**Dynamic Development.** In the past three years, the material class of compound polyamides has developed with great dynamics, just as its markets have. At the K2010 plastics trade show, producers of polyamide presented a large number of new products and applications, especially (but not only) for automotive construction. On the one hand, these new developments are determined by the trend towards lightweight construction which has become even stronger as a driving force for automotive industry – especially considering the issue of electromobility. On the other hand, many specialties are being developed for independent applications in entirely new fields, and this shows the large potential for innovation included in the polyamide material family.

**Polyamides (PA)**

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Considering PA6 compounds, BASF SE in Ludwigshafen, Germany, DSM Engineering Plastics B.V. in Sittard, Netherlands, and Lanxess AG in Leverkusen, Germany, remain some of the major suppliers of compounds, whereas DuPont in Wilmington, DE/USA, Rhodia S.A. in Saint-Fond, France, and BASF are leaders in PA66.

Almost every supplier expanded capacities or announced to do so; and this was before, but mainly after the economic crisis, with demand having recovered from the downturn amazingly fast. BASF is expanding its compounding plants in China and Korea, and is about to start a first stage of expansion in Europe. DuPont has plans for enhancement in Asia, Lanxess will do the same in the USA, India and China. Rhodia will create new capacities in China, South Korea, India and Brazil. Invista S.à.r.l., situated in Wichita, KS/USA, has moreover announced to enter the PA compound business in Asia, North and South America. PlasticsEurope association found out that — following the high rate of 12 % from 2009 to 2010, the global growth rate of PA considered as an average value over the past 25 years — which means despite many ups and downs — will amount to 6 % until 2015. Capacities for the production of basic polymers are due to rise correspondingly.

Nevertheless, even with these increased quantities available at the market, suppliers will be able to meet the higher demands only if they can provide the right products to satisfy customers’ higher requirements for customized solutions. Product designers therefore make great endeavor to find new material variants with highly specific property combinations.

This comprises brands that feature high stability to thermal and hydrolytic impact, high flowability, as well as flame retardant products. At the same time, the trend continues towards supporting the customer’s own development activity by means of computer-aided prediction methods. The Ultrasim tool by BASF, which is continuously being enhanced, is one example to show this process. The tool can do much more than just provide for virtual crash tests. It uses so-called integrative optimization, thus enabling designers today to optimize on the computer a component’s mechanical performance, as well as the boundary conditions of the injection molding process, at the same time. This is how high-quality products can be linked to superior support, to eventually obtain customized solutions.

Recently, a special polyamide with excellent heat stabilization and a competitive price was introduced, meeting the high demands of temperature posed to the charge air duct components of charged engines (all photos: BASF)
Automotive Construction: Reductions in Weight and Expenses

Engine: After 2007 the focus had been on high-speed polyamides – in particular easy-flowing materials – making mold filling much easier, especially of complex molds. However, a recent trend is currently obvious towards PA variants with a high degree of permanent heat resistance. Those components inside the engine compartment that originally used to be made of metals and could easily be replaced by plastics parts, e.g. engine covers, intake manifolds, or cylinder head covers, have meanwhile been exchanged for plastics parts, either entirely, or in part.

New challenges are emerging through downsizing and exhaust gas recycling constantly stepping up temperatures in areas close to the engine. Materials have to cope with permanent temperatures of more than 200°C, which means that only certain high-temperature thermoplastics used to be suitable here. Since K2010, BASF has offered Ultramid Endure for this application. It is highly resistant to heat ageing while featuring the good processing properties of PA66. Focusing on similar applications, more products have been made available, for instance Zytel Plus 95G35 from the Zytel Plus series by DuPont, or Stanyl DabolO OCD2100 by DSM. As part of its Grivory series, Ems-Chemie Holding AG, situated in Domat/Ems, Switzerland, also offers heat-resistant variants. In the spring of 2011, Radici Group SpA in Gandino, Italy, also announced a PA66 variant of the Radilon series, with low heat ageing. These materials are particularly suited for components found in the charge-air duct, such as charge-air cooler covers, resonators, charge-air pipes and intake manifolds. For slightly lower permanent temperatures (190°C), but high overpressure changes, BASF moreover offers Ultramid A3W2 G10, which has proved a suitable material for use in end caps of charge-air intercoolers for common rail turbodiesel engines (Fig. 1). Many of these components are produced by blow molding too. Until recently, air-charge ducts with integrated bellows have been produced by sequential co-extrusion techniques only, combining polymers of different flexibilities. Lanxess has now developed highly flexible polyamides such as Durethan DP BC 60 HTS, which do not need to be combined with other materials.

