Development of a procedure to accurately measure the low temperature operating limits of elastomeric seals

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1. ABSTRACT

The search for usable reserves of oil and gas is taking operators into more remote and arduous environments, many of which are in the coldest regions of the world or where temperatures fluctuate widely from high to low. This raises a challenge for elastomeric seal manufacturers as conventional elastomeric materials start to lose effectiveness as they become stiffer and lose resilience as the temperature drops. The members of the European Sealing Association’s Elastomeric and Polymeric Seals Division are rising to this challenge as they develop new compounds and seal designs to accommodate extreme low temperature operation.

These seals need to be tested to demonstrate their effectiveness at low temperature. There are numerous acceptable test methods to show the properties of the materials themselves at low temperature, such as torsion modulus, brittleness, compression set and temperature retraction. But these do not give a direct indication of whether a seal will continue to function. There are also proprietary functional test procedures which aim to identify the minimum operating temperature for seals; however all of these rely on the seal being energised by the pressure of the test fluid prior to being subjected to low temperature. This is not normally the case as in most real applications the seal will have been kept at low temperature prior to being exposed to the pressurising media and because it has already stiffened may not then be able to energise to maintain a seal.

This paper describes work to prepare and validate a suitable test method for this common but more severe condition. Having drafted the standard a validation programme has commenced in the form of round-robin tests conducted by the members on typical seals obtained from a single source. Each laboratory is testing seals and comparison of the results allows refinement of the specification. This will result for the first time in an industry agreed specification that all reputable seal suppliers will be able to use to give end-users reliable guidance on the low temperature operating limits of their compounds.

2. BACKGROUND

There is a wide variety of sealing applications that require elastomeric sealing components to operate at low temperatures. Of particular importance are sealing devices in well-head and other oil and gas exploration and production applications in latitudes where the ambient temperature above and below ground is below 0°C for prolonged periods. All elastomeric materials tend to stiffen as temperature is reduced and therefore
become less responsive. Eventually a temperature will be reached at which this stiffening causes the seal to start to leak as it is no longer sufficiently responsive to effect a seal.

All elastomers are based on polymers made up of long chain molecules randomly arranged in coils which have been chemically cross-linked to form a three dimensional structure. Within their normal operating temperatures, the molecules are free to rotate and the individual chain segments remain flexible but as the temperature is decreased, the ability of the molecules to rotate is reduced as they move closer together. The material reaches a point known as the glass transition temperature (Tg) which is the point at which it ‘freezes’ though is not yet brittle. Chain mobility is restricted, and the elastomer starts to crystallise, becoming ‘leathery’ and unresponsive. The temperature at which the elastomer crystallises is predominantly influenced by its chemical structure. Introducing ‘irregular’ monomers reduces the tendency to crystallise, and as a consequence improves the flexibility of the polymer at low temperatures. The molecular structure of a rubber polymer has by far the greatest influence on the low temperature flexibility of the fully compounded elastomer. But other factors such as the introduction of plasticisers, compound hardness, modulus and even the medium being sealed can have minor effects.

3. SEALING MECHANISM

The majority of elastomeric seals used in high pressure applications in the oil and gas industry are for static or pseudo static duties and are of the squeeze type. The most common is of course the versatile ‘O’ ring, which is placed in a rectangular housing and is ‘squeezed’ by initial compression to form a seal. The sealing force applied by this initial squeeze is then increased by deformation of the seal under system pressure. The initial sealing force created by the squeeze on the seal, and maintained by the residual stress within it takes the overall sealing force above that of the system pressure. It is this balance of forces that forms the seal.

![Sealing mechanism](image)

**Figure 1. Sealing mechanism**

Whilst the seal is energised by the system pressure, the residual stress within the elastomer is critical to maintain a sealing force above the pressure being contained. This sealing force can reduce over time due to stress relaxation brought about by physical and chemical changes to the seal material, and at low temperatures the residual sealing force can also reduce to a point where the system will fail.
4. SEAL SELECTION

When selecting a suitable elastomer material for a particular application several aspects have to be considered, in particular; chemical resistance, mechanical properties, operating temperature range and any significant aspects of the duty such as resistance to Rapid Gas Decompression (RGD).

