

Polyamides (PA)

Problem Solver for Lightweight Construction and Numerous Highly-Specialized Cases

Polyamides have gone through a remarkable development in recent years. On the one hand, they are under pressure from other polymer materials increasingly entering the domain of engineering plastics. On the other hand, new, highly-specialized PA types are opening up applications hitherto reserved for high-performance materials. Continuous fiber composite materials are experiencing a dynamic development, polyamides from renewable raw materials are constantly on the increase.



The backrests of driver and front passenger seats in the BMW i3 feature injection molded seat structures of a special polyamide. Their high surface quality makes it unnecessary to varnish the visible parts (figures: BASF)

In 2014, again, polyamides belong to the most important engineering plastics. There has been little change, however, in the group of top compound suppliers, within the past three years: BASF SE in Ludwigshafen, Germany, DSM Engineering Plastics B.V. in Sittard, the Netherlands, and Lanxess AG, Cologne, Germany, dominate the PA6 market. Considering PA66, DuPont in Wilmington, DE/USA, Solvay (formerly Rhodia S.A.) in Saint-Fons, France, and here as well, BASF, are among the leading suppliers. In the area of partly aromatic polyamides (polyphthalamide,

PPA), DuPont de Nemours, Geneva, Switzerland, Solvay and Ems-Chemie AG, in Domat, Switzerland, must be named as the top suppliers. Long-chain polyamides (e.g. PA12) are mainly produced by Evonik Industries AG in Marl, Germany, Arkema SA in Colombes, France, and Ems-Chemie.

Global and Local

A trend which emerged some time ago and has obviously gained speed in recent times is the establishment of local devel-

opment centers. These centers follow the production facilities, relocation of which started several years ago. Virtually all major producers of polyamide are intensifying their activities outside Europe, mainly in the Chinese metropolises of Hongkong and Wuxi (Lanxess) as well as Shanghai (BASF, DSM, DuPont and Solvay) in order to develop together with the local customers innovative materials fast and in the market environment with the highest dynamics globally.

All producers of polyamide compounds have meanwhile established local branches in the major industrial regions and growth markets, with significant volumes of production. BASF, for example, recently increased the capacity of its compounding plant in Pudong near Shanghai, China. Together with a new plant in Yesan, Korea, which will more than double the company's capacities for engineering plastics in Korea by 2015, this project will help BASF to increase its compounding capacities in Asia, from the present volume of 130,000 t to 225,000 t. Lanxess, just as BASF, is also focused on South America, apart from India and China. At the site of Porto Feliz in Sao Paulo, Brazil, a new plant with an annual capacity of 20,000 t for PA6, PA66 and other compounds recently started operation.

The requirement of products that are standardized globally can be considered as another worldwide trend. This trend is driven by the global OEMs' wish to reduce costs. Identical specifications and formulas help slim down approval pro-

Fig. 1. Metal substitution in a vehicle:

The dampening element was made of a polyamide with 60 % glass fiber content (right), weighing approx. 50 % less than the tin variant (left) used up to now



Fig. 2. Ultramid D3EG10 FC Aqua is an example of a polyamide that can be used for components in contact with drinking water, thanks to its good chemical and hydrolysis resistance. The Aqua variant is suitable as a substitute of lead-containing alloys in water meter housings, for example

cesses, while a material needs to be tested and/or approved only once in a central location, and can then be supplied from local sources at high and homogeneous qualities. However, defining universal quality standards for all regions is extremely demanding: these standards must consider, e.g., local differences in raw material sources, differing climates, or the differences in process equipment available in the respective locations. Today, some large suppliers like BASF offer products that meet these requirements, while they work intensely to enhance their range of global products.

Metal Replacement with Less Material

The substitution of metals with polyamides remains the main driver for polyamide sales: The plastic material reduces weight, can integrate functions, simplify assembly and make elaborate post-processing dispensable, all of which reduces costs significantly. Especially in recent times, many suppliers have presented improved highly-specialized products to simplify lightweight construction. However, simple metal components have been replaced by now. This is why the most progress is made in details. State-of-the-art applications are, e.g., turbo-charge air distributors, cylinder head covers, radiator tanks and oil sumps in vehicles.

