Defining True Minimum Temperature Capabilities of Elastomeric Seals

European Sealing Association

Summary

Elastomer seals are being used in ever more arduous conditions in many industries, with more aggressive media, higher pressures, and wider temperature ranges being encountered. Equipment manufacturers and operators are reliant on the seal suppliers’ advice on compatibility of their products with these conditions and such advice is normally based on reliable and established tests. However, when it comes to applications at low (sub-zero) temperatures the situation is not so clear.

Elastomeric materials become stiffer and lose resilience as the temperature drops and, thus, their sealing ability reduces. There are numerous test methods to investigate elastomer material properties at low temperature, such as torsion modulus, brittleness, compression set and temperature retraction. But these in themselves do not give a direct indication of whether a seal will continue to function. There are also proprietary sealing tests which aim to identify the minimum operating temperature capability; however all of these rely on the seal being energized by the pressure of the test media prior to being subjected to low temperature. This is not necessarily the case in real applications; if the seal is kept at low temperature prior to being exposed to the pressurizing media it may be too stiff to energize and form a robust seal.

The members of the **ESA Elastomeric and Polymeric Seals Division** are therefore working together to prepare and validate a suitable test method for this common and more severe condition. An initial draft of the standard has been prepared and is currently in the process of being validated. This program takes the form of round-robin tests conducted by the members on seals obtained from a single source. Each laboratory is testing seals and the results are being compared for consistency and repeatability before refinement of the specification.

This paper will give details of the test procedure itself and results for a number of generic elastomer types will be presented and discussed.

The aim is, for the first time, to produce 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. It is anticipated that the test procedure can subsequently be put forward to the International Organization for Standardization (ISO) for development into a truly international standard.

1. Motivation

Low temperature sealing operations are required in a wide variety of applications from oil and gas exploration to off-highway vehicles in Siberian Tundra. Seals need to operate successfully in subzero temperatures for prolonged periods. Elastomers and thermoplastics have a tendency to stiffen and become harder as they are approaching their glass transition temperature (T_g). However all the sealing materials react differently under compression and pressure therefore there is a need to determine lowest sealing temperature irrespective of the T_g.

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 move and the individual chain segments remain flexible but as the temperature is decreased, the ability of the molecules to move is reduced as they move closer together, and the energy in the system reduces. The material reaches a point known as the glass transition temperature (T_g) which is the point at which it 'freezes' though is not yet fully brittle. Chain mobility is restricted, and the elastomer starts to crystallize, becoming brittle and unresponsive. The temperature at which the elastomer crystallizes is predominantly influenced by its chemical structure. Introducing 'irregular' monomers reduces the tendency to crystallize, 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. Other factors such as the introduction of plasticizers, compound hardness, modulus, and even the medium being sealed can have minor effects.

2. Mechanism of Sealing

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 reaction of the seal to 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.

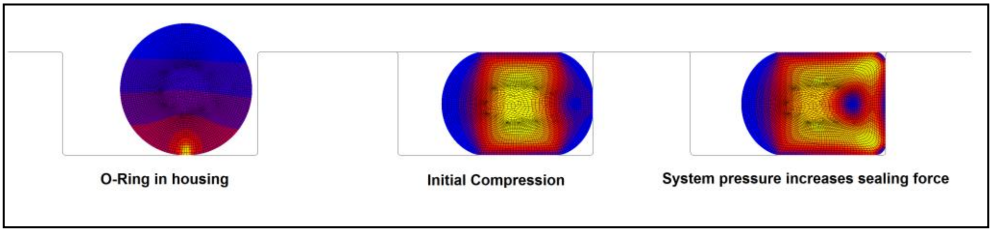


Figure 1: Sealing Mechanism.

Whilst the seal is energized 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.

3. 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.

4. Low Temperature Test Methods

There are two types of testing for determining the low temperature operation limits for elastomers. Firstly are methods which determine changes in the properties of elastomer material itself and then set arbitrary limits to the changes to derive an operating limit. Secondly methods which are more relevant to the actual mechanism of sealing, but still do not represent the usual mode of operation of low temperature environment.