In case not only high temperature resistance is required, but also resistance to chemicals such as fuel or cooling agents, partly aromatic polyamides are used. The major suppliers of these material types are DuPont (Zytel HTN) and Ems (Grivory NT). However, BASF also offers a partly aromatic PA, i.e. Ultramid T. Low water absorption and outstanding dimensional stability make long-chain, partly aromatic, polyamides the appropriate material for lead-free soldering in the E/E segment (Fig. 2).

Suppliers of special polyamides have added partly aromatic products to their range of PA products too, for instance Evonik Industries AG in Marl, Germany, (Vestamid HT) and Arkema SA in Colombes, France, offering the flexible Rilsan HT designed for fuel systems. With an increasing number of vehicles using AdBlue, which is an aggressive urea solution employed to reduce NOx emissions, special polyamides with corresponding properties have recently been introduced for pumps, dosing units or filters. These materials comprise Ultramid A3EG7 AB (BASF) and Durethan AKV 35 H3.0 (Lanxess).

Car body: Online paintable plastics represent a particular challenge to suppliers and users. The thermal stability required, and a low CTE (coefficient of thermal expansion), will enable the component to cope with the 30 minutes of drying in the paint shop at 200°C. To meet these requirements, BASF developed Ultramid TOP 4000. This high-temperature polyamide is impact-modified, partly aromatic, mineral-filled and conductive, offering superior stiffness and dimensional stability. Considering the market situation, this polyamide is the car body material that features the most constant and the lowest CTE value over a wide range of temperatures (Fig. 3). Sabic Innovative Plastics Holding BV in Bergen op Zoom, Netherlands, offers
Noryl GTX, an alternative material for car body application. It was designed on a PA-PPE blend basis. Ineos Olefins & Polymers Europe in Grangemouth, Great Britain, moves forward with mineral-reinforced (PA+ABS) blends. However, for these materials, penetration of the automotive construction market is still low, because using them would call for profound changes to the process of vehicle painting.

Electrics/Electronics: Intelligent Solutions

Despite the crisis and of growth rates slumping, if considered over several years, automotive electronics is due to be a growing field of activity, because demands for reductions in fuel consumption and emissions, as well as for improved comfort and safety, will continue to increase. Intelligent electronic control is the main factor of success here, only just making potentials for saving and for certain functions possible, that used to be unthinkable several years ago. Considering automotive electronics, classical polyamide materials are mainly used for highly stressed mechatronic applications, e.g. gearbox control units, but also for sensors used in chassis, as well as certain plug-and-socket connectors. These materials’ main characteristics are their high chemical resistance to impact from substances such as oils, but also their mechanical tough behavior (Fig. 4), which is a typical feature of polyamide. Despite many discussions on the subject of flame retardant materials, no such general tendency exists in the automotive electronics area, at present. They are rather used for very specific applications merely, or by few automotive manufacturers, respectively.

Polyamide materials can be found more frequently in home electric wiring and industrial automation, in these cases with flame retardant effect. If compared to other material classes, many halogen- and antimony-free products are common among polyamides, or are being developed. They are based on a variety of different flame retardants, with their specific advantages and disadvantages. Red phosphorus is the main flame retardant for glass fiber-reinforced PA66 products. Thanks to its high efficiency, a low share is sufficient to achieve the required flame retardant classification, which maintains the compounds’ excellent mechanical property profile. Though researchers are undertaking elaborate investigations on other types of flame retardants, these properties are unmatched as yet, with PA. Photovoltaics manufacturers have recently started using BASF’s Ultramid A3X types for their products too. Additionally, these products show low smoke gas density and toxicity as well as very good electrical properties. With its eye-catching color, the red phosphorus cannot be used for final products in light colors, though. This is why many PA producers today offer halogen-free flame retardant types, including, for instance, certain phosphoric compounds in neutral colors, which can thus be colored in light shades. BASF also offers such new products, one of them being Ultramid A3U40G5. Based on PA66, this material achieves V-0 according to UL94 at wall thicknesses of only 0.4 mm, and easily meets the IEC 60335-1 standard ruling the requirements for domestic appliances.
BASF will introduce another new product at Fakuma 2011, i.e. Ultramid B3U30G6. This is a PA6 with flame retardant properties, designed for circuit breakers; it fulfills the requirements of the glow wire test without any difficulties, and is extraordinarily stiff. This property enables low wall thicknesses, thus opening up new options of design, in view of the available constructed space constantly growing smaller.

