Polyarylsulfones (PSU, PESU, PPSU)

Water – A Growth Market. It is not only the automotive industry which is increasingly demanding heat-stable polymers that can be injection molded. The amorphous high-temperature (HT) polymers of the polyarylsulfone family are characterized by extraordinary, inherent flame retardancy and high transparency. In addition, membranes having adjustable pore sizes can be produced, with the result that the market for water purification membranes has shown growing interest in them in the last three years. Global consumption of these polymers is currently running at about 57,000 t (including polyetherimide, PEI). The HT polymers are expected to grow at a steady annual rate of 5 % in the coming years.

Polyarylsulfones play a special role in the range of polymeric materials available on the market: they have high glass transition temperatures ($T_g$) of around 200°C and so are suitable for producing extremely heat-stable components, and in fiber-reinforced form they are providing competition for metals in particularly challenging applications.

Polyethersulfone (PESU, e.g. Ultrason E, Veradel, Sumikaexcel), with a $T_g$ of 225°C, meets the highest HT requirements of this family of materials. It has good inherent flame retardancy (up to V0 according to UL94, without additives) and good hot-water, coolant and chemical resistance, e.g. against oils and fats (up to about 170°C). PESU offers continuous service temperatures of 180 to 190°C. Special grades, such as Ultrason Dimension from BASF SE, Ludwigshafen, Germany, have a modulus of elasticity of more than 10,000 MPa and a low coefficient of thermal expansion at 120°C, yet are easy to injection mold due to their lower melt viscosities. Polyphenylsulfone membranes for ultrafiltration of water are characterized among other things by their variable pore size, high flow, their chemical resistance and repeated sterilizability (figures: BASF).

Table 1. The most important polyarylsulfone and polyetherimide producers in the world (2012)

<table>
<thead>
<tr>
<th>Producer</th>
<th>Products</th>
<th>Capacity [t/a]</th>
</tr>
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<tbody>
<tr>
<td>BASF</td>
<td>PSU, PESU, PPSU</td>
<td>12,000</td>
</tr>
<tr>
<td>Sabic</td>
<td>PEI</td>
<td>21,000</td>
</tr>
<tr>
<td>Solvay</td>
<td>PSU, PESU, PPSU</td>
<td>30,000</td>
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<tr>
<td>Sumitomo</td>
<td>PESU</td>
<td>3,000</td>
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is also characterized by high superheated steam and stress-cracking resistance, as well as high notched impact strength. Polysulfones (PSU, e.g. Ultrason S, Udel), with a glass transition temperature of 187°C, lie at the back of the field when it comes to heat resistance, but compensate for this to some extent by absorbing only small amounts of moisture.

The glass transition temperature of polyetherimides (PEI; \( T_g \) 217°C) is similar to that of polyarylsulfones. These polymeric materials, which also count as amorphous HT thermoplastics, therefore often compete with PESU or PPSU, especially in injection molding applications. For that reason, despite their different chemical structure, polyetherimides are also covered in this article (Fig. 1).

**Market, Producers and Capacities**

The slowdown in global economic growth in 2008/2009 also impacted on polyarylsulfone sales. However, the decline was not as pronounced as it was for many other polymers; the years 2010 and 2011 following the crisis were characterized by significantly above-average growth. The reason for this lies in the nature of the main application fields for this family of materials: some, such as water and dialysis filters, and medical technology as a whole, are relatively immune to economic cycles. In fact, the proportion of polyarylsulfones consumed by the medical sector rose from about 20 % in 2010 to the current value of 24 %. PPSU, for example, can be sterilized very well by superheated steam, without loss of properties. PEI, too, sold under the brand name Ultem from Saudi Basic Industries Corporation (Sabic), Riyadh, Saudi Arabia, is used in sterilization boxes (Fig. 2).

The barriers to entry for PSU, PESU and PPSU are relatively high compared with those for other thermoplastics. Due to their special property profile, they often find use in safety and regulatory-driven applications in the automotive, medical and aerospace sectors. Thus, the development of new products is quite time-consuming. One exception was the strong growth in the baby bottles segment in 2010, where PESU proved to be a compelling alternative to polycarbonate. Growth in this application is flattening out again, however, because there has since been a shift toward polypropylene.

