets: shortages of the respective precursors – due among other things to limited availability of transport containers – have led to price increases, in some cases substantial. Due to the resulting production backlog and the need to catch up, disruptions in the value chain are expected to continue to lead to limited availability of end products in the near future.

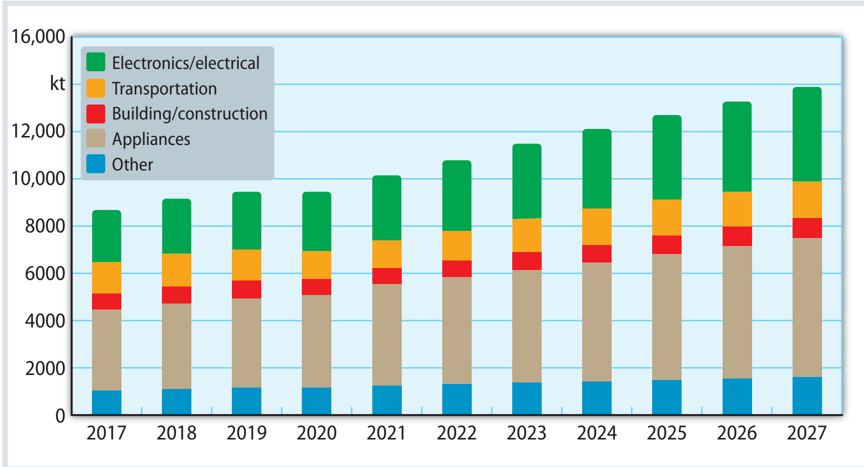

Fig. 1. Global ABS demand broken down by industry segment: continued growth in household appliances and electronic products is driving up demand for ABS. Source: IHS database; graphic: © Hanser

Emulsion or Bulk?

As mentioned, the most widely used ABS production technology globally is »

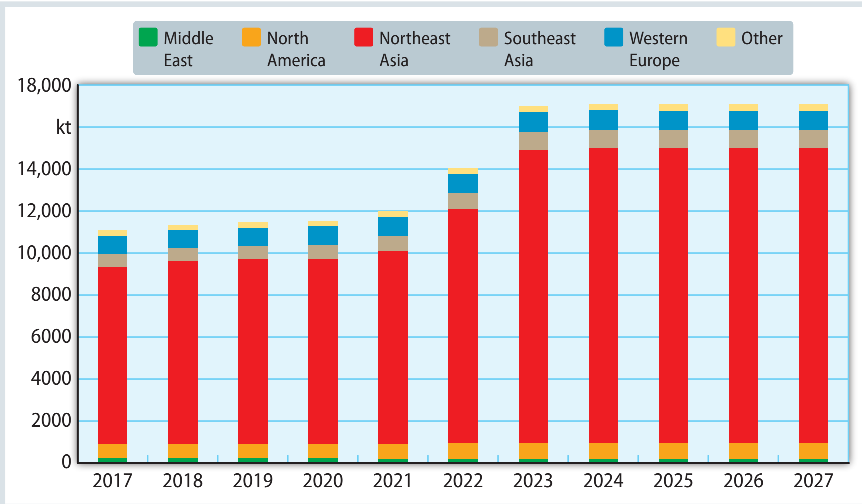

Fig. 2. An overwhelming share of global ABS production takes place in China.
Source: IHS database; graphic: © Hanser

Fig. 3. ABS is in demand for automotive components such as rear spoilers because it combines a very attractive appearance with good mechanical properties, such as high stress crack resistance. © Thaco

emulsion polymerization. In this process, styrene, acrylonitrile and, if necessary, other monomers such as alpha-methylstyrene are polymerized in a continuous process. Toughening is achieved by admixing discontinuously produced emulsion-polymerized polybutadiene rubber, which is grafted for compatibility with styrene and acrylonitrile. The most outstanding property of emulsion ABS is its high gloss. This is due to small rubber particles of average diameter below the visible light wavelength, which produce maximum surface gloss by minimal light scattering.

As mentioned, mass ABS technology is also used for production. It is very similar to the impact-resistant polystyrene process and produces both the styrene-acrylonitrile matrix and the rubber dispersed within it in a continuous process. The size of the resulting rubber particles is in or above the range of visible light wavelengths. Light is therefore scattered more strongly and the surfaces appear more matt. This is a desirable effect in automotive interior applications, among others.

The successful use of ABS in various applications is due to its combination of properties. With heat resistance up to about 112 °C, a very good impact strength to stiffness ratio, good resistance to stress-cracking media, and good esthetics, ABS is the material of choice for applications up to just below 100 °C continuous service temperature. ABS has therefore long been used in various interior and exterior automotive applications. A recent example is the high-quality rear spoiler from a major automotive OEM made of Novodur 550 from Ineos Styrolution (**Fig. 3**).

Mechanical Recycling Is the Best Choice

The drive for sustainability and a circular economy dominates the entire plastics value chain. The aim here is to return plastics to a sensible use after the initial use phase and, if possible, to a qualitatively equivalent use. At the same time, this means the consistent avoidance of uncontrolled disposal into the environment, such as marine littering, but also the avoidance of controlled landfilling and incineration.