**Food Contact, Domestic Products and Aesthetics**

Apart from automotive construction and electrics/electronics, compound polyamides, with their benefits, have gained ground in many more areas of application. Furniture designers have recently discovered polyamides as an interesting, robust and versatile material for their design ideas. The Vegetal chair (Fig. 5) by the Bouroulllec brothers can serve as an example here. It is outstanding for its shapely design and special chromaticity, in addition to the fact that it is produced by GIT.

If the products are due to be in contact with food, polyamides need more specific admissions. According to EU regulation, it is necessary not only to select raw materials in a well-aimed way; in 2008 a regulation was established, demanding production to comply with GMP conditions. By the time being, several suppliers have introduced PA compounds that meet these requirements. Moreover, for household products which are in contact with food, providers and consumers wish for products with a shapely design. The cutlery “Join” (Fig. 6) was developed by the ding3000 design studio and consists of Ultramid A3EG6 FC, which was approved for food contact. The cutlery’s design is appealing and withstands the required loads, despite its centrally positioned openings. There is a vast number of examples showing that more and more industrial designers are discovering polyamide materials – and other engineering plastics, which is why BASF is further enhancing endeavors at their designfabrik assistance center.

In drinking water systems and sanitary installations, the trend towards replacing metal components by engineering plastics continues. In this area too, using these materials means a way of saving costs, integrating functions and generating complex geometries. A particular necessity of substitution is caused by new regulations, because there is often lead found in brass components, which is re-
garded as a risk to heath. Mainly polyamides certified for use with drinking water are employed here, e.g. Ultramid A3EG7 FC. The materials must meet high requirements regarding hygiene, migration and neutrality in terms of odor and/or taste, with the respective regulations differing significantly from region to region. A particular challenge is incurred in the demands posed to long-term resistance to hydrolysis at high temperatures, and in the resistance to chlorine that may be included in drinking water as a disinfectant. For especially demanding applications, mainly PPAs and their blends are available at the market (e.g. Grivory HT by Ems).

Polyamide for Building and Construction

Other than in vehicle construction, the reason for the increased use of engineering plastics in construction is less a matter of weight than of the option incurred to produce 3-D components by injection molding. Or users can make use of so-called thermal separation, which is made possible by the low thermal conductivity of the materials. One of the major challenges in this segment are the requirements of a long service life and high resistance to weathering. In this respect, more and more information is available from measurements and experience today, for instance, on the resistance of PA compounds to UV radiation and humidity, even over periods of more than ten years.

A relatively new working area in the construction segment is photovoltaics. Certain PA types are admitted for use in connectors and junction boxes of photovoltaic plants, such as Ultramid A3X2G7 or Ultramid A3XZG5 (Fig. 7). These types of materials can moreover serve for complete substructures of solar modules. BASF has been part of the team that developed a promising new product by Schott Solar in 2011. Together with the photovoltaics company, the enterprise developed a multifunctional pan for a roof-integrated solar module (Fig. 8), which can be fixed in a fast and safe way. It moreover provides for tool-free mounting of the PV modules. In spite of its size, which is 1.7 m², the component is produced by injection molding, because the Ultramid B High Speed material has excellent flow properties.

Prediction of Component Behavior

It has been several years now that BASF introduced the first PA materials that were optimized in regard to crash resistance. Featuring improved impact resistance and/or energy absorption, and a wide range of stiffnesses and toughnesses, the latest PA6 variants are designed for automotive construction mainly: just as their predecessors, for instance Ultramid B3WG6 CR, they are developed e.g. for lower bumper stiffeners. Such safety components would be far from meeting the high requirements regarding pedestrian protection and short development periods, without these new polyamides and the respective sophisticated simulation by Ultrasim. With PA66 applications, similar demands exist for structural inlays for the car body, e.g. for B-pillars or hatch doors. And finally, these types of materials have replaced numerous engine bearings, transmission supports and stabilizers formerly made of metals (Fig. 9) — a milestone in metal substitution under the hood, which used to be regarded as impossible some years ago.

Also in sectors other than automotive construction, these materials have been successful, for instance in highly-stressed safety components for firefighting (Fig. 10). Beside BASF, there are other suppliers looking into the CAE issue: Rhodia has introduced a CAE service named MMI*. Lanxess has also worked in this field for some time.