4.1. Material Testing

4.1.1. Temperature Retraction (ISO 2921/ASTM D1329/BS ISO2921)

In this test the sample is stretched by typically 50% and then conditioned in 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 percentage. The temperature to recover by 10% (TR10) is often used to establish the minimum static operating temperature of the elastomer. Normally the percentage 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.

4.1.2. 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 in TR method. 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.

4.1.3. 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 T_g and 'Brittle Onset Temperature' can be made.

4.1.4. 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 T_g.

4.1.5. Bend Brittle Test (e.g. DTD 458)

This 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.

4.1.6. Brittleness Temperature by Impact (ASTM D746, ISO 812)

These test methods specify a method for determining the lowest temperature at which rubber materials do not exhibit brittle failure or the temperature at which half of the test pieces used in a test fail when impacted under specified conditions.

The temperatures thus determined do not necessarily relate to the lowest temperature at which the material can be used since the brittleness will be affected by the conditions of test and especially by the rate of impact. Data obtained by this method should, therefore, be used to predict the behavior of rubbers at low temperatures only in applications in which the conditions of deformation are similar to those specified in the test.

4.2. Existing Low Temperature Sealing Tests

DuPont introduced a sealing test using O-rings with a fixed amount of compression (typically 10%) using nitrogen at a particular pressure and ambient temperature. The temperature of an energized seal is reduced until failure occurs. Results obtained from the testing were typically significantly below T_g (between 10 and 15°C). Most of the testing was carried out on FKM seals and the results can be applied to real life applications in which, the seals are compressed by the same ratio, having the same size, lubricated the same way and pressurized to 200 psi before cooling down. However very few seals would be pressurized before the temperature was reduced in real life.

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.

5. ESA Proposed Test Method

In order to meet real life conditions and recommendations ESA EPSD chose to use an O-ring in accordance with ISO 3601 series for dimensional, groove, tolerances and quality acceptance criteria.

5.1. Scope

This specification details a test method for O-ring seals in elastomeric materials, which are subject to pressurized 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 utilized to test seals of alternate size and design, or using alternative media, but such deviations shall be detailed separately on the report form. The results shall not be used to determine the minimum operating temperature of seals of any other configuration than that tested.

5.2. Definitions

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

5.2.1. Minimum seal temperature

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

5.2.2. Zero leakage

For the purpose of this test a negligible leak rate is no discernible bubbles. This is considered to be equal to a displacement of less than 20cm^3/h, as defined in API 6A F1.13.6.

