Semi-Crystalline, and yet Thermoformable

Special Polymers Enable Thermoforming of PEKK Parts

Ultra high performance polymers such as polyaryletherketones (PAEK) are typically not thermoformable for thick gauge applications because of their semi-crystalline nature. Specially developed PEKK grades now allow processing in this method. These can be used to produce large semi-crystalline PAEK parts with large wall thickness exhibiting extreme mechanical, chemical and flame retardant properties.

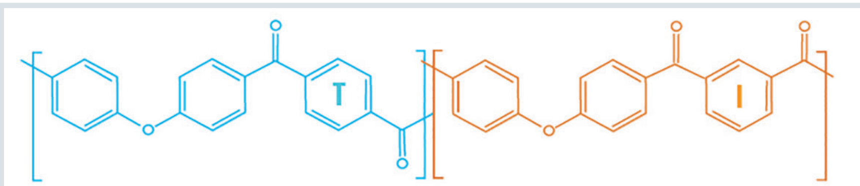

Fig. 1. PEKK copolymers contain both terephthalic (T) and isophthalic (I) monomers. The ratio and distribution of the monomers significantly determines the properties of the plastics © Arkema

Polyaryletherketones (PAEK) are used in technically challenging industry sectors, e.g. aerospace industry and the oil and gas market. The generic PAEK family includes different polymers, depending on the ketone to ether ratio, such as polyetheretherketone (PEEK), polyetherketone (PEK), polyetherketoneetherketoneketone (PEKEKK) and polyetherketoneketone PEKK (**Table 1**). These polymers are typically used when all other polymers fail, in particular when there is a need for a combination of properties such as resistance to high temperature, to wear, to chemicals, to hydrolysis and to fire.

Unfortunately, PAEKs are generally not easily thermoformable. Thermoforming is one of the first original methods of forming useful plastic parts and is widely recognized as a very robust, reliable and cost competitive process. This processing technology starts with a sheet of plastic material, heating it up until it is formable, and then forming it into a cavity (or over a tool) using vacuum, air pressure or mechanical means. Amorphous polymers are very suitable for such a forming process. Commodity plastics such as acrylonitrile-butadiene-styrene (ABS), polystyrene (PS) or polyvinyl chloride (PVC) are routinely used for packaging and thin gauge applications, while engineering plastics – such as polycarbonate (PC) – and specialties polymers – such as polyetherimide (PEI) or polyarylethersulfone (PAES) can also be processed this way for more demanding applications and for thicker gauge markets.

	PEEK	PEK	PEKEKK	Kepstan PEKK
Ketone/ether ratio	1/2	1/1	3/2	2/1
Glass transition temperature [°C]	143	152	162	160-165
Melt temperature [°C]	343	373	387	305-358

Table 1. Comparison of the properties of different PAEK polymers Source: Arkema

Challenges for PAEK Thermoforming

When it comes to PAEK, and in particular to PEEK, crystallization happens too fast at the extrusion stage, resulting in an already partially semi-crystalline sheet, which virtually leaves no useful processing window for thermoforming. There are two major challenges to overcome to bring PAEK thermoforming to maturity. The first one is to extrude a PAEK sheet, which remains amorphous even up to several millimeters in thickness. The second one is to form the sheet and crystallize in situ during the thermoforming process and within a reasonable cycle time. To meet these challenges both at the extrusion and at the thermoforming levels, Arkema, Colombes, France, collaborated with American sheet extruder Westlake Plastics, Lenni, PA/USA, and Plastiform, Thise, France, to develop specific PEKK grades. They come from the Kepstan family of the company.