There is a tendency to further improve strengths and stiffnesses, which will make it possible to further reduce wall thicknesses, and, along with this, diminish the amount of material used. This can be achieved by increasing the fiber content to 60% and above, and applying carbon fibers instead of glass fibers. Lanx-

ess' Durethan DP BKV 60 EF with a high content of glass fiber reinforcement is suitable for thin-walled components that are at the same time highly rigid. Durethan BCF 30 H2.0 EF is based on carbon fibers and features a comparable property profile, while its density is reduced by 30%. Epic Polymers Ltd. in Kaiserslautern, Germany, recently presented similar developments. Their Strator XC material (PA66 and PPA compounds) has a new type of carbon fiber reinforcement with a stiffness comparable to that of Magnesium (45 GPa), while its tensile strength is similar to that of steel (350 MPa). Technyl Star AFX, a PA66 by Solvay, with its glass fiber content up to 60%, offers a high degree of stiffness, too.

A polyamide which was developed to compete with zinc and aluminum die casting is Ultramid D3EG12 HMG (High Modulus Grade) by BASF. This partly aromatic, creep-resistant polyamide has an E-modulus higher than 20 GPa, in a dry and conditioned state. Despite its high glass fiber content of 60% it is also suited for applications in visible furniture parts, for example. Flat faces made of this product are smooth enough, requiring no further treatment.

Ems-Grivory, the company sector at Ems-Chemie concerned with high-performance polyamides, developed and improved their long glass fiber polyamides: With their Grivory GVL-6H HP, the company claims to have achieved an unprecedented value of 300 MPa ultimate tensile strength by employing special glass fibers at high concentrations – without using carbon fibers. This is combined with an optimized surface, which is due to the fact that the cross section of the fibers is not round.

An example for the benefits of the latest PA types is a dampening element for car seats BASF developed together with vehicle supplier Somic Ishikawa Inc., Hamamatsu-Shi from Japan (Fig. 1). Not only does the Ultramid component (60% glass fiber content) have excellent mechanical characteristics, such as a high E-modulus. Its low water absorption also makes it highly dimensionally stable. In this application, the polyamide competes with zinc. Nevertheless, its weight is approx. 50% below that of the metal version.

However, metal replacement is not a topic of the automotive industry, only. One example is the current discussion about water meter housings, which are mostly made of brass today. Brass contains a large amount of copper and a low percentage of lead to simplify processing. In December 2013, a pronounced reduction in the limit values for lead in drinking water became effective in the EU. Polyamides approved for use with potable water, such as BASF's Ultramid D3EG10 Aqua, have since grown in importance: This partly aromatic polyamide is outstanding for its reduced water ab-



Fig. 3. Applying laminates and tapes, complex components can be produced by injection molding. These parts are reinforced mechanically by continuous fibers sitting at precisely defined spots. The figure shows a multifunctional test specimen of 360 mm x 360 mm size, suitable to reproduce numerous characteristics and challenges of composite production

sorption, high resistance to hydrolysis, and high stiffness (Fig. 2).

Composites and Service

Based on the experience gained in the past years, the industry can now concentrate on metal substitution in load-bearing structures. These components are often safety-relevant and semi-structural, with high demands on part design. In addition to components reinforced with short or long fibers, an increased number of products are optimized with continuous fibers. Such materials include unidirectional or fabric-reinforced continuous fiber tapes and laminates. In case short cycle times are achieved for processing these materials, too, thermoplastics will gain ground over thermoset polymer matrixes in regard to welding, forming, maintenance, recycling, and even from an economic point of view.

The commercial launch of unidirectional and fabric-reinforced continuous fiber components is gaining speed only slowly, because the value chain from polymer to component is still under development. It is not enough today, to supply the granules. New operating steps have emerged between the raw material supplier and the manufacturer of the component. Some of these steps are the

production of semi-finished products and prepregs, cutting and forming the non-woven prepregs prior to overmolding. The material suppliers' approaches differ: Lanxess took over Bond Laminates, producers of continuous-fiber-reinforced semi-finished fabrics (type: Tepex).

BASF has developed the necessary know-how in-house. They added the respective competences to their technical center, and presented their own new range of products and services, named Ultracom, at K2013. This comprises semi-finished products with the respective thermoplastic overmolding materials tailored to them, in addition to a comprehensive range of services from BASF's application development, including component testing, simulation by Ultrasim (Fig. 3) as well as processing in a fully automatic manufacturing cell.

