PHOTO: LEHMANN & VOSS

Originally launched onto the plastics market back in the 1990s, polyketone was discontinued in 2000. It is now available once more and its unique performance offering is drawing attention, writes **Jennifer Markarian**

Unique properties drive the polyketone revival

Aliphatic polyketone (PK), which was available from Shell under the brand name Carilon in the mid-1990's but was discontinued in 2000, underwent a rebirth in 2013 when South Korea's **Hyosung Corporation** - after ten years of development and more than fifty patents - began marketing product from a pilot-scale plant. In July last year, the company started up a 50,000 tonne per annum (110 million lb/yr) commercial plant for its brandname Poketone resins and announced plans for a second plant to start up after 2020.

The unique properties of PK are a result of its semi-crystalline molecular structure, which alternates between carbon monoxide (CO) and olefin. Hyosung says it can make both terpolymer (ethylene, propylene, and CO) and copolymer (ethylene and CO) polyketones. However, all grades currently offered by the company are terpolymers, which have better processability (in both moulding and extrusion applications) compared to copolymer form.The copolymer does have some interesting mechanical properties, with better heat resistance and strength than PA66, but its processability is a drawback, says Cliff Watkins, marketing director at US-based distributor **PolySource**. Hyosung's technology is also capable of producing terpolymers with other monomers, but these are in an early R&D stage. Such polymers could be designed for lower processing temperatures, which could take advantage of PK's interesting adhesive and cohesive properties for use as a tie-layer resin, according to Watkins.

Hyosung's current slate of terpolymers produced at its commercial-scale plant is broad and includes a high-flow grade (M230A); a medium-flow grade (M330A) for injection moulding; a low-flow extrusion grade (M630A); and a very low-flow grade (M730A) for profile extrusion and blow moulding. All of these grades melt at 220°C. The company also makes a low-flow, lower melting point grade (M620A) for extrusion applications, where a slightly lower temperature is needed. It melts at 204-210°C and is currently produced at pilot scale but could be produced at commercial scale if demand warrants, the company says. Another pilot-scale grade is M930A, with a medium-high MFI (165 g/10 min). Two new grades developed by Hyosung include M340 for high impact strength and M640 for high heat resistance. The company plans to further expand its product portfolio as the market demands.

Customers that previously had used Carilon are finding improved mechanical properties and enhanced colour matching with Poketone, says J H Park, president of Hyosung Chemical performance group.

The alternating structure on the PK polymer backbone (CO and olefin) results in properties such as

Main image: Good processing and a novel property set means newly available polyketone compounds are attracting interest

Above: Hyosung's 50,000tpa commercial-scale PK facility in South Korea started up in July last year

short moulding cycles, low warpage, good resilience and snap fit, good impact performance over a broad temperature range, high chemical resistance and barrier performance, hydrolytic stability, and good friction and wear characteristics, says Dr Cary Veith, CEO at **Esprix Technologies**, which introduced its Ketoprix Polyketone compounds in 2015. This broad spectrum of beneficial properties makes PK useful in a wide variety of end uses. "For example, in industrial applications, the resistance of PK to most chemicals helps reduce corrosion and improve environmental sustainability," says Veith. "In high-temperature composite parts, glass and/or carbon fibre reinforcement of PK can create compounds that are good for replacing metals. In consumer machines (for example, printers, copiers, kitchen appliances), PK's low coefficient of friction and high wear resistance make it an excellent choice for bushings, wear rings and the like."

Barrier to fuels

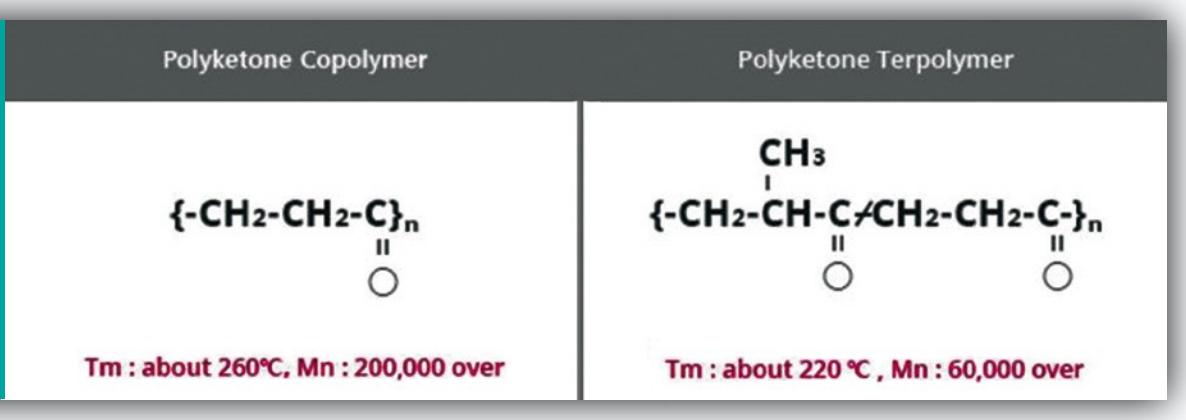
PK's barrier to fuels opens up a host of potential end uses. "In oil & gas applications, PK can be used as a barrier layer in pipe and tubing to reduce migration of oilfield chemicals out of transport systems and/or reduce corrosion of conveying equipment," says Veith. "In automotive under-the-hood and fuel systems, high use temperatures and chemical resistance plus high resilience make PK excellent for snap-fit connectors and other structural parts. And in gasoline service station fuel delivery systems, the low permeation of PK to fuels means safer, more environmentally friendly operations with less pollution and contamination risks."

