WHITEPAPER

PUSHING THE BOUNDARIES WITH NEW ADDITIVE MANUFACTURING OPTIMISED PAEK POLYMERS

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PAEK (Polyaryletherketones) and PEEK (Polyetheretherketone) in particular is regarded as one of the highest-performing polymers in the world. However, when invented, traditional PEEK polymers were not designed for additive manufacturing. They were designed for injection moulding where they have a track record of 40+ years in replacing metals and other materials in the most demanding applications.

This paper outlines why 3D printing PEEK is challenging and how Victrex has developed new, easier to print PAEK polymers for filament fusion (FF) and laser sintering (LS) by utilising our Polymer Innovation Centre's specific capabilities and collaborating with our partners to enable new possibilities with 3D printed PAEK.

We sincerely thank Martin Riley for his valuable contributions to this paper.

WHY IS PRINTING WITH TRADITIONAL PEEK SO HARD?

Little more than 40 years ago, the versatile, break-through polymer PEEK was invented with VICTREX 450G™, the first commercially available PEEK. The materials were specifically formulated to promote fast cycle times, and easy processing in injection moulding, which directly contributes to cost-effective mass production.

Since injection moulding is a relatively fast process, lasting seconds to minutes, residence times at high temperatures are short and cooling is generally more uniform.

3D printing, or additive manufacturing, is different. In both laser sintering and filament fusion, printed material needs to fuse with cooled material across layers or powder particles respectively, rather than being processed in a uniform molten phase as in injection moulding.

Printing a fast crystallising, high shear thinning, injection moulding optimised PEEK material results in poor interlayer adhesion in most filament fusion printers. The potential issues are low z-axis mechanical properties, significant dimensional changes as the part cools and crystallises non-uniformly – shrink, warp, delamination, and internal stress of layers – and/or thermal degradation over the many hours of printing.

The thermodynamics of melting and cooling a polymer can be observed with Differential Scanning Calorimetry (DSC). DSC measures the temperature and magnitude of key thermal transitions and the thermal energy that must be added or removed from the polymer for each degree change in temperature.

Figure 1 shows the DSC curve for our best-known polymer, VICTREX 450G™ PEEK.

