

Above-average Growth. Thanks to its outstanding mechanical, chemical and tribological properties, polyoxymethylene (POM) can bridge the gap between plastics and metals. Its field of applications is broad – from automotive through electrical and electronics, consumer goods and the food industry right up to medical technology industry. New developments such as low-emission grades, metal-detectable grades, grades subject to special quality controls and high-impact types are opening up further fields of application. Consumption is rising rapidly – particularly in China which is experiencing an estimated average increase of 7 % per year.



Autoliv produces these bearing plates for seat belt retractors from a low-emission and impact-modified polyacetal homopolymer from DuPont. This combines the demand for high-impact resistance with additional noise-damping properties (figure: DuPont)

Polyoxymethylene (POM)

Polyoxymethylene (POM) is a semi-crystalline thermoplastic available as a homopolymer or copolymer which can be processed by injection molding or extrusion. The first POM homopolymers were commercialized by DuPont in 1956 under a brand name that is still used today – Delrin. They are produced by direct polymerization of formaldehyde

and achieve typical degrees of crystallinity of 55 to 60 %. POM copolymers (e.g. Hostaform from Ticona GmbH, Sulzbach, Germany; Ultraform from BASF SE, Ludwigshafen, Germany) are produced by the copolymerisation of trioxan with dioxolan and offer degrees of crystallinity of 45 to 50 %. They have a slightly (approx. 10 K) lower melting point.

The Properties

Common to all types are high hardness and good mechani-

cal properties (POM offers the highest stiffness and strength of all non-reinforced conventional engineering plastics), very good dimensional stability, a low coefficient of friction and very good wear resistance, together with good dielectric properties. While copolymers have high resistance to alkaline media, fuels (including biodiesel) and hydrolytic exposure, the homopolymers are characterized in particular by their very high stiffness, strength and creep resistance as well as their high resistance to fatigue.

Due to the special combination of mechanical properties that cannot be offered either by metals or by most other plastics, POM is establishing itself in a growing number of applications. More and more impetus is coming from the automotive industry where POM is increasingly contributing to weight savings through the substitution of metals.

POM is supplied as compounds that are formulated to meet specific demands. These include impact-modified, UV-stabilized, wear and fric-

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tion-optimized, filled and reinforced, anti-static or electrically conductive grades and, to an increasing extent, low-emission types that satisfy the most stringent demands of the automotive industry for use in automobile interiors. In recent years both homopolymers and copolymers have been developed for use in the food and health care sector where production is subject to special monitoring and documentation.

Manufacturers and Capacities

The global demand for POM has been growing more or less constantly for years, and in 2012 reached an estimated mass of 1,040 kt (Fig. 1).

This growth, however, shows a very different picture when viewed by region. In Europe it is currently around 3 %, but in China it is currently over 7 % because of the relocation of electronics production facilities and the strong growth in the country's automotive industry. China is now also the largest consumer worldwide, followed in 2nd and 3rd places by Europe and the USA. The largest consumer in Western Europe is Germany with over 50 % (Fig. 2).

In line with the consumption, China has also developed into the largest producer of POM with a capacity of 445,000 t/a, followed by the production facilities in Europe (Germany, Netherlands

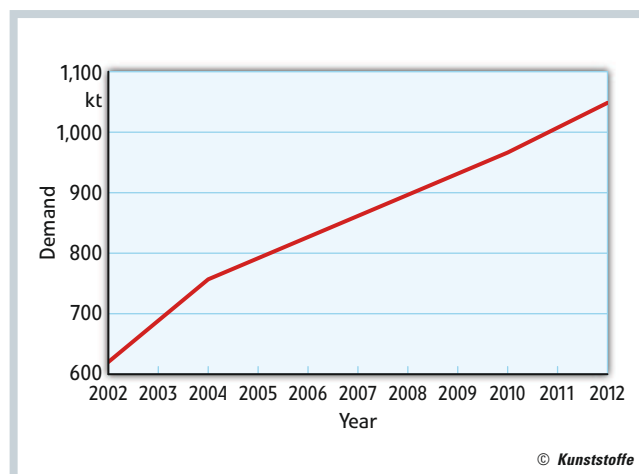


Fig. 1. Development of the worldwide consumption of POM homopolymers and copolymers (estimates by DuPont)

and Poland) with together some 300,000 t/a and the USA and South Korea each with 180,000 t/a (Fig. 3).