In making this decision the user will normally have to rely on information provided by the seal supplier in the form of data sheets and manufacturers’ literature. This will include a reference to minimum operating temperature but the means by which this has been arrived at, and possible limitations of the data are often not clear. It will normally be assumed that the minimum operating temperature quoted represents the lowest temperature at which elastomer components will seal in all situations, unless otherwise indicated. This is unlikely to be the case.

5. CURRENT METHODS

The methods currently used to determine a minimum operating temperature fall into two categories. The first are methods which determine changes in the properties of the elastomer material itself and then set arbitrary limits to the changes to derive an operating limit. The second are more relevant actual low temperature testing of sealing capability, but as previously noted existing methods do not represent the usual mode of operation of low temperature equipment.

5.1 Material Tests

5.1.1 Temperature Retraction 
(ISO 2921/ASTM D1329/BS ISO2921)
In this test the sample is stretched by typically 50% and then frozen in position using an alcohol bath cooled with solid carbon dioxide to -70°C (other temperatures can be specified depending on the cooling media). The specimen is then allowed to retract freely while the temperature is raised at a uniform rate. Its ability to recover is measured as a temperature at a given %. The temperature to recover by 10% (TR10) is often used to establish the minimum operating temperature of the elastomer. Normally the % recovery is recorded every minute against temperature, and the results plotted on a graph. It is worth noting that the elastic modulus of an elastomer may influence the results independently of its low temperature properties.

5.1.2 Gehman Torsional Modulus 
(ISO 1432/ASTM 1053/BS 903 A13)
Small samples cut from sheet are placed in a carousel holder and immersed in an alcohol bath cooled as above. They are conditioned at the test temperature before being twisted using a calibrated wire, which after a simple calculation gives the torsional modulus. The temperature at which a torsional modulus of 70MPa (T70) is achieved has also been used to set a value for the minimum operating temperature of an elastomer. The absolute torsional modulus of a given material may to some extent influence the result. A minimum operating temperature can also be estimated by finding at which point a given ratio of torsional moduli between room temperature and a lower temperature is reached. This may in some circumstances be a more reliable option.
5.1.3 Dynamic Mechanical Thermal Analysis (DMTA or DMA)
A small sample of elastomer is flexed and properties such as modulus and damping are measured over a range of temperatures at fixed frequencies. Elastic (E') and viscous (E'') moduli are recorded along with a ratio of these, Tanδ. From these data, an assessment of Tg and ‘Brittle Onset Temperature’ can be made.

5.1.4 Differential Scanning Calorimetry (DSC)
(ISO 22768/ASTM D7426)
DSC measures the heat flow associated with transitions in materials as a function of time and temperature. Basically DSC measures heat flow into or out of a sample as it is heated, cooled or held at a set temperature. This technique can provide a wide range of data including Tg.

5.1.5 Bend Brittle Test
(e.g. DTD 458)
This somewhat crude test locates an elastomer sample between two jaws connected via a helical screw. After conditioning at the specified temperature in a cooled alcohol bath, the jaws are screwed together by a predetermined amount which subsequently flexes the sample which is then examined for splits or cracks. This is not a measure of elasticity and merely measures brittleness at a given temperature.

5.1.6 Compression Stress Relaxometer
(BS ISO 3384)
The Compression Stress Relaxometer (CSR) permits the measurement of the residual sealing force at a given temperature and as such gives a more representative evaluation of potential sealing performance than the previous methods.

An elastomer button is compressed in a specially designed jig, and the residual sealing force is measured by momentarily placing the jig in a CSR unit. The jig complete with sample under a preset level of compression can be placed in an environmental chamber to condition the sample for specified periods of time at a given temperature. By this means, the residual sealing force at this temperature can be measured.

It should be noted that BS ISO 3384 does not specify a procedure for testing at low temperatures stating ‘the methods [described] have been used for low temperature testing but their reliability under these conditions is not proven’.

