Exchanging elastomer knowledge

By Alfred Kruijer, Shell

Abstract

At the recent Valve World Conference, Alfred Kruijer of Shell organized a workshop on "Soft Sealing Performance & Technology". Attended by more than fifty peers in the industry coming from end-users, suppliers, and engineering companies, it addressed in two-and-a-half hours of very stimulating discussion many of the challenges confronting those working with soft seals for valves as well as testing, design, and performance. Orchestrated expertly by Mr. Kruijer, it proved to be a huge learning experience and session for the transfer of knowledge and expertise.

About the Author

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Introduction

Elastomer o-rings provide FE Class A performance but their application is limited by temperature, pressure, and fluids. The latter limitation is often overlooked. Polar molecules (water, aromatics, amines, CO_2, glycol, methanol, etc.) can either swell the matrix to bursting point in the confinement of the o-ring groove, or chemically attack the polymer itself.

Often low-temperature limitations are overlooked (blowdown situations) when the elastomer becomes hard and can no longer follow stem lateral movement. Explosive decompression is another natural limitation for elastomers, when dissolved gaseous components in the fluid vaporise upon decompression. Shell, like other major users specify specially developed ED resistance elastomer grades for all Class 600 and valves above these limits. Graphite stem packing has been developed rapidly over recent years. FE Class B is easily achieved and even Class A for quarter turn valves. FE Class A can now be achieved with specially developed packing sets.

The component in valves leading to the most limited "operating window" are elastomer o-rings. In many piping classes such o-rings are only found in trunnion mounted ball valves used in EP. O-rings are popular as they provide excellent sealing performance at low cost. However, strength, softness and resilience characteristics need to be maintained to ensure proper sealing. These mechanical properties depend on temperature, pressure, and fluid exposure. PTFE lip seals may be used instead of o-rings in case of service incompatibility.

At low temperatures, elastomers become harder, less resilient and lose their memory. For static seals, low-temperature tolerance is somewhat better, as there is no strong reliance on resilience needed. Often the limit between static and dynamic applications is approximately 10°C. There are special low-temperature grades that are softer, but at elevated temperatures, this softness leads to lower strength, which in turn limits pressure. It is not recommended to apply elastomers below a lower design temperature of –20°C.

The upper temperature limit of elastomers is strongly dependent on fluid exposure. This is particularly the case with polar molecules and hydrocarbon molecules, which have a molecular weight below 120 as this affects elastomers commonly used in our industry. The more dissimilar the elastomer is to the fluid, the less it will be affected. Mixtures of hydrocarbons with polar molecules create particular challenges. Constituents requiring detailed attention are water, methanol, glycol, amines, ammonia, CO_2, and H_2S. When relatively small and/or polar molecules migrate in to the open polymer structure of elastomers, swelling occurs. This swelling leads to reduced mechanical properties and, hence, limits design pressure. But more important, the swelling can lead to o-ring groove overfill and internal tearing of the material, or extrusion and cutting of the o-ring surface.

Even cracks can appear in the o-ring groove. Dynamic o-ring seals can accept up to 10% volume swell, static o-ring seals up to 20%. Valves fitted with o-rings are often offered to temperature limits in air. Special attention should be given to fluid exposure other than air. Some of the sealing manufacturer literature lists the upper temperature limitations of elastomers as a function of chemical fluids. It is prudent to limit the upper design temperature to between 120°C and 150°C, depending on the pressure class.

Pressure

Pressure also limits the application of elastomers. The limit is driven by tear strength, hardness and modulus. Excessive pressure can lead to o-ring extrusion when diametrical clearances meet with practical limitations. Another effect is that high pressure raises the so-called glass transition temperature. This is relevant for some of the oil resistant fluoroelastomers used in our industry that have a glass transition temperature close to ambient. The closer the application temperature is to the glass transition temperature, the less resilient the material. Hence, pressure may affect low-temperature performance. A serious high-pressure constraint exists in gaseous, or volatile services when light components in the fluid diffuse into the elastomer over time and expand in the matrix upon rapid decompression before they can diffuse out again. The effect is called Explosive Decompression (ED) and it appears at particularly low pressures when CO_2 or $H2_S$ are present. Pressure classes 600# and above require ED-resistant o-rings that are tested to conditions representing the actual fluid, pressure, and temperature. Where the actual fluid cannot be used in the test because of safety reasons, equivalent fluids with the same solubility parameter may be used. Testing should be performed according to NORSOK M-710. The most important rules for ED-resistant o-rings are: a shore-A hardness in excess of 90 and a cross section less than 7 mm. Many o-ring manufacturers claim ED-resistance for some of their ranges, but examination of the applied test conditions often teaches us that a lot of these claims are optimistic. Elastomers can be applied in valves up to 1500#, but their application may be limited to much lower pressures depending on fluid and temperature.