If we consider the breakdown of the capacities by producer, a certain shift can be seen over the last three years. In 2010 the three largest producers, Ticona, DuPont, Wilmington, DE/ USA, and Polyplastics Co. Ltd., Tokyo, Japan, shared more than half of the world's capacity. Although these three still hold their leading positions, their total share of the worldwide POM capacities has fallen – to around 47 % despite the successful commissioning of the new Ticona POM plant, with 140,000 t/a the world's largest, in the Industrie-Park Hoechst, Germany, in 2011.

This shift resulted from new installations, including a 60,000 t/a plant at Shenhua Group Co. Ltd., Beijing, China, and a 40,000 t/a plant at

Tianjin Bohai Chemical, Tianjin, China, commissioned in 2011, coupled to capacity expansions at the Yunnan Yuntianhua Co. Ltd plant, Shuifu County Zhaotong, China, by 20,000 t/a to reach 105,000 t/a and at the Kolon Plastics Inc. plant in South Korea by 40,000 t/a to reach approx. 60,000 t/a in 2012 [1].

Further significant increases in capacity are to be expected in the near future:

Mitsubishi Gas Chemical (MGC) Co. Inc., Tokyo, Japan, and Celanese Co., Irving, TX/USA, have reached an agreement to expand the production capacities for POM at Korea Engineering Plastics Co. Ltd. (KEP, a joint venture between Tongyang Nylon (Korea), MGC and Mitsubishi), Seoul, Korea, by 35,000 t/a to reach 140,000 t/a by 2014.

MGC is planning to expand the capacities at its Thai sub-

siary, Thai Polyacetal Co. Ltd., Bangkok, by 55,000 t/a to reach 100,000 t/a in 2013.

Polyplastics is also planning to expand its POM facility in Malaysia by 90,000 t/a in 2014. In total Polyplastics will eventually have a capacity of 290,000 t/a at its four production plants in Japan, Taiwan, China and Malaysia.

In mid-2013, the Japanese chemicals company Asahi Kasei Chemicals Co., Tokyo, reached an agreement with DuPont on the acquisition of the shares in the joint venture Asahi-DuPont POM Zhangjiagang (ADZ) Co. Ltd., Zhangjiagang, Jiangsu, China, in which both companies had previously held equal shares. DuPont will continue to supply the Chinese market with POM homopolymers from its production site in Shenzhen.

Application-specific Material Developments

The most widely used POM variants are the universal types that are available in different viscosities and therefore cover a broad spectrum of demands from a processing perspective – from thin-wall injection molding through to extrusion. In the case of the POM homopolymers from DuPont, the materials range from, for example, the easy-flow 900 Series grades (MFR_{190/2,16} to approx. 25 g/10 min) for delicate parts, long flow paths and low wall thicknesses up to the 100 Series grades

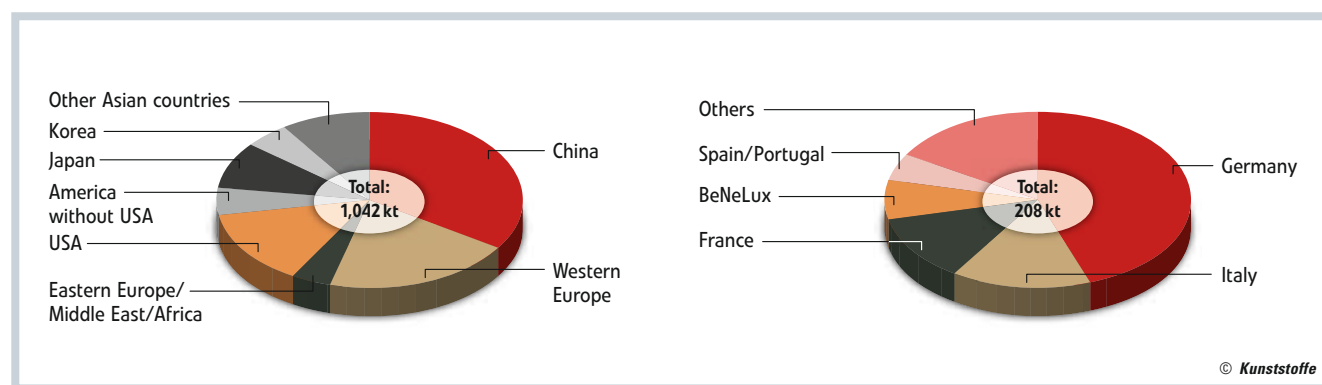


Fig. 2. Breakdown of the worldwide consumption of POM by region: World (left), Europe (right) (current estimates by DuPont)

