WHITEPAPER

WHY VICTREX PEEK™ IS ANTICIPATED TO SUPPORT ENERGY TRANSITION TO HYDROGEN

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As the world seeks to limit the effects of climate change, hydrogen produced with renewable energy is anticipated to become a major source of cleaner energy not only to provide heat to domestic buildings and industry but also to fuel for cars, airplanes, trains, and ships. Hydrogen as an energy source for industry is new technology which brings many layers of economic and technical complexity. In particular, a common idea is that the transition will include at least one intermediate step, blue hydrogen, on the journey from grey to green (Table 1). Each stage of the transition will present a set of technical and commercial challenges.

GREY & BROWN	BLUE	GREEN
Produced from fossil fuels (natural gas + coal)	Produced from fossil fuels (natural gas + coal)	Produced by electrolysis of water
Large amount of CO_2 emissions produced	Dependent of adoption of carbon capture and storage	Powered by renewable energy (e.g. wind + solar)
Relatively low in cost	An important step in energy transition from Grey to Green	Cleaner but currently more expensive

Table 1. Types of Hydrogen[1]

It is fortunate that infrastructure for compressed gases, including hydrogen, has already been developed for chemical and petrochemical operations.[2,3] Victrex polyether ether ketones (PEEK) based components have performed critical sealing, isolation, compression, storage, and distribution functions for many years. It is anticipated that translation and adaptation of PEEK-based technologies will enable accelerated development of future hydrogen supply chains.

HYDROGEN SUPPLY CHAIN

For hydrogen as a fuel source to be cost competitive, secure, energy efficient, and environmentally friendly, options for technology need to be carefully considered. A future hydrogen supply chain will likely be complex – there may be multiple means of production, conversion, storage, transport, and end use (Figure 1).

Common goals for these multiple pathways are anticipated to include:

- Reducing emissions (lower permeability)
- Increasing efficiency (high strength-to-weight ratio, low friction and wear)
- Increasing reliability and service life (chemical resistance, temperature resistance)
- Mitigating EH&S risk (reduced emissions)

From production of gas to usage there are multiple stages of storage and offloading, each of which demands accurate and safe transfer of hydrogen. Here polymers and elastomers are essential components of the supply chain, from liquefaction to gasification. [1,5]