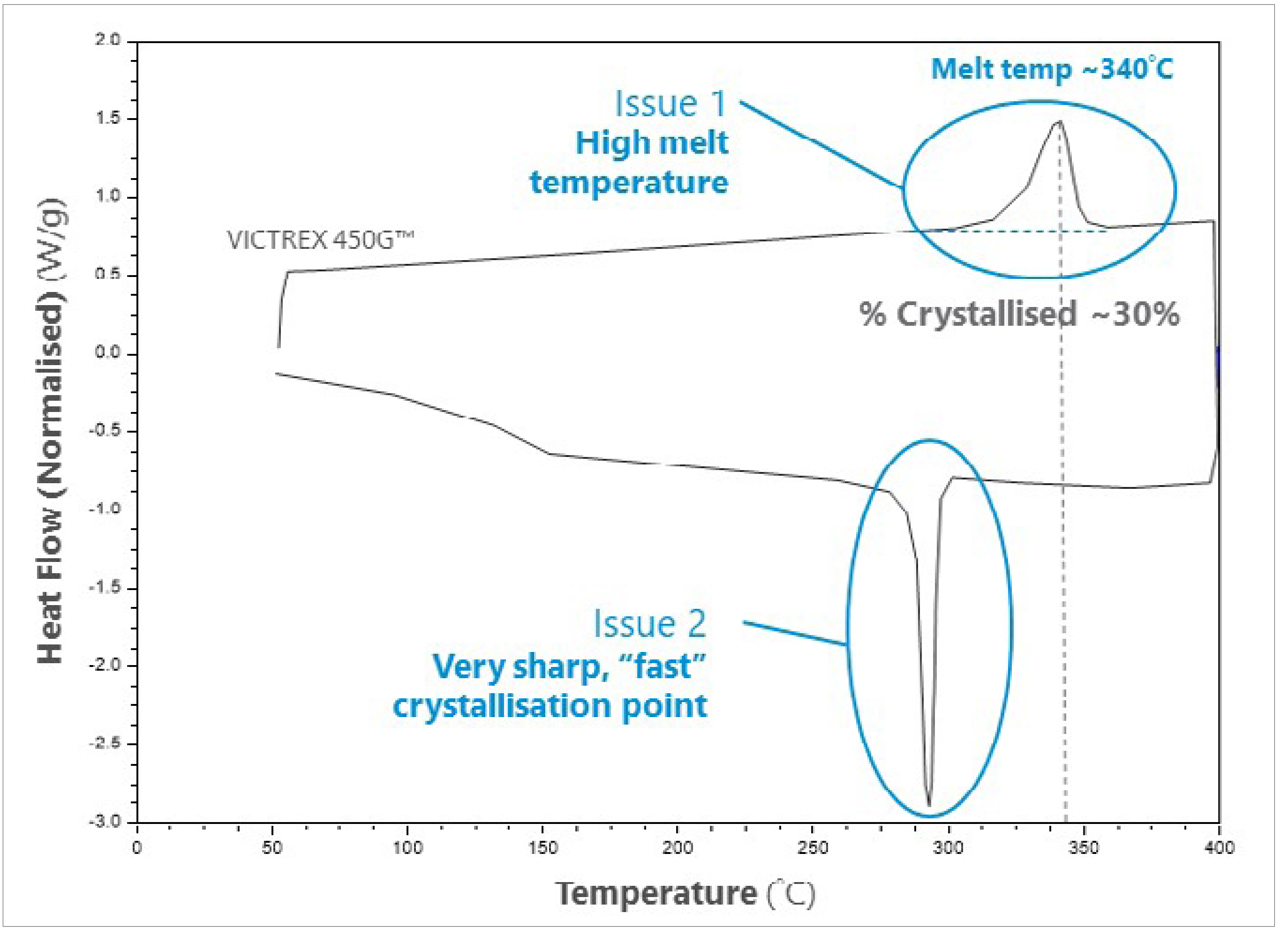


Figure 1: Differential Scanning Calorimetry (DSC) of VICTREX 450G™ PEEK illustrating the high melt temperature in melting and a sharp crystallisation point in cooling. Source: Victrex internal data.

From the DSC chart in Figure 1:

- We can observe the melting temperature
- We can infer the achievable crystallinity, which in PAEK directly influences properties such as mechanical stiffness and chemical resistance
- We can infer the crystallisation rate

PEEK's high level of achievable crystallinity and high glass transition temperature contribute to many of its exceptional properties, however its fast crystallisation can make it harder to print PEEK parts with good interlayer strength.

Along with crystallisation, polymer viscosity was a consideration in designing the materials for additive manufacture. Much of the cooling phase of the printing process in which the crystallisation and interlayer bonding occurs is in the open air, where shear forces on the polymer are low and melt viscosity increases, as shown in Figure 2.

These conditions are quite different from injection moulding, where cooling and consolidation occurs within a heated and pressurised mould.

Additionally, for laser sintering, the powder bed is held at elevated temperatures for many hours in the print chamber., and this is known to cause degradation in some high-temperature polymers.