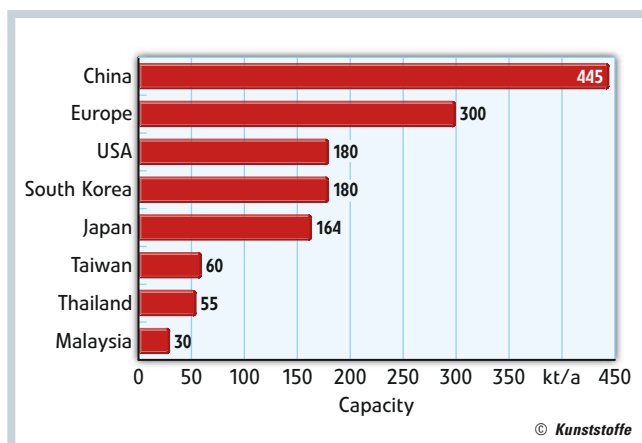


Fig. 3. POM capacities by region ([1], 2013 figures)

(MFR_{190/2,16} approx. 2.5 g/10 min) and grades for extrusion (Type 150). Some producers also have grades from this segment for rotation molding, physical foaming or gas and water injection process (GIT/WIT) in their portfolio.

Depending on the intended application, the use of different fillers, reinforcing materials and additives is possible. Starting from the non-reinforced grades, the range extends through impact-resistant and super impact-resistant modified grades, UV-stabilized, friction and wear-optimized grades, glass-filled and fiberglass-reinforced grades to low-emission types. Some variants offer hot-diesel resistance, electrical conductivity, detectability using metal detectors or laser marking capabilities, others a higher crystallization speed, dimensional stability or creep resistance. Furthermore there is a trend right across the range towards special grades for medical engineering applications.

Low emissions for automobile interiors: A central question in conjunction with the use of POM in automobile interiors is the aldehyde emission for which German and increasingly Asian OEMs set strict limits. The lowest limit at present comes from German OEMs at 2 mg/kg. All producers of POM have therefore developed low-emission grades and have delivered a

number of variants for special demands to the market in recent years.

DuPont, for example, introduced three heat-stabilized POM grades with Delrin 100PE, 300PE and 500PE. In these grades, a “formaldehyde scavenger” ensures that the emission of volatile substances lies well below the lowest admissible value without having to make compromises on the mechanical properties or the creep and fatigue resistance compared to the corresponding standard grades. Their typical applications include parts for safety systems, door linings, adjusters and seat elements.

A current application for Delrin 100PE is stop elements for steering columns which absorb the impact when the columns reach the limits of their longitudinal adjustment (Fig. 4). Crucial aspects for the choice of this material were not only the low emissions and the generally good mechanical properties, but also the vibration-damping effect of the material, its high notched-bar impact strength and its very good sliding properties.

Apart from the heat-stabilized grades, highly impact-modified and low-emission POM grades are now also available on the market, such as the new Delrin TE types from DuPont. Measurements of samples of Type 300TE, for example, →



Fig. 4. A small spring element of the particularly low-emission Delrin 100PE from DuPont damps the impact when steering columns from ThyssenKrupp Presta reach their stops during longitudinal adjustment
(figure: DuPont)

showed formaldehyde emissions of 1.0 mg/kg and less. Applications range from large visible parts through to miniature functional parts such as clips, levers and gear wheels as well as applications in the automotive interior, including

those in cabin, which have to withstand high impact loads. The **Title figure** shows a current application of Delrin 300TE where not only the high impact resistance, but also the higher damping properties – thanks to the impact modifi-

cation – as well as acoustic and mechanical vibrations led to the choice of this material.