Hydrogen Supply Chain Schematic

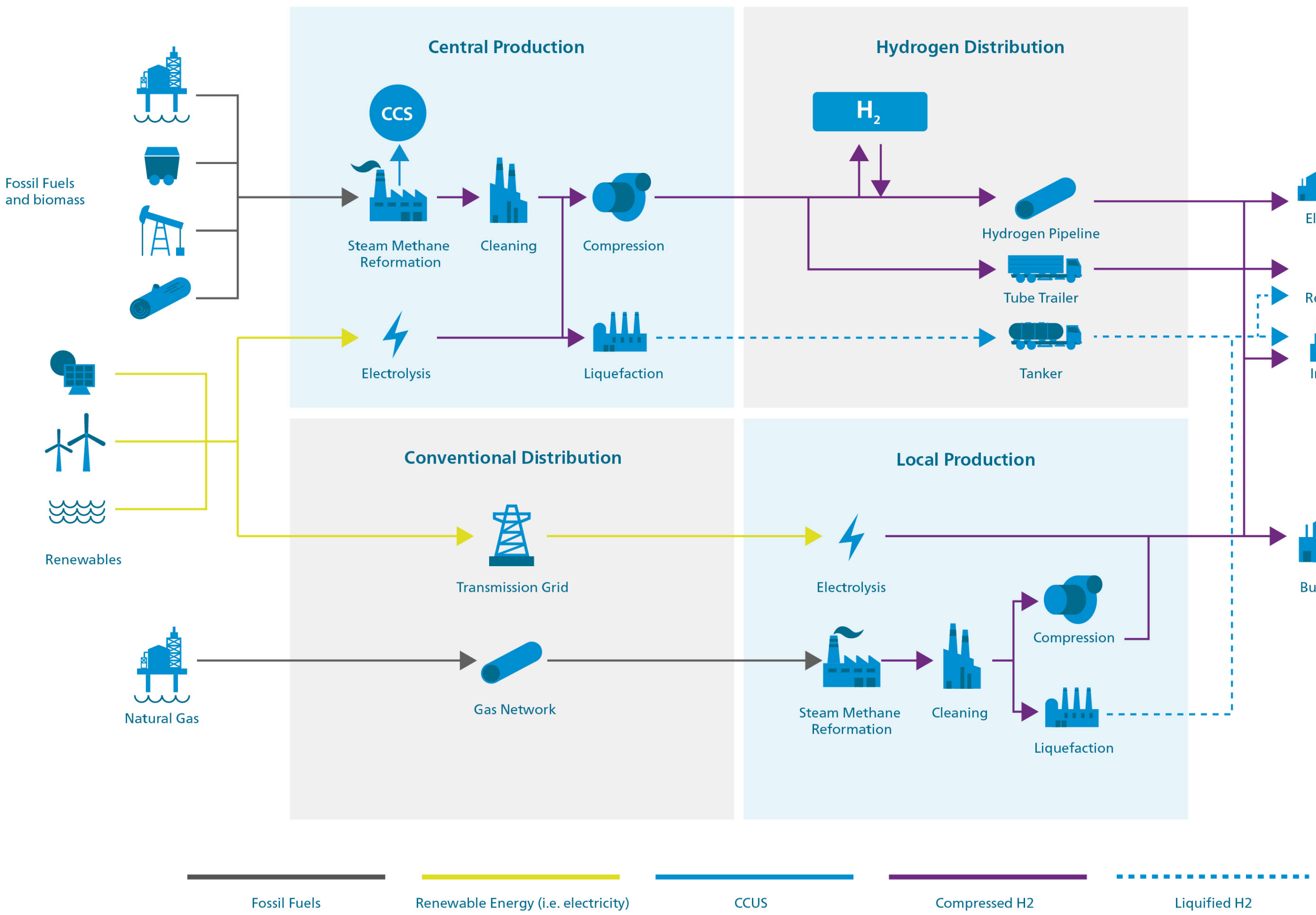

Figure 1. Production, distribution, and end-uses of hydrogen.[4]

VICTREX PEEK POLYMER SOLUTIONS

VICTREX™ PEEK and its formulations provide a unique combination and range of high performance properties – its structure from molecular to macroscopic scales contributes to high strength/toughness at extreme temperatures, low permeability, low friction, and high wear resistance needed for seals, valves, and packings (Figure 2).

- Extreme Temperature: strength/toughness at very low (cryogenic) to high temperatures.
- Weight Reduction at Equivalent Stiffness: up to 70-85% lower weight at equivalent stiffness compared to some metals. Higher strength-to-weight ratio enables higher efficiency.
- Tribological Performance: ability to perform in hydrodynamic, mixed friction, boundary lubrication, and even dry conditions.
- Stable Properties: retention of properties in corrosive, contaminated, and low/high temperature service conditions.
- Tunable Properties: PAEK and PEEK polymers are thermoplastic and consequently can be melt formulated with additives to enable design of properties for purpose.

Figure 2. Advantages of VICTREX PEEK solutions – a unique combination of properties.

SELECTION OF POLYMERS FOR USE AT CRYOGENIC TEMPERATURES

An important portion of the future hydrogen infrastructure will handle cryogenically cooled, liquified hydrogen. The denser cryogenic liquid state (~0.07 g/cm^3) has a greater concentration of hydrogen than the gas compressed to maximum pressures of conventional storage vessels (~0.03 cm/^{3} at 50 MPa and 25°C)[6] making it potentially a more valuable source of energy. Various steel and nonferrous alloys have been developed over the years to meet the challenges of property retention (especially ductility) at such extremes of temperature.

Mechanical properties of polymers are related to the positions of transitions and relaxations which lay below the glass transition temperature[7] and which can be identified from relaxation spectra using a variety of techniques such as dynamic mechanical thermal analysis (DMTA). Kreibich[8] notes that nearly all polymers which are tough in their glassy states exhibit clearly defined low temperature relaxations.