PEKK resins have the uncommon make-up of being copolymers that contain terephthalic (T) and isophthalic (I) moieties (**Fig. 1**). The T/I ratio is set at the synthesis level and controls thermal properties and crystallization kinetics of the resulting polymer. Arkama's PEKK

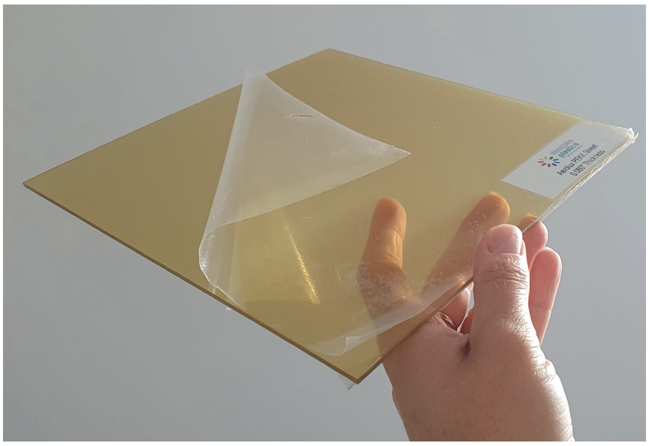

Fig. 2. Amorphous PEKK sheet: to thermoform PAEK components, sheets or films must first be extruded that remain amorphous even at a thickness of several millimeters © Westlake Plastics

Fig. 3. Amorphous thermoformed PEKK final part © Arkema

comes in three "series", each one having a different T/I ratio to better-fit application processing requirements or end use properties. All PEKK series are inherently flame retardant and halogen free with very low smoke toxicity, which make them suitable for demanding aerospace or train applications.

By selecting the right PEKK series, extrusion is possible without any particular issue: PEKK remains amorphous, even when extruding a 3 mm thick sheet (**Fig. 2**). Such sheets e.g. are manufactured by Westlake Plastics. Thermoforming technology requires a specific expertise, which Plastiform has successfully developed after very few trials. The sheets must be dried carefully prior to thermoforming process to avoid any moisture effects, as for most high performance polymers. Both temperature control and heat distribution must be very precise to form the sheet, which has to be heated up above its glass transition temperature. Tooling equipment never reaches extreme temperatures, as there is no need to go above PEKK melting point. In order to crystallize in situ, the mold has to be maintained at the right temperature level to ensure crystallization is achieved in a reasonable time. Typically, for a 2 mm thick sheet, production cycle time is less than 5 min.

As thermoforming process starts from an amorphous PEKK sheet, it is also possible to obtain an amorphous PEKK final part after forming (**Fig. 3**). Such parts exhibit and amber tint much like PEI or PAES thermoformed parts. Process is even simpler as there is no in situ crystallization, and ductility is increased. However, PEKK highest thermo-mechanical and chemical performances can only be obtained when PEKK reaches its equilibrium semi-crystalline state.

ESCR Test Shows High Chemical Resistance

The newly developed materials have great potential for markets historically limited to amorphous polymers, such as PAES or PEI. The benefit of PEKK compared to these polymers, is among others, the achievement of an extremely high chemical resistance. Semi-crystalline PEKK has outstanding resistance to aggressive fluids such as kerosene, skydrol or methyl ethyl ketone (MEK), which can be present in aerostructure of commercial aircrafts, and more generally to all kinds of chemicals.

Figure 4 exhibits the results of an environmental stress cracking resistance (ESCR) test after one week of full immersion in aggressive fluids at room temperature, in comparison with PPSU and PEI). Test results clearly show that semi-crystalline PEKK exhibits the best chemical resistance, even at a 40 MPa stress »

	Semi-crystalline Kepstan PEKK	Amorphous Kepstan PEKK
Tensile modulus [GPa]	3.6	3.0
Stress at yield [MPa]	110	95
Strain at break [%]	> 9	> 60

Table 2. Mechanical properties of amorphous and semi-crystalline Kepstan PEKK after thermoforming Source: Arkema

The Authors

Philippe Bussi is General Manager at Arkema, Paris, France;
philippe.bussi@arkema.com
Pierre Gonnetan is Business Development Manager for Europe at Arkema, Paris. He is the key contact for thermoforming projects & questions;
pierre.gonnetan@arkema.com
Dr. Eléonore Möller is Senior Account Manager at Arkema GmbH, Düsseldorf, Germany; eleonore.moeller@arkema.com
Bernd Opinkowski is Senior Account Manager at Arkema GmbH, Düsseldorf;
bernd.opinkowski@arkema.com

