TECHNICAL PAPER

IMPROVING CRYOGENIC PERFORMANCE WITH VICTREX CT™ POLYMERS

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VICTREX CT™ GRADES: WHITEPAPER

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INTRODUCTION

Substantial growth in demand has resulted in significantly increased amounts of natural gas produced to be liquefied and transported around the world by a network of specialist tankers. Liquefied Natural Gas (LNG) provides extreme low temperature challenges to the Energy Industry. Where polymers and elastomers are essential components of the supply chain, from liquefaction to gasification.

Commonly, PAEK polymers are associated with high temperature performance, high chemical resistance and a unique range of mechanical properties. This paper provides an overview of two novel PAEK polymers which provide a particular range of properties over the temperature range from +200°C to -196°C. Across this temperature range, while chemical resistance is important, other aspects such as low temperature stiffness, toughness, tribology, and thermal properties such as conductivity and expansion are all significant in applications such as valve seats and packings. The paper introduces some possible selection criteria for polymers used at very low temperatures and explains performance on a molecular as well as macro level. The Victrex CT polymers are described together with properties and application specific data which indicates where they may be used.

SELECTION OF POLYMERS FOR USE AT CRYOGENIC TEMPERATURES

LNG is a mixture of hydrocarbons, predominantly methane but with varying levels of ethane, propane, butane and other naturally occurring gases. LNG normally has a boiling temperature between -166°C and -57°C at atmospheric pressure.

According to EN / ISO 16903[1], many common materials of construction fail in a brittle manner when they are exposed to these very low temperatures and recommends that materials used in contact with LNG should be proven resistant to brittle fracture.

Various steel and nonferrous alloys have been developed over the years to meet the challenges of property retention (especially ductility) in such extremes of temperature. For polymers, mechanical properties are related to the positions of transitions and relaxations which lay below the glass transition temperature[2] and which can be identified from relaxation spectra using a variety of techniques such as DMA. Kreibich[3] notes that nearly all polymers which are tough in their glassy states exhibit clearly defined low temperature relaxations.

There are three basic requirements for polymers to function well at very low temperatures[4]. These are:

- Processability
- Mechanical properties at room temperature
- Flexibility and toughness at low temperatures.

Several thermoplastic polymers are commonly found in cryogenic applications, and two of these are frequently found in sealing applications. These are Polytetrafluoroethylene (PTFE), and Polychlorotrifluoroethylene (PCTFE or PTFCE), the latter being best known by trade names such as Kel-F[5] and Neoflon[6].

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 prevent thermal mismatch with adjoining metallic components
- High thermal conductivity to allow rapid equalisation of temperature with surrounding components.
- Widest possible operating range of temperature and pressure.

Reducing temperature produces a progressive increase in tensile and flexural strength as well as stiffness, creep resistance and fatigue strength. There is also a progressive decrease in elongation, fracture toughness, impact strength, compressive strength and coefficient of linear thermal expansion (CLTE). In practice however, as temperatures fall a decrease in strength is often noted since low temperatures cause a loss in flexibility which may result in brittle failure before the yield point is reached.

The chemical environment may also have an effect upon the properties of the polymer at low temperatures: in a similar way to that in which solvents promote crazing in polymers at elevated temperature, when gases are in a highly active state (i.e. near their condensation point) they may also promote the loss of yield strength. Absorbed gases reduce surface energy (assisting with the creation of new surfaces in crazes) and can also act as a plasticizer.

With this background of development of the cryogenic space and existing sealing materials, Victrex has developed and introduced a new family of PAEK polymers known as VICTREX CT™ polymers.

VICTREX CT POLYMER FAMILY

Following the introduction of the Victrex CT100 grade in 2017, Victrex CT200 was introduced in 2019. Based on the same polymer technology, the latter is specifically intended for dynamic valve applications.

The use of PAEK polymers at elevated temperatures in conjunction with high chemical resistance and a unique range of mechanical properties is common, so what makes these materials suitable for operation at the other end of the temperature spectrum?

