New PP grades with improved flowability increase productivity without sacrificing the stiffness-toughness balance. The picture shows an ice-cream container made of Clyrell EC340R, with improved low-temperature toughness

Polymer Design. The development of polypropylene is currently subject to several trends: new grades on the market show improved processing, manifested as, e.g., faster cycles. Their improved stiffness–toughness balance helps to reduce part weights. Innovative manufacturing processes are making PP specialties accessible, whose outstanding transparency make them a serious competitor for other polymeric materials.

Polypropylene (PP)

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The polypropylene market continued to show steady growth in the last three years. Thus, world PP sales in 2007 increased by 5.4 % to around 45 million t – a significant increase compared to the average rate of 4.8 % from 2003 to 2006. This demand contrasts with capacities of 48.7 million t/a – the highest are in Asia (20.2 million t/a), North America (with Mexico: 9.9 million t/a) and Western Europe (9.7 million t/a). The Middle East is also increasingly using its raw materials resources for polyolefin manufacture. The PP capacities installed here are currently 3.3 million t/a – in 2003 it was only 2 million t/a. The world's biggest supplier is still LyondellBasell (Fig.1).

Almost three quarters of world polypropylene production is now manufactured using the flexible Spheripol process developed by LyondellBasell Industries. This fact illustrates a discernible relationship: current demand – particularly in the Western economic area – is closely linked to the continuing technical development of PP. Although for many this polyolefin is still the quintessential commodity material, it has become apparent that Western manufacturers can only exploit their opportunities if they can tailor their products more closely than before to their customers' needs. This insight resulted in a large number of remarkable new developments and improvements, giving this supposedly mature material surprising properties that for a long time were the reserve of engineering plastics.

Doors have been opened here, in particular, by modern manufacturing processes such as the Spherizone process licensed by LyondellBasell, and now established with around a dozen producers worldwide, or the extended possibilities of metallocene catalysis. Thus, polypropylene is now proving itself in a wide range of applications, with an outstanding cost/benefit balance. Now, it is even finding use as an alternative to outstanding design materials, such as ABS, without losing ground in its traditional markets, such as the packaging industry. Many of the innovations are aimed at increasing the productivity of PP processing, e.g. by reducing cycle times and material con-

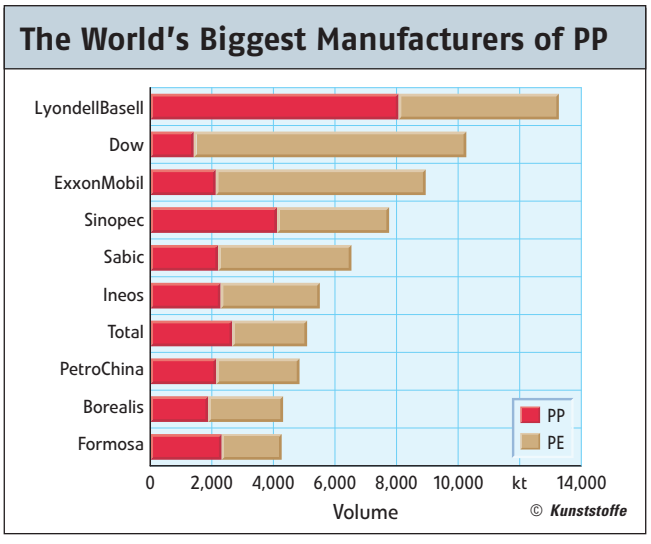

Fig. 1. The top ten polyolefin manufacturers – the graphic includes all sales rights of joint ventures and stockholdings – combine over 50 percent of the total capacity of 133 million t (polyethylene and polypropylene)

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sumption. Further savings, which have not been a main focus of considerations before, may result from the use of stiffer grades, which can positively influence storage and transport costs as a result of lower part weights. Lower processing temperatures may even reduce energy costs.

Caps and Closures

Polypropylene has been the standard material for producing bottle caps and closures for years. This sector particularly requires stiff PP grades with high toughness; both properties are important for reducing part weights. To ensure high output, polyolefins for this sector must also have good flow.

However, there are trends here that require more from the materials used than just high productivity. To attract attention in the highly competitive beverage market, producers are increasingly turning to eye-catching packaging designs. For this, they require materials for transparent closures or outer caps for sport drinks. To survive in this challenging field, the PP grades must offer an attractive aesthetic appearance. Also, improved organoleptic properties are necessary, which will not affect the fine aromas of the increasingly popular wellness drinks.