5.2.3. Room Temperature

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

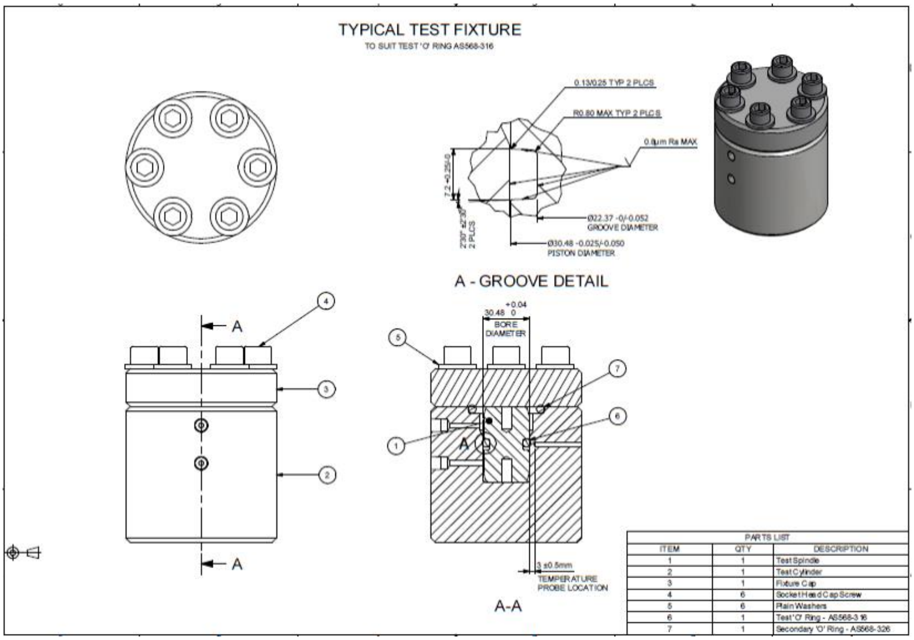
5.3. Test Apparatus

5.3.1. Test fixture

A suitable test fixture shall be similar to the typical example shown in Figure 2 and shall consist of 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. For ease of seal installation and removal a split plug could be used.
- 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 centralization 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.



PARTS LIST		
ITEM	QTY	DESCRIPTION
1	1	Test Spindle
2	1	Test Cylinder
3	1	Fixture Cap
4	6	Socket Head Cap Screw
5	6	Plain Washers
6	1	Test 'O' Ring - AS568-316
7	1	Secondary 'O' Ring - AS568-326

Figure 2: Typical Test Fixture.

Picture 1: Typical Test Fixture.

5.3.2.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 2 Typical Test Cell.

5.4. Test conditions

5.4.1. 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).

5.4.2. Test medium

The test medium shall be nitrogen gas.

5.4.3. Pressure

The test pressure applied to the seals shall be 15 MPa +5/-0%

5.5. 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. 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.

5.6. Test procedure

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

5.6.2. Apply the test pressure and check for leakage.

5.6.2.1. If leakage is observed release the test pressure and raise the temperature by 5°C. 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 4.6.2 onwards.

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

5.6.3. 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.

5.6.4. Repeat the test procedure from clause 4.6.2 onwards until a temperature is reached where the seal fails to hold pressure.

5.6.5. 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.

5.6.5.1. If leakage is observed release the test 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. Then repeat the procedure from clause 5.6.5 onwards.

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

5.6.6. Continue the process from clause 5.6.5 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**.

5.6.7. The start point for each repeat test shall be 5°C higher than the previous minimum seal temperature.

5.6.8. 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.

6. Results and Discussion

The study of a “**Specification for a Test Procedure to Determine Low Temperature Sealing Capability of Elastomeric Seals**” started in 2014, with the involvement of five ESA members. A lot of interlaboratory testing has been carried out within ESA to create the draft ESA standard and to test the assumptions and analyze the repeatability of the method.

During the course of testing HNBR, FKM, EPDM, and FFKM materials have been tested by different laboratories and variation from lab to lab and from sample to sample have been studied carefully. Revisions to the standard had been made to minimize variation.

In this study we will focus on a generic FFKM O-ring with a **T_g of -19 °C** supplied by one of the ESA members.

6.1 Initial Testing

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.

The material under test was a nominal 70 IRHD perfluoroelastomer (FFKM). Its glass transition (T_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.

6.1.1 Test Results 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 1: Results of running the ESA low temperature test procedure on 5 FFKM samples at laboratory A.

Test 1		Test 2		Test 3		Test 4		Test 5	
Temp (°C)	Result	Temp (°C)	Result	Temp (°C)	Result	Temp (°C)	Result	Temp (°C)	Result
-9	Pass	-9	Pass	-9	Pass	-9	Pass	-9	Pass
-14	Pass	-14	Pass	-14	Pass	-14	Pass	-14	Pass
-19	Pass	-19	Pass	-19	Pass	-19	Pass	-19	Pass
-24	Fail	-24	Pass	-24	Pass	-24	Pass	-24	Pass
-23	Fail	-29	Fail	-29	Fail	-29	Fail	-29	Fail
-22	Fail	-28	Fail	-28	Fail	-28	Fail	-28	Fail
-21	Fail	-27	Fail	-27	Fail	-27	Fail	-27	Fail
-20	Fail	-26	Fail	-26	Fail	-26	Fail	-26	Fail
-19	Fail	-25	Fail	-25	Fail	-25	Fail	-25	Fail
-18	Fail	-24	Fail	-24	Fail	-24	Pass	-24	Fail
-17	Pass	-23	Pass	-23	Fail			-23	Fail
				-22	Fail			-22	Pass
				-21	Fail				
				-20	Fail				
				-19	Pass				