In general, the temperature related transitions in polymers appear as in Figure 1:

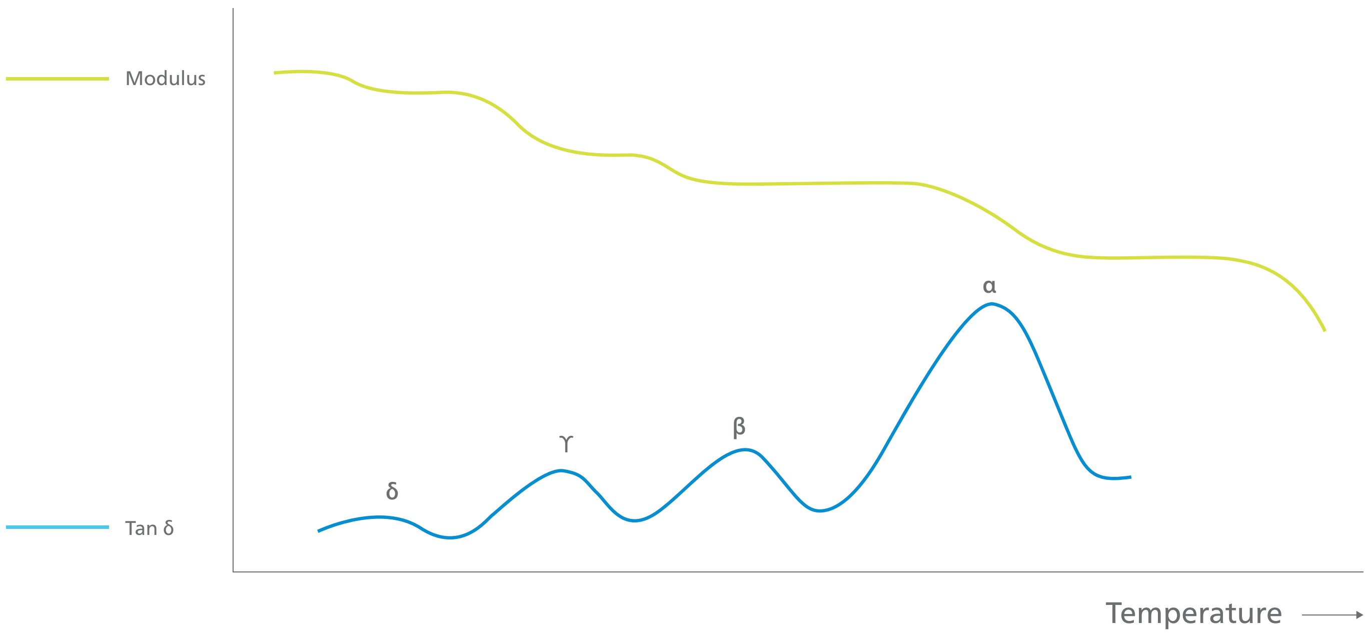

Figure 1: Transitions in thermoplastic polymers

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. Above Tg 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[7] notes that the β transition might be considered as an 'activation barrier' for solid phase reactions such as deformation, flow and creep. It is has been suggested that in the region from Tβ to Tα, there is enough free volume available to permit movement of whole side chains and between 4 and 8 backbone atoms. Moving from Tβ to Tϒ (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[8]. Boyer[2] notes that there is, in many cases, a link between toughness and the location of Tβ,but that this is not always the case. Nelson[9] 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 relaxations have been identified in PEEK polymers by Adams and Gaitonde[10] and are reproduced in Figure 2 below:

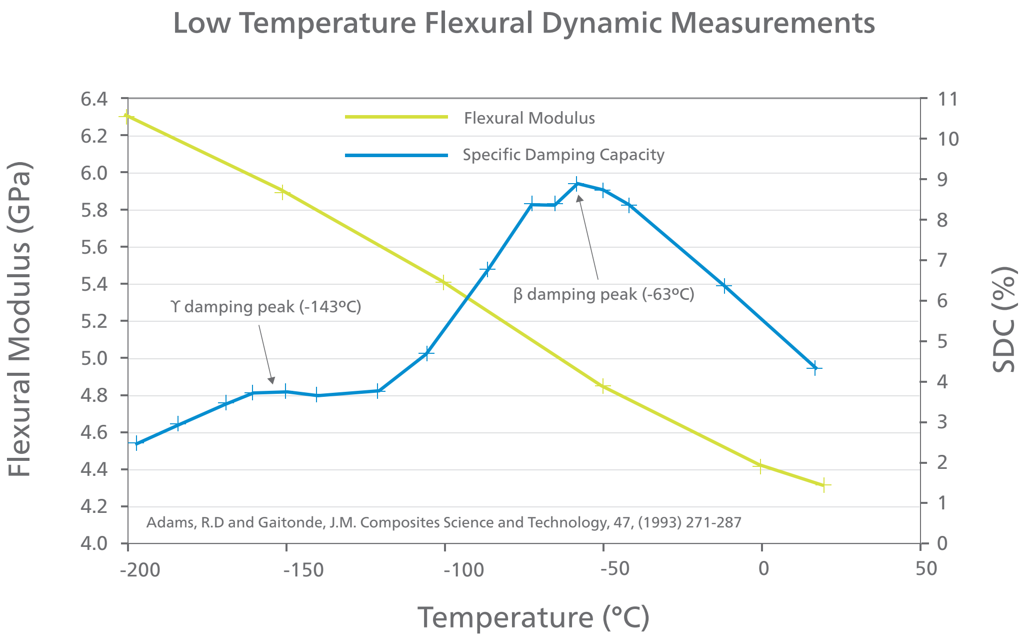

Figure 2: Beta and Gamma relaxations in PEEK polymer

Their work shows the β relaxation in PEEK at -63°C is well defined and of significant scale, while the somewhat less well defined (but still clear) ϒ relaxation is at -143°C. The ability of polymer segments and side chains to move at these lower temperatures is associated with an ability to exhibit some strength / toughness and 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 1 below:

Material	Method	ϒ	β	α	Melting
PTFE[11]	Tan δ	-97	19-30	127	327
PEEK[5]	Tan δ	-143	-63	143	343

Table 1: Transition Temperatures(°C) for PTFE and PEEK

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

Existing research papers might therefore suggest that molecular motion (even of only side chains or short backbone segments) is more feasible in PAEK's than PTFE and therefore that a greater level of ductility at low temperatures would be seen.

VICTREX CT™ 100 PAEK polymer provides very low temperature performance required for applications associated with the production and transportation of Liquid Natural Gas (LNG). It is well suited to static sealing applications at very low temperatures and in addition, significantly widens the useful temperature envelope at the high temperature end. A heat deflection temperature (at 264 psi) of 152°C for PEEK compared to 65°C for PTFE (glass or carbon filled) indicates that the former will retain very high creep and creep extrusion resistance in high temperature (or pressure) operation.

According to Victrex test data, the ambient temperature VICTREX CT™ 100 polymer is less compliant than fluoropolymer materials the latter requiring a lower sealing force. The elongation at break of the fluoropolymers is also significantly higher than either CT100 or CT200 as shown in Figure 3 below:

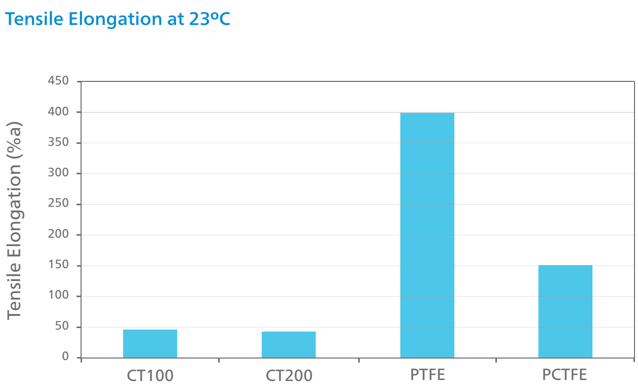

Figure 3: Tensile Elongation at break for CT Polymers and Fluoropolymers

The modulus of the fluoropolymers is significantly lower than the CT grades, indicating a good ability to seal (Figure 4):

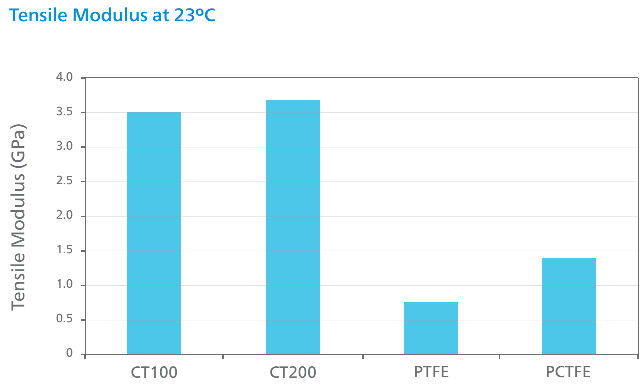

Figure 4: Tensile Modulus for CT Polymers and Fluoropolymers

The use of PAEK polymers as primary sealing components is however widespread with good design and production practice. In ambient to high temperature application the CT Polymers could offer significant improvements in dimensional stability and creep resistance. Specifically, the higher strength and modulus of these polymers presents an opportunity to design and manufacture seals for higher pressure systems where the fluoropolymers are unable to withstand the high creep loads required. Between ambient and 77K the modulus of the fluoropolymers increases steeply whereas for the CT family the change in stiffness is relatively minor as shown in Figure 5.