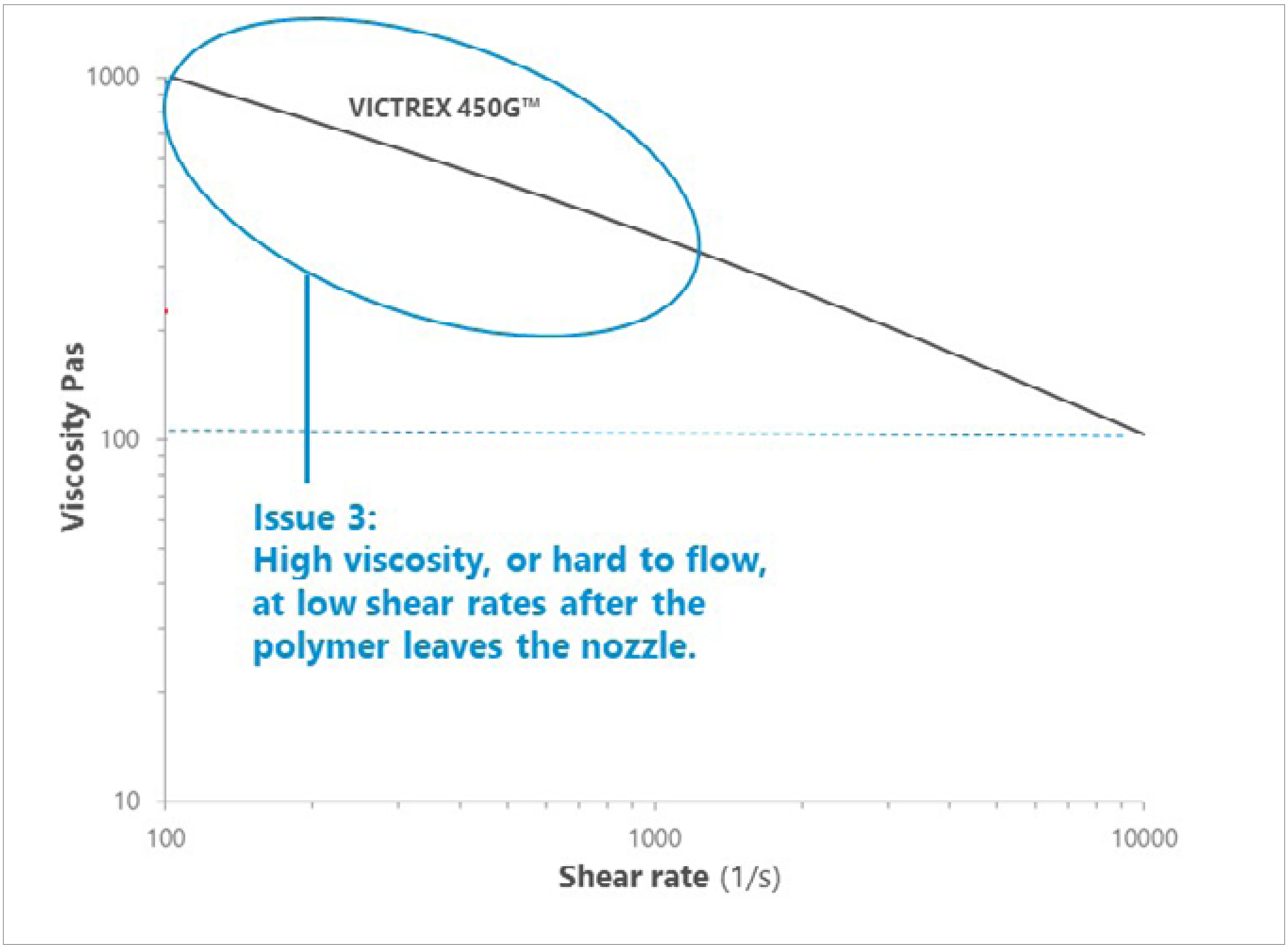


Figure 2: Melt viscosity vs. shear rate curve illustrating the shear sensitivity of VICTREX 450G™ PEEK, where the melt flows much less easily in low shear environments such as open air after the melt leaves the nozzle in a 3D printer. For reference, shear rates in the print chamber are nearly zero while shear rates in the FF nozzle might be in the hundreds of (1/s) depending upon print speed and nozzle diameter. Injection moulding may see thousands of (1/s).
Source: Victrex internal data.

CUSTOMISING PAEKS TO SUIT ADDITIVE MANUFACTURING PROCESSES

Our approach to improving our materials for additive manufacturing has focused on redesigning the polymer at a molecular level, achieving better prints without using additives or plasticisers.

PEEK is a member of the polyaryletherketone (PAEK) polymer family. PAEK polymers are made from aryl ether and ketone linkages. Depending on how these building blocks are assembled, polyaryletherketones (PAEK) include PEEK, PEKK, PEK, and many other variants. The ratio, structure and sequence of the aryl ether and ketone groups determine the melt temperature, the crystallisation behaviour, and many other properties. Using our Polymer Innovation Centre, our team combined these ether and ketone building blocks to create new PAEK polymers better suited for additive manufacturing.

As mentioned, these new materials do not use additives, avoiding additional uncertainty for customers since the use of additives may present complications as their stability and compatibility needs to be verified in the extreme environments generally encountered in PAEK applications.

