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High Performance Elastomers Answering the Big Questions

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Who are the ESA?

Association of European based companies which manufacture fluid sealing devices.

Established in 1990, Registered in the UK and Germany.

5 Divisions:

- **Mechanical Seals**
- **Packings**
- **Flange Gaskets**
- **Elastomeric & Polymeric Seals**
- **Expansion Joints**

48 Members

Aims of the ESA

Achieving what cannot be done by individual companies alone:

- **Joint Non-Competitive Research Programs**
- **Lobbying:**
  - **National Governments**
  - **European Union**
- **Creating, Developing and Influencing International Standards**

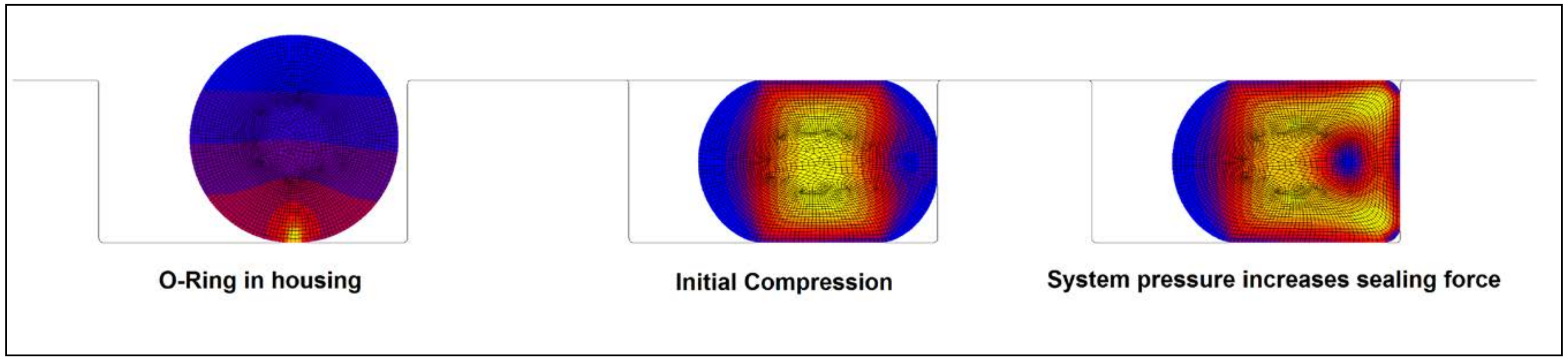
The Big Questions!

- How long will it last?
- What is the lower temperature capability?

Agenda

- What happens at High Temperatures?
- What happens at Low Temperatures?
- Assessing High Temperature Performance:
  - Heat Ageing (AIR / MEDIA)
  - Arrhenius – ESA E&PSD Testing
  - Compression Set / Compression Stress Relaxation (CSR)
- Assessing Low Temperature Performance:
  - Existing methods (e.g. TR10, $T_{g,}$ T_{70})
  - ESA E&PSD Proposed method
- Conclusions

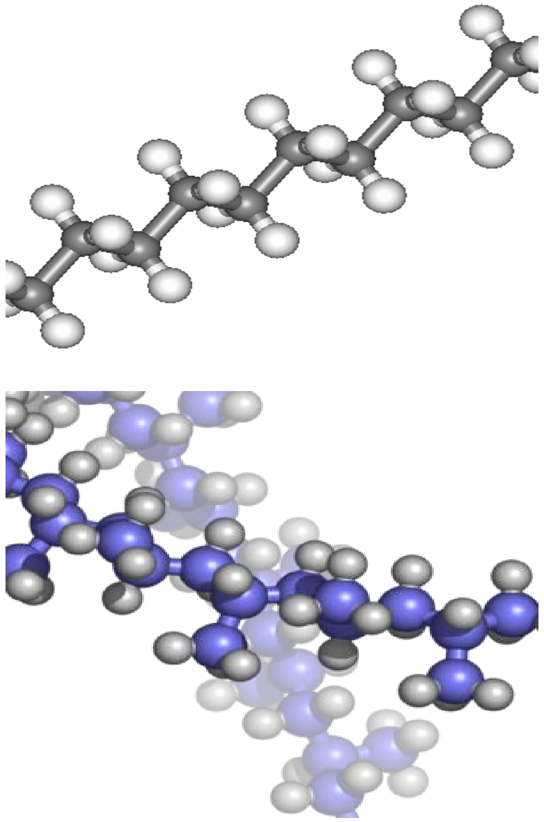
What Happens at High Temperatures?



- Irreversible formation of new/different chemical bonds.
- Changes physical properties.
- Reduction in elasticity.
- Reduction in sealing efficacy.
- All Elastomeric seals have a finite lifetime.

What Happens at Low Temperatures?

- As temperature decreases parts become steadily less flexible, as system energy reduces.
- Ultimately movement is not possible, at the glass transition.
- Reduction in sealing efficacy.



Assessing High Temperature Performance

- Measure changes in:

Standard	Property	Specimen Type
ASTM D412	Tensile Strength, Elongation	(ASTM D412 Type C) DIN 53504 S2 Dumbbells
ASTM D412	50%, 100%, 200%, 300% Modulus	(ASTM D412 Type C) DIN 53504 S2 Dumbbells
ASTM D2240	Hardness (Shore A)	ASTM D395 Type 1 Discs
ASTM D297	% Volume Change (IRM 901 Only)	(ASTM D412 Type C) DIN 53504 S2 Dumbbells

- After exposure to chemicals of interest at temperatures of interest.
- To asses lifetimes an Arrhenius approach is often suggested.

The Arrhenius Equation

The Arrhenius Equation

Rate of Reaction

Activation Energy

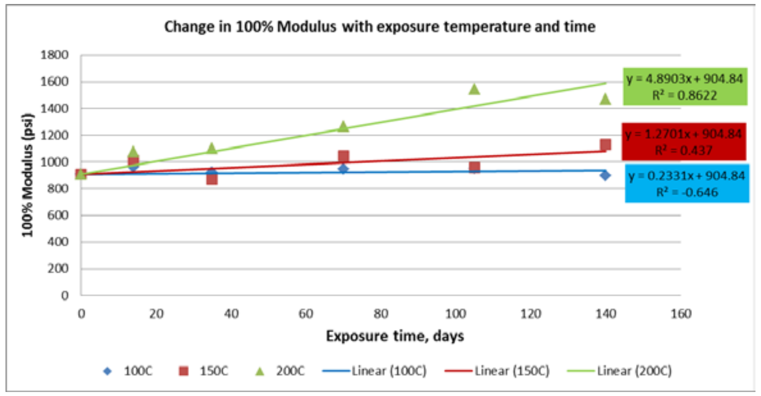
$$k = Ae^{-\frac{E_a}{RT}}$$

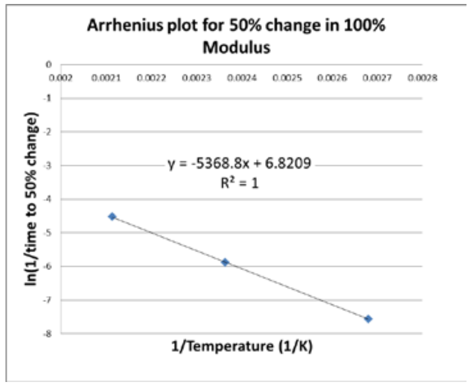
Pre-exponential or Frequency Factor

Gas Constant x Absolute Temperature

Application of Arrhenius

- Plot a series of “Averages” for Temp v Time..
- “Obtain a Reaction Rate” for each Temperature…
- Determine time to X Change (50%)..
- Plot ln K v’s 1/T…
- Pre-exponential Factor is C
- “Slope” x –R is E_a





$$\ln k = \ln A - \frac{E_a}{RT}$$

$$y = c + mx$$

Use to predict time to 50% of property change at any temperature....!