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 $T_{g.}$

6.1.2 Test Results 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 3 FFKM samples at laboratory B.

Test 1		Test 2		Test 3	
Temp (°C)	Result	Temp (°C)	Result	Temp (°C)	Result
-20	Pass	-20	Pass	-20	Pass
-25	Pass	-25	Pass	-25	Pass
-30	Fail	-30	Pass	-30	Pass
-29	Fail	-29	Fail	-35	Fail
-28	Fail	-29	Fail	-34	Fail
-27	Fail	-28	Fail	-33	Fail
-26	Fail	-27	Pass	-32	Fail
-25	Pass			-31	Pass

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.

6.1.3 Test 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

Test 1		Test 2		Test 3		Test 4		Test 5	
Temp (°C)	Result	Temp (°C)	Result	Temp (°C)	Result	Temp (°C)	Result	Temp (°C)	Result
-21	Pass	-11	Pass	-11	Pass	-11	Pass	-11	Pass
-26	Fail	-16	Pass	-16	Pass	-16	Pass	-16	Pass
-25	Fail	-21	Fail	-21	Fail	-21	Pass	-21	Fail
-24	Fail	-20	Fail	-20	Pass	-26	Fail	-20	Pass
-23	Fail	-19	Pass			-25	Fail		
-22	Fail					-24	Pass		
-21	Fail								
-20	Pass								

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.

6.1.4 Overall Results for initial testing and discussion

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

Laboratory	Minimum seal temperature °C					
	Test 1	Test 2	Test 3	Test 4	Test 5	Median
A	-17	-23	-19	-24	-23	-23
B	-25	-27	-31	-	-	-27
C	-20	-19	-20	-24	-20	-20

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 5 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 given 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. As the hardware is already well defined it was decided to investigate in more detail the effect of cooling rate.

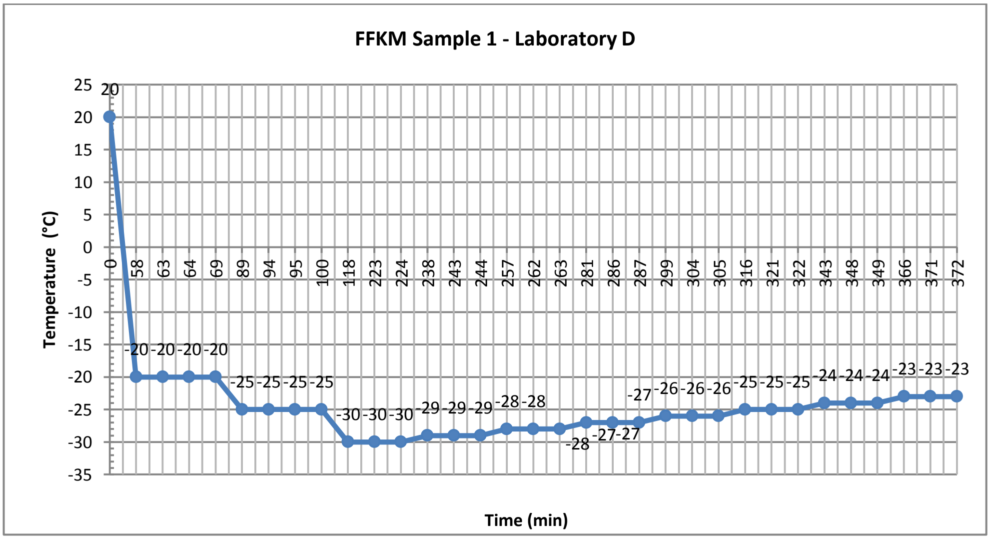
It should be noted that after this round of testing it was decided to have a test temperature 5°C above the expected point of failure; this is reflected in the procedure given in this paper.