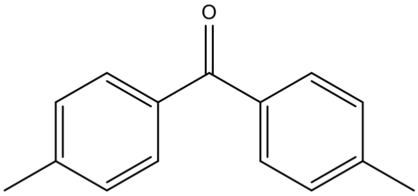


Figure 3: Ketone

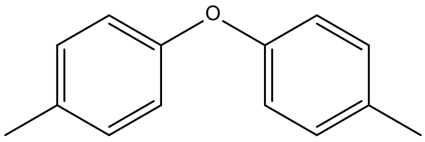


Figure 4: Ether

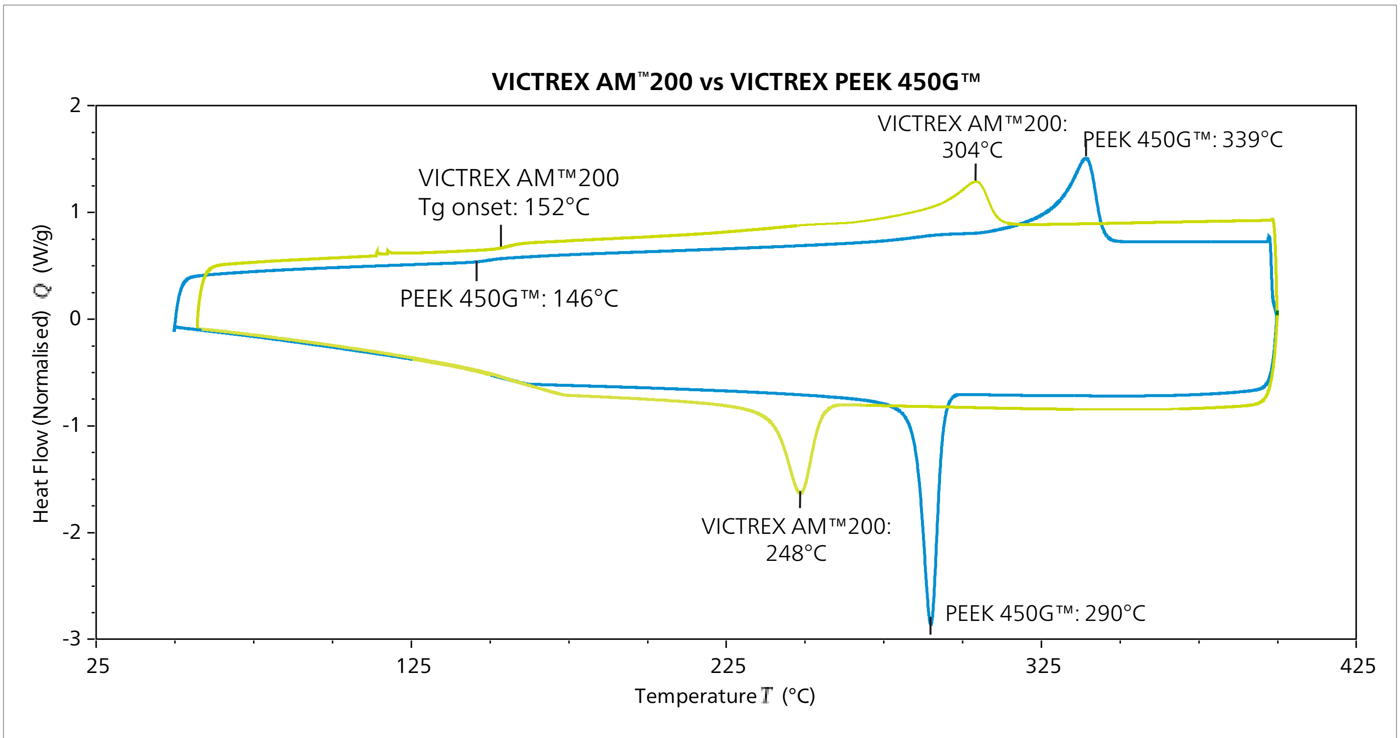


Figure 5: Differential Scanning Calorimetry (DSC) for the PAEK optimised for filament fusion. The comparison of percent crystallinity is inferred by the area under the melting transition and infers that the new PAEK is capable of similar crystallinity to traditional PEEK polymer, which is important for chemical and thermal resistance

IMPROVING PAEK FOR FILAMENT FUSION

One of these new polymers is VICTREX AM™ 200, a 1.75mm filament, while others remain in development. These newly developed polymers, optimised for filament fusion, have lower melt temperatures, slower crystallisation, and a viscosity tuned to the FF process, such as easier flow in lower shear conditions, allowing for better consolidation.