Above the glass transition temperature (T_g) there is sufficient free volume for large scale movement of polymer chains in the amorphous regions of the polymer. The next transition is the β transition. Bershtien[9] notes that the β transition might be considered as an 'activation barrier' for solid phase reactions such as deformation, flow and creep. It has been suggested that in the region from T_β to T_α, there is enough free volume available to permit movement of whole side chains and between 4 and 8 backbone atoms. From T_β to T_Υ (lower temperature) free volume decreases and movement of molecular chains is restricted to stretching and bending of bonds and commonly associated with re-orientation of chain ends[10]. Boyer[2] notes that there is, in many cases, a link between toughness and the location of T_β, but that this is not always the case.

Nelson[11] relates the transition to vibration damping and therefore suggests that the scale of the β transition is a measure of how readily the polymer will absorb vibration.

These low temperature relaxations identified in PEEK polymers by Adams and Gaitonde[12] are reproduced along with additional data at higher temperatures in Figure 3. Moving from high to low temperature successive transitions are denoted with the Greek letters α, β, ϒ, and δ. 'α' is the glass transition temperature.

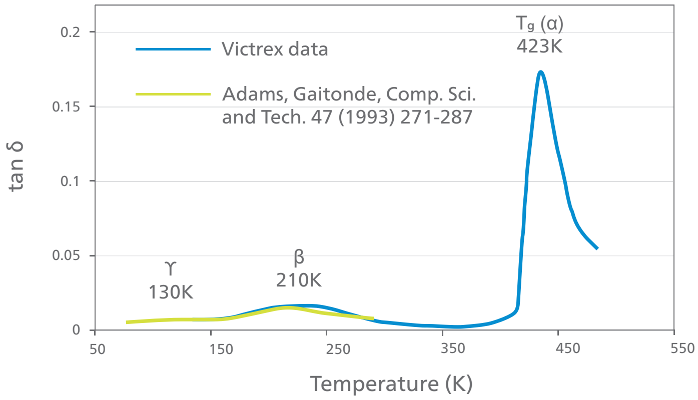

Figure 3. Alpha, beta and gamma relaxations in PEEK polymer.[12]

The β relaxation in PEEK at 210 K (-63°C) is well defined and of significant scale, while the somewhat less well defined (but still clear) ϒ relaxation is at 130K (-143°C). The ability of polymer segments and side chains to move at these lower temperatures is associated with strength and toughness. The authors note that the specific damping capacity of PEEK is significantly greater than many existing materials which are used in low temperature applications.

The transition temperatures for PTFE, which is often found in cryogenic sealing applications, are shown in comparison to PEEK in Table 2 below:

MATERIAL	METHOD	ϒ (°C)	β (°C)	α (°C)	MELTING (°C)
PTFE[13]	DMTA, Tan δ	-97	19-30	127	327
PEEK[14]	DMTA, Tan δ	-143	-63	150	343

Table 2. Transition Temperatures for PTFE and PEEK.

Although these two polymers have similar melting points, the 'glassy' region, between T_α and T_β is around twice as broad for PEEK compared to PTFE. Furthermore, the T_γ for PEEK is at significantly lower temperature albeit a less well-defined feature than for PTFE.

Prior studies might therefore suggest that molecular motion (even of only side chains or short backbone segments) is more prominent in PEEK than PTFE and therefore that a greater level of ductility at low temperatures would be seen.

HYDROGEN EMBRITTLEMENT

Hydrogen embrittlement is a term used to describe the process by which metals, for example steel, become brittle and fracture due to the ingress and diffusion of hydrogen. A significant consequence of this exposure can lead to a substantial reduction in ductility and load bearing capacity. Materials such a high strength steels, titanium and aluminium alloys are the most vulnerable to this phenomenon.[15]

PEEK[16] and other polymers[17] are not expected to be permanently affected by exposure to hydrogen and consequently can be considered to extend the lifetime and reliability of components in hydrogen service across many applications such as sealing solutions and compressors.[18] To assess fitness for purpose for specific applications, evaluation should be conducted relevant operating temperatures and pressures.