E&PSD Study

- *Two Elastomer Compounds*
  - *FKM copolymer , bisphenol cured, carbon black loaded, rated to 240°C*
  - *A high saturation (≥90%) HNBR, peroxide cured, carbon black loaded, rated to 175°C*
- *Three Temperatures -* ISO 23529 ISO 188

HNBR	70°C	100°C	150°C
FKM	100°C	150°C	200°C

- *Five Time Periods*

2 weeks	5 weeks	10 weeks	15 weeks	20 weeks

- *Two Media*

Air	IRM 901

- *Five Different Ageing Laboratories*
- *All Tested at one Laboratory*

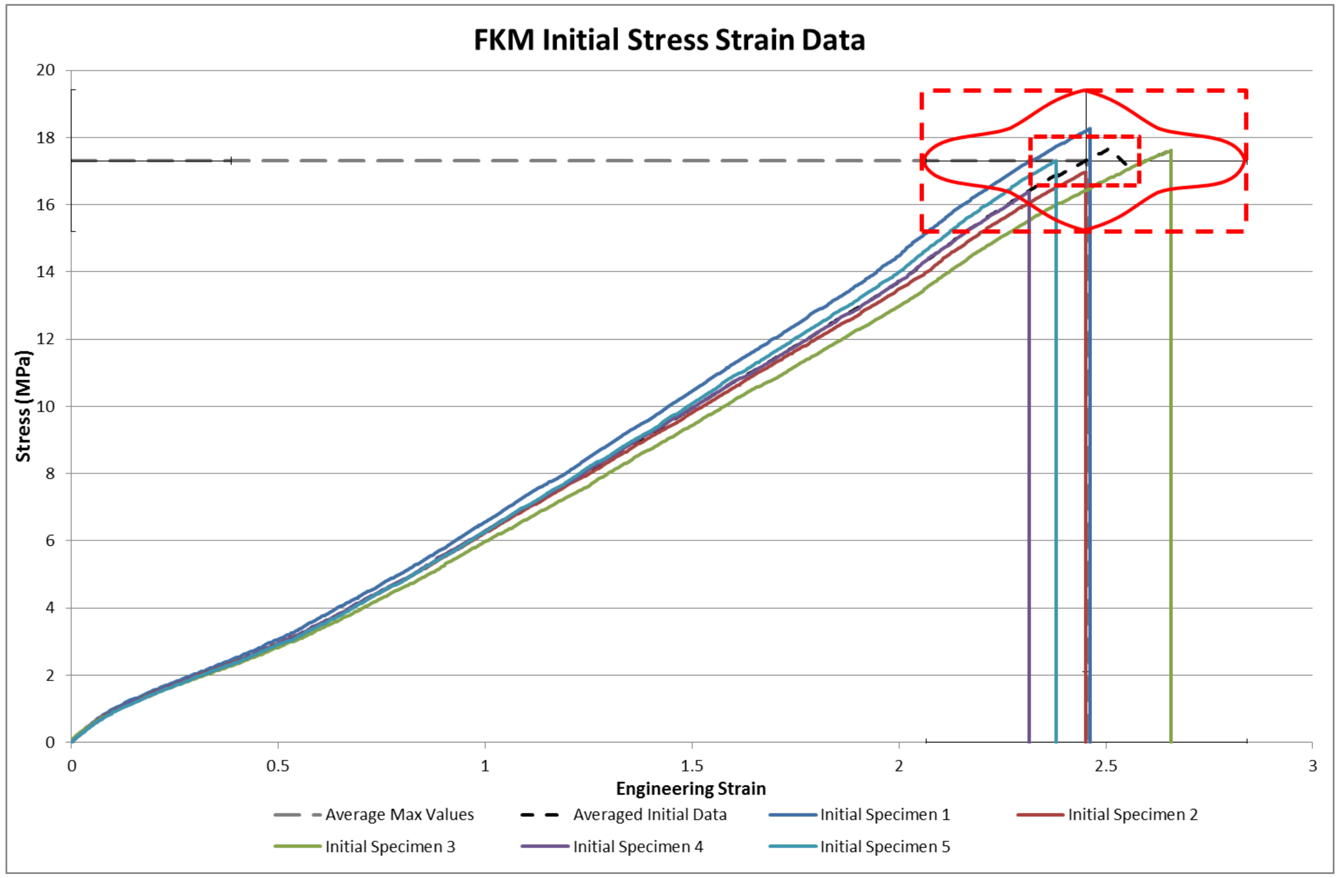
The Statistics

- Consider the variation in Elastomeric Material properties…..
- Take 1 Specimen
- Add 4 more
- Average them
- Add Statistics

1 σ

3 σ

Really something like this



Lifetimes

- Full FKM Air Ageing findings….

FKM Air Ageing Arrhenius Life Predictions (All Data) (Years)

Property	Tensile Strength			Elongation			50% Modulus			100% Modulus			200% Modulus		
Data Set (fitted to Initial)	40°C	100°C	150°C	40°C	100°C	150°C	40°C	100°C	150°C	40°C	100°C	150°C	40°C	100°C	150°C
Mean Values	3.13	1.73	1.20	9.16	4.10	2.49	7.67	2.34	1.12	38.91	7.33	2.62	5.31	4.91	4.68
Upper Bound	2.87	1.62	1.13	6.70	2.91	1.74	12.02	2.71	1.08	108.96	12.51	3.29	3.72	3.47	3.32
Lower Bound	3.54	1.91	1.31	23.91	13.05	8.98	2.35	0.72	0.35	19.10	5.03	2.21	10.37	9.61	9.16
Mean Values*	4.214	2.135	1.404												

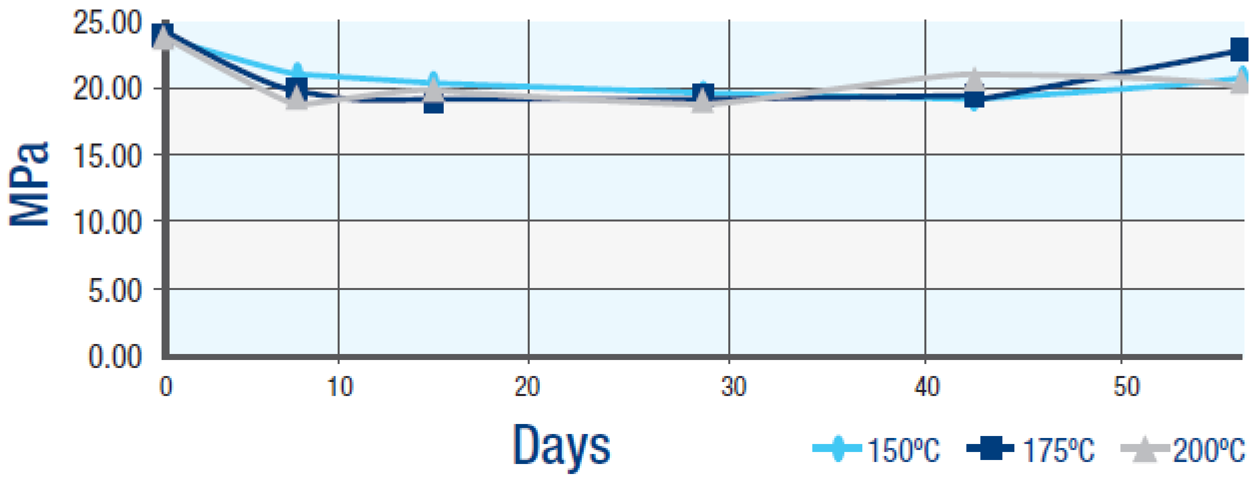
- Full HNBR Air Ageing findings….