These traits contribute to improved interlaminar adhesion, and easier printing (less shrink and warp). Certain variants of our new polymers may also be printed amorphous, as they are less likely to crystallize during filament fusion printing, and then may be post-annealed to achieve the final desired level of crystallinity.

Figure 5 shows a DSC curve of one of the new polymers. You can see when tested the improvements in thermal transitions that contribute to easier printing:

- Lower melt temperature
- Lower crystallisation temperature
- Broader, "slower" crystallisation, allowing more time for interlayer bonding and better dimensional stability

Additionally, the new polymer maintains its lower viscosity – or higher flow – even in low shear situations, such as hitting the open air after leaving the nozzle, compared with both PEEK and PEKK.

This contributes to reported "easier printing," and may also contribute to the higher observed mechanical properties.

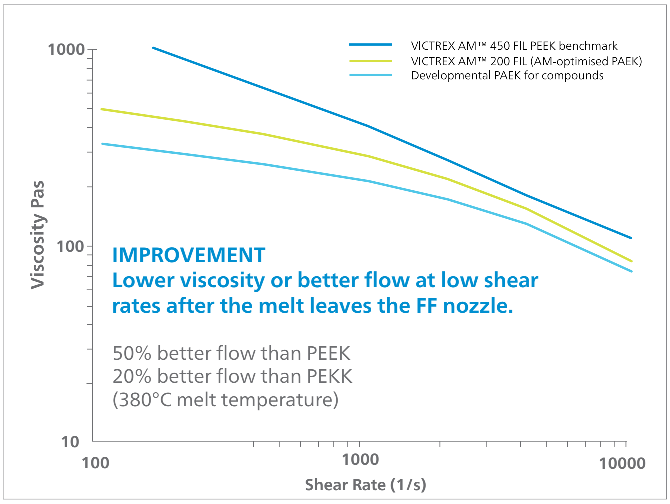


Figure 6: Melt viscosity vs. shear rate for the new filament fusion optimised PAEK, VICTREX AM™ 200.

IMPROVING PAEK FOR LASER SINTERING

Other polymers degrade when held at the elevated chamber temperatures for many hours. Our new developmental polymers for laser sintering have lower melt temperatures, which allows lower chamber temperatures to be used, contributing to easier printing, greater thermal stability, and more accessible machine options. In laser sintering, the print chamber, or oven, is usually set just below melt temperature, and remains there for the duration of the print. A much lower melt temperature means that the bed temperature at which the entire Laser Sinter build is held for many hours is significantly reduced, contributing to reduced thermal degradation in the polymer. Additionally, there are more machines available with an oven temperature close to 300°C than machines available with oven temperatures to 350°C and above.

The crystallisation point for our new laser sintering polymer is also broader and lower, helping with consolidation in sintering of the polymer powder. The improved thermal stability and lower process temperatures make the new PAEK much less susceptible to the refresh rate problem typical of PEEK and PEK. Figure 7 shows a comparison of polymers after long exposure to printing temperatures where the group on the left is the new more recyclable PAEK polymer optimised for sintering, and the group on the right is the PEK benchmark. The improved stability of the new polymer is visibly apparent, and initial refresh rate studies show these benefits are more than skin deep, contributing to stable mechanical properties over multiple cycles. We expect significant improvement over 100% refresh rates required in PEEK and PEK in the past, toward 50-60% refresh rates typical in common nylon materials laser sintered today.