6.2 Investigating Cooling Rates

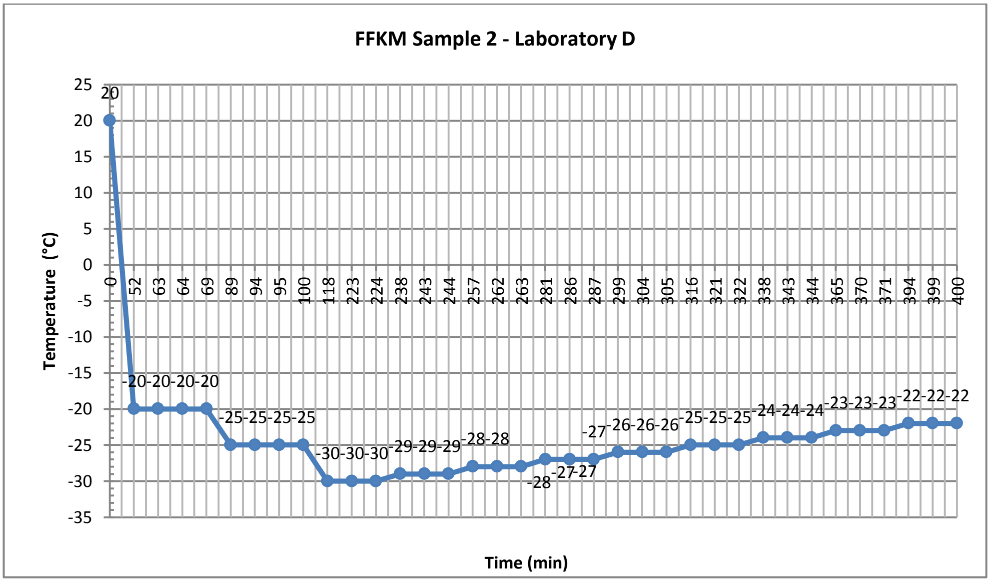
A second round of testing was carried out on a new set of samples. Laboratory D in this round of testing was using a test cell with liquid nitrogen cooling, which allowed for rapid cooling; the average time taken to get to the initial test temperature of -20°C was around 50 minutes. In Laboratory E the average test duration is 5000 minutes, due to the test cell ability' and single shift operation; resulting in extended periods of fixed temperature during testing leading to extended test duration.

6.2.1 Results from Laboratory D

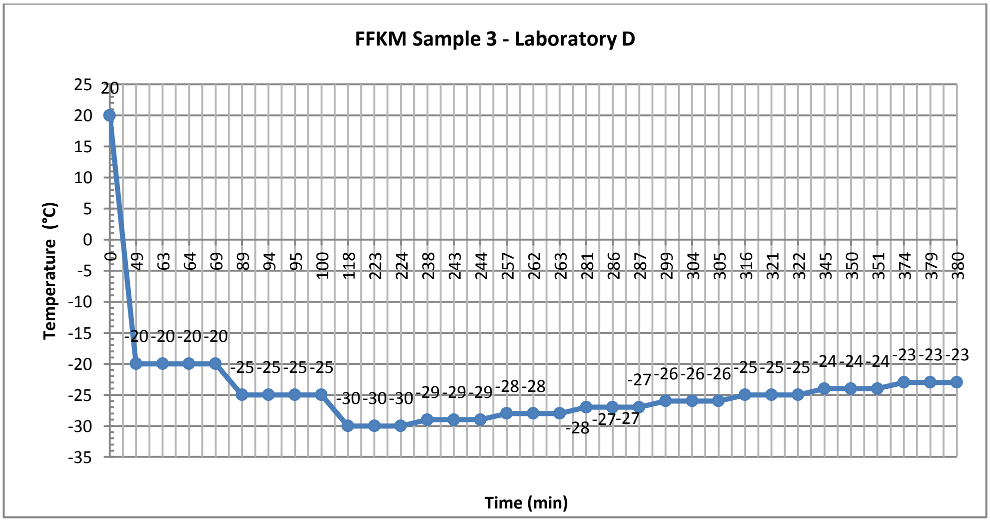
Three FFKM samples have been tested by Laboratory D. The results are shown in Graphs 1-3. The variation between results is only 1 °C and repeatability is precise with respective results of -23 °C, -22 °C and -23 °C.



