TECHNICAL PAPER

IMPROVING CRYOGENIC VALVE PERFORMANCE WITH VICTREX CT™ 100 POLYMER SEALING SYSTEMS

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INTRODUCTION

A substantial growth in requirements has resulted in increasing amounts of natural gas being produced to be liquefied and transported around the world by a network of specialist tankers. Liquefied Natural Gas (LNG) provides a range of low temperature engineering challenges to the industry. Here polymers and elastomers are essential components of the supply chain, from liquefaction to gasification. There are numerous areas where such materials are required for the transportation, distribution and use of liquefied gases. Applications range from complex piping and transportation systems to seals, gaskets and packings.

It is estimated that the Arctic may contain up to 1,670 trillion cubic feet of natural gas and 90 billion barrels of oil[1]. This vast, and yet untapped, resource provides a starkly different and new set of challenges to the Oil and Gas Industry, which apart from having to deal with down hole conditions which may be familiar, is confronted with a series of new material requirements topside, to provide functionality and reliability at temperatures which may drop below -50°C. With great focus on environmental issues, safety and reliability are key.

To date, many sealing applications in the Arctic to Cryogenic temperature ranges have been fulfilled by fluoropolymers.

Commonly, PAEK polymers are associated with high temperature performance, high chemical resistance and a unique range of mechanical properties. This paper will provide an overview of a PAEK polymer that provides a unique range of properties over the temperature range from +200°C to -196°C, that can rival those of fluoropolymers at the low temperature end. In this temperature range, chemical resistance is still important but other aspects such as low temperature toughness and friction, and thermal properties such as conductivity and expansion are the most important to applications such as valve seats and packings. Properties and application specific data have been generated through work commissioned by Victrex by an independent laboratory. Comparisons between commonly used fluoropolymers and the PAEK polymer as well as a range of potential application areas will be discussed.

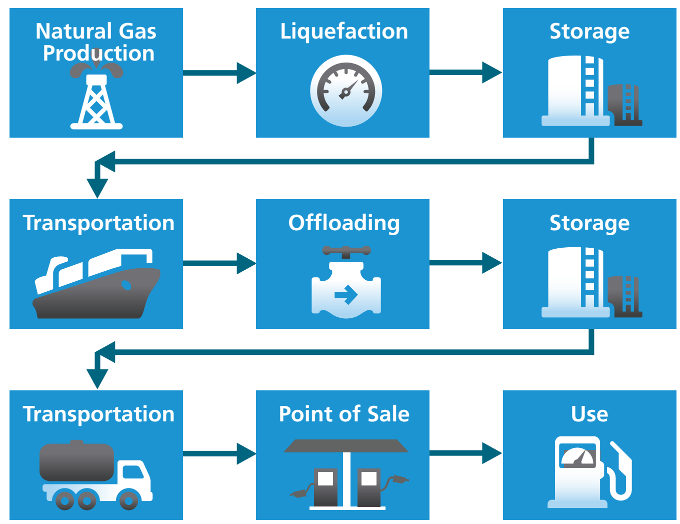
LNG MARKET OVERVIEW

The year 2014 marked the second highest LNG trade record at 241 million metric tons globally and in the same year global liquefaction capacity grew by 10 million metric tons[2]. Liquefied natural gas usage has grown at 7% per annum since 2000 and natural gas now accounts for around 25% of global energy demand: 10% of this gas is supplied as LNG compared to 4% in 1990[2].

The advantages of LNG supply over conventional pipeline transportation of gas are clear, not least since pipelines are not versatile in when or where they deliver product to and their upkeep can be highly expensive. In comparison, LNG transport around the world (noting that Qatar is the biggest exporter) can be both versatile and reactive. A recent LNG Market survey[3] notes that the LNG tanker fleet is undergoing "massive expansion" and at the end of 2013, the total fleet consisted of 354 large vessels and 24 smaller ones.

A simple flow diagram for the production and transportation of LNG is shown below in Figure 1:

Figure 1: Production and transportation of LNG (schematic)



From production of gas through to usage are multiple stages of storage and offloading, each of which demands accurate and safe transfer of LNG and an integral part of these are valves for both isolation and control.