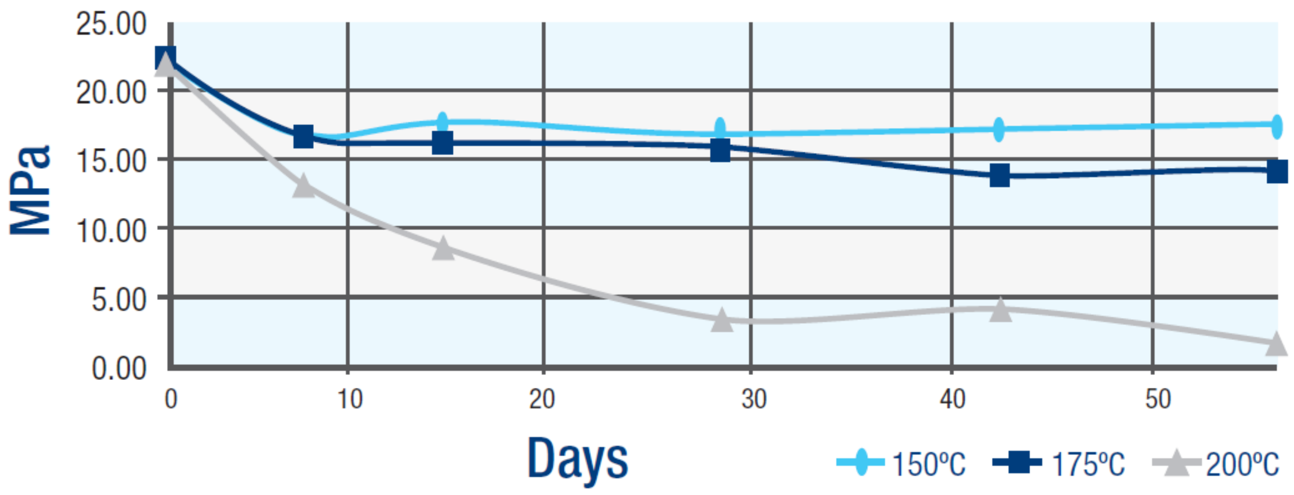
HNBR Air Ageing Arrhenius Life Predictions (All Data) (Years)

Property	Tensile Strength			Elongation			50% Modulus			100% Modulus			200% Modulus		
Data Set (fitted to Initial)	40°C	100°C	150°C	40°C	100°C	150°C	40°C	100°C	150°C	40°C	100°C	150°C	40°C	100°C	150°C
Mean Values	5.08	3.24	2.46	3.60	0.55	0.17	14.48	0.20	0.01	7.75	0.28	0.04	14.00	0.55	0.07
Upper Bound	0.68	4.05	12.19	4.21	0.61	0.19	12.30	0.25	0.02	9.46	0.30	0.04	23.81	0.73	0.09
Lower Bound	153.31	6.56	0.94	4.00	0.58	0.18	9.35	0.23	0.02	32.84	1.04	0.12	9.45	0.44	0.07
Mean Values*	29.25	79.46	147.14												

Further Considerations

What if the response is like this:





Further Considerations

- Still required to match a “failure mode” with “a” physical property/ies and the level at which its becomes an issue.
- Apply this to situations other than ASTM specimens in tightly controlled ovens in single fluids at a single temperature.
- The Arrhenius equation is best applied to single step processes or those which can be easily broken down into such.
- Elastomer sealing is highly complex with a large number of variables.

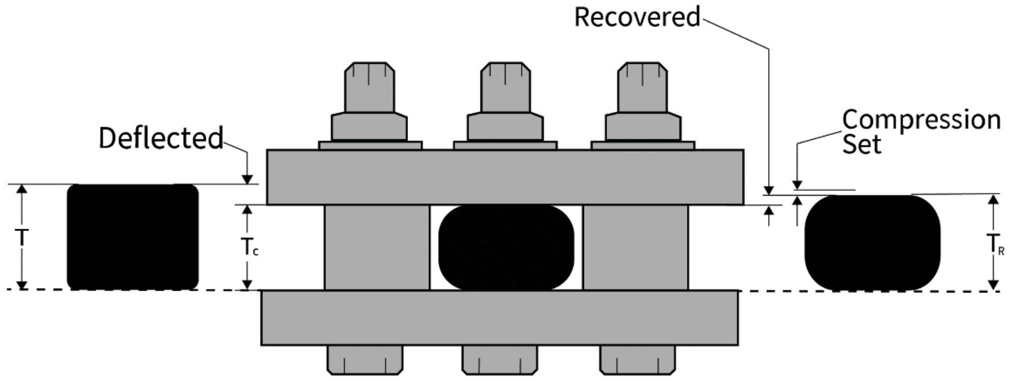
Next Steps – Compression Set

- A test method outlined by ASTM D395 (ISO 815)

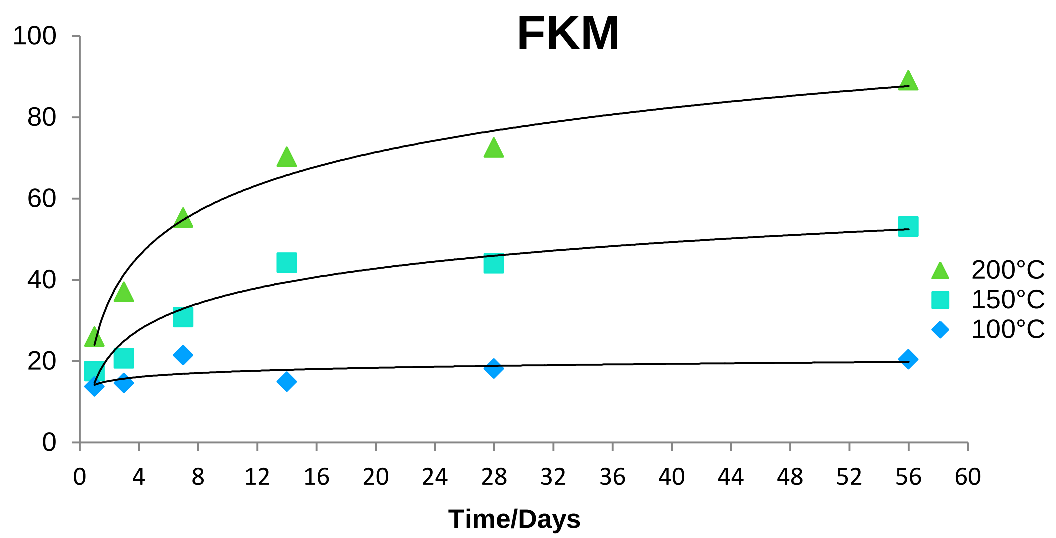
- Is the recovered height of an elastomer sample after the application of a strain, at a given time/temperature/media:

  - This is typically a 25% deflection as shown below.
  - Can be the application of a constant force.

$$\text{Compression Set} = \frac{T_I - T_R}{T_I - T_C} \times 100$$



T_I = Initial thickness
T_C = Compressed thickness
T_R = Recovered thickness

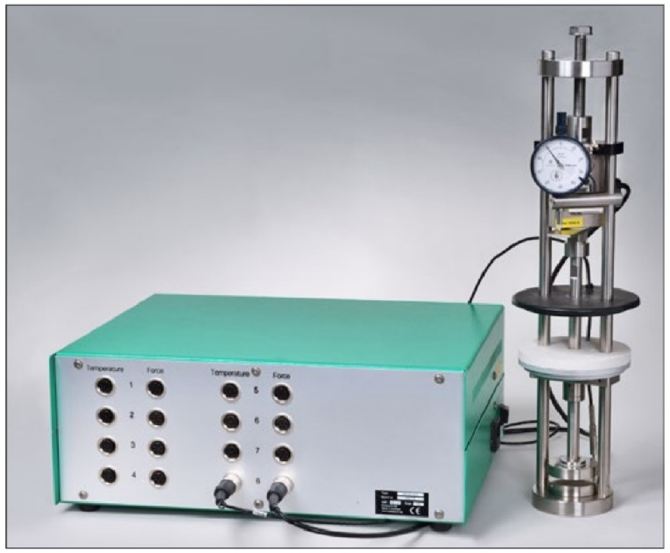


Next Steps – Compressive Stress Relaxation

Measures the force returned by an elastomer sample.