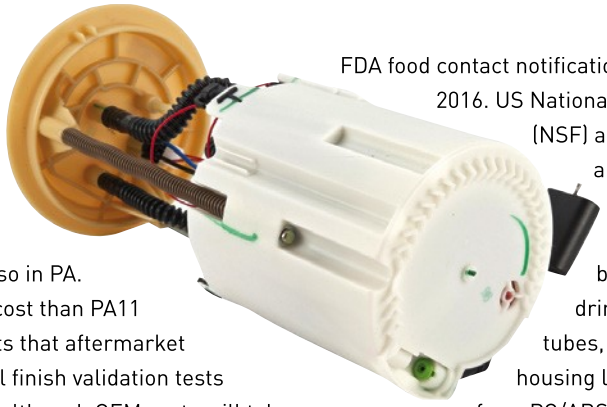
PK's key to success in fuel-transport systems is its lower permeation coefficient compared to other materials, explains Veith, who published a white paper estimating PK's performance in fuel transport systems using property values derived from previously published Shell data. Lower permeation results from PK's dipolar nature, which allows it to resist attack and permeation by aliphatic and aromatic hydrocarbons (for example, in fuels), and its morphology, which results in resistance to swelling and dissolution in all but the strongest polar environments, explains Veith. "A lower permeation coefficient for PK versus other materials, for a given thickness, means that there will be less fugitive emissions of fuel from the delivery system into the surrounding environment using PK."

Veith reports that integrated values of fuel lost (g/m2 per day) are essentially nil at 23°C and 0.9 at 93°C for PK compared to 1.4 at 23°C and 243 at 93°C respectively for PA12, which is a commonly used liner material. PK also performs much better than PA12 with oxygenated fuels such as E10. "Permeation of E10 through PK at 23°C is about the same (within experimental error) as permeation of UL gasoline (no alcohol or oxygenate) through PK at 23°C," Veith says. Several companies are said to be evaluating the company's Ketoprix PK as the inner liner in multi-layer pipe and tubing applications for fuel delivery and also in oil and gas transport applications.

PK is being evaluated for automotive applications that had used Shell's PK in the past, as well as for new applications. "When Tier 1 companies and OEMs switched from PK to other materials for fuel handling applications, they had to compromise in mechanical properties, and they are interested in coming back to PK," says Watkins. "PK's fuel resistance is approxi-

Hyosung can produce PK in copolymer and terpolymer forms but all of its current commercial Poketone grades are based on the terpolymer variant





Right: PK offers high resistance to automotive fuels, especially the new bio-diesel and ethanol grades

mately ten times better than PA11 and PA12. In addition, PK can resist acids that can form from sulphur-containing biodiesel fuels; these are a big problem in POM and also in PA. In addition, PK is lower in cost than PA11 and PA12." Watkins predicts that aftermarket fuel-pump applications will finish validation tests before the end of the year, although OEM parts will take longer to commercialise.

Consistent mechanical properties

A key benefit of PK for a variety of applications is that its mechanical properties withstand a broad range of temperatures and humidities in use. Building and construction applications can benefit from this broad performance range, for example. "Testing is currently underway with glass-filled PK as a potential replacement for glass-filled nylon in window and door hardware, because the nylon tends to lose its toughness properties in regions such as the southwestern United States, where there is low humidity and broad temperature swings from very hot to cold," says Watkins. PK's toughness is demonstrated by high values for notched Charpy, elongation, and tear strength. This toughness, combined with its low moisture absorption and excellent chemical resistance, makes PK better than resins such as PBT, POM, or some nylons in various building applications.