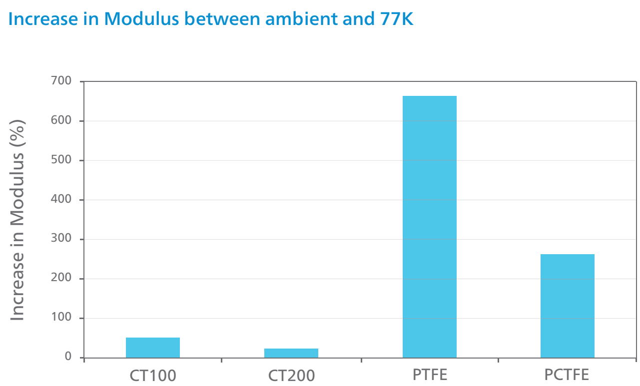

Figure 5. Change in modulus between ambient and 77K

The result of these changes is that at 77K, PTFE has a modulus 23% higher than the CT grades while PCTFE is 15% more stiff.

The increase in stiffness means that higher loads must be placed upon the material for it to conform to a mating metal part and achieve a seal. It follows then, that the CT polymers require lower sealing force at cryogenic temperatures than the fluoropolymers.

Victrex CT100 is specifically targeted at static sealing components, providing improved ductility and toughness at cryogenic temperatures and providing a wide application temperature range. CT100 is not, however, a simple substitute polymer for dynamic sealing applications exhibiting more challenging tribological behaviour at ambient temperatures.

Victrex CT200 is specifically targeted for dynamic sealing applications. This material exhibits improved ductility and higher strength than fluoropolymers at -196°C, with lower stiffness providing for lower sealing forces in operation. Furthermore, CT200 has a significantly higher operating temperature range which allows superior sealing at up to150°C.

Victrex CT200 builds upon the excellent low temperature properties of CT100 using a proprietary additive system to provide targeted tribological properties in the ambient to high temperature range with equivalent or lower operating torque than fluoropolymer products.

At room temperature the coefficient of friction of CT100 on a steel counterface is around 0.2 compared to between 0.05 and 0.2 for PTFE. Adhesive wear is the primary wear mechanism in such materials, as shown in Figure 6,