These requirements are met by e.g. PP random copolymers, such as Moplen RP340N or RP348R (manufacturer: LyondellBasell); both have excellent transparency and provide good organoleptic properties and good flowability. In applications requiring special low-temperature toughness, Clyrell EC340R has a proven track record. This is a specially developed transparent PP copolymer that also has low stress whitening and high surface quality. This property combination is now used for developing new closure types that could not be realized with conventional products. Other suppliers, such as Borealis, have similar PP grades on the market.

Fig. 2. In film extrusion, random copolymers have made a good name for themselves. They combine stiffness with transparency and good barrier properties. If necessary breathing films can also be produced

(figures: LyondellBasell Industries)

Blow Molded Containers

Similar trends could be seen in recent years in the blow molding sector. The lower material costs have already made polypropylene a competitor for polycarbonate, allowing PP to gain above-average growth in applications such as blow molded laboratory vessels, microwavable food packaging and baby bottles. And polycarbonate is not the only polymer from which PP has been able to take market shares: new PP grades are increasingly making inroads into applications that were hitherto dominated by PET, PVC and SAN. PP is also quickly making friends in upcoming market segments – the transition from glass to plastics is progressing at full speed here. In Western markets, new design options that can be inexpensively realized with PP are an important driving force. In blow molding, they help to attract customers' attention to new products with attractively shaped containers.

These trends are supported by PP manufacturers on a broad front. For example, distinct specialties, such as the development product based on metallocene catalysts, known as RM2091 until now (manufacturer: LyondellBasell), are targeting markets so far dominated by PC, PVC or even glass. RM2091 is characterized by high stiffness, low-temperature toughness and transparency. At the same time, the high stability can be used to achieve weight advantages without significantly worsening the mechanical properties of the blow molded products. Spherizone polypropylenes, which were only introduced a few years ago, have found a home in blow molding applications. An example is Moplen RP1977, a multimodal random copolymer, which besides high stiffness and transparency compared to unimodal grades is chiefly characterized by improved low-temperature toughness. It also has a wide processing window, so that the reject rates in the manufacturing process are lower. The high crystallization temperature also allows cycle times and energy costs to be reduced.

Fig. 3. Metal-coated films help to preserve sensitive aromas. Thanks to new PP grades, no solvents are required for their manufacture and the aluminum layer no longer needs to be laminated

Film for Tough Requirements

Transparency also plays an important role in the manufacture of film. Special copolymers such as Clyrell RC1314 have gained a name in the extrusion of film for the food sector – here, too, the Spherizone process combines typical PP properties, such as good stiffness with outstanding transparency and good barrier properties (Fig. 2). In multilayer coextruded film structures, the new material grades can also help to significantly increase extrusion performance. Together with EVOH or polyamide, they are even suitable for making vacuum-sealable laminates.

New PP grades can offer even more strengths for the production of aroma-protection films. Here, economic and environmental considerations have stimulated the demand for alternatives to, e.g., reduce solvent consumption in the production of the aluminum laminates that have dominated the market until now. Heat-resistant, metallizable PP grades such as Clyrell RC1601 have proven themselves in this application as a boundary layer between the homo-PP and a very thin aluminum foil (Fig. 3). Solvents are no longer required for producing these films. Now – unlike in the past – it is not even necessary to laminate the aluminum layer.

With the aid of innovative PP grades, it is possible to greatly simplify the structure of complex laminated films, e.g. for storing household chemical or beverages. Until now, at least four film materials, including ▶

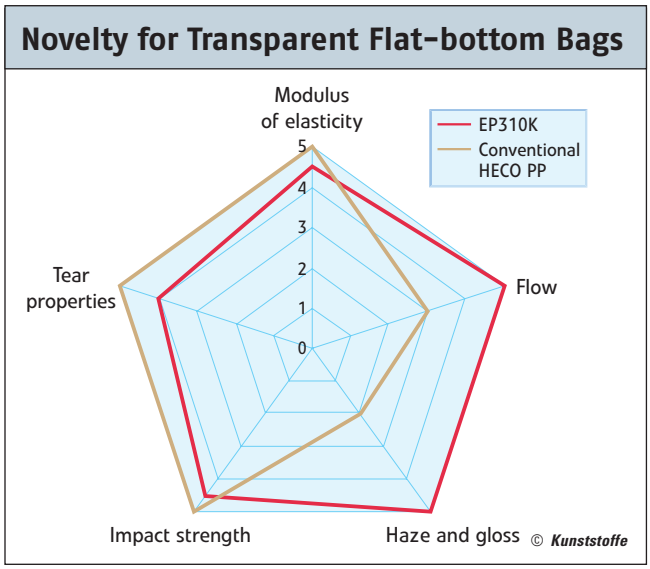

Fig. 4. Properties of the new PP film grade Moplen EP310K in comparison to conventional PP