In parallel with this expansion of production and transportation of LNG, comes a raft of new legislation on emissions control. According to The Flow Control Network[4], valves account for more than 51% of fugitive emissions and it is noted that the first step in controlling such emissions is to minimise the potential for leaks by applying proper design and materials selection standards. New standards and controls such as ISO 15848 Parts 1 and 2[5] provide guidance and testing methods for equipment screening. Clearly then the selection of the most appropriate and secure sealing material in cryogenic valves is of importance.

Usage of LNG in transportation is an area of growth globally, with benefits such as 30% reduction in greenhouse gas emissions[6]. Currently there are around 15 million fueled LNG vehicles globally[7] and this number is set to rise: the Latin America and Asia Pacific regions account for some 70% of this total[7]. For example, it has been suggested that the number of LNG vehicles in Sweden alone will triple between 2010 and 2018 to nearly 100,000[8]. However, the existing global infrastructure for distribution of this source of energy runs the risk of falling behind demand with only 47 LNG stations in the USA compared to 160,000 gasoline stations[9]: the National Petroleum Council of America specifically calls out examples of scope for technology improvements which are necessary to allow this fuel source to be further used and cites "cryogenic fuel handling systems: material or system developments can improve static and dynamic seals, non-intrusive fuel sensing and vapour pressure management". It goes on to mention that one of the primary challenges for Natural Gas vehicles is the ability to comply with modern emissions legislation.

SELECTION OF CRYOGENIC SEALING MATERIALS

Two polymers have become well-known in the cryogenic sealing market. These are Polytetrafluoroethylene (PTFE), more specifically, modified PTFE (MPTFE) and Polychlorotrifluoroethene (PCTFE or PTFCE).

Such materials have been used in cryogenic sealing systems for some time on account of their low temperature properties, providing useful ductility and load bearing characteristics in environments where all materials become increasingly brittle (including metals).

The requirements for a good sealing material for use in cryogenic valves may include:

- Suitable stiffness characteristics to allow effective sealing at very low, ambient and high temperatures
- Rapid recovery on removal of load
- Low friction 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.

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

According to EN/ ISO 16903[10], 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 in such extremes of temperature. In the polymers and elastomers arena, behaviours are dictated by the positions of the major thermal transitions and the molecular movements/rotations which are associated with these. Commonly used polymers in this area include PTFE, FEP, polyethylene, polycarbonate and polyimides and various elastomers which have been specifically formulated to retain ductility at such low temperatures. Despite a number of such materials being specifically formulated for such conditions, MPTFE and PCTFE remain among the commonly used materials.

There are three basic requirements for polymers to function well at very low temperatures[10]. These are:

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

Reducing temperatures produces a progressive increase in tensile and flexural strength and stiffness, creep resistance and fatigue strength, and dielectric strength and resistance. There will be a progressive decrease in elongation, fracture toughness, impact strength, compressive strength, coefficient of linear thermal expansion (CLTE) and permittivity/dielectric loss factor. In practice however, it is noted that as temperatures fall a decrease in strength is often seen 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 a significant effect on 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. In these conditions it is possible that greater elongation might be observed in a liquefied gas than in a vacuum at the same temperature. Absorbed gases reduce surface energy (assisting with the creation of new surfaces in crazes) and also can act as a plasticizer.

The suitability of polymers for use at low temperatures is highly dependent upon toughness and flexibility at those temperatures and these properties, in turn, depend upon molecular movements in the polymer molecules while in their glassy state. These are the specific Beta and Gamma relaxations which can be seen in the thermo-mechanical response.

Kreibich (11) notes that nearly all polymers which are tough in their glassy states exhibit clearly defined low temperature relaxations.