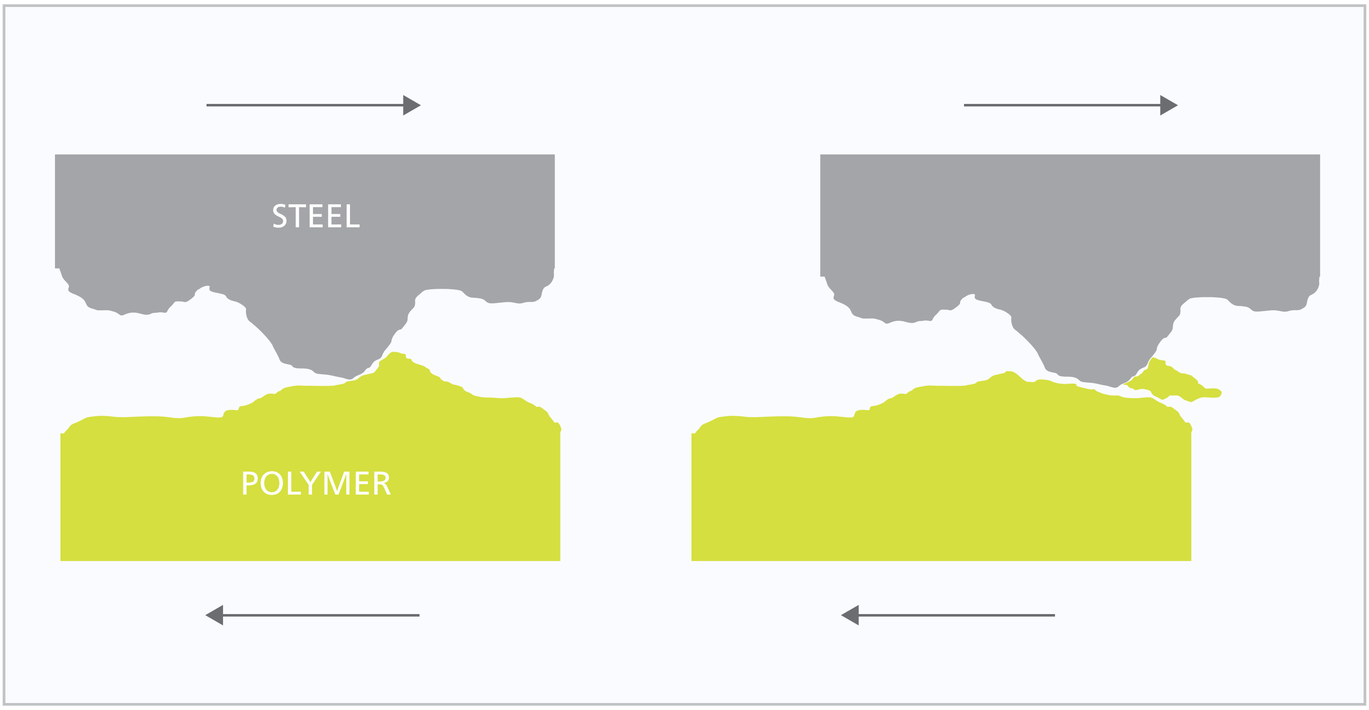

Figure 6. Adhesive wear mechanism

Pressure between the polymer and the counterface causes an adhesive interaction between them: relative movement requires shearing of these micro-joints. The typical shear strength of PTFE is <10MPa compared to ~50MPa for PAEK's. The lower shear strength in PTFE means that it has a greater propensity to shear and form a lubricating film layer on the steel surface. This results in a lower coefficient of friction. In a ball valve seat this is manifested as the required torque to turn the valve to open or close (Figure 7):

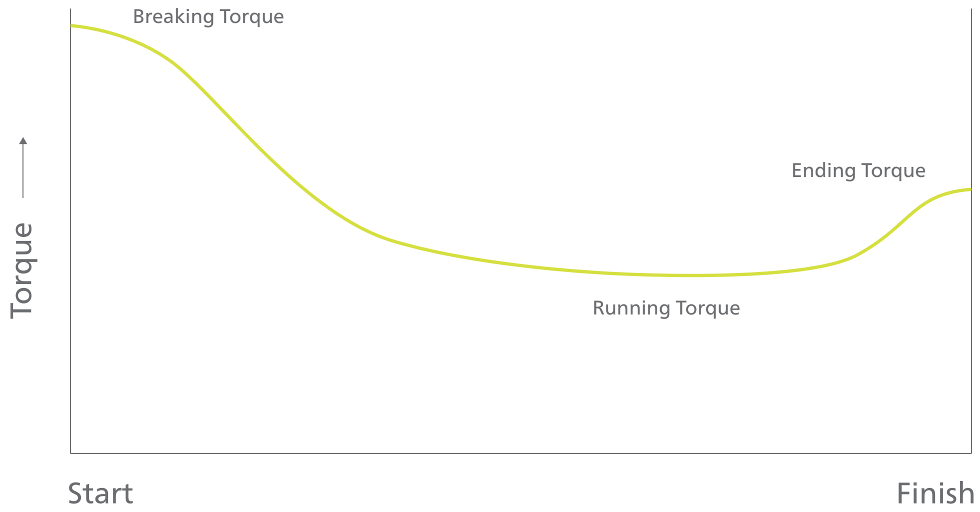

Figure 7. Torque Cycle in a ¼ turn ball valve

Victrex CT200 has potential to provide an appropriate level of sealing force and lubricity at ambient to high temperatures, typically reducing required torques for valve operation to levels associated with PTFE and PCTFE.

At very low temperatures the tribological performance of polymers is quite different: Zhang and co-workers[12] studied the tribology of several polymers including PEEK in such conditions. Their measurements of friction coefficient are shown in Figure 8:

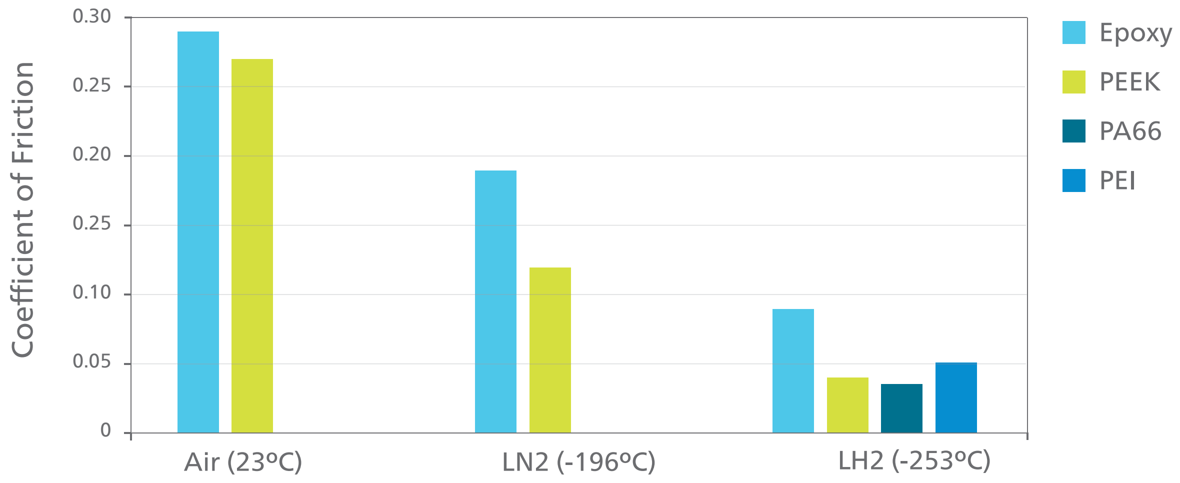

Figure 8. Coefficient of friction versus temperature (from Ref 12)

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 PAEK's and Fluoropolymers.

Victrex CT200 therefore provides a compelling combination of toughness and tribological performance which specifically lends it to use in dynamic valve sealing parts for operating across the entire range of cryogenic to +150°C.

The sealing and tribological performance of CT200 were evaluated in 2019 against an equivalent PCTFE insert in a 10" diameter trunnion ball valve (Figure 9).

Figure 9. 10 inch diameter trunnion ball valve test

The test parameters involved holding pressure from 2 to 275 bar for 5 minutes at each level over a temperature range spanning ambient to 125°C and down in stages to -196°C before returning to a final test at ambient. CT200 exhibited superior sealing at both the high and low end of temperature with near equivalent sealing at ambient.

Comparison of the required operating torque of the valve with the CT200 and PCTFE seats indicates that there is little difference in tribological performance across the entire temperature range (Figure 10):

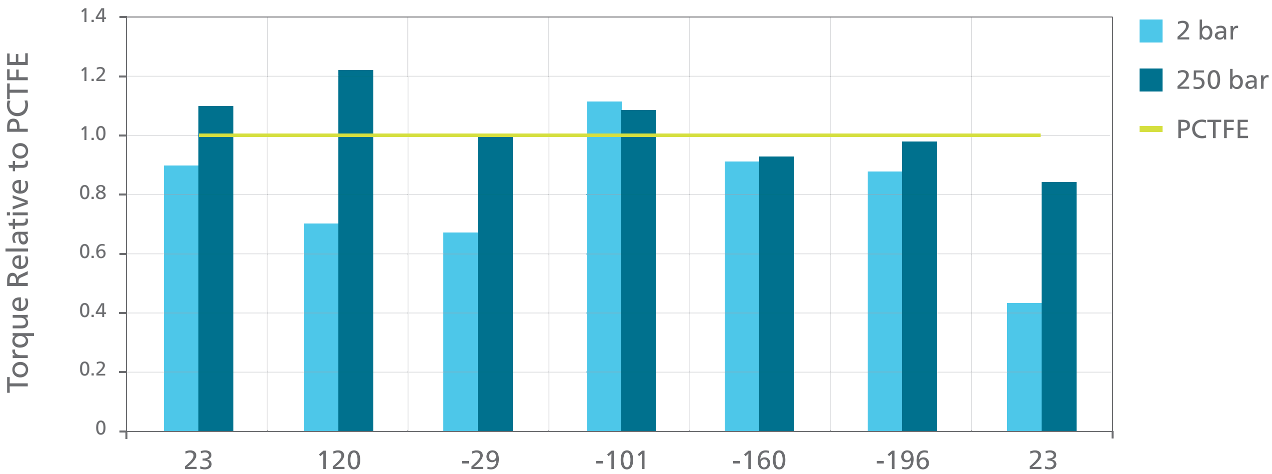

Figure 10. Operating torque required for CT200 valve seat relative to PCTFE seat at 2 and 250 bar over the tested temperature range.

SUMMARY

- Victrex CT Polymers can provide superior ductility and lower sealing force compared to commonly used polymers for cryogenic applications.
- For static sealing applications, Victrex CT100 provides high levels of low temperature ductility.
- For dynamic sealing CT200 combines superior low temperature properties with ambient temperature tribological performance to provide an alternative polymer system with wider operating temperature range.

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