The producers of POM copolymers also offer low-emission types. These include, for example, the new Hostaform/Celcon XAP2 product family from Ticona. The producer quotes a specification limit of less than 2 mg/kg for non-pigmented natural grades. One example of this is the easy-flow Hostaform C 27021 XAP² grade, which was specially developed for parts in automotive interiors. At BASF the low-emission grades are identified by the suffix LEV. With Ultraform W2320 U035 LEV,

ical technology: For medical technology equipment, surgical instruments and for apparatus engineering in the diagnostic and pharmaceuticals industry, some POM producers offer special polyacetals, which are subject to particularly stringent quality control measures and in some cases are even produced on separate production lines. The intention here is to ensure the availability in the long term without making changes to the plastic formulation, which may be stored in a drug master file (DMF) at the FDA (Food Drug Administration). The materials are produced in accordance with good manu-

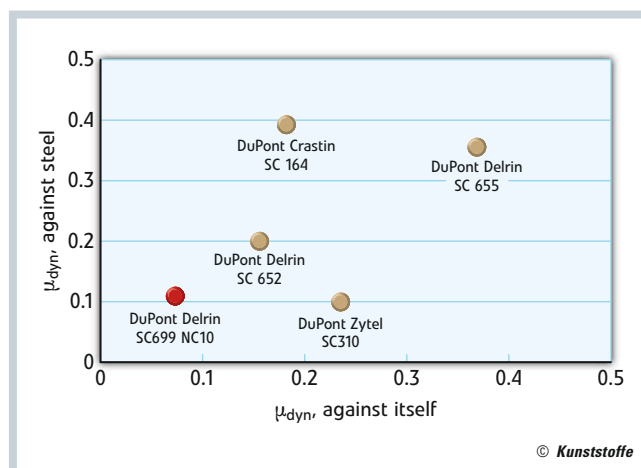


Fig. 5. The comparison of a number of Special Control plastic types intended for medical engineering applications shows the special position held by the new Delrin SC 699 polyacetal, whose typical dynamic coefficient of friction – both for movements against itself and against steel – is only approx. 0.1 (depending on the pv value) (figure: DuPont)

for example, the company offers a UV-stabilized, easy-flow and rapidly solidifying POM copolymer for injection molding or, with N2650 Z6 LEV, an elastomer-modified POM with very high toughness and low rigidity. Examples from the Asian market include the very low-emission Kocetal POM copolymers from Kolon Plastics and the POM-LOF types introduced by the Korean joint venture Kepital (Korea Engineering Plastics Co. Ltd.), Seoul, in 2010.

Uniformity and purity for pharmaceuticals and med-

facturing practice (GMP) and generally satisfy the requirements of the European Food Safety Authority (EFSA) and FDA for contact with food and, depending on the product, the United States Pharmacopeia and ISO 10993-5 and -11 and USP Class VI. Certificates on the absence of heavy metals in accordance with the American Coalition of Northeastern Governors (CONEG) of 1 January 1994 and with EU Directive 94/62/EEC can also form part of the extensive packages of services from the individual producers.



Fig. 6. For the laser-marked adjusting sleeve of the UnoPen disposable injector pen, Ypsomed uses the new, particularly low-friction Delrin SC 699 polyacetal

(figure: Ypsomed)

These special grades are available in two versions from DuPont, both of which are formulated for the demands of a large number of medical-technology products not intended for implantation. Very high standards with respect to product uniformity apply to the production of the Special Control (SC) types. The Premium Contorl (PC) types satisfy even higher demands. Their production and properties are more intensively monitored, and their listing in the drug master file is ensured. Both product ranges include medium- to high- or easy-flowing Delrin POM homopolymers, also in nucleated or friction and wear-optimized versions.

In combination with additional substances such as certain additives for internal lubrication or PTFE fibers or micro-powders, aramid fibers or silicon oils, the coefficient of friction of the polyacetal against itself and against other plastics and metals can be significantly reduced. This makes it possible to eliminate external lubricants, a crucial aspect in the food and pharmaceuticals sector. At the same time, the service life of parts subject to tribological loads can be maximized with such compounds.

One such special medical technology grade, internally lubricated with silicon oil, has been recently launched by DuPont – the particularly low-friction and low-wear Delrin SC or PC 699 (Fig. 5). This material was developed for precision injection molding of reliable, durable and

movements between two surfaces can be more or less eliminated.

The Swiss company Ypsomed AG, Burgdorf, is one of the first producers to use the grade SC699 for the adjusting sleeve of the UnoPen, a disposable pen with variable dosing for manual injection of insulin or other drugs from a prefilled glass vial (Fig. 6). The adjusting sleeve allows easy setting of the desired insulin dose. It is mechanically connected to the metering thread which ultimately ensures the

dispensing of the required dose. For this application, the material was made laser-markable by means of a corresponding additive in order to be able to apply a clear, high-contrast scale.