A legacy Shell application that will benefit from PK's return is in commercial beverage dispensers for frozen drinks. "The alternate material (POM) has poorer toughness at low temperatures and so has had a higher rate of failure at -30°F," explains Watkins, who is working with a major OEM to qualify PK and anticipates it to see commercial use in Q1 of this year.

PK has approval for EU direct food contact, and an FDA food contact notification was published in January 2016. US National Sanitation Foundation (NSF) approvals for drinking water are expected by the end of March. PK also shows advantages in commercial beverage dispensers for hot drinks. "PK can be used in flow tubes, for example. PK can replace housing lids that are currently made from PC/ABS, but are cracking because of inadequate chemical resistance," says Watkins. "The combination of PK's glossy surface appearance and exceptional chemical resistance is ideal at resolving the poor resistance of PC/ABS to disinfectant cleaners, oily foods and sanitizers."

Toughness in a range of temperatures and humidities is also a potential benefit in electrical and electronic applications. "PK can be compounded with flame retardant additives and it is easy flow, so complicated parts with thin walls can be moulded," says Watkins. He notes that PK is competitive with LCP and PPS from a processing standpoint (for example, for thin wall connectors), although PK has a lower use temperature than LCP and PPS. Usage temperatures of PK are currently being evaluated, but a relative thermal index (RTI) of approximately 130 °C is expected.

PK's high resilience is demonstrated in its high elongation at yield (25%), and it can be subjected to larger, cyclic deformations than many other engineering thermoplastics, making it useful in electrical connectors, according to Veith. PK is also ductile over a broad temperature range, with elongation at break of approximately 300% at 23 °C.

In automotive interior applications, PK offers high resilience combined with low volatile organic compounds (VOC); this is an advantage over POM, which can have problematic emissions from the final part due to formaldehyde content, says Thomas Collet, global product and marketing manager for the Customized Polymer Materials business unit at **Lehmann & Voss.**

Above: High operating temperatures and chemical resistance makes PK a candidate for structural under-hood components

Tribological applications

Polyketones are said to be uniquely suited for tribological applications because of their wear resistance, combined with other properties, such as chemical resistance or fatigue resistance. In particular, PK-PK pairs have lower wear than other like-paired materials (see Nov. 2015 article).

At the Compounding World Forum (held in Philadelphia in the US on 8-9 December last year), Oliver Frey, head of the compounding department at **Ensinger**, presented data showing the tribological properties of

Above: PK offers the flow required in thin wall connectors

PK compounds. He noted that PK's benefits are unique in applications that require mechanical or tribological properties in combination with low water absorption and chemical resistance.

Akro-Plastic offers its normal flow and easy-flowing Akrotek PK grades formulated to meet various needs. These incorporate glass reinforcements, carbon-fibre reinforcements and flame retardants. At the upcoming Compounding World Congress (Cologne, Germany, 18-20 April 2016), Thilo Stier, sales director and innovation manager at Akro-Plastic GmbH, will be presenting "The return of polyketones: developing new compounds and applications including long-fibre grades and tribological components."

Compound with care

There are some difficulties to consider when compounding PK polymers. "The biggest issue when compounding PK is avoiding thermal oxidation of the polymer due to dead spots or cessation of flow in the processing equipment. If you keep the polymer moving, you can process it satisfactorily," reports Veith. H "Have every piece of ancillary equipment up and running at steady-state and turn on the PK feed as the last item in the start-up checklist, then get to steady state as fast as you can. If you must go down due to a mechanical failure elsewhere, purge out the PK first, then solve the mechanical problem. Pay special attention to the restart, and look out for gels and degradation products in the extrudate or processed polymer. If you have these defects and they don't clear up in short times, then shut down and clean out the equipment and try again tomorrow," he advises.

Ensinger's experience with compounding PK highlights the importance of handling it on very clean equipment. "We observed a negative impact on mechanical properties when the equipment was not cleaned absolutely carefully, which is usually not needed to that extent with other polymers. We believe that traces of contamination cause degradation in PK," says Frey.