Improved Flowability: Longer, Better, Faster

Easy-flowing PA types have meanwhile improved too: BASF has added new PA6 types such as Ultramid B3WG6 High Speed and Ultramid B3ZG6 High Speed to its highly filled PA66 High Speed variants. The toughness-modified PA6 variant is used for products such as ax handles (Fig. 11), achieving improved surface qualities, apart from the reductions in cycle times thanks to the material’s enhanced filling behav-
ior. Using a ribbed component as an example, BASF has been able to show that, if demolding temperature and injection pressure are kept to a constant level, cycle times can be reduced by up to 25%. Basically all suppliers work on the issue of flow improvement, i.e., BASF, as well as Lanxess, DSM and Rhodia.

**High Load: Long Glass Fibers and CAE**

If the aim is to make optimum use of engineering plastics’ main advantage – i.e. its performance together with its low weight – then they will have to replace more metals: this is why BASF has entered the market for long fiber-reinforced (LF) polyamides with its Ultramid Structure product series in 2010. These materials feature outstanding mechanical performance, if compared to short glass fiber-reinforced compounds, which is due to the 3-D glass fiber network that forms during injection molding (Fig. 12). One of these particular properties is significantly improved energy absorption under high dynamic stress, which is one of the features required for vehicles in a crash situation. These types of materials are provided by Celstran GmbH, Kaiserslautern, Germany, and RTP Company in Winona, MN/USA, and, most of all, Ems, which offers grades such as Grivory GVL-5H, with – similar to Ultramid Structure B3WG10 LF – an energy absorption several times as high as that of standard types. The glass fiber network also affects long-term behavior: it generates a higher creep modulus and higher resistance to long-term alternating stress (Wöhler curve), which represent the improvement achieved. What is more, BASF’s universal Ultrsim simulation tool today enables the user to calculate and predict the behavior of such demanding components on the computer: This is a type of support that was not available as yet in the LF-polymide market in this comprehensive form.

**Environmental Aspects**

“Organic” or “bio” is on everyone’s lips – and this not only refers to packaging plastics today, but also to demanding engineering plastics such as polyamides. At least in their considerations, producers regard materials based on renewable raw materials an interesting issue. As one of these materials, BASF offers Ultramid Balance, a PA610 with its C10 share of sebacic acid obtained from caster oil. The main share of this product thus consists of renewable resources – just as the products offered by Arkema (PA11), DuPont (PA610), Ems (PA610, PA10T, etc.), Rhodia (PA610) Radici (PA610) or DSM (PA410).

PA610 offers engineering properties that are different from those of PA6, which is why it is interesting to users. Its characteristics include low density and reduced water absorption, but also hydrolysis resistance and stress cracking resistance to aggressive chemicals such as water spray containing calcium chloride and zinc chloride. With its property profile, it can serve as an alternative to PA12, for some engineering applications. This comprises injection molded components, as well as extruded pipes, for instance media ducts in cars.

Development of more 100 % bio-based products, apart from PA11, is in fact technically feasible. So-called drop-in solutions are considered as providing the best chances for fast and durable market penetration: if the basis of existing monomers, as used in classical polyamides, could be exchanged for a basis of renewable raw materials, the known and estimated polyamide properties would be maintained. New start-up businesses are undertaking research on obtaining the two major components of PA synthesis – caprolactam (PA6) and adipic acid (PA66) – from animated nature. Even here, it is essential to draw up an overall balance corresponding to an eco-efficiency analysis, to show whether the solutions are in fact economically compatible, and which ecological benefit they finally provide. For most engineering plastics, crude oil is still inevitable as a source of raw material.

**Conclusion**

More and more polyamide compounds will be part of customized solutions in engineering in the years to come. This includes materials with specially tailored properties that will replace more metals, but also those applications that would be impossible with metals in this form. This also applies to sectors totally different from automotive construction and E/E. Comprehensive support in terms of CAE and testing is connected to these special materials, because this is the only way to face the high pressure on costs and time that exists throughout the entire supply chain.

In lightweight construction with increased load on components, the next big step will lead to enhanced application of organosheets and unidirectional (UD) tapes. The most sophisticated and innovative components are obtained where suppliers and users of plastics materials work closely together. The market for polyamides thus grows in terms of size, but, most of all, quality, opening up options for new products and business models.

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