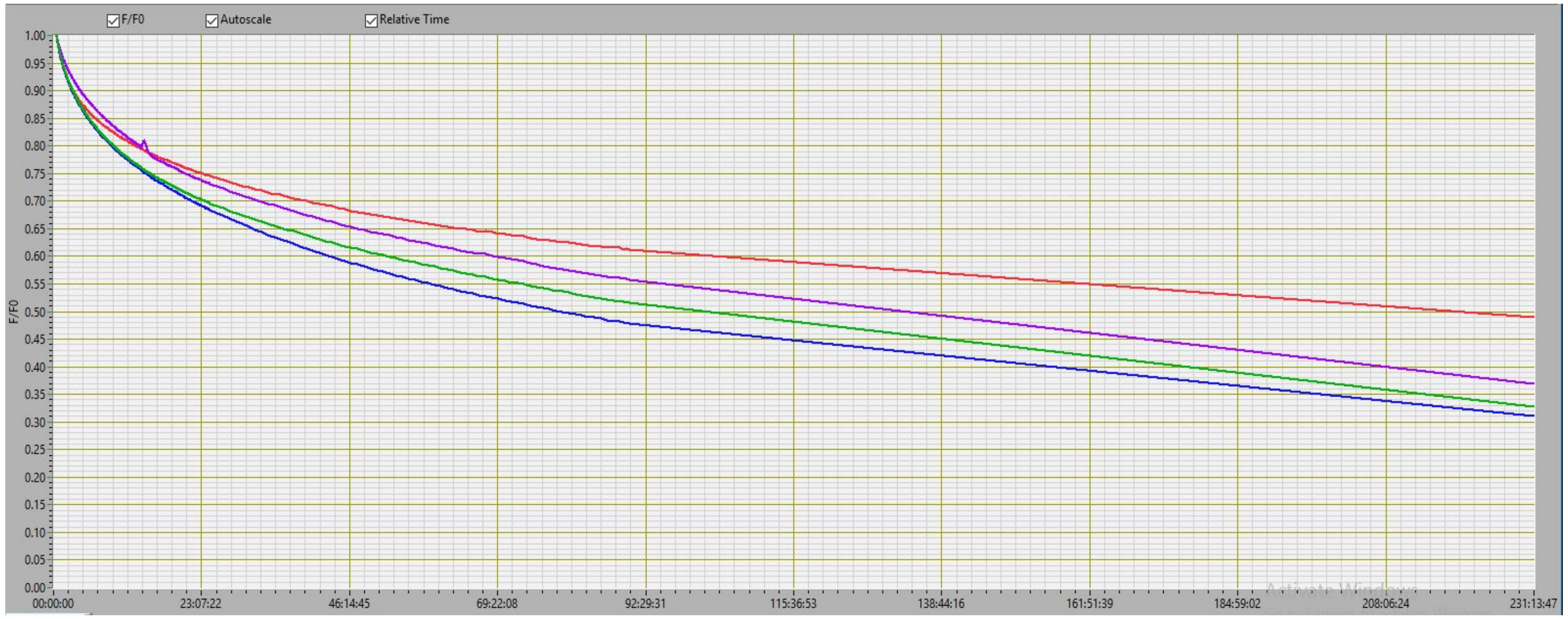
Defined by ASTM 6147/ISO 3384. 25% Compression is also applied.

Results are usually expressed as a percentage F/F_o.



Continuous CSR equipment.

Non-continuous CSR equipment.



CSR curves for FEPM (red), FKM Terpolymers (green and purple), and FKM copolymer (blue).