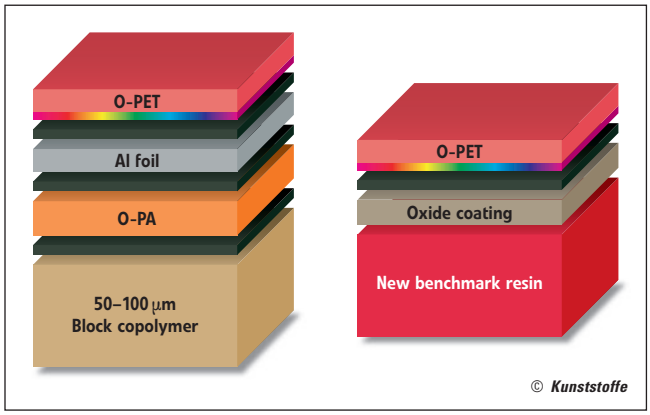

Fig. 5. New PP grades simplify the structure of films for transporting liquids and foods. The absence of an opaque PP layer and aluminum barrier layers permits the manufacture of products with high transparency

an aluminum layer had to be combined to produce the required barrier properties. New PP grades, such as Moplen EP310K allow leaner alternative structures to be realized, dispensing with the previous opaque PP layer (Figures 4 and 5). The aluminum can here be replaced with a transparent oxide coating. This results in clear, extremely robust films with very good barrier properties. Moplen EP310K is also superior to conventional PP grades as regards tensile strength, impact strength and modulus of elasticity.

Contradictory barrier properties are required in films for packaging fresh foods, such as salads. These products are very sensitive to changes in water and oxygen content in the enclosed atmosphere. "Breathing" films of unblended Clyrell EC1941 slow down the loss in O_2 content and delay the rise in the CO_2 concentration, which also levels out at lower values than with standard films. The gas exchange can be further simplified by blending with other film materials. At the same time, the transparent material offers a high stiffness, which facilitates filling of the bags. Metallocene-based film polymers are also noticeably acquiring markets.

Gaining Ground in Pipes

Polypropylene block copolymers have been used in pipe construction for around 40 years, though they have only been able to gain a foothold for wastewater/drainage pipes in the last 15 years. The decisive factors were clear cost advantages – and a higher durability – in comparison to classical pipe materials, such as concrete or cast iron. This trend has also speeded up recently, not least because of the availability of special PP grades such as Hostalen PP H2464 produced by the Spheripol process, which is specially tailored to the needs of manufacturers of double-wall pipes. Besides high stiffness, their good dimensional stability over a wide temperature range and excellent impact strength are required here – even at particularly low temperatures. In addition, there are special requirements such as resistance to aggressive substances.

In recent years it has become possible to satisfy this special requirements profile even better. A highly promising candidate again owes its properties to the Spherizone process: Hostalen PP H2483 – the first high-modulus polypropylene (PPHM), which became accessible as a result of this technology is impressive for its flexural modulus of 1,800 MPa (for comparison, Hostalen PP H2464 has 1,450 MPa) and very good notch impact strength, which minimize the risk of serious damage or leaks during laying. Because of its special molecular structure, the material is also less sensitive in the long term to point loads or earth movements. The lifetime is given as 50 to 75 years by the pipe manufacturers. Hostalen PP H2483 is suitable for manufacturing solid products and double-walled pipes. Under certain conditions, the material can be used to reduce the wall thickness of pipes while still meeting the relevant standards. PPHM pipes weigh considerably less than PVC ones for the same performance. High-molecular PPHM (HM = high modulus) also offers a wide processing window and can also be extruded on high-speed lines; because of the high melt stability, large pipe diameters can also be readily manufactured.

Fibers are Opening up New Markets

Polypropylene fibers are used in agriculture, in technical goods such as sorbents and protective masks, but also in cloths, diapers and specialized articles of clothing. Users working in this area, who usually operate high-productivity plants, require lower process temperatures to be able to reduce their energy costs. A high flowability (with melt flow rates in the range between 400 and 3,000 ml/10 min) is also desirable to improve the processing efficiency. This makes particular demands on the purity of the polymers. Grades are required with a low content of volatile oligomers.

Metallocene grades, such as Metocene MF650Y (manufacturer: LyondellBasell) characterized by good flowability, have therefore been able to gain a foothold in this area. Metallocene grades are further characterized by a narrower molecular weight distribution compared to Ziegler-Natta PP. Users report that, with mPP, they can produce softer fabrics with a uniform structure and good barrier properties. The more homogeneous structure also absorbs dyes better.