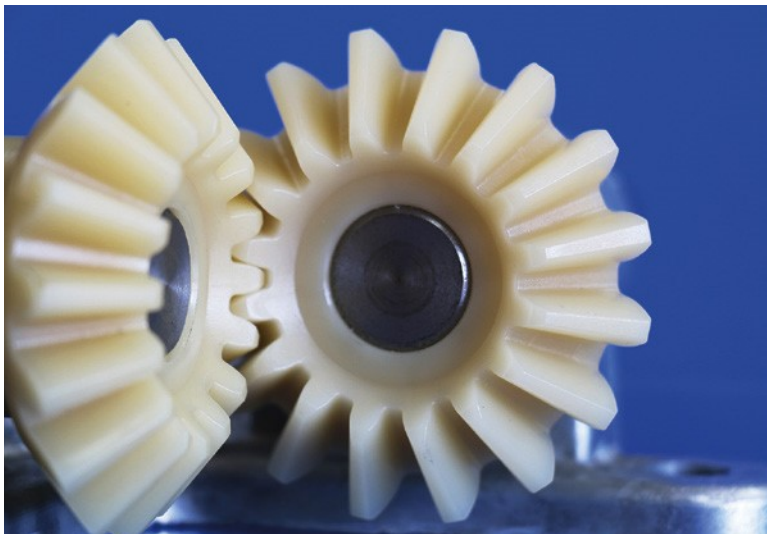
Similarly, moulding and extrusion of PK must be carried out carefully. For example, an injection-moulding machine barrel must be sized properly to avoid a long residence time, warns Watkins. "If residence time is too long, the PK may start to darken (although POM has a similar issue)," he says. "Because PK crystallises quickly, you can reduce moulding cycle times compared to POM or PBT but, if you're not careful, PK can freeze at the moulding nozzle. There is a learning curve, but PK is relatively trouble-free once you optimise equipment to run it."

Hyosung has established an internal task force to improve properties and processing stability as quickly as possible, including evaluating better stabilization additive packages, as it sees this as a critical area for improvement. The company says it is collaborating with a number of partner companies to enhance long-term thermal stability, UV resistance, and processibility using different approaches in polymerisation, additive packages, and alloy technologies.

In general, the resin is compatible with a wide range of fibre reinforcements, fillers, colorants, and additives, such as flame retardants, thermally and electrically conductive additives, wear-resistance additives, and others. In addition to unfilled grades, Hyosung offers a 30% glass-filled, flame-retardant grade and an unfilled, flame-retardant grade. Compounders offer many combinations.

Right: The good wear performance of PK could lead to applications in appliance bushings and bearing rings

PHOTO: AKRO-PLASTIC



Above: PK's good tribological performance makes it suitable for polymer gear applications

Promising future

Although many projects are in development and a few are close to commercial, it will take some time for many products to be commercialised. "We have new, tailor-made products being qualified, but a typical product takes 1-3 years to become commercial. PK is known to many processors and end-users, but it is a relaunch and customers need to get used to it and want to be sure that the resin will be there," says Collet at Lehmann & Voss. He says his company is working on antistatic and reinforced PK compounds for automotive, industrial and electrical applications, some of which are reinforced with carbon fibre for high strength and electrical properties and with lubricants for tribological applications.

A Schulman has developed its carbon fibre reinforced Schulaketon and Schulaketon Flame Retardant compounds. The Schulaketon flame retardant extrusion compounds, for example, may be used in corrugated tubes for cable protection and meet requirements of the new European railway standard, says the company.

Hyosung anticipates demand will likely grow first in the European and US markets, where many customers already understand PK's properties and features and have experience in adopting PK for new applications. But the company also expects growth elsewhere in the world. "China is an attractive market with a great volume and growing possibilities, and therefore we are actively introducing and promoting Poketone in this region by focusing on the customers who are interested to maximise the value of this new polymer," says Park. "Hyosung is also developing new applications and trying to discover promising markets in Oceana, the Middle East, South America, South Korea and Japan."

Hyosung is developing applications with official business partners (compounders and distributors) as it works to position this "new" engineering plastic in the market. The most recently appointed partner is German distributor **K D Feddersen**, which is distributing three standard resins (high flow, medium flow, and high impact) in Europe and Latin America. It says its key focus is on the extrusion industry and compounding.

The high volume of inquiries into investigating PK for the first time or in qualifying for applications that had previously used PK has been surprising, according to Watkins, who says the fact that PK promises to solve some long-standing problems with existing resins has been a real boon. "Designers don't need to make compromises with PK as they do with other polymers because they don't have to account for any variation in mechanical properties due to moisture changes," he explains. In an industry where new polymers don't come along very often, it seems worth taking a look at PK.

Click on the links for more information:

- **www.poly-ketone.com (Hyosung)**
- **www.polysource.net**
- **www.esprixtech.com**
- **www.lehvoss.de**
- **www.ensinger-online.com**
- **www.akro-plastic.com**
- **www.aschulman.com**
- **www.kdfeddersen.com**