Graph 1: FFKM Sample 1.



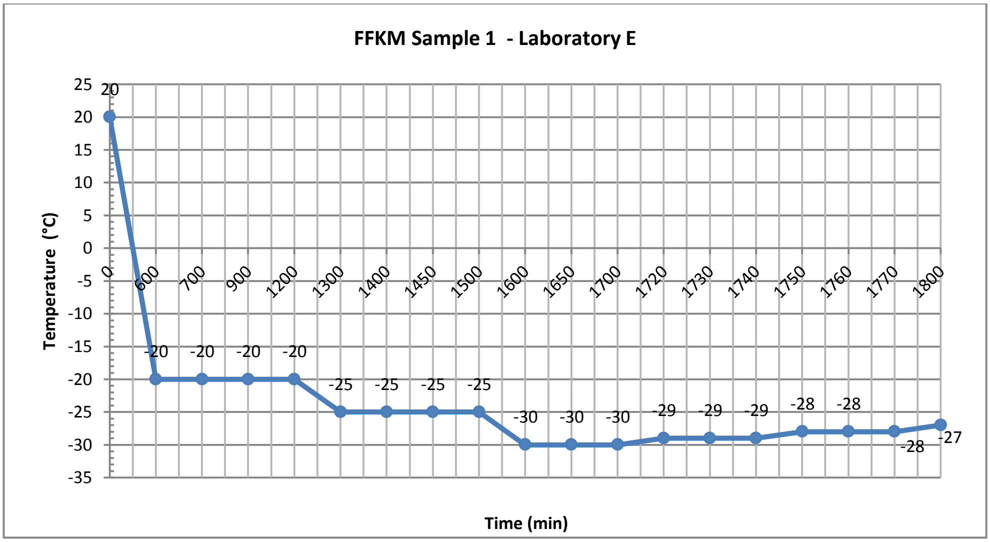
Graph 2: FFKM Sample 2.



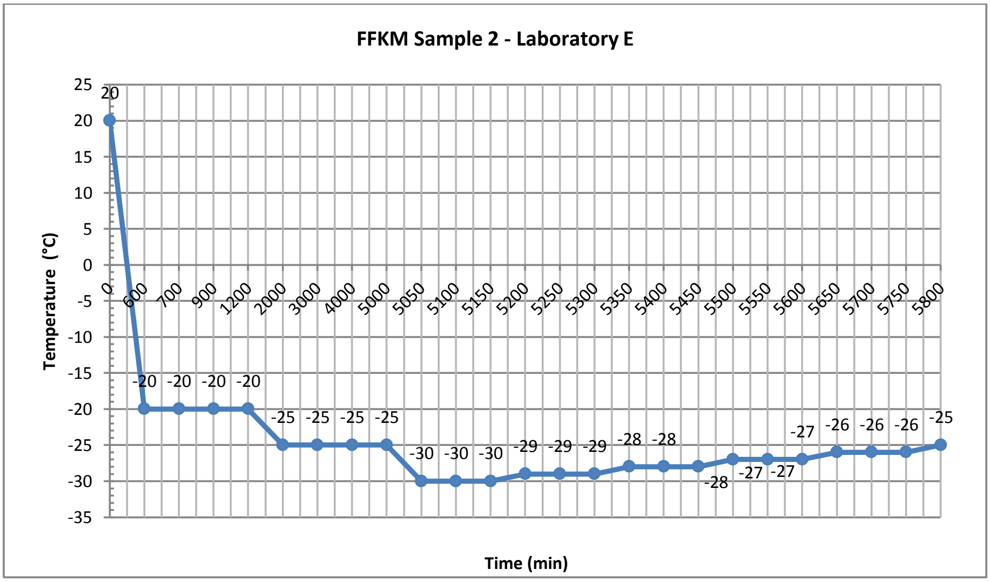
Graph 3: FFKM Sample 3.