For several years now, BASF has been offering POM copolymers for medical technology applications with various types from its Ultraform PRO portfolio. BASF now also has an easy-flow (or “high-flow”), internally lubricated variant for particularly high tribological demands with its →

Ultraform W2320 003 PRO TR. Type N2320 003 PRO has been in the range since 2011. This impact-resistant injection molding grade, which offers higher viscosity, is suitable for the production of thick-walled parts which at the same time make high demands on the mechanical load-bearing strength, such as functional parts in insulin pens, atomizers or dry-powder inhalers. The type H4320 PRO introduced at the same time has an even higher viscosity and is designed for processing by extrusion with high production speeds. The applications targeted here are plug-in connectors, handles for surgical instruments and parts manufactured from semi-finished components.

At Ticona the grades corresponding to the SC and PC types at DuPont and to the PRO types at BASF bear the suffix MT. The portfolio includes impact-resistant, easy-

flow standard types and low-friction PTFE powder-filled or modified grades, optimized for low noise development, wear and/or flowability. Hostaform MT 8U05 contains a special additive that permits simple and reliable inspection of parts under UV light. Optical UV sensors allow complex assemblies such as dry-powder inhalers or other drug dosing systems to be checked for the presence and proper installation of all the components even during the assembly process. Finished product scrap can thus be reduced, the costs of production significantly lowered and plant productivity increased. The use of UV-detectable polymers in OEM parts also allows counterfeit products to be identified.

For contact with food: The majority of the POM types from all producers are approved for contact with food. Products available extend



Fig. 7. The Swedish producer WeLoc uses a metal-detectable polyacetal homopolymer from DuPont for a new range of film bag clips for the food industry (figure: DuPont)

from non-reinforced standard types with different viscosities through to application-specific optimized special types. Such materials generally satisfy a large number of regional and international regulatory demands, such as the FDA, European Regulation (EU) No. 10/2011 (Food Contact for Plastics) and European Regulation (EU) No. 2023/2006 (GMP). Typical applications include conveyors and metering systems, knives, scoops and scrapers as well as forms and molds for chocolate, etc.

Detectability is one of the development focal points for POM applications intended for contact with food. The demand for detectability rises with the increasing substitution of metal parts with those made from lightweight, low-friction and low-wear (even without lubrication), low-noise and corrosion-resistant POM. At the same time the users want to continue to work with the conventional metal or X-ray detectors used

for quality control, therefore correspondingly modified POM types are needed.

DuPont recently introduced two polyacetal types which meet these demands: Delrin FG400MTD BLA079 (FG = Food Grade) is a medium-viscosity POM for injection molding applications that is filled with metal powder and can therefore be identified using metal detectors. Parts made from medium-viscosity naturally colored Type FG400XRD NC010 can be identified using X-ray detectors. In both cases 3 mm cube particles can be detected using the conventional equipment. Ticona has a POM copolymer that can be identified using metal detectors in its product portfolio under the name Hostaform C 9021 MD.

A current application of the detectable POM homopolymer types is the clip for film bags produced in various sizes by the company WeLoc – Weiland M. AB, Smålandsstenar, Sweden, which are used i.a. in



the food industry for resealing bags that have not been totally emptied (**Fig. 7**). Reasons for the choice of material were not only the detectability, but also the very good suitability for the snap fastener mechanism and the unrestricted function even at -50°C .

Reduced friction and lower wear: Transport systems for the food or pharmaceuticals industry offer huge application potential for POM. While the detectable types are used predominantly in the food industry, special friction and wear-optimized types are also used for example in high-

BASF is Ultraform N 2310 P as a universal grade for injection molding. Examples from the extensive portfolio of highly wear-resistant POM copolymers from Ticona are Hostaform LW15EWX which also has good weld strength, and the silicon oil-modified type LW90BSX optimized for POM-POM friction pairings.