Du Pont is working on similar technologies marketed under the name of Vizilon.

Interpolymer Competition

In the past years, various applications hitherto reserved for polyamides, have been opened up for other materials, e.g. polypropylene. Sometimes, however, it is the other way round, as with the front-end cross carrier of the new Golf 7, which

is the first ever without a metal reinforcement (Fig. 4). As compared to the preceding model, the component considerably reduces the weight of the entire front-end module, consisting of the highly reinforced Ultramid B3WG8 by BASF. It substitutes a polypropylene hybrid component that had subsequently to be stabilized with sheets of steel. Here as well, the key to success was the Ultrasim simulation tool, which served to generate an optimized topology based on the main loading cases. Only little changes were necessary to make the component ready for serial production.

The replacement of high-quality plastics is more demanding, but (even more) attractive. With the performance of their polyamides constantly growing, PA suppliers are entering more and more areas previously dominated by other polymers. For example, Evonik found a new substitute material of polysulfon (PSU). Its Trogamid RS6121 is a transparent and steam-sterilizable polyamide with a density 20% lower than that of PSU. Steering in the same direction, Ems introduced to the market its new Grilamid TR material, which features a transparency similar to that of polycarbonate, but with a stress cracking resistance significantly higher. The material includes another benefit that shows when mixed with black pigments; this yields a basic material for the production of highly brilliant components.

A Variety of Flame Retardants

Polyamide is used for demanding plastics components in the area of electric and electronics if these applications require good isolation, high resistance to chemicals and heat, as well as particular mechanical properties. Many of these components also have to meet demanding specifications in terms of safety and flame retardancy, e.g. electric equipment for industrial and building wiring, photovoltaic systems, consumer electronic units, and, most of all unattended household appliances. This is why they need to be equipped with flame retardants.

Unlike other material classes, polyamides are used with many different flame retardants today. The usual systems are based on halogen/antimony compounds, in addition to additives containing red phosphorus, organic phosphorus

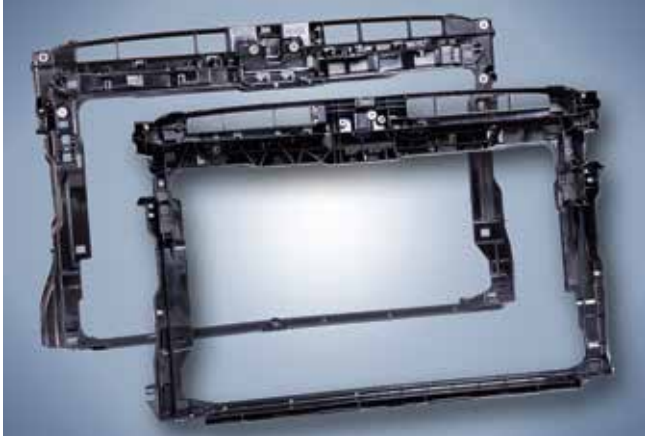


Fig. 4. The front-end cross carrier of the new Golf 7 consists entirely of Ultramid B3WG8. Other than in the previously used polypropylene component, no metal reinforcement is required here



Fig. 5. Switchgears of Ultramid A3X make the electrical function permanently and highly reliable

or nitrogen, or metal hydroxides. One of the major flame retardants for polyamide 66 is red phosphorus. Thanks to its high efficiency, the retardant shows good fire behavior as well as excellent mechanical properties, even at relatively low filling degrees (**Fig. 5**). BASF is enhancing their portfolio in this area. For example, a long-glass-fiber-reinforced A3X type has recently been made available, providing for high strength even at low temperatures, and low creep at high temperatures.

However, its color makes the red phosphorus unsuitable for light-colored plastics products, which is why most polyamide suppliers offer alternative solutions.

In case the component is required to feature free colorability and good suitability for state-of-the-art soldering techniques with lead-free solder at high temperatures, users may apply partly aromatic polyamides such as Ultramid T KR 4340 G6 by BASF, based on color-neutral organic phosphorus compounds. Starting from 0.4mm wall thickness, the material reaches V-0 according to UL94, and 5VA, starting from 1mm. What is more, it fulfills high requirements considering glow wire and creep resistance.

DSM also added a suitable flame retardant to its heat-resistant polyamide 4T, to make it ready for the UL94-V0 standard (Stanyl ForTii). It reaches this classification at only 0.2mm wall thickness.