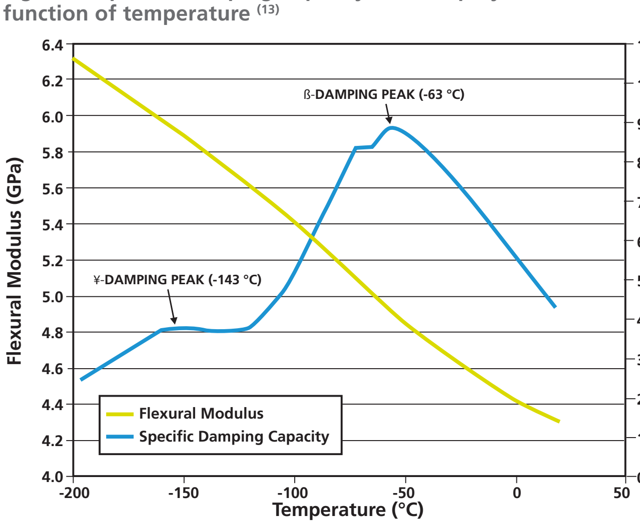
It is against this background of development of the cryogenic market and existing sealing materials that Victrex has developed and introduced a PAEK known as VICTREX CT™ 100 polymer.

VICTREX CT™ 100 POLYMER

In an industry which generally associates PAEK polymers with high temperature performance, high chemical resistance and a unique range of mechanical properties, a product which provides a beneficial set of low temperature properties is a significant departure from the accepted application areas.

Referring to the molecular movements which describe mechanical behaviour at very low temperatures, it can be seen that the Beta relaxation in PEEK is very well defined and signifies the movement of segments of the polymer backbone (and side chains) typically between 3 and 10 units, while the somewhat less well defined (but still clear) Gamma relaxation is associated with localised bond movements such as side chains (without affecting the main chain). The ability of polymer segments and side chains to move at these lower temperatures signifies an ability to exhibit some flexibilty and toughness at low temperatures. These relaxation peaks have been identified in PEEK polymers by Adams and Gaitonde[12] and are presented in Figure 2 below:

Figure 2: Specific Damping Capacity of PEEK polymer as a function of temperature (13)



The authors note that the specific damping capacity of PEEK is significantly greater than many existing materials of construction used in low temperature applications and that the damping capacity of the composites of PEEK is still useful.

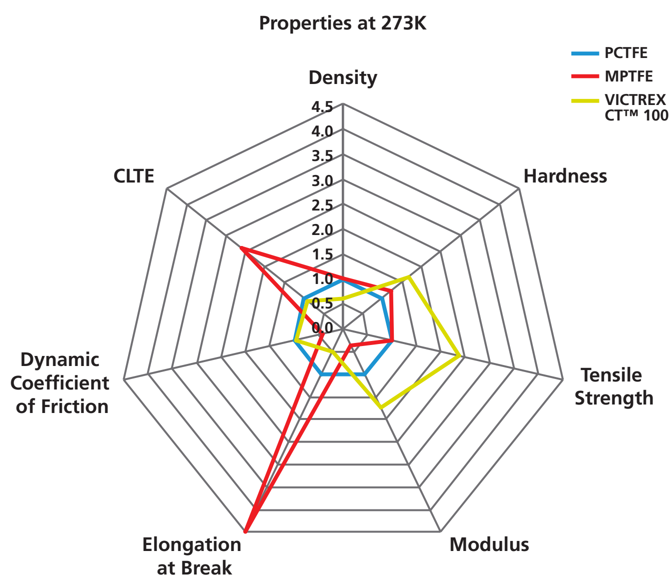
Fu[13] reports that crystallinity in semi-crystalline polymers exhibits an effect on properties at cryogenic temperatures and examines the tensile stress curves at 77K for polyether nitrile (PEN) of varying levels of crystallinity. It seems reasonable to assume that the lower free volume afforded by higher levels of crystallinity makes the required molecular movements for good damping properties more difficult.

VICTREX CT™ 100 PAEK polymer provides cryogenic (-196°C) temperature performance required by the industry both for operations in Polar Regions and also in the production and transportation of Liquid Natural Gas (LNG). The remainder of this paper describes the mechanical properties of VICTREX CT™ 100 polymer in the context of both the anticipated applications and compared to the fluoropolymers herein.