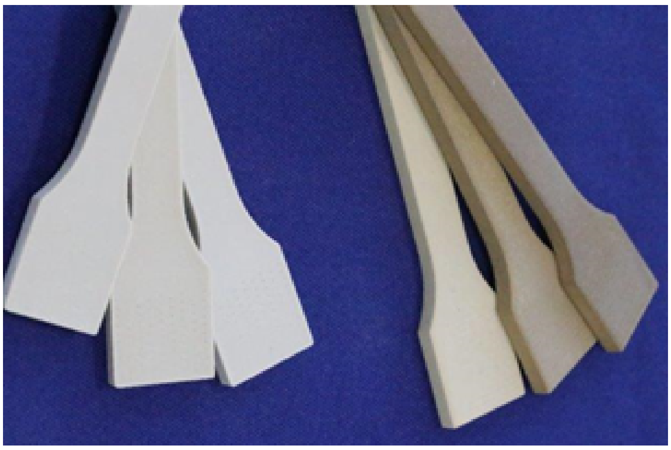


Figure 7: Visual comparison of optimised PAEK (left) vs. PEK (right) after long exposure to printing temperatures.

	Injection-moulded VICTREX PEEK 450G™ benchmark	Typical FF of 450G™ (machine dependent)	Observed FF of new AM optimised PAEK	LS PEKK, commercial datasheet	Observed LS of new AM optimised PAEK
Tensile Strength XY	98 MPa	60-70 MPa	60-90 MPa (machine dependent)	75 MPa	
Tensile Strength ZX	98 MPa	10-30 MPa	40-70 MPa (machine dependent)	62 MPa	70-80MPa
Tensile Modulus XY	4 GPa	3 GPa	3.1 GPa	4.8 GPa	3.7 GPa
Elongation to Break XY	45%	2-10%	12%	2.5%	>10%

Table 1: Illustrative comparison of properties. Injection moulded benchmark is drawn from the published datasheet for VICTREX 450G™. Observations of new AM optimised PAEK are Victrex internal on various machines. A datasheet for VICTREX AM™ 200 filament on a low chamber temperature machine is available by request. The laser sintering benchmark for PEKK references a published datasheet from a PEKK manufacturer. Observations on laser sintering of VICTREX AM™ optimised PAEK are from internal observations, and work conducted at University of Exeter on developmental powders.

IMPROVEMENTS IN PERFORMANCE

These improvements in the printability of PAEK do result in improved performance in printed parts. Most notably, z-axis strength of 70 MPa has been shown to be achievable using the new FF grade under the right conditions.

As these results came from a pure polymer without additives or overly complicated blends, this represents a big step forward compared to similar materials. For instance, the z-axis strength of printed PEEK is typically <30-40 MPa, and often as low as 10-20 MPa.

In laser sintering, refresh rates are improved dramatically, helping to improve the business case for printing PAEK parts. Most notably, elongation to break over 10% is achievable with the new LS grade, whereas most commercial sintering PAEK solutions are brittle, at around 2-3% elongation to break.

Figure 8: Manifold printed with VICTREX AM 200 filament, befor and after annealing (Photo courtesy of Intamsys).

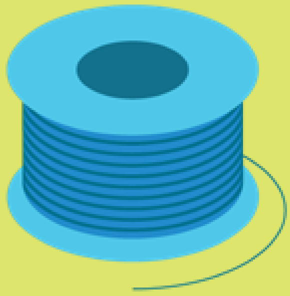
UNFILLED FILAMENT NOW AVAILABLE

Whilst Victrex continues to further optimise the new PAEK products, our first AM optimised 1.75mm filament, VICTREX AM™ 200 FIL is now commercially available. It is currently available for evaluation by owners of PAEK capable 3D printing machines in high-performance applications.

Additional developmental products will be available over time, and R&D managers, engineers, and designers hoping to combine additive manufacturing with PAEK are encouraged to contact Victrex to discuss the options.

WHAT ARE YOUR CHALLENGES?

Contact our team directly at VictrexAM@victrex.com to discuss or visit the Victrex Website and get a first impression if additive manufacturing with PAEK polymer is right for you.



As a global high-performance polymer solutions provider, Victrex serves more than 40 geographies worldwide across the automotive, aerospace, medical, electronics, industrial and energy markets.

VICTREX™ PEEK is regarded as one of the highest-performing engineering thermoplastics in the world, and is used by leading companies to develop fuel-efficient automobiles and aeroplanes, advanced medical devices, next generation technology and tools for the harshest environments.

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