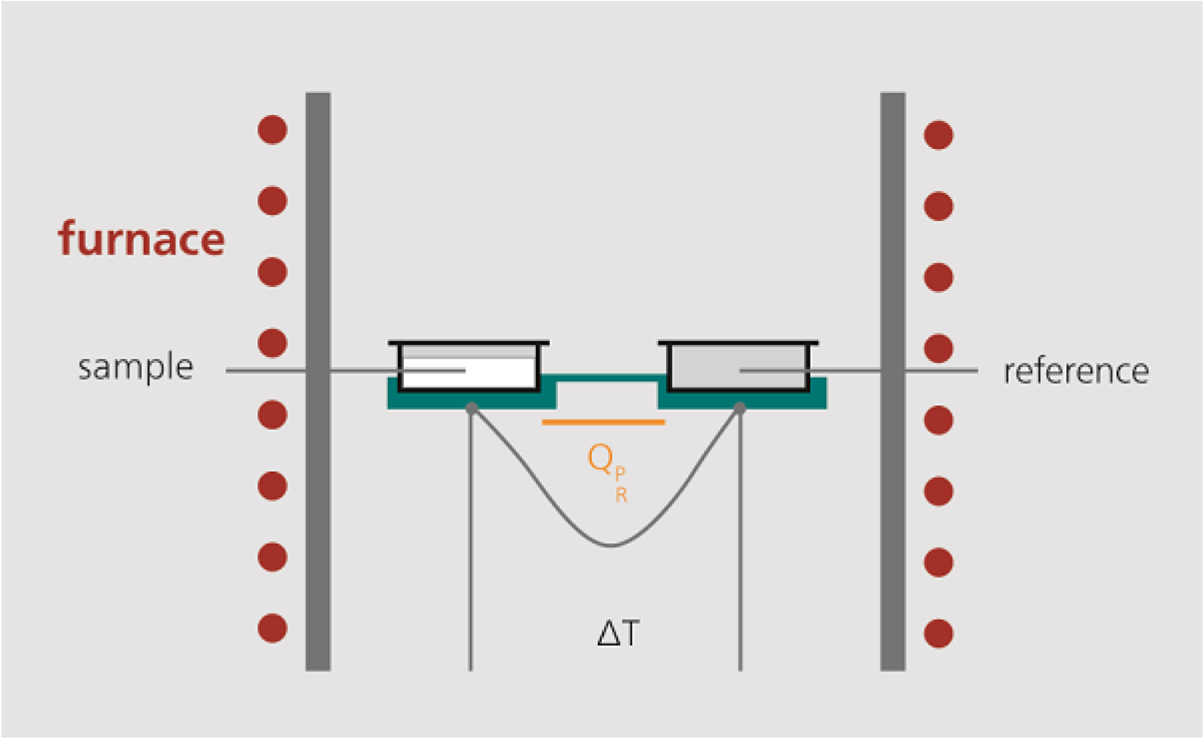
Next Steps – Further Study

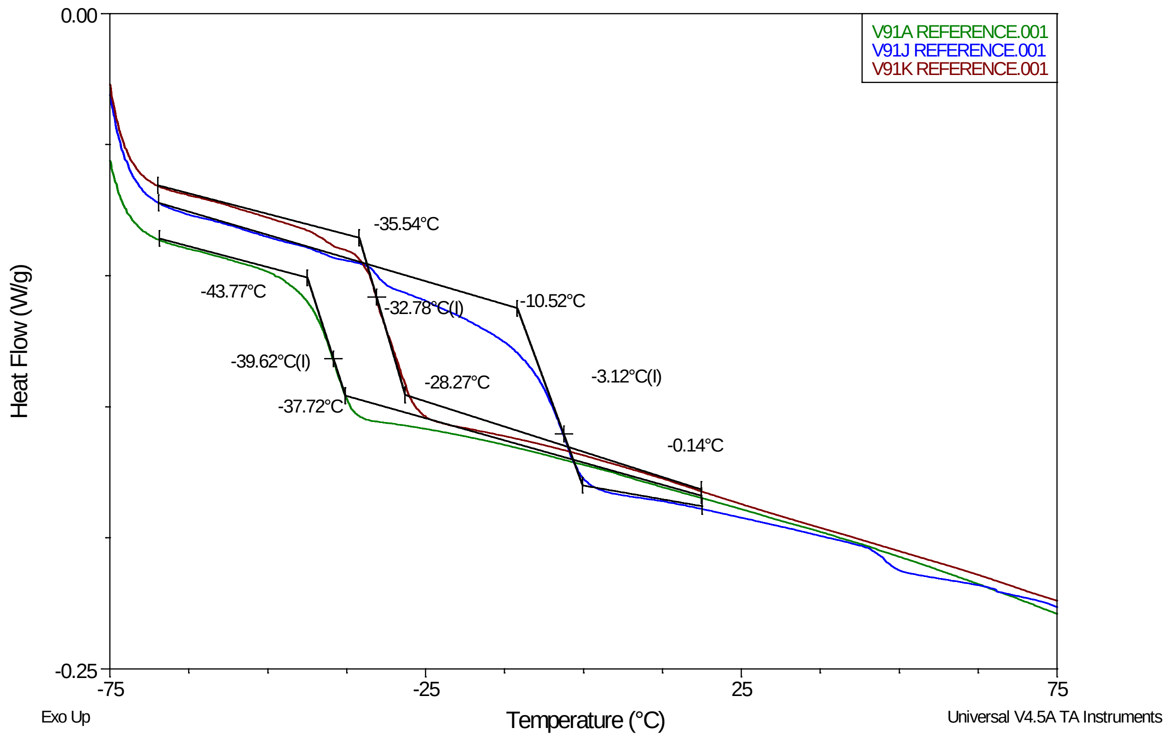
- Further test programme initiated.
- Same FKM on which tensile properties where measured.
- Run CSR and Compression Set in Air at same times and temperatures.
- Does this have better predictive abilities?
- Some of the issues identified previously will applied.

Assessing Low Temperature Performance

- Tg by differential scanning calorimetry ASTM 7426
- Temperature Retraction (TR) ASTM D1329
- Gehman Plot (Torsional Modulus) ASTM D1053
- Low Temperature Brittleness ASTM D746

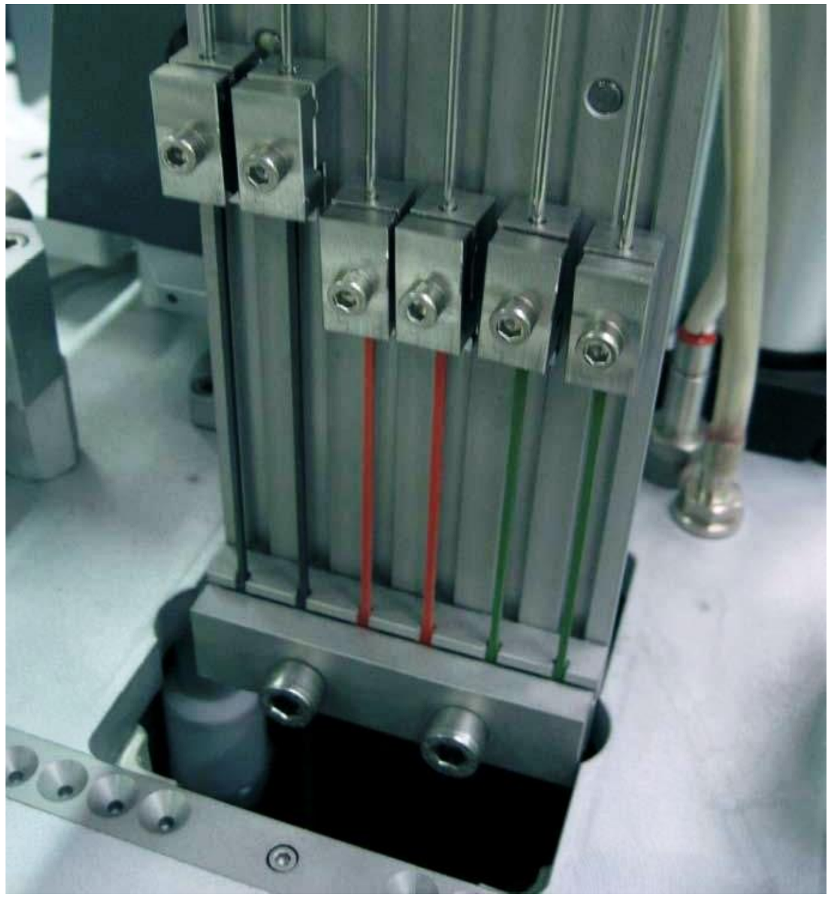
Existing methods – ASTM D7426





Existing methods – ASTM D1329

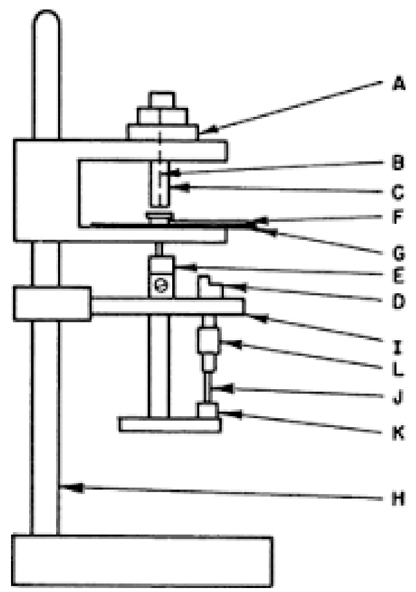
- Specimen is elongated to typically half the elongation at break.
- Conditioned at -70°C before being released and allowed to retract freely as the temperature is raised by 1°C/min.
- The dimension of the sample is measured every 2 minutes until it has retracted 75% of the original elongation.
- Normally TR10, TR30, TR50, and TR70 is reported.