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PERMEATION RESISTANCE TO HYDROGEN

Permeability, diffusivity, and solubility are used to describe the dissolution and transport of a gas through a material. Low permeability is generally required in static and dynamic sealing solutions to reduce emissions. PEEK is advantaged in low permeability applications due to its relatively high Tg (α transition) and semicrystalline solid-state structure.

In 2011, Entegris completed a study on the permeation resistance of PEEK to hydrogen at ambient conditions.[19] Permeability, diffusion, and solubility coefficients were measured on two grades of VICTREX PEEK-based APTIV™ extruded films and compression and injection moulded specimens from VICTREX PEEK 150G as shown in Table 3. The generally low permeability of all the PEEK samples can be attributed in part to the glassy state as the ambient temperature was below Tg. The PEEK specimens were differentiated with crystallinity resulting in progressively lower permeability.

Sample	Permeability Coefficients: P ($10^{-10}cm^3$ cm/cm^2 s cm Hg)	Diffusion Coefficients: D (10^{-8} cm^2 s^{-1})	Solubility Coefficients: S (10^{-3} cm^3/cm^3 cm Hg)
Victrex APTIV FILMS 1000 Series	1.81 ± 0.25	29.6 ± 3.4	0.61 ±0.04
Victrex APTIV FILMS 2000 Series	3.60 ± 0.05	53.2 ± 6.4	0.69 ± 0.09
VICTREX PEEK 150G (compression moulded)	1.16 ± 0.04	24.2 ± 4.9	0.50 ± 0.10
VICTREX PEEK 150G (injection moulded)	2.01 ± 0.04	51.6 ± 2.8	0.39 ± 0.02

Table 3. Overall averages of Permeability, Diffusion & Solubility Coefficients of the Hydrogen gas for PEEK films at 25°C. [20]

Among the samples tested, VICTREX PEEK 150G compression moulded film had the lowest permeability to hydrogen and almost three times lower than the amorphous 2000 series of APTIV film.

PEEK may also be advantaged over fluoropolymers in reducing emissions. Figure 4 shows that PEEK has a 63-90% lower permeability to hydrogen gas compared to fluoropolymers. Higher permeability can be attributed to the lower Tg's of PFA to be -80 and 90°C and of PTFE reported to be 34 and 137°C.[18,20]