PROPERTIES AT AMBIENT TEMPERATURE

The properties of VICTREX CT™ 100 polymer compared to PCTFE and MPTFE are presented for comparison in Figure 3 below:

Figure 3: Comparison of relative ambient temperature properties for VICTREX CT™ 100 polymer, modified PTFE and PCTFE



The simple star chart shows VICTREX CT™ 100 polymer with a significantly higher tensile strength and modulus than PCTFE and MPTFE, higher hardness and a lower elongation at break. Dynamic coefficient of friction is similar while thermal expansion coefficient is significantly lower. Notably the density of VICTREX CT™ 100 polymer is some 40% lower than the fluoropolymers.

At ambient temperature therefore, VICTREX CT™ 100 polymer is somewhat less 'compliant' than the fluoropolymers. This requires good design and production of primary sealing elements but is no barrier to the use of PAEK polymers as primary seals.

Specifically, the higher strength and modulus of VICTREX CT™ 100 polymer presents an opportunity to design and manufacture seals for higher pressure systems where the fluoropolymers are unable to withstand the high creep loads required. This different combination of properties means that VICTREX CT™ 100 may not be a simple 'slot-in' alternative for a fluoroploymer material. However, the requirement to seal effectively at ambient temperatures may require additional design freedom or different manufacturing processes to be used.

PERFORMANCE AT -196°C (77K)

A range of mechanical property evaluations and sub-component tests were carried out on VICTREX CT™ 100 polymer at the laboratories of Aerospace and Advanced Composites based in Austria with a range of physical properties being evaluated at the Austrian Institute of Technology (AIT). All mechanical properties, (with the exception of impact strength) were carried out in a fully immersed liquid nitrogen environment. Due to equipment limitations, the evaluation of some physical properties was only possible down to a lower limit of -170°C.

The following mechanical properties were evaluated at -196°C:

Flexure: ISO 178

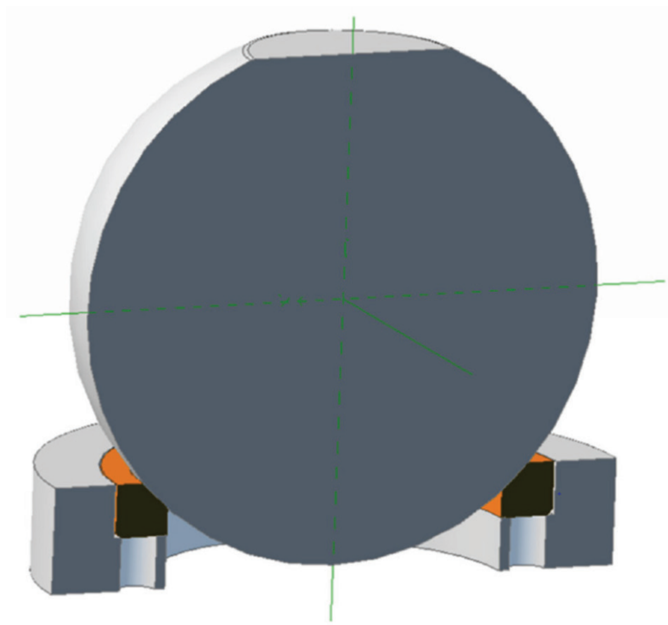
Tension: ISO 527 Compression Tests

Compression: ISO 604

Impact Tests: ISO 179-1/1fUc

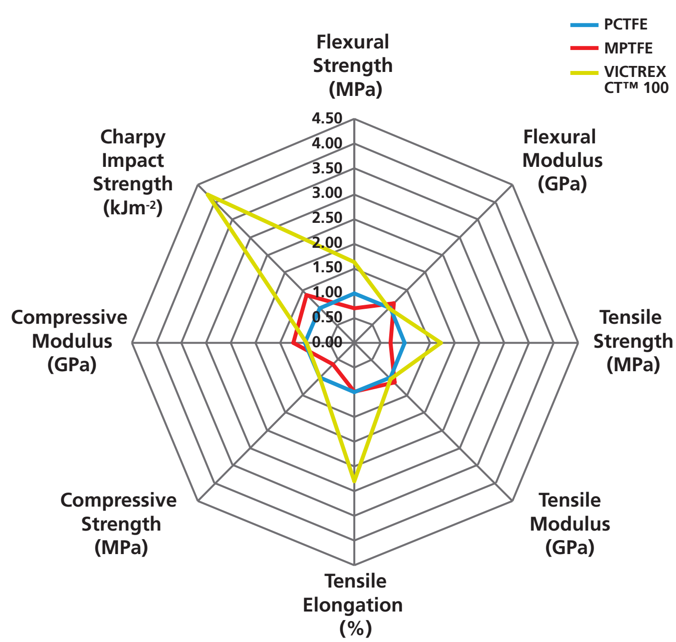
Additionally a non-standard test was designed to evaluate the mechanical response of seal materials in a ball valve seat configuration. In this test, a 50mm diameter valve seat was machined to mate with a steel bearing and the bearing was slowly compressed into the seat while recording the load displacement response. Unloading was also evaluated to assess recovery. The test configuration is shown in Figure 4:

Figure 4: Test Configuration for valve seat sub-component



Mechanical properties at -196°C (77K) of the VICTREX CT™ 100 polymer and PCTFE and MPTFE are summarised in Figure 5 below, which normalises results in relation to the properties of PCTFE which is taken as unity:

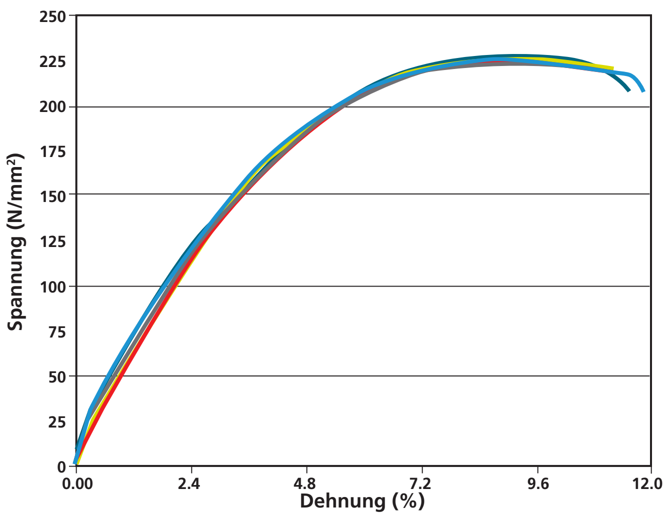
Figure 5: Comparison of relative properties at -196°C (77K) for VICTREX CT™ 100 polymer, modified PTFE and PCTFE



It is evident that there is a greater change in the properties of the fluoropolymers from ambient to 77K than for VICTREX CT™ 100 polymer: the latter material exhibits more than three times higher impact strength and elongation at break than the fluoropolymers while maintaining higher strength.

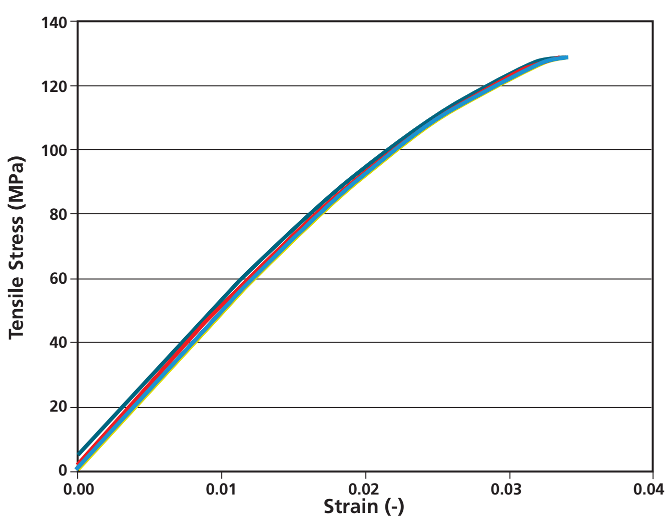
Significantly, in tensile testing a clear yield point can be identified for the VICTREX CT™ 100 polymer (Figure 6), demonstrating the enhanced ductility of this product at cryogenic temperatures:

Figure 6: Tensile Stress Strain Curve at -196°C (77K) for VICTREX CT™ 100 polymer



In the case of PCTFE (Figure 7) no such clear yield is visible and the load rises steadily followed by a brittle failure mode at just over 3% strain.