Typical applications of POM include slat-band and flush-grid belts which, thanks to their damping properties and the low friction of the food grade types used here, can be operated up to 80 % quieter than comparable

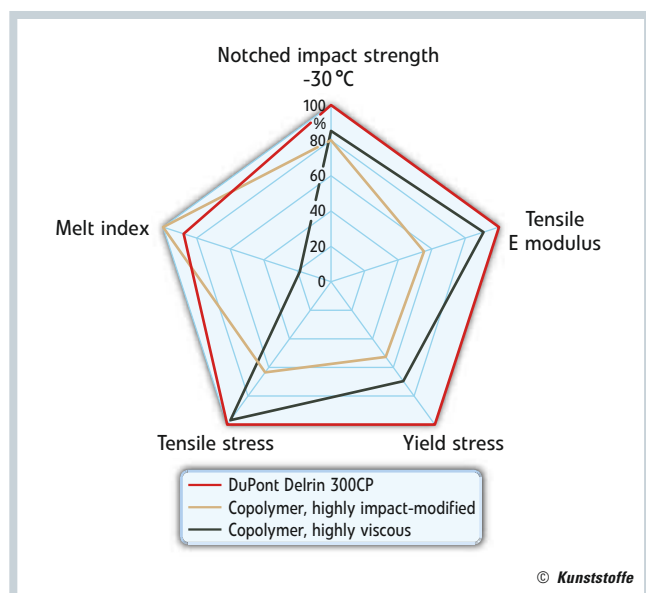


Fig. 8. A POM homopolymer from DuPont combines a very high low-temperature impact resistance and very good mechanical properties with very good processability (figure: DuPont)

speed bottling plants. Typical POM types from DuPont for this application include the non-reinforced standard type Delrin 511P, the multi-purpose type 500AL with its special lubricant modification, the PTFE micropowder-modified type 500TL with its low coefficient of friction and increased resistance to wear in slide pairings with steel or with itself, and the high-viscosity Kevlar brand fiber-modified and therefore extremely abrasion-resistant Type 100KM.

A corresponding friction and wear-reduced type from

metal belts. Furthermore they can be up to 40 % lighter so that the drive power can be reduced or the conveying speed increased. The high abrasion resistance and very good sliding properties of the material allow a practically contamination-free and low-maintenance use without lubricants, enabling use under high hygiene demands in the food, beverages and packaging industry. The high corrosion resistance also permits the use of highly effective cleaning media which either precludes the use of metal chains or makes cleaning →

far more maintenance-intensive.

High impact resistance and easy processing: A specialty from DuPont is the homopolymer type Delrin 300CP which combines very high processing efficiency with very good mechanical properties otherwise only offered by polyacetal copolymers with significantly higher viscosity (Fig. 8). Versions available in natural and black have high rigidity, strength and extension values, very good low-temperature impact

resistance and very good creep and fatigue resistance. The Charpy notched impact resistance of 10.5 kJ/m² at room temperature declines only to 10 kJ/m² at -30°C. This value can drop significantly with specially impact-modified copolymers in this temperature range (e.g. from 13 to 8 kJ/m² with a highly impact-modified copolymer).

The high yield stress coupled with high rigidity and high creep resistance also offers a wide range of possibilities for the production of re-

silient elements subject to permanent load. Under high load, comparatively high flow path lengths or low wall thicknesses can be achieved, thus reducing material consumption. At the same time, the lower viscosity melt supports the formation of high-strength weld seams, indirectly simplifying mold optimization, for example through the use of several gates. Thanks to its high heat distortion temperature and better mechanical properties, 300CP can be used for higher temperatures

than comparable copolymers. Potential applications include fasteners, components for seat belt mechanisms, levers, clamps, gear wheels and switches in automobiles, buckles, straps or protective caps for sports articles, fittings for doors and windows, parts for water systems in the domestic and commercial sector and, in general, parts with snap fasteners.

Outlook

The ongoing rise in the consumption of POM in China and in the production capacities in the whole Asian region will continue to open up great opportunities for new applications of POM. This applies equally to the homopolymers with advantages in their mechanical properties and to the copolymers with their strengths in the chemical resistance. A driving force across all fields of application remains the substitution of metal parts with lighter, more easily produced and multi-functional plastic parts made from POM. The future will also bring further modifications of POM materials, adapted to new customer demands in order to support innovative application possibilities.

The very good sliding properties and very high strengths of non-reinforced polyacetals make this polymer the material of choice for applications with moving parts at operating temperatures up to approx. 100°C. Apart from the saving in weight compared with metals, noise generation can also be significantly reduced. The increasing automation in the emerging industrialized countries will continue to drive the growth of the worldwide POM market. ■

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REFERENCES

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