Comparison of Permeability of Hydrogen Gas at 25°C

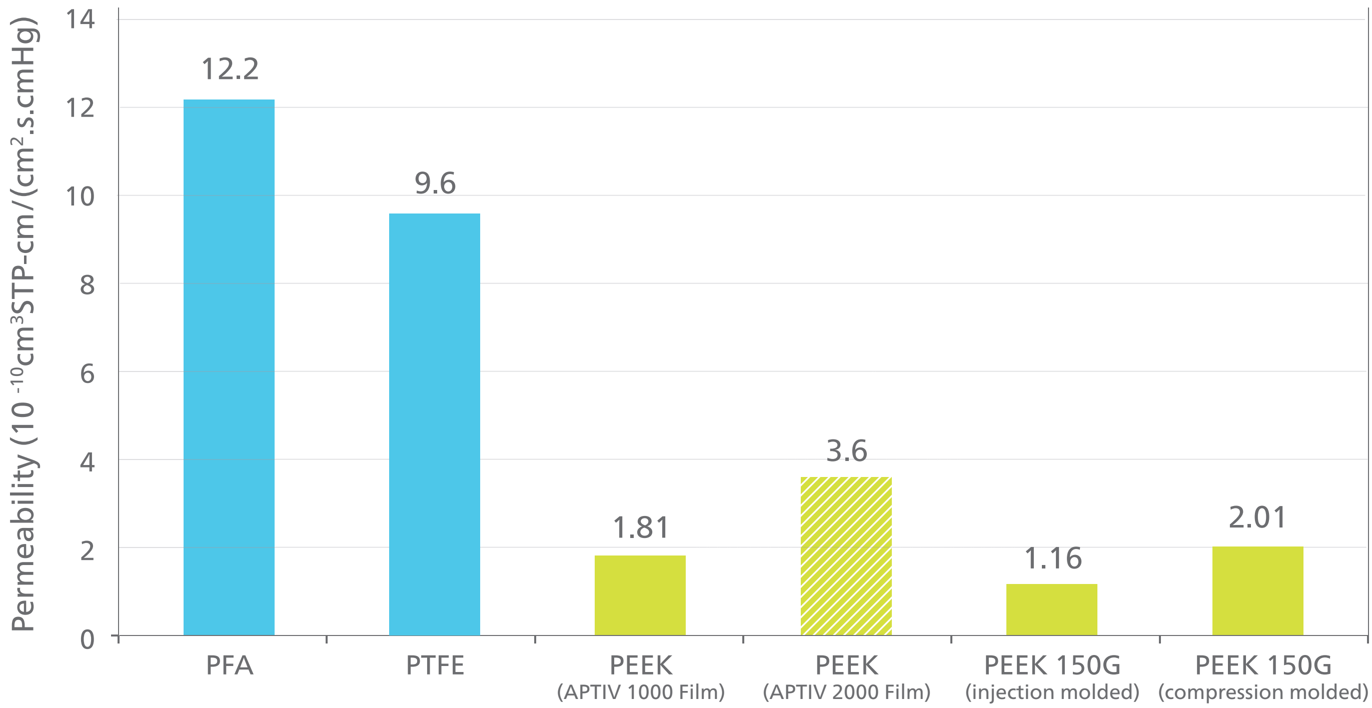


Figure 4. Permeation study of PEEK vs. PFA and PTFE to hydrogen at 25°C. [18]

PEEK APPLICATIONS IN HYDROGEN

Relating the needs of the hydrogen supply chain to steps within the infrastructure suggests potential value PEEK may bring to specific applications (Table 4).

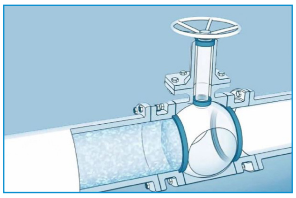
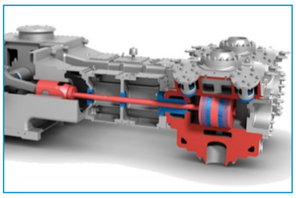
	Minimal Emissions / EHS		Efficiency		Reliability	
Step	Sealing Performance	Minimal Permeability	High Strength-to-weight ratio	Minimal Friction	Low Wear Rates	Robust Mechanical Performance
Target Applications	PEEK Seal 		PEEK Composites	PEEK Packing & Bearings 		General PEEK-based Components
Liquifaction	✓	✓	✓	✓	✓	✓
Compression	✓	✓	✓		✓	✓
Transport	✓	✓		✓		✓
Dispensing	✓	✓				✓

Table 4. Potential PEEK solutions in the Hydrogen Supply Chain.

SEALING SOLUTIONS

Several thermoplastic polymers are commonly found in cryogenic applications and two of these are frequently found in sealing applications. These are polytetrafluoroethylene (PTFE), polychlorotrifluoroethylene (PCTFE or PTFCE), the latter being best known by trade names such as Kel-F[15] and Neoflon[21].

The requirements for a good sealing material for use in cryogenic valves may be described as:

- Suitable stiffness characteristics to allow effective sealing at very low, ambient, and high temperatures (i.e. a wide usage temperature range)
- Rapid recovery on removal of load
- Low friction / torque and high wear resistance
- Toughness and strength commensurate with the application
- Low thermal expansion to maintain fit with adjoining metallic components
- High thermal conductivity to allow rapid equalisation of temperature with surrounding components
- Minimal chemical and physical effects by the gases being conveyed

Given the relaxations in polymers discussed previously, consideration of properties across the full service temperature range is necessary when selecting a sealing material..