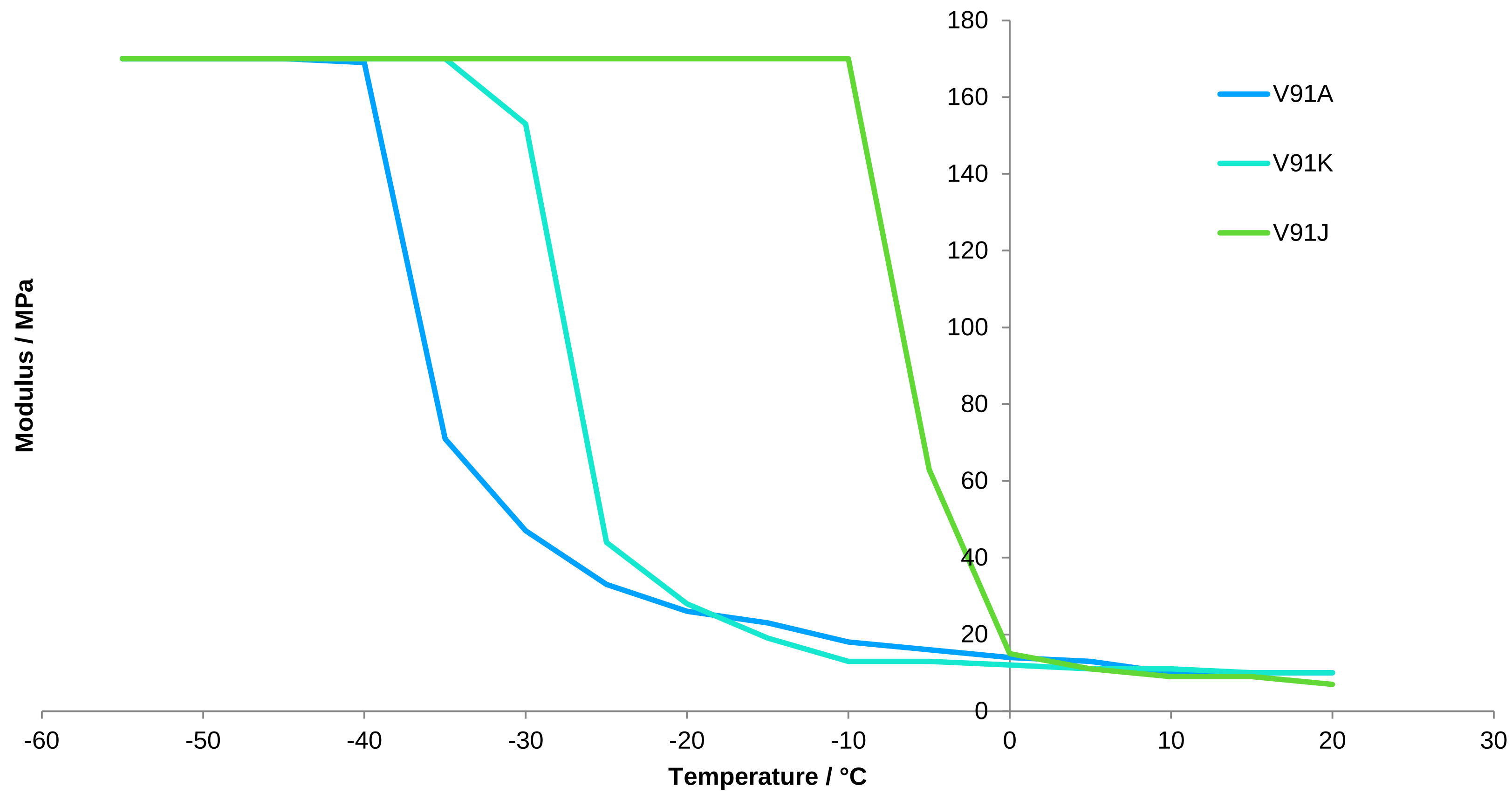


TR 10s V91J = -7 °C V91K = -33 °C V91A= -46 °C

Existing methods – ASTM D1053

Measures the torsional modulus as the temperature is raised.





Existing methods – ASTM D746

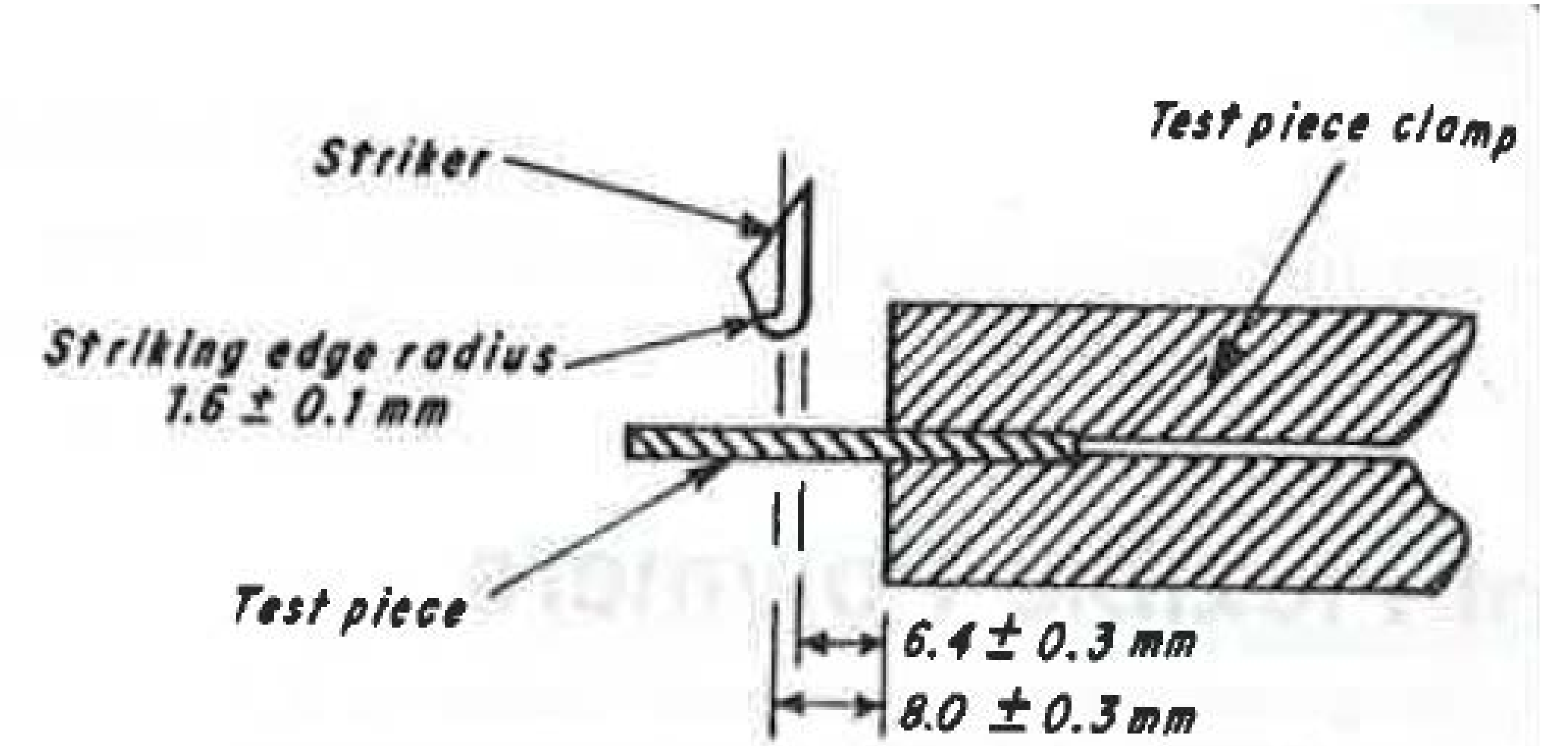
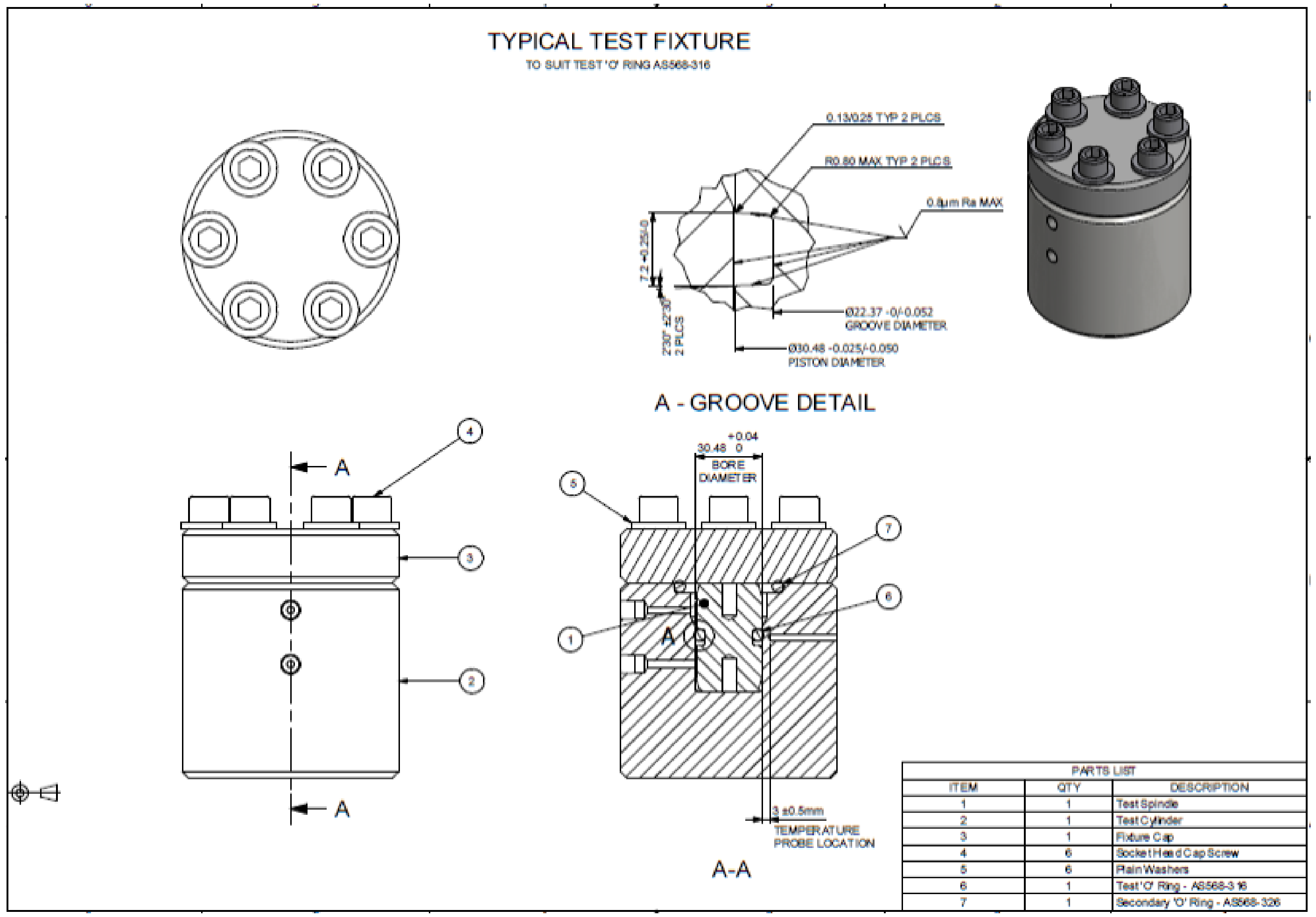