Elastomers can be applied in valves that are rated up to 1500#

Fluid

Fluid has a significant impact on the suitability of elastomers for o-ring seals. In addition to the excessive physical swelling that can occur, chemical attack is another degradation mechanism that affects performance. Hot water, steam, H_2S, ammonia and amines harden Viton (FKM). Although HNBR has a better chemical resistance to most oilfield chemicals compared to FKM, its intolerance to particularly aromatic compounds is a serious limitation. Special grades like Aflas (TFE/P, FEPM) and Kalrez (FFKM) offer much improved chemical resistance, but are very expensive. Also their resilience properties and compression set is less favorable compared to standard FKM and HNBR. PTFE lip seals are often the more beneficial sealing concept.

Of the reviewed elastomers, FKM and HNBR have the most favourable pressure/temperature/chemical inertness envelopes relative to cost. EPDM has a niche application in lined butterfly valves for water service.

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1. Thermoplastics

Thermoplastics severely limit the operating window of valves. They can be found in seats and seals of floating ball, trunnion mounted ball, double offset butterfly, and plug valves. The seals should be made from virgin PTFE or filled/modified PTFE in all services up to 200°C, except butadiene and styrene service. In styrene and butadiene services, PFA or styrene/butadiene compatible modified PTFE should be used. In services above 200°C, graphite has to be used.

PTFE has the lowest coefficient of friction of all solid materials, but is relatively soft and has poor extrusion resistance. When reinforcing fillers, such as glass or graphite, are combined with PTFE, the composite will have very good extrusion resistance and wear without compromising its low friction characteristics.

PTFE needs to be housed (captivated) on all sides in order to minimise creep or cold flow. Extrusion gaps should be kept to a minimum. In dynamic applications face seals are effective, these are normally preloaded by springs incorporated into the valve design. Lip seals (radial seals) use a built-in spring to seal on both their inner and outer diameters.

An effective way of proving valve seat design is by breaking open the valve at maximum temperatures and pressures. This exposes the seats to possible extrusion. At the point just prior to ‘break out’, the force on the seat is a maximum and the greatest possibility of extrusion occurs. When the valve is subsequently cooled down for a low-temperature test, any distortion at the high-temperature test is effectively frozen in. This will show up as seat leakage in a low-pressure test.

For classes 150 and 300, virgin PTFE or filled/modified PTFE seals easily, has low frictional properties, is chemically resistant and cost effective. For class 600, virgin PTFE can no longer be used.

For classes 900 and 1500, nylon 12G or 612 is the most cost effective choice. Nylons, however, are not chemically resistant to a number of services. For common oil & gas services, this means acids, amines, aromatics (acceptable up to 25%), glycol, methanol, aldehyds, esthers, water and H_2S. In these services, PEEK has to be used. Nylons are susceptible to water absorption and will swell. They are therefore not recommended for the less tolerant (non sprung-loaded) floating ball valve seats.

An exception in classes 900 and 1500 must be made for low-temperature service (LNG applications). The lower design temperature for PEEK is approximately –60°C. So for that specific service, PCTFE has to be selected.

For class 2500, nylon 612 or PEEK can be considered. Nylon 612 is, however, not recommended due to its load capacity being close to that required for class 2500. Therefore, PEEK is the preferred choice.

Because the valve manufacturing industry has settled on soft-seated floating ball valve designs without the use of elastomers and only use thermoplastics, the limitations with respect to upper and lower temperatures are less restricted compared to trunnion-mounted ball valves. However, floating ball valves are limited with respect to pressure. Because the forces due to differential pressure are all conducted through the seats, pressure class is limited by size. Class 2500 up to DN 40, class 300 up to DN 100 and class 150 up to DN 250.