The product properties that can be achieved with the new mPP grades help the polymer to penetrate into hitherto untapped markets – for example in the production of functional, moisture-wicking sports clothing, which was primarily the domain of polyester and polyamide fibers. This is because the toughness of metallocene PP, such as Metocene HM562S, as a result of the advantageous molecular weight distribution, can be around 30 % above that of standard PP for fiber applications, i. e. in a

Fig. 6. High-modulus polypropylene is increasingly becoming established for pipes. Good notch impact toughness ensures that minor damage during pipe laying does not develop into serious damage
(photo: Hakan/LyondellBasell)

range that textile manufacturers are familiar with for traditional fiber synthetics. The throughput for the manufacture of Metocen fibers is therefore comparable to the fast-running plants for producing their polyester or polyamide counterparts. In addition, they offer good abrasion, solvent and seawater resistance and the low weight of the Metocene yarns. In comparison to other synthetic fibers, they can achieve weight savings of up to 20 % according to an Italian sport clothing manufacturer (Fig. 7). The promising fiber market is pronounced by strong competition between the raw materials manufacturers: Borealis, Total and Exxon Mobil are also active here besides LyondellBasell.

New Developments in Injection Molding and Thermoforming

Polypropylene is also about to drive other materials out of its domains. High-transparency PP variants produced by single-site catalysis, with good stiffness, are thus challenging not only glass, but also PC, PMMA or styrene plastics. Metallocene-based specialty plastics, such as the development product RM2073 (manufacturer: LyondellBasell), offer a considerable density and cost advantage over these materials for comparable functionality, and thus present themselves as an alternative for the production of DVD cases, plastic tableware and technical products. As regards their robustness and design possibilities, they are often superior to transparent amorphous thermoplastics. Furthermore, high-melt flow rates help processors to reduce cycle times for injection molding. This market, too, is seeing strong competition between suppliers. Borealis, for example, only recently enlarged its product range.

Polymer substitution is also an issue in thermoforming – PP provides an inexpensive alternative to PVC, PET and PS, which are more than a match for most polymers as regards quality and productivity. PP is thus making ever greater inroads into an area that is characterized by high growth rates, since thermoformed products are desirable particularly in the packaging sector because of the design options they offer, and are increasingly competing with thin-wall injection molding. In thermoforming, metallocene-based PP variants offer the possibility to reduce layer thicknesses and therefore material costs. Form-fill-seal packaging, until now a domain of PET and PS, can now be made of PP thanks to specially developed transparent grades such as Clyrell RC514L. Polypropylene can thus be used for coextrusion as well as film lamination and both hot filled and pasteurized. Compared to A-PET, considerable weight savings can be made because of the material's high stiffness (Fig. 8).

Fig. 7. Until now, a domain of polyester and polyamide fibers, now also made of tough metallocene PP: functional sports clothing
(photo: Slam/LyondellBasell)

In the field of consumer goods, developers are aiming at new PP grades, which offer better flowability without sacrificing the stiffness-toughness balance. Examples are Moplen EP340P LB and the highly transparent Clyrell EC340R, which offers good impact strength at low temperatures (Title photo). Both grades are characterized by good stress whitening.

Even experts are surprised that PP offers an alternative to ABS in some of its applications. Novel copolymers such as Moplen EP1904, a nucleated injection molding polypropylene (manufacturer: LyondellBasell), or similar special grades from Sabic are characterized by good processability, low shrinkage and a balanced ratio of stiffness and toughness and high gloss. They can be used to produce toys and household goods, food containers and housings that are unbreakable even at low temperatures and whose surface quality can compete with ABS. Translucent, opaque and metal-effect parts are possible. Not every application for ABS requires all the properties of this efficient styrene copolymer – the new PP variants are an interesting alternative here.

Fig. 8. New PP grades are increasingly competing with other plastics in many areas. Transparent polypropylene can supersede, e.g., PET in form-fill-seal applications

In some respects, Moplen EP1904 is even superior to standard ABS. For example, only small amounts of material are required for coloring the material. This opens up all the potential of economic and efficient self-coloring for processors. The better sound-insulating properties of polypropylene are responsible for the pleasant sound of polypropylene products.

In the rigid packaging and consumer goods sectors, battery housings are to some extent a special case. PP has a considerable market share here in the automotive sector. It is required to have high impact strength, in particular thermal resistance, low warpage, low stress whitening, good welding and high resistance to acids and grease. In the medium-term, some changes can be expected in the battery market. Thus, safety-relevant units in the car make it necessary to revert to backup batteries in an emergency. Hybrid batteries and fuel cells lead to a rethinking of previous material concepts. Among others, creep-resistant PP grades are increasingly required. In addition, PP is set to replace materials such as SAN in the medium term, including for non-transport applications. ■

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