FIG. 1 Specimen Clamp and Striker

Existing methods

How can we apply the results from the above methods to real world sealing applications?

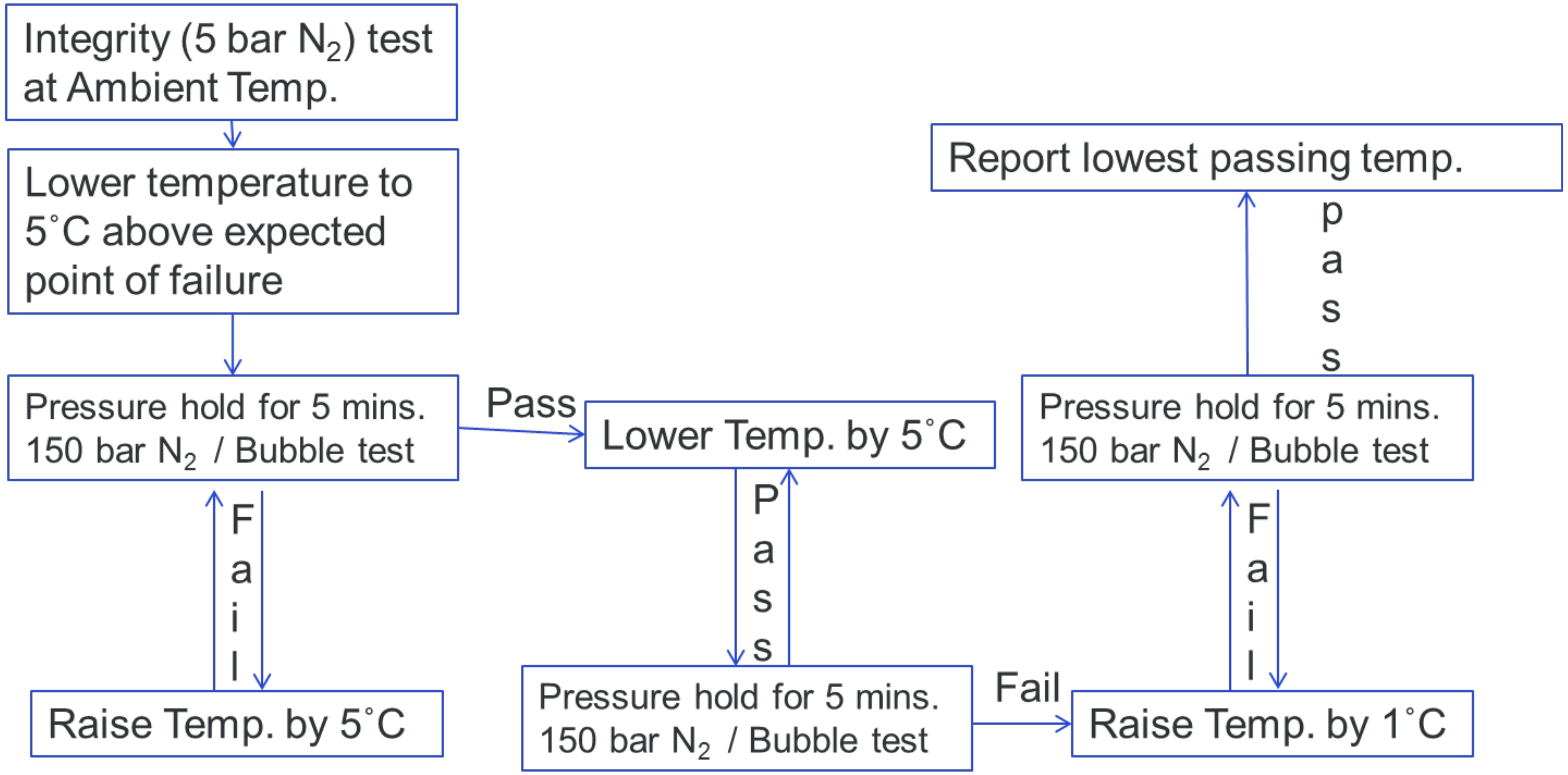
ESA E&PSD Proposed method



PARTS LIST

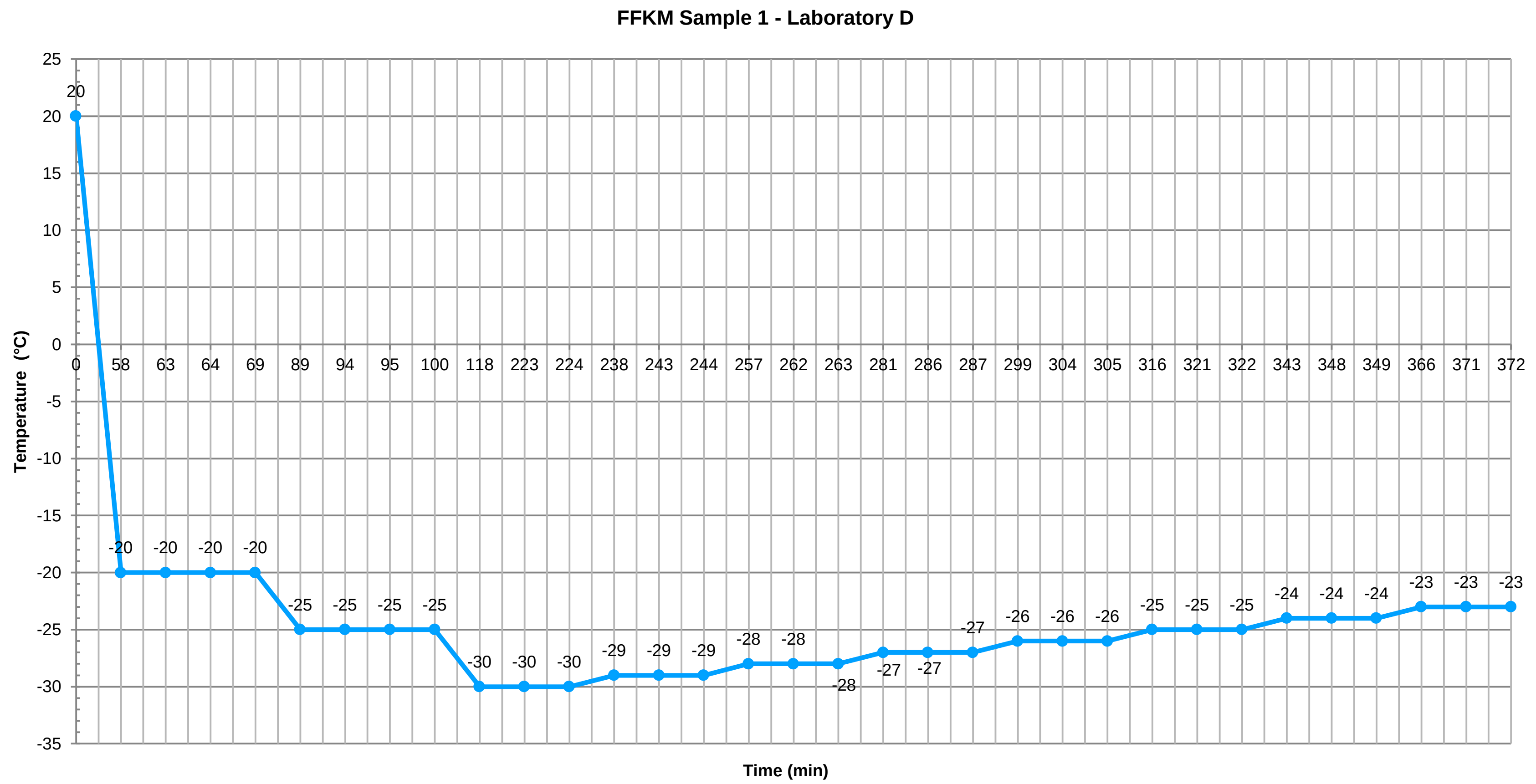