5.2 Existing Sealing Tests

A sealing test using ‘O’ rings was developed by DuPont in the 1990s and is quite often used by seal manufacturers. Typically a particular size of ‘O’ ring is compressed by a fixed amount (typically 10%) and seals nitrogen at a particular pressure and ambient temperature. The energised seal temperature is then reduced at a slow rate until leakage is detected.

The values obtained in this test are typically significantly below the TR\textsubscript{10} temperature. The initial tests carried out by DuPont were on a number of fluorocarbon elastomers and gave results of 10 to 15 degrees below the TR\textsubscript{10} value. It must be noted that claims of working 15°C below TR\textsubscript{10} are only theoretically applicable if the seal is of the same size, lubricated in the same way and pressurised with nitrogen at 200psi prior to reduction in temperature. In reality few seals would be pressurised before the temperature was reduced.
A report by Sandia Laboratories studied the failure temperatures of selected elastomer O-rings by pressurising after the seal had been conditioned at the test temperature and the failure temperatures were significantly higher.

Several members of the ESA Elastomeric and Polymeric Seals Division (ESA EPSD) have also developed in-house low temperature sealing test methods of varying sophistication. The draft proposed test method described below incorporates elements of these programs.

**6.0 PROPOSED TEST METHOD**

The ESA EPSD chose to use ‘O’ ring seal dimensional, quality and groove design recommendations in accordance with ISO 3601 to ensure the proposed test method mirrored ‘real-world’ conditions.

**6.1 Scope of testing**

This specification details a test method for ‘O’ ring seals in elastomeric materials which are subject to pressurised media at low temperatures. It gives guidance on the design of test equipment, standard test parameters and reporting criteria. It does not specify performance criteria which should be agreed between supplier and customer.

The test procedure may be utilised to test seals of alternate size and design or using alternative media but such deviations shall be detailed separately on the report form and the results shall not be used to determine the minimum operating temperature of seals of any other configuration than that tested.

**6.2 Definitions**

The following terms used in this specification have the meanings defined:

**6.2.1 Minimum seal temperature**

The minimum temperature is the temperature at which the test seal holds the test pressure during the test.

**6.2.2 Zero leakage**

A leak rate considered to be negligible for the purposes of the test and equal to a displacement of less than 20 cm³/h equivalent to no discernible bubbles as defined in API 6A F.1.13.6.

**6.2.3 Room Temperature**

The standard temperature of the test facility usually considered to be in the range 20±5°C.

**6.3 Test Apparatus**

**6.3.1 Test fixture**

The test fixture shall be similar to the typical example shown in Figure 2 and shall consist of a suitable test fixture with 3 major components:
- A solid cylindrical test plug containing a groove on its outer diameter to suit a test ‘O’-ring in accordance with ISO 3601-316 when used in a static piston sealing application.
- An outer cylindrical test shroud with bore to suit the test ‘O’-ring and an external means of sealing to retain the test fluid under pressure – normally an ‘O’ ring which will remain flexible at a temperature at least 20°C below the minimum test temperature.
- A cylindrical cap which fits around the test shroud and is sealed on its bore by the flexible ‘O’-ring and contains suitable fittings to allow the ingress of the test medium.
- Means shall be provided to ensure centralisation of the test plug within the test shroud such that the extrusion gap on the low pressure side of the test seal does not exceed the requirements of ISO 3601-2

![Figure 2: Typical test fixture](image)

### 6.3.2 Test cell

The test cell shall be provided with:

- An external method of cooling such that the temperature at the test seal can be reduced at a controlled cooling rate between 15°C per hour and 90°C per hour.
- A means of measuring the temperature of the test seal positioned within 3 ± 0.5 mm of either the inner or outer diameter of the test seal.
- A means of detecting leakage bypassing the test seal – normally by means of a leakage tube directly connected to the test fixture and terminating within a water bath where bubbles of leakage may be observed and collected.
- A means by which the test fluid may be applied under pressure to the test cell and the pressure within the fixture measured.