6.2.2 Results from Laboratory E

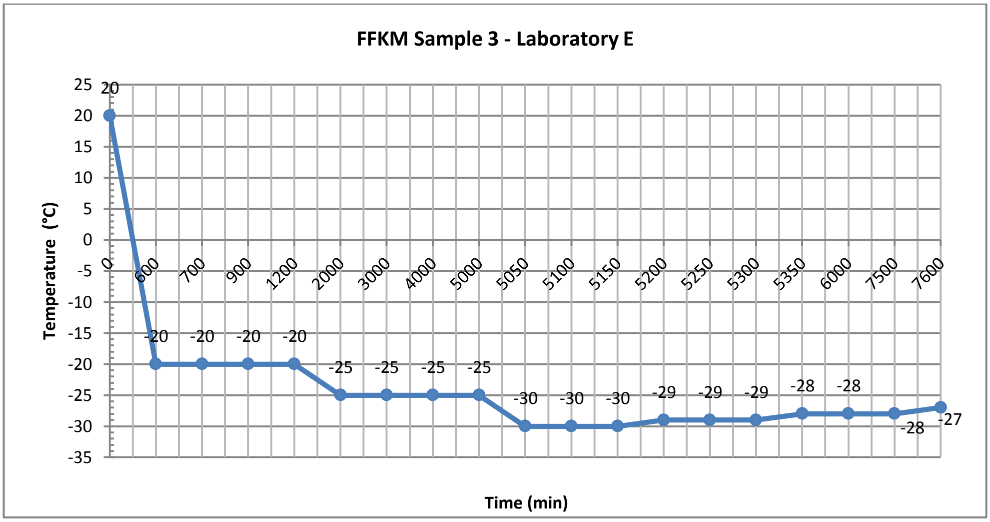
Three FFKM samples have been tested by Laboratory E. The results are shown in Graphs 4-6. The variation between results is only 2 °C and repeatability is precise with respective results of -27 °C, -25 °C and -27 °C.



Graph 4: FFKM Sample 1



Graph 5: FFKM Sample 2



Graph 6: FFKM Sample 3

6.2.3 Discussion

Although each laboratory had very good repeatability on the tests carried out, there was a small but significant difference between the two laboratories. This suggests that the cooling rate needs to be better defined in the standard. There are, however, two competing considerations. Firstly the length of time in which it takes to complete the testing, and the cost of the equipment that would need to be purchased in order to carry out the testing.

6.3 A Comparison with Current Sealing Tests

Finally it is felt it would be useful to compare the results as found from previously practiced methods as described in section 3.2. In this testing the system was pressurised before cooling it down, this is not typical of all applications. The results are very different and much lower in comparison to ESA method. This could be expected, as the system pressure is able to maintain a seal; and so the results are heavily dependent on the pressure applied due to the increased energisation of the system. Experiments were carried out at 500psi 1,000psi, and 3,000psi. Each pressure was held at ambient temperature for 1 hour before being gradually reduced until leakage occurred, a resealing temperature was not determined.

Table 5: Test Results - Laboratory F

Pressure	500 psi	1000 psi	3000 psi
Min. Sealing Temp.	-45 °C	-60 °C	< -80 °C

7. Conclusions

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, which all reputable seal suppliers will be able to use to give end-users reliable guidance on the low temperature operating limits of their compounds.

In order to fully define the low temperature capability it could be worth developing a second test procedure which covers the situation in which pressure is applied before the temperature is reduced. The hardware and seals used could be as in the previously described procedure. Main points to be defined would be the rate of temperature reduction, and what constitutes failure.

8. Future Work

- Additional testing to fully understand the effect of cooling rate on the results.
- It is intended to investigate whether using a fresh seal for each test is necessary or whether the same seal can be used for subsequent tests.
- Results for other elastomer types will be evaluated and reported.
- Work will be undertaken to investigate exactly what pass/fail criteria should be implemented for this kind of testing.

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