ITEM	QTY	DESCRIPTION
1	1	Test Spindle
2	1	Test Cylinder
3	1	Fixture Cap
4	6	Socket Head Cap Screw
5	6	Plain Washers
6	1	Test 'O' Ring - AS568-316
7	1	Secondary 'O' Ring - AS568-326

ESA E&PSD Proposed method

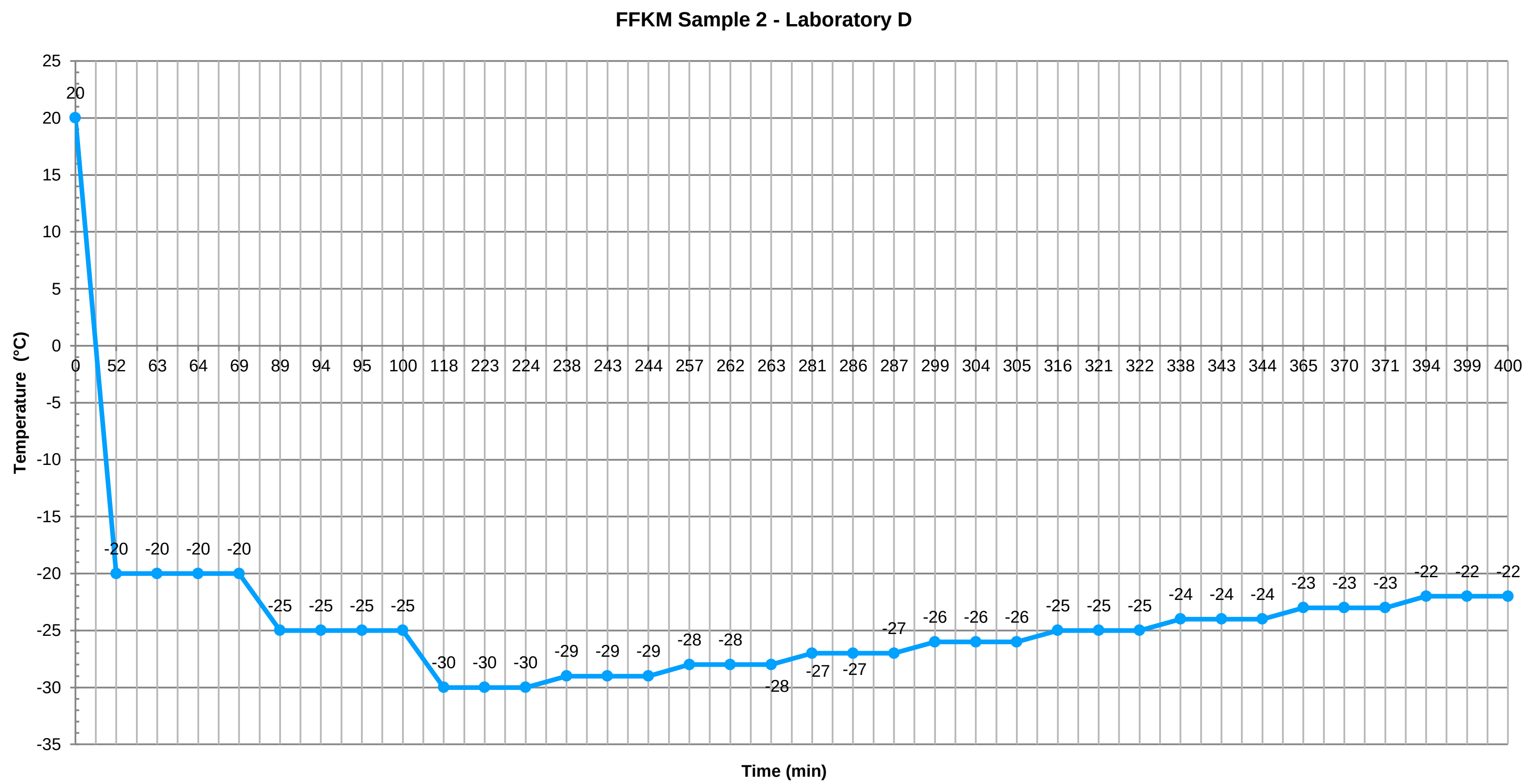


Low Temperature Results