![Picture 1: Typical test cell](image)

6.4 Test conditions

6.4.1 Temperature
Tests shall be carried out at a range of temperatures from Room Temperature down to at least 10°C below the expected minimum seal temperature. The expected minimum seal temperature may be estimated by use of other material or functional tests (e.g. temperature Retraction or DSC analysis).

6.4.2 Test medium
The test medium shall be nitrogen gas.

6.4.3 Pressure
The test pressure applied to the seals shall be 15 MPa +5%/-0
6.5 Pre-test procedure

Inspect the test seals for conformity to their dimensional specification in accordance with ISO 3601 – 1 and visually in accordance with ISO 3601-3 Grade N and record their actual cross-section and inside diameter. Install the leakage and test seals in their respective grooves – the test seals shall not be lubricated. Assemble the test cell and all relevant connections and monitoring devices.

Pressurize the cell with nitrogen to 1.5 MPa at ambient room temperature at a rate of approximately 0.5 MPa per minute. Hold the cell at 1.5 MPa for 2 minutes and check that there is zero leakage. Apply the test pressure for 2 minutes and check that there is zero leakage.

6.6 Test procedure

6.6.1 Reduce the temperature of the test cell and seal to a temperature 10°C above the expected minimum seal temperature and hold for a minimum of 5 minutes after the fixture temperature has remained stable (±0.5°C) for at least 1 minute.

6.6.2 Apply the test pressure and check for leakage.

6.6.2.1 If leakage is observed release the test pressure and raise the temperature by 5°C and hold for a minimum of 5 minutes after the temperature has remained stable (±0.5°C) for at least 1 minute then repeat the procedure from clause 6.6.2 onwards.

6.6.2.2 If zero leakage is observed hold pressure for 5 minutes.

6.6.3 If zero leakage is observed release the test pressure and reduce the temperature by a further 5 degrees and hold for a minimum of 5 minutes after the temperature has remained stable (±0.5°C) for at least 1 minute.

6.6.4 Repeat the test procedure from clause 6.6.2 onwards until a temperature is reached where the seal fails to hold pressure.

6.6.5 Release the pressure and raise the temperature by 1°C, hold for a minimum of 5 minutes after the temperature has remained stable (±0.5°C) for at least 1 minute and then apply the pressure.

6.6.5.1 If leakage is observed release the test pressure and raise the temperature by 1°C and hold for a minimum of 5 minutes after the temperature has remained stable (±0.5°C) for at least 1 minute then repeat the procedure from clause 6.6.5 onwards.

6.6.5.2 If zero leakage is observed hold pressure for 5 minutes.

6.6.6 Continue the process from clause 6.2 onwards until a temperature is reached at which the pressure can be held for 5 minutes with zero leakage – this is the minimum seal temperature.

6.6.7 The start point for each repeat test shall be 5°C higher than the previous minimum seal temperature.
6.6.8 A minimum of 5 test runs shall be carried out for each material. The final minimum seal temperature reported shall be the median of these 5 samples.

7.0 RESULTS AND DISCUSSION

The testing as outlined above was carried out by three separate laboratories to investigate firstly, how consistent the method as outlined is and secondly how practical the testing is as it is hoped that the method will be widely adopted. Improvements will be discussed at the end of this section.

The material under test was a nominal 70 IRHD perfluoroelastomer (FFKM). Its glass transition (T\textsubscript{g}), as measured by Differential Scanning Calorimetry (DSC) was -19°C. This was the only low temperature characterisation carried out; other methods do exist, and are discussed at the beginning of this paper.

Results are presented by laboratory below with a final summary table combining the three data sets.

**Laboratory A**

Laboratory A took its starting point to be -9°C, 10°C above the glass transition (as determined by DSC). The results for the five runs undertaken are given in Table 1.