Renewable Raw Materials

Most of all, bio-based polyamides have lately attracted the attention of experts. Numerous suppliers today offer different types of polyamides based on castor oil that serves as a basis for sebacic acid, i.e. for the respective diamine. Some of these suppliers are Arkema, DuPont, Ems, Evonik, Radici Group in Gandino, Italy, and BASF.

Even if the general trend to become independent of fossil sources of raw material is perfectly understandable today, the actual significance of biobased polyamides severely lags behind the attention it is given. Their production volumes are still relatively small, making bio-based »

Fig. 6. Bio-based polyamides help enhance the raw material basis, and complement the existing PA portfolio. A. Raymond's quick connectors are one example of a successful application



polyamides more expensive, in most cases, than their competitors based on crude oil. Often, the question is ambiguous, or hard to answer, whether polyamides based on renewable raw materials are in fact more sustainable than other types – in particular, if considering factors such as landscape consumption, use of fertilizers and water, transport, working conditions or the competition with food production. Variations in the qualities of the natural raw materials can cause difficulties in the production of the polymers, and, also subject to the respective crop yield, cause severe variation in the cost of the raw material. In some cases, suppliers replace established materials that have, for years, proved well-suited for demanding applications. After all, customers must be convinced of the new products. At the same time, standards and specifications may be a huge challenge for the new class of materials to meet.

Nevertheless, enhancing the basis of raw materials suitable for polyamide production and investing in renewable raw materials can be a good idea because, in addition to improving the security of energy supplies, this may yield new polyamides with interesting properties. For example, Evonik recently started operation of a pilot plant for the production of amino lauric acid (ALA) from palm kernel oil. ALA is a precursor of PA12. Several suppliers added a PA1010 to their portfolio, which is entirely based on castor oil, and features a property profile that fits in the gap between PA12 and PA6 or PA66, respectively.

In addition, applying renewable raw materials is justifiable, in particular, if there is no alternative petrochemical access to the monomer, or if specific engineering requirements such as reduced water absorption or improved stress cracking resistance make it necessary to employ these materials. An example of an application with property profile as the decisive factor of material selection is the fuel quick connector (**Fig. 6**) of A. Raymond SCS in Grenoble, France, made of Ultramid S3WG6 Balance by BASF. Thanks to good stress cracking and fuel resistance, the material easily passed the demanding tests typically required for automotive applications, which are usually reserved for PA12-based components.

Concept of Sustainability

In addition to Ultramid Balance and many other products based on renewable raw materials, BASF has recently started an entirely new approach called the Mass Balance method. Together with TÜV Süd, Munich, Germany, BASF developed this concept for the application of renewable raw materials. The process is immediately

available for many products, and can be flexibly adapted to customers' wishes. Biomass is used as a feedstock in the production of basic products on existing plants, here. Following the new certified process, this bio-based share is then allocated to the sales products according to their respective formulas. The quality of the products remains unchanged.

The products mass balanced in this way save fossil raw materials, diminish greenhouse emissions, and can boost sustainable development. Up to 100% of fossil raw materials can be replaced in a final product, which can then be marketed correspondingly. Existing equipment and technologies along the value chain can be used as before, and product formulas and specifications of customers do not need to be adjusted.

High-Quality Surfaces

Over the past years, developers and product designers have shifted their focus on component surfaces. Demand has increased for plastics that do not have to be treated after demolding. Here, as well, the latest polyamide variants can help to reduce costs – as is the case with the back-



Fig. 7. One of the first serial products of the Ultramid SI series is the swivel office chair MOVYis3 created by BASF, together with furniture producer Interstuhl. The backrest is made of Ultramid B3EG4 SI, combining valuable surface appearance, sleek component design and high load-bearing capacity

The Authors

Dr. Matthias Scheibitz is head of the product development team concerned with Ultramid at BASF SE in Ludwigshafen, Germany.

Dr. Jens Cremer is a product developer for Ultramid at BASF SE, Ludwigshafen.

Service

Digital Version

» A PDF file of the article can be found at www.kunststoffe-international.com/909228

German Version

» Read the German version of the article in our magazine *Kunststoffe* or at www.kunststoffe.de

rests of driver and front passenger seats in the BMW i3 (**Title figure**). This hybrid component is 2 kg heavy and consists of a UV-stable PA6 compound by BASF (type: Ultramid B3ZG8 UV): The material not only provides the necessary elongation and strength. It moreover shows an attractive, scratch-resistant surface that does not have to be varnished.