For the reuse of post-consumer ABS, mechanical recycling is currently the best choice, as other processes such as dissolution and precipitation or controlled thermal degradation (pyrolysis) are not yet sufficiently advanced for ABS (**Fig. 4**). ABS's big brother, polystyrene (PS), also has enormous potential for the plastics circular economy. Due to its properties, i.e. high glass transition temperature, controllable thermal decomposition to what is essentially styrene, as well very good sortability, PS is ideally suited for the circular economy and can also be considered for chemical recycling. The glass transition temperature of PS – which is well above its service temperature – freezes the molecular mobility of the polystyrene chains and minimizes the migration of trace contaminants from or through the PS. This makes PS highly suitable for mechan-

	Elastic modulus [MPa]	Charpy notched impact strength [KJ/m^2]	Melt volume flow rate [cm^3/10 min]	Heat resistance (Vicat B/50) [°C]
Terluran GP-22 (virgin material ABS)	2300	22	19	96
Terluran Eco GP-22 MR50 (50 % recyclate)	2100	18	19	95
Terluran Eco GP-22 MR70 (70 % recyclate)	2100	17	17	95
Novodur H801 (virgin material ABS)	2400	35	10.5	106
Novodur Eco H801 (40 % recyclate)	2100	35	10	105

Table. Comparison of the important characteristic values of virgin ABS and ABS with recycled content. Source: Ineos Styrolution

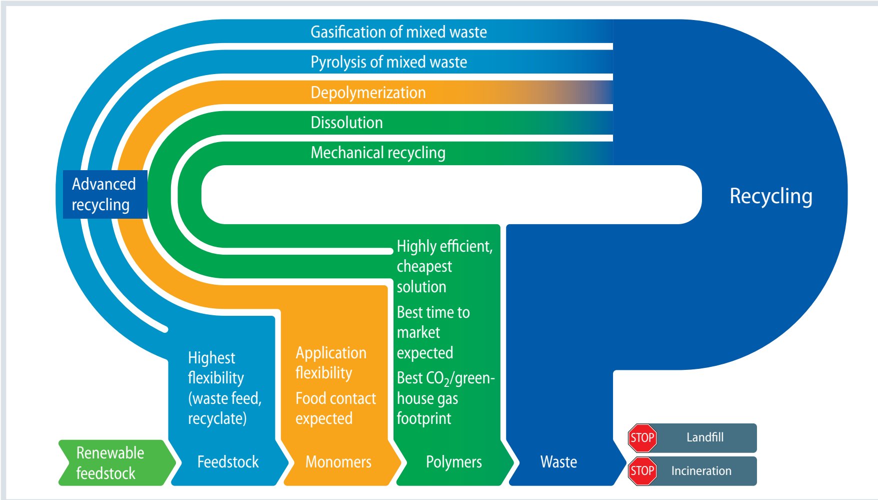

Fig. 4. Overview of the main recycling processes for styrene polymers, using PS and ABS as examples (without depolymerization): ABS is suitable for both mechanical and chemical recycling. However, the chemical processes are, for the most part, still under development. Source: Styrolution Group; graphic: © Hanser

ical recycling into very pure food-grade packaging materials.

Food Approval Expected

One such product is the recently introduced Styrolution PS Eco 440, which is produced using Tomra's near-infrared sorting process, delivering polystyrene purity of more than 99.9 %. Corresponding food contact dossiers (FC petitions) have been submitted to the European Food Safety Authority EFSA for evaluation and approval [1, 2]. Styrolution PS Eco is not only made from recycled material but is also fully recyclable. The material thus allows true circularity without the need for downcycling. The first grade available is Styrolution PS Eco 440 MR100 White. The MR100 suffix indicates that the material is made from 100 % recycled material.

The material can also be used behind a functional barrier, making it also suitable for food contact applications such as food packaging trays made from XPS foam. The concept, which meets the requirements of Regulation (EU) No. 10/2011, is based on a layer of virgin PS surrounding the recycled polystyrene.

How the recycling process changes the technical properties of ABS recyclates has been studied in more detail by a team of researchers led by Robert Scaffaro of the University of Palermo [3]. The scientists analyzed blends of virgin and recycled ABS containing 0, 30, 50, 70, and 100 % recycled content and considered the entire range of rheological and mechanical data. While rheology remains largely unaffected, despite the generally higher melt volume-flow rate (MVR) of PCR-ABS due to aging-related chain-splitting effects, mechanical properties are »