<table>
<thead>
<tr>
<th>Test 1</th>
<th>Test 2</th>
<th>Test 3</th>
<th>Test 4</th>
<th>Test 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp (°C)</td>
<td>Result</td>
<td>Temp (°C)</td>
<td>Result</td>
<td>Temp (°C)</td>
</tr>
<tr>
<td>-9</td>
<td>Pass</td>
<td>-9</td>
<td>Pass</td>
<td>-9</td>
</tr>
<tr>
<td>-14</td>
<td>Pass</td>
<td>-14</td>
<td>Pass</td>
<td>-14</td>
</tr>
<tr>
<td>-19</td>
<td>Pass</td>
<td>-19</td>
<td>Pass</td>
<td>-19</td>
</tr>
<tr>
<td>-24</td>
<td>Fail</td>
<td>-24</td>
<td>Pass</td>
<td>-24</td>
</tr>
<tr>
<td>-23</td>
<td>Fail</td>
<td>-29</td>
<td>Fail</td>
<td>-29</td>
</tr>
<tr>
<td>-22</td>
<td>Fail</td>
<td>-28</td>
<td>Fail</td>
<td>-28</td>
</tr>
<tr>
<td>-17</td>
<td>Pass</td>
<td>-23</td>
<td>Fail</td>
<td>-23</td>
</tr>
</tbody>
</table>

The final results are -17°C, -23°C, -19°C, -24°C, and -23°C, the median result is -23°C. The results have reasonable correlation and there is good correlation with the T\textsubscript{g}. 

Table 1: Results of running the ESA low temperature test procedure on 5 FFKM samples at laboratory A
**Laboratory B**

The starting temperature chosen was -20°C. In this case a replication of 3 was used due to time constraints. The results are given in Table 2.

**Table 2: Results of running the ESA low temperature test procedure on 5 FFKM samples at laboratory B**

<table>
<thead>
<tr>
<th></th>
<th>Test 1</th>
<th></th>
<th>Test 2</th>
<th></th>
<th>Test 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp (°C)</td>
<td>Result</td>
<td>Temp (°C)</td>
<td>Result</td>
<td>Temp (°C)</td>
<td>Result</td>
</tr>
<tr>
<td>-20</td>
<td>Pass</td>
<td>-20</td>
<td>Pass</td>
<td>-20</td>
<td>Pass</td>
</tr>
<tr>
<td>-25</td>
<td>Pass</td>
<td>-25</td>
<td>Pass</td>
<td>-25</td>
<td>Pass</td>
</tr>
<tr>
<td>-30</td>
<td>Fail</td>
<td>-30</td>
<td>Pass</td>
<td>-30</td>
<td>Pass</td>
</tr>
<tr>
<td>-29</td>
<td>Fail</td>
<td>-29</td>
<td>Fail</td>
<td>-35</td>
<td>Fail</td>
</tr>
<tr>
<td>-28</td>
<td>Fail</td>
<td>-28</td>
<td>Fail</td>
<td>-34</td>
<td>Fail</td>
</tr>
<tr>
<td>-27</td>
<td>Fail</td>
<td>-27</td>
<td>Pass</td>
<td>-32</td>
<td>Fail</td>
</tr>
<tr>
<td>-25</td>
<td>Pass</td>
<td>-31</td>
<td>Pass</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The final results are -25°C, -27°C, and -31°C, with the median being -27°C. These results correlate reasonably well with each other however are further from the $T_g$ those of laboratories A and C. It was conveyed however, that the rate at which the temperature was applied had a large bearing on results; a slow and steady initial cooling is required to achieve consistent results.

**Laboratory C**

This laboratory chose its initial starting temperature for the first run by first cooling the system with pressure applied until leakage, which occurred between -26°C and -31°C, so an initial starting temperature of -21°C was used for Test 1. This seal was then discarded. Subsequent tests used -11°C as the start point, 10°C above the previous initial pass temperature. Results are given in Table 3.