Seat stability requirements limit the maximum temperature up to 150°C for class 600 and below and 120°C for higher classes. Double offset butterfly valves also do not contain elastomer o-rings. Sealing is by means of graphite, seats are thermolastic. Pressure class is limited to 300#, but there is no size limitation. Seat stability requirements limit the temperature application to between –50 °C and 150 °C.

Soft seated valves are maintenance intensive. Especially valve designs incorporating elastomer o-rings require periodic seal replacement (6–8 year average). Lip seals are thin and are subject to wear. These also require periodic replacement. Metal seated valves with graphite packing should only require repacking on a reactive basis. Gland tightening can be done on the run.

2. Tolerance to solids

Tolerance to solids in the fluid is a major consideration driving type of valve selection. Every valve type is suitable for clean service, but in our industry, clean service is limited to e.g. instrument air, nitrogen, potable water, potable and treated (demineralised) water, steam, lube oil, diesel oil, oxygen and many chemicals including dosing chemicals used for injection into fluids systems. Pipe rust, mill scale, welding slag, sand, grit and proppant are often unavoidable. Solids are usually erosive and abrasive, rendering soft seated valves unsuitable. Seats protected from continuous erosion while in the fully open position tend to last longer compared to valves with exposed seats (note that during travel, seats are always exposed and that many types of isolation valves should therefore not be used for throttling). A scraping action by the seat is beneficial for fouling that tends to stick to metallic surfaces to form a scale. Solids also have a tendency to migrate into narrow clearances between moving parts, especially the fines around 10 microns. Particularly when forces to overcome friction cannot be increased by the operator to crush (i.e. spring energised or pressure energised movements), critical parts can become stuck. Enclosed pockets with moving parts like springs can become compacted with solids, freezing up free travel. Fines tend to migrate to and settle in quiet zones like valve cavities and the ability of the flow to flush the body cavity is beneficial. Lumps can become trapped in recessed pockets.

Packing

Operating temperatures and pressures are the primary selection criterion for packing types. Using graphite as a sealing material allows a wide operating window to be covered with the two most popular packing types: dye-formed graphite and braided graphite yarn. The same goes for chemical resistance; graphite is a very noble material that can be used in many mixes of fluids and gases.

Longevity of packing becomes increasingly important since run lengths of units are extended and not all packings are replaced at each shut down. Hence the aging behaviour of packing materials becomes more and more important. Automatically a preference emerges for graphite sealing materials as these are relatively robust to oxidation, creep and chemically resistant to a wide range of species. The use of high-purity graphite will increase the longevity even further.

Graphite

The leakage rate (denoted as fugitive emissions) of assembled packings depends heavily on the quality of the sealing material, usually graphite. Especially at milder temperatures the tightness and longevity of graphite depends heavily on its purity and absence of detrimental materials. Detrimental materials are mainly chloride containing species, fluorides and sulphur. The chloride and fluoride atoms may decompose especially at higher temperatures and form strong acids in the presence of water leading to corrosion. Sulphur will easily oxidise to SO_2 and escape causing loss of packing volume and reduce tightness. To compensate for detrimental elements that promote aqueous or galvanic corrosion, manufacturers often add corrosion inhibitors. Corrosion inhibitors are typically zinc-based. When they oxidise the volume expands. In stem packing material this leads to increased friction. Eventually the corrosion inhibitor disappears, leaving voids in the graphite, which in turn leads to increased emissions.

Good practice is to prescribe an ‘industrial grade’ graphite quality of at least 98% purity (2% ash). For service at temperatures above 400°C (750°F) a ‘nuclear grade’ graphite purity of 99% is required. The high temperature graphite qualities have to contain an oxidation inhibitor i.e. a proprietary chemical that retards the formation of CO_2 at the air or steam exposed surface. Elements, like catalytic metals, that reduce high temperature stability of graphite are less well understood. Hence, an oxidation test qualifies products and grades.

In conjunction with a number of large Dutch petro-chemical industries and a few graphite manufacturers a standard graphite specification was developed. This effort resulted in a CAPI specification that has been adopted by some end-users.