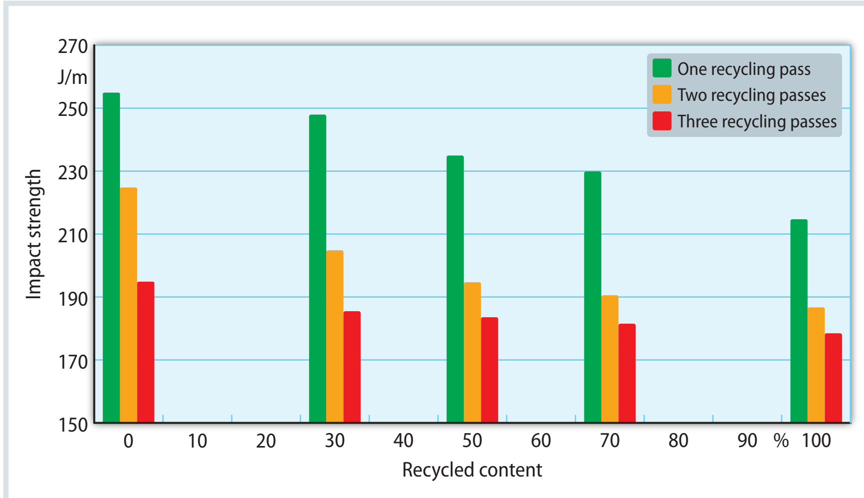

Fig. 5. Impact strength of blends of virgin ABS with different recyclate contents after one, two and three processing steps respectively: it can be clearly seen that the impact strength drops significantly, especially after the second recycling step. Source: [3]; graphic: © Hanser

lower for the recyclate blends, as expected. Interestingly, mechanical properties after the initial blend compounding step show a relatively linear dependence on the PCR-ABS content. In addition, the authors investigated two more compounding cycles and found that performance drops significantly for all blends (**Fig. 5**).

The challenge is thus to produce ABS recycled grades with virtually no drop in product properties. Ineos has launched products with 50 % and 70 % recycled content, respectively, that meet these requirements (**Table**). This genuine recycling, as opposed to downcycling, generates demand, even in premium segments. One example is the set of travel cases developed by suitcase manufacturer Tuplus and Ineos (**Fig. 6**) based on a 50:50 blend of recycled and virgin ABS (product name: Terluran Eco GP-22 MR50). Compared to suitcases made from fossil raw materials, the models made from Terluran Eco have a significantly reduced carbon footprint.

Biobased ABS

Despite all the successes in the field of mechanical recycling, it should not go unmentioned that the colorants and additives contained in the recyclate mean a certain restriction in the areas of application. For example, it is very difficult to produce white or even natural-colored ABS from mechanically recycled, black-colored ABS. Chemical recycling – splitting ABS into monomers followed by repolymerization – is suitable for these cases.

Bioattribution is another way to reduce the carbon footprint. In this process, part of the fossil feedstock is replaced by biobased feedstock at the beginning of the value chain. However, due to the enormous capacity of the chemical plants concerned, it is currently not yet possible to fill them completely with biobased feedstock. In the process, the biobased portion is allocated to the products via an official, certified process. This has the advantage that

Fig. 6. An ABS blend with 50% recycled content from Ineos Styrolution is used for the Tuplus travel case set. © Tuplus

- the existing infrastructure (refinery, steam cracker, etc.) can be used,
- biobased feedstock can be used, the sources of which do not compete with the cultivation of foodstuffs such as cereals and oilseed,
- the product properties do not change and therefore the approvals and technologies for production and processing do not change.

Both solutions – sustainable product lines made from styrene plastics with the use of bioattributed feedstock or with the use of recycled raw material sources – help avoid the use of fossil resources and enable significant reductions in the carbon footprint of the respective products to be achieved. A number of styrene polymers based on bioattributed raw materials are now available, such as PS, styrene-acrylonitrile copolymers (SAN), styrene-methyl methacrylate copolymers (SMMA), styrene-butadiene copolymers (SBC), acrylonitrile-styrene-acrylate copolymers (ASA), and ABS. All these products can be easily used as 1:1 replacements in existing applications without the need for renewed technical clearance tests. ISCC (International Sustainability and Carbon Certification) certified bioattributed raw materials are used in a mass balance process also certified by ISCC. One example is the recently launched Styroflex Eco. Styroflex Eco 2G66 B60 is an ISCC certified product using a bioattributed styrene. Compared to the use of styrene from fossil raw materials, Styroflex Eco has a 77 % lower greenhouse gas footprint.

In addition to the use of renewable raw materials, the use of recycled styrenes is establishing itself as a sustainable solution in various applications. It should be noted that more demanding application areas such as the automotive sector are also becoming achievable with newly developed products. One example is that of the Novodur Eco products launched by Ineos Styrolution, which are based on mechanically recycled ABS from used and discarded electrical and electronic equipment. They are intended for automotive interiors to produce, for example, parts that require increased heat resistance. ■

Info

Text

Dr. Norbert Niessner is Director of Global Innovation and IP at Ineos Styrolution.
Dr. Eike Jahnke is Vice President Business Management Styrenic Specialties EMEA at Ineos Styrolution.
Dr. Frank Eisenträger is Director Polystyrene EMEA at Ineos Styrolution.
Yohann Bach is Product Director Standard ABS EMEA at Ineos Styrolution.
Oliver Carstensen is Technical Product Manager Standard ABS EMEA at Ineos Styrolution.
Dr. Christian Ruthard is Product Manager ECO Specialties EMEA at Ineos Styrolution.

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