Overall, HT thermoplastics are expected to enjoy global market growth of around 5 % per annum in the coming years, with comparable…
growth rates expected in Europe. Asia is likely to grow somewhat more strongly (by about 7 %); whereas only about 3 % is predicted for the most developed market, the USA.

Market share barely shifts over the years, however. This is an indirect consequence of the high development cost for products that typically involve polyarylsulfones (Fig. 3). The entry of BASF into the PPSU market in 2007, however, brought movement into the market (Table 1). With its new 6,000 t/a Ultrason plant in Yeosu, Korea, BASF intends to provide a more flexible response to the rapidly growing Asian market. The plant will be operational in 2014. Sabic took its PEI facility in Cartagena, Spain, on stream in 2010 [1]. As a result, the company now has capacity for around 21,000 t HT thermoplastics. Sabic has been producing its polyetherimides exclusively in the USA until now. Furthermore, in 2011, it opened a pilot plant for producing Ultem polyetherimides in Mt. Vernon [2]. Solvay SA, Brussels, Belgium, has announced that it is nearing completion of a powder PESU production line in Panoli, India. Target capacity for the specialty (Viran- tage), required particularly for the production of epoxy composites, is set at a few hundred tons per year [3]. Sumitomo Chemical Corp., Chūō/Japan, has not announced any capacity changes since 2010.

Applications and Innovations

Aviation: The continuing trend toward replacing metal and toward lightweight engineering will provide a further stimulus for polyarylsulfones. The aviation industry has been interested in these materials for quite some time. What recommends them here, too, is their inherently good flame-retardant properties. A current example of lightweight constructions made with polyarylsulfones is the trolleys used to serve drinks and meals to airline passengers: inside the walls is foamed Ultrason E (PPSU) with a density of only 40 kg/m3, while the injection molded handle cavities are of Ultrason P (PPSU) (Fig. 4). Consequently, at 10 kg, the trolleys are only half as heavy as the conventional metal versions. The required flame-retardant properties are achieved without the addition of additives. Large aircraft can have more than 100 such trolleys, so the weight savings associated with the use of PPSU and PESU are considerable.

The parts are colored using color masterbatches (Sicover- sal X) from BASF Color Solutions Germany GmbH, Cologne, Germany, which has included Ultrason-based masterbatches in its program for about a year now: the color masterbatches of the same type of material is important for safeguarding a high level of product quality. The medical sector, especially, remains keen on coloring; Solvay therefore offers polyarylsulfones (PPSU) for the medical sector in various colors [4].

For particularly demanding lightweight construction projects, BASF also offers a PESU grade reinforced with 30 % carbon fibers (Ultrason E 2010 C6). The aviation sector also makes use of OH-termin- nated polyethersulfones as impact modifiers for epoxy systems – BASF and Sumitomo help to simplify prepreg production and significantly increase productivity at the end customer.

Another polyarylsulfone variant for the aviation sector is a PESU reinforced with continuous carbon fibers (Complete LCF-PPSU, Fig. 5), which is supplied by PlastiComp, Winona, MN, USA. Based on Ultrason E from BASF, the compound offers values for modulus of elasticity that are very high, even in comparison with glass-fiber-reinforced standard grades, and also outperforms aluminum (based on part weight) in its capacity to serve as a highly durable lightweight material for rigid components. Possible applications are to be found, for example, in aircraft seating, which is one of the few applications in passenger aircraft that are still dominated by metal. The material has already proved itself in initial tests.

Automotive: Polyarylsulfones have a wide range of applications in the automotive industry, too. PESU, for example, is used in the cooling-water and oil circuits, in vehicle electrics (housing and connectors) and transmissions.
Automobile headlights constitute a particular challenge: for the reflectors, developers—sometimes after trying out supposedly cheaper materials—keep returning to PESU. This is because there are few alternative materials that are capable of surviving continuous operating temperatures of 190–200°C without property degradation, while also being very readily metallizable and, due to their amorphous structure, offering high dimensional stability (Fig. 7).