Figure 7: Tensile Stress Strain Curve at -196°C (77K) for PCTFE



Each of these properties contributes to a cryogenic sealing material which could offer significant additional security in application, and potential protection against failures from a range of sources, not least of which would be over-tightening / overload situations.

An additional factor in sealing capability also is the somewhat lower compressive modulus (-25%) compared to MPTFE. For similar seal designs this could mean up to 25% less load would need to be applied to effect a suitable seal.

The output of the valve seat compression test is shown in Figures 8 and 9 below:

Figure 8: Compressive Displacement at 7kN load on 50mm diameter seat

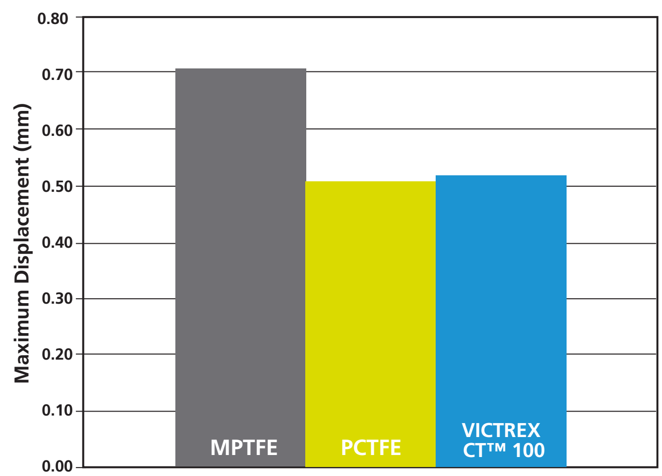
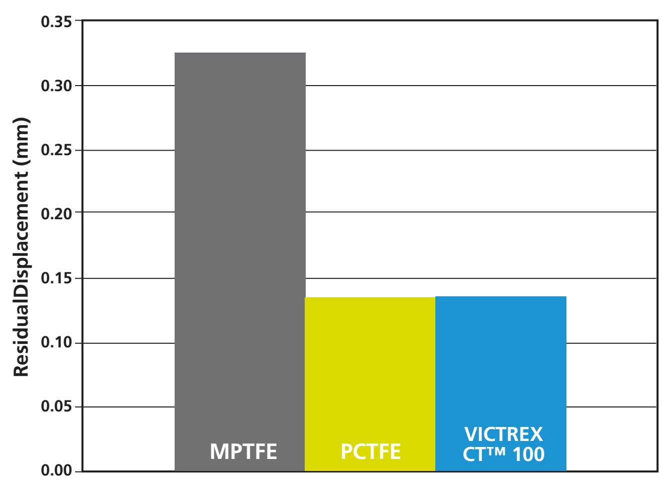


Figure 9: Residual Displacement on removal of load from seat



CONCLUSIONS

VICTREX CT™ 100 polymer offers a strong combination of low temperature ductility and high temperature performance for the cryogenic industry. Extensive laboratory testing has shown that:

1) Unlike fluoropolymers, VICTREX CT™ 100 polymer exhibits a clear yield point at -196°C and some post yield deformation.

2) The lower compressive modulus of VICTREX CT™ 100 polymer results in lower required sealing loads for equivalent seals.

3) Higher strength and toughness of VICTREX CT™ 100 polymer at -196°C provide additional design security and in service performance.

4) The recovery characteristics of VICTREX CT™ 100 polymer on removal of sealing load are a significant improvement over MPTFE and are at least equivalent to PCTFE

5) VICTREX CT™ 100 polymer offers a greater range of operating temperature, but:

   - May present greater sealing challenges at ambient temperatures
   - May require design freedom to take advantage of properties
   - May not be a simple 'slot-in' substitute material

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