**Table 3: Results of running the ESA low temperature test procedure on 5 FFKM samples at laboratory C**

<table>
<thead>
<tr>
<th></th>
<th>Test 1</th>
<th></th>
<th>Test 2</th>
<th></th>
<th>Test 3</th>
<th></th>
<th>Test 4</th>
<th></th>
<th>Test 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp (°C)</td>
<td>Result</td>
<td>Temp (°C)</td>
<td>Result</td>
<td>Temp (°C)</td>
<td>Result</td>
<td>Temp (°C)</td>
<td>Result</td>
<td>Temp (°C)</td>
<td>Result</td>
</tr>
<tr>
<td>-26</td>
<td>Fail</td>
<td>-16</td>
<td>Pass</td>
<td>-16</td>
<td>Pass</td>
<td>-16</td>
<td>Pass</td>
<td>-16</td>
<td>Pass</td>
</tr>
<tr>
<td>-25</td>
<td>Fail</td>
<td>-21</td>
<td>Fail</td>
<td>-21</td>
<td>Fail</td>
<td>-21</td>
<td>Fail</td>
<td>-21</td>
<td>Fail</td>
</tr>
<tr>
<td>-24</td>
<td>Fail</td>
<td>-20</td>
<td>Fail</td>
<td>-20</td>
<td>Pass</td>
<td>-26</td>
<td>Fail</td>
<td>-20</td>
<td>Pass</td>
</tr>
<tr>
<td>-23</td>
<td>Fail</td>
<td>-19</td>
<td>Pass</td>
<td>-25</td>
<td>Fail</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-22</td>
<td>Fail</td>
<td></td>
<td></td>
<td>-24</td>
<td>Pass</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-21</td>
<td>Fail</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-20</td>
<td>Pass</td>
<td></td>
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<td></td>
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<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>
The results obtained are -20°C, -19°C, -20°C, -24°C, and -20°C, with a median of -20°C. These results are both very consistent with each other and correlate very well with the $T_g$ of the material.

Table 4: Overall results table (laboratories A, B and C)

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>Minimum seal temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Test 1</td>
</tr>
<tr>
<td>A</td>
<td>-17</td>
</tr>
<tr>
<td>B</td>
<td>-25</td>
</tr>
<tr>
<td>C</td>
<td>-20</td>
</tr>
</tbody>
</table>

The three laboratories have returned median results of -23°C, -27°C, and -20°C, this shows that there is some variation and the method outlined in section 6 does not return exactly the same result lab to lab. This can be compared to for example $T_g$ by DSC which would return very similar results (within 1°C typically – although a range may be quoted depending on whether initial, mid-point or end point temperature has been quoted) no matter where it was tested. This is because the DSC is a very precise piece of analytical equipment in which temperature change is very tightly controlled.

Based on discussions within the ESA EPSD it is felt that the variation in the results returned can most likely be attributed to differences in hardware or differing rates of cooling. However given the inherent variation in elastomeric components there is reasonably good agreement between the results returned. It is felt that the method offers useful data that is closer to real world conditions than generated by traditional low temperature characterisation methods.

8.0 FUTURE WORK

The results reported above cover the period to December 2015. On the basis of this work the following changes were proposed. It is intended that the results of these changes will be reported during 2016.

- A maximum cooling rate of 1.5°C per minute will be applied
- The stabilisation period at a given temperature before application of pressure will be increased from 1 minute to 5 minutes.
- In order to reduce the overall test time, future testing will stipulate an initial start test temperature 5°C above the expected minimum sealing temperature rather than the current 10°C.
- The test fixture design will be amended to allow use of a split centre bobbin. This will allow easier fitting of low elongation materials.
- The effects of using the same seal for each test run against using a new seal for each test run will be evaluated
- Results for other elastomer types will be evaluated and reported.
- The test program will be expanded to include additional ESA EPSD member laboratories.
9.0 CONCLUSION

The ESA EPSD believe that the work described within this paper shows that it will be possible to develop a testing method that gives a closer link to ‘real world’ low-temperature sealing capability than existing laboratory tests.

This will result for the first time in an industry agreed specification that all reputable seal suppliers will be able to use to give end-users reliable guidance on the low temperature operating limits of their compounds.

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