A particularly important application is the use of polymers in dynamic sealing applications such as valve seats. At very low temperatures the tribological performance of polymers is quite different: Zhang and co-workers[22] studied the tribology of several polymers including PEEK in such conditions. Their measurements of friction coefficient are shown in Figure 5:

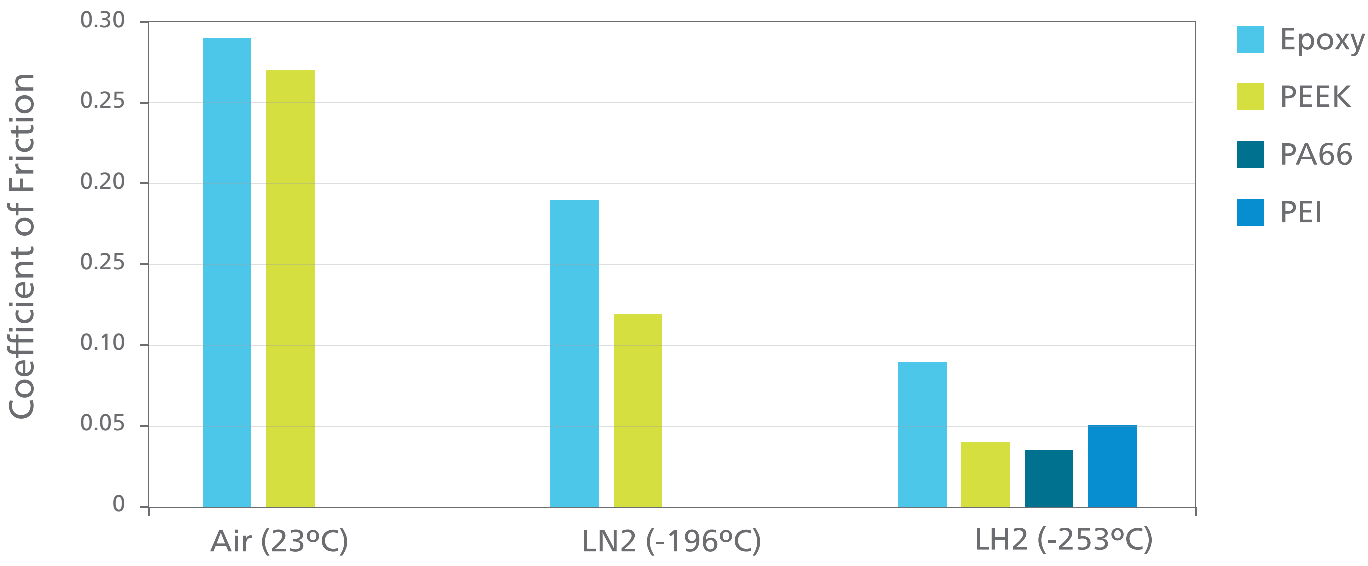


Figure 5. Effect of temperature on the coefficient of friction of some polymers.[25]

The graph shows that the coefficient of friction of the selected polymers reduces significantly as temperature is reduced. The PEEK in this study contained both graphite and PTFE, however, the authors note that the friction coefficient seems to be dominated by the polymer matrix. This significant drop in coefficient of friction is most likely due to the increased stiffness of the polymer which reduces interaction with the metal counter-surface. It is likely therefore that at very low temperatures, there is little difference in the tribological performance of PAEKs and fluoropolymers.

Considering the other performance characteristics of PEEK especially at higher temperatures (Figure 2), suggests potential advantages in applications serve across a broad temperature range.

COMPRESSOR PACKING AND WEAR COMPONENTS

VICTREX PEEK has likely been used in natural gas and hydrogen value chain for downstream (i.e. gas treatment), refining and industrial applications for over 40 years.

VICTREX PEEK solutions have provided stable performance in temperatures ranging from -196°C (-321°F) up to 260°C (500°F) with the capability of withstanding differential pressures up to about 207 MPa (30,000 psi). This key property makes these solutions appropriate for use in both low and high temperature compressor environments.

A significant portion of the operating conditions for a compressor in hydrogen service is anticipated to comprise temperatures within this range.