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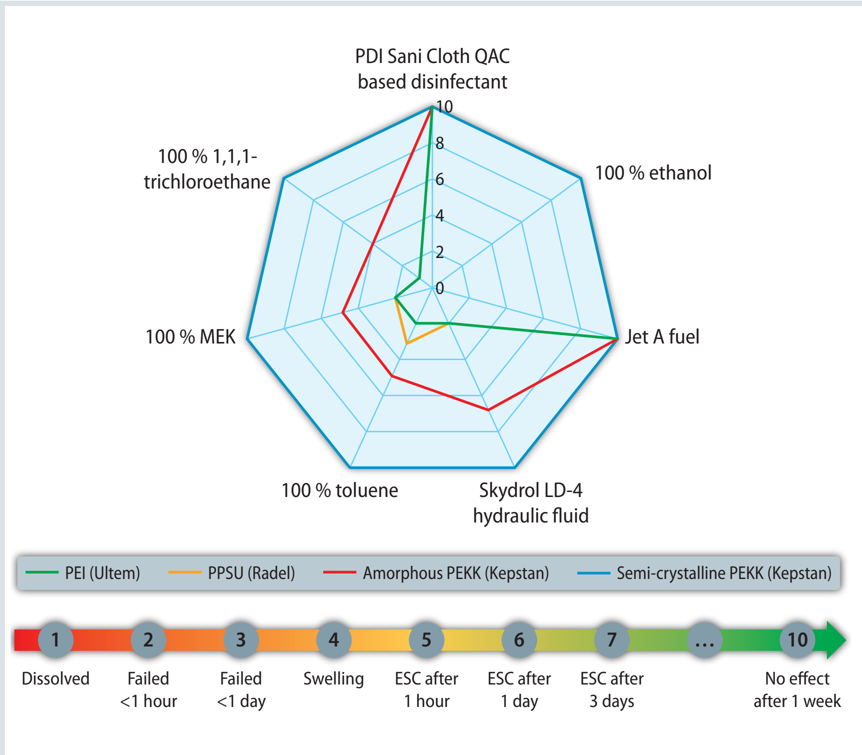

Fig. 4. Results of an ESCR test after one week of full immersion at room temperature and a load of 40 MPa at 1.1 % strain: semi-crystalline PEEK has the best chemical resistance of all polymers Source: Arkema; graphic: © Hanser

level (1.1 % strain level) strain. Note that the test also show that amorphous PEKK perform better than PEI or PPSU, which of course are not reaching the level of performance of semi-crystalline PEKK.

Thermoformed PEKK sheets exhibits very high mechanical properties. Semi-crystalline PEKK parts always remain ductile with a tensile modulus of 3.6 GPa and tensile strength of 110 MPa at room temperature (**Table 2**). At 150 °C, semi-crystalline PEKK remains 25 % more rigid than PEI and 280 % more rigid than PC.

Due to the previously mentioned high crystallization speed limitation with PEEK, it has not been possible up until today to produce very large PAEK parts at an affordable price. Machining of a large PAEK slab could in principle be considered but would not be cost effective. As an example, to produce the part shown on **Figure 5** by machining, one would have to start from a PAEK block (40 cm x 30 cm x 5 cm) weighting close to 8 kg. By thermoforming a PEKK sheet, scrap is drastically reduced and much less material is needed (about 350 g), resulting in high cost reductions.

Lighter and Cheaper PEKK Components

This technology not only opens up the opportunity to produce large parts with intricate designs, but also allows for the production of many small parts in one shot. A single large PEKK sheet can be used to produce several smaller technical parts as soon as the mold is suitable. In addition thermoforming tooling costs are generally very cost competitive versus molds designed for injection molding.

This innovation is also a step towards further metal replacement. Steel density is about 8 g/cm^3 and metal forming is a costly process, while PEKK density is 1.3 g/cm^3. PEKK polymer, as a formable, light and very strong material alternative, and showing extreme chemical performance, has already raised the interest of diverse industries.

PAEK thermoforming is a new space to explore. This breakthrough finally opens the door to a wide range of high performance parts for demanding applications such as large-scale galleys, interior paneling for aircraft and rail interiors, electrical enclosures, industrial component and electronics trays (**Fig. 6**). ■

Fig. 5. Semi-crystalline thermoformed PEKK part. The process allows the production of highly chemical-resistant components at lower costs © Arkema

Fig. 6. Semi-crystalline thermoformed PEKK electronic tray © Plastiform