BASF has developed a portfolio of surface polyamides consisting of four special Ultramid types: Ultramid SI (Surface Improved). It will push the limits of design in terms of aesthetics, stability and surface quality. This novel polyamide links the engineering properties typical of PA to extraordinarily sophisticated surface appearance, thus meeting the highest requirements of furniture manufacturing. The four types are equipped with different properties, e.g. flame retardance. One of the first serial products of the Ultramid SI series is the swivel office chair MOVYis3 created by BASF, together with furniture producer Interstuhl (**Fig. 7**).

Ems-Grivory also offers a product series for visible components: The highly filled Grivory GVX (with up to 70% GF content) was designed as a substitute material for metals. It has a low tendency to warp, and its flowability was improved, which is why the material yields good surface qualities without streaks. Leona 90G60 is the name of the new surface-optimized polyamide by Asahi Kasei Plastics in Fowlerville, Michigan, USA. The material is a glass-fiber-reinforced partly aromatic polyamide (66/6I), which is outstanding for its delayed crystallization behavior. This enables high-quality class-A surfaces, despite a high fiber content. DSM recently presented two UV-stabilized PA6 types (Akulon) designed for the production of exterior mirror casings and vehicle door handles, which do not have to be varnished after production.

High-Temperature Applications

In this area, polyamides are finding their way into applications that used to be dominated by heat-resistant high-performance plastics. Slowly but surely, charge air temperatures of high-performance engines are moving towards the 230-centigrades-mark – while, ten years ago, these temperatures were usually around 200°C. One can assume that the Euro 6



Fig. 8. One of the most heat-resistant, polyamide-based injection molding materials on the market is now also available as a blow molding type: Ultramid Endure D5G3 BM can withstand temperatures up to 220°C in permanent operation

standard will lead to another increase in temperature. This is the point when aliphatic polyamides will have reached the limits of their capacity. Most of all, materials based on modified polyphthalamides are thus supposed to prove superior to other high-temperature plastics such as PPS.

Solvay enhanced its range of polyphthalamides by adding two new high-temperature resistant types for application in the engine compartment: Heat ageing tests on these two PPA variants yielded results better than those for PPS. Ems-Grivory developed Grivory HT-2VS-HH, which is a modified PPA variant that features almost constant tensile stress at 250°C over 3,000 h, while its stress-strain behavior corresponds to that of PPS.

But also aliphatic polyamides offer good options at long-term service temperatures up to 220°C. A good example is a heat shield used in the charge air distributor of Daimler's four-cylinder engines. The aluminum sheet hitherto used was replaced with a corresponding component made of Ultramid Endure D3G7 supplied by BASF. The material can be processed in a way similar to PA66. Its special stabilization technology prevents premature heat ageing as a result of reaction with oxygen, which makes the material resist 220°C permanent load and peak loads up to 240°C. As a result, among injection molding materials on a PA basis, it is considered as one of those with the highest heat resistance.

BASF, with its Ultramid Endure D5G3 BM, now also has a blow molding type on the market with a respective heat resis-

tance (**Fig. 8**). This material will make it possible to efficiently produce the pipes in the charge air ducts between turbocharger and charge air cooler. Under the name of Stanyl Diablo OCD 2305 BM, DSM also brought to the market a polyamide 46, which is supposed to fit blow molding and withstand temperatures of permanent use of up to 230°C. The low density of hot air ducts made of this material help to save further weight as compared to PPS variants.

Conclusion

The trend towards constantly refined polyamide compounds with ever-increasing performance will continue in the next years. Polyamides will also continue to stimulate (automotive) lightweight construction, with major surprises expected to come from long-fiber-reinforced components and continuous-fiber-reinforced structures, most of all. In the future, lightweight construction will be the domain of smart material combinations, with thermoplastic materials such as polyamides featuring a vast number of benefits over thermosets. Interesting developments are taking place, too, with heat-resistant polyamides. Partly aromatic polyamides are expected to find a growing number of applications in the future.

The coming years will show which of the PA types currently being introduced at the market will finally succeed, or even grow to be the new standard. The material class of polyamides will maintain its outstanding significance for the world of plastics. ■