PEEK-based formulations are shown to have a unique combination of properties (Table 5). They are known for a balance of mechanical strength, ductility (elongation at break), relatively low density, compliance (Shore D), low coefficient of friction, heat resistance, and wear resistance in compressor wear components. Translation of these existing applications of PEEK to green hydrogen service is expected to be a feasible, expedient, and economical means to develop future infrastructures.

	PEEK	PTFE	PI	PPS
Tensile Strength at Break (MPa)	55 - 90	11 - 17	76	76
Elongation at Break (%)	3 - 15	4 - 175	4	2
Specific Gravity (g/cm3)	1.32 - 1.48	1.82 - 2.18	1.41	1.51
Shore D	80 - 87	57 - 72	80	84
COF	0.25 - 0.3	0.08 - 0.25	0.28	0.35
CLTE (ppm/K)	45-63	72-99	~45	~63

Table 5. Comparison of Properties of PEEK, PTFE, PI, and PPS based formulations.

BEARINGS

The performance and reliability of the rolling-element bearings and bearings cages are dependent on the bearing component materials. VICTREX PEEK polymer can replace metal to reduce system cost and save weight, as well as substitute standard polymers which cannot meet decreasing temperature and hydrogen rich gas applications.

NEED FOR CHEMICAL RESISTANCE, MECHANICAL AND WEAR PERFORMANCE

Bearing cages are mechanically stressed by friction, tensile, and inertia forces. They are exposed to organic solvents, coolant, lubricants, lubricant additives and their decomposition products which can be corrosive. The extent to which these factors affect performance depends on such parameters as temperature, impact resistance, vibrations or a combination of these and other factors.

Figure 6. Example of a PEEK bearing cage.

PEEK BEARING CAGE FOR ROLLER BEARINGS

Bearing cages made from PEEK polymer are characterized by their balanced combination of strength and elasticity. The low coefficient of friction of the polymer on a steel surface produces minimal friction between the cage surface and the balls so that there is very little heat and wear inside the bearing. Moreover, the low density of the material reduces the weight which, in turn, reduces the moment of inertia force and gives greater angular velocity to the bearing. Tribologically optimized compounds allow the bearings to run dry for a brief period without the danger of friction wear or damage. This suggests that the amount of applied grease could be reduced to make a favourable environmental contribution while maintaining performance.

Regardless of form, VICTREX PEEK polymer as a bearing cage material can provide the following benefits:

- Accommodates high continuous temperatures and very high speeds
- Reduces heat generated by the bearing
- Reduces energy consumption
- Accommodates shock forces and high centrifugal forces
- Enables bearing to survive longer under poor lubrication conditions
- Extends bearing service life

CONCLUSIONS

Victrex polyether ether ketones (PEEK) based components have been used in existing infrastructure for distribution of gases including hydrogen for many years. Adaptation of existing PEEK-based sealing, isolation, and compression technologies is anticipated to be a practical means to realize the energy transition to hydrogen on an accelerated timeline.

In seals, valves, compressor packing and other components. VICTREX PEEK offers the potential to:

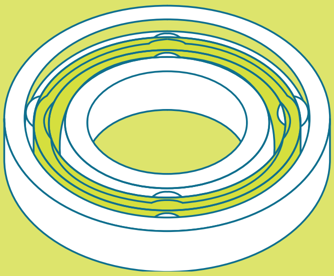
- Reduce emissions (lower permeability)
- Increase efficiency (high strength-to-weight ratio, low friction and wear)
- Increase reliability and service life (chemical resistance, temperature resistance)
- Mitigate EH&S risk (reduced emissions)

These benefits, technical attributes, and an existing manufacturing base of processors/moulders, tier 1 suppliers, and OEMs should enable rapid scalable production. With over 40 years of experience, Victrex expertise can support the development of the next generation of components needed for the hydrogen supply chain.

LET'S TALK!

Considering PEEK-based sealing, bearing, or compression technologies for your hydrogen component?

Contact our team directly at CleanEnergy@victrex.com.



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In renewable energy, VICTREX™ PEEK-based solutions could facilitate LCoE (Lower Cost of Energy), improved reliability and reduced maintenance costs as well as extended service life. Learn more: www.victrex.com/energy

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