The requirements imposed on the heat resistance of the materials used will continue to increase in the future, because car designers are increasingly specifying ever-smaller, more compact headlights that become even hotter than before in operation. BASF has responded to this challenge by introducing the highly heat-resistant Ultrason E 2010 MR SW HM (HM: heat management). This high-temperature PESU contains a special additive and so absorbs significantly less heat radiation than the already very stable predecessor Ultrason E 2010 SW Q31. Thus it is suitable for much higher continuous-service temperatures. The material is already being used by a major manufacturer of automotive lighting systems.

Oil pumps are another application area that is still enjoying remarkable growth: PESUs qualify for this application mainly by virtue of their excellent hot-oil resistance and constant mechanical properties over a wide temperature range of -40 to 160°C. By incorporating carbon fibers, graphite and PTFE, BASF has managed to improve the tribological properties of this material even further. Ultrason KR 4113 shows better wear and sliding friction characteristics than metal in variable-speed oil pumps made by Schwäbische Hüttenwerke, Germany, and the polymer also resists heat up to 200°C. Pump parts made of Ultrason E are now used by the million in vehicles from reputable European automotive manufacturers. It may be true that the European car market is stagnating at the moment, but the Asian mar-

Fig. 6. PESU reinforced with continuous carbon fibers is a highly durable lightweight material for rigid components and is in competition with aluminum
integrated boiler, which was an example is a solar panel with in solar technology. A good is naturally an important issue ing.

Drinking water and sanitary applications: The search for alternatives to metallic materials in the sanitation sector is ongoing. Although the construction industry itself is currently stagnating, brass pipes continue to be replaced by plastic pipes for functional reasons. BASF is active in this field with its Ultrason P, but Solvay too has a strong presence with its Radel grades. One of the uses for PPSU here is fittings for hot water pipes or heating distribution systems (e.g. Ultrason P 3010 (Fig. 8). In this regard, the material is reaping the benefit not only of its good hot-water resistance and its compressive strength but also its high level of ruggedness for use in the construction sector. Ultrason P 3010 has various approvals for food and drinking water contact and is even resistant to superheated steam (up to 134°C). The glass fiber-reinforced PESU has become established in impellers of pumps for sanitary engineering.

Pronounced heat resistance is naturally an important issue in solar technology. A good example is a solar panel with integrated boiler, which was unveiled in 2012 by Soterna, Spain. The 80-kg system, consisting of two extruded PPSU profiles (Radel, Solvay) between two injection molded end pieces, works with chlorinated hot water at a temperature of 95°C under a pressure of 6 bar. According to the manufacturer, thanks to PPSU, this is the first time a thermoplastic material has replaced steel in the pressurized boiler of a solar panel [5].

Polymeric materials that lend themselves in particular to water-contact applications will become very important in the short to medium term, as access to clean drinking water becomes critical to the world’s growing population. With special processes it is possible to make PESU membranes whose pore number and size can be varied over a wide range. Such membranes are crucial to water treatment. PESU is one of the very few polymer materials that lend themselves to such applications (Title figure). For BASF, the megatrend toward clean water is of strategic importance. Dialysis patients, whose numbers are constantly increasing due to demographic changes, are the beneficiaries of similar products. Solvay, too, has some polyarylsulfones for this application in its range [6].

Outlook

Since polyarylsulfones will in all probability remain a specialty in the coming years, their medium-term growth will remain closely linked to that of their customer industries. Therein lie special opportunities: the automotive sector is expected to remain a key market due to continued growth in China and India while the health sector will likely grow above-average in importance as the proportion of elderly citizens in developed countries increases.

The same applies to drinking-water recovery: the market for water-treatment technologies is considered to be one of the fastest-growing in the world. According to a study by BCC Research and cited by Inge GmbH on its website [7], sales of water and wastewater technology (excluding construction) have already more than trebled to around 81 billion US dollars, from 2007 to 2012. Access to clean drinking water has been a human right since the passing of a resolution by the UN General Assembly in July 2010. PESU membranes can help to make it a reality. An interesting novelty in the field of polyetherimides is the launch of new, more transparent Ultem or Extem grades (Sabic) for optical applications in the telecommunications sector [8].

Further growth stimuli could come from capacity expansions like the one by BASF in Korea: these present applied research with an opportunity to establish the high-temperature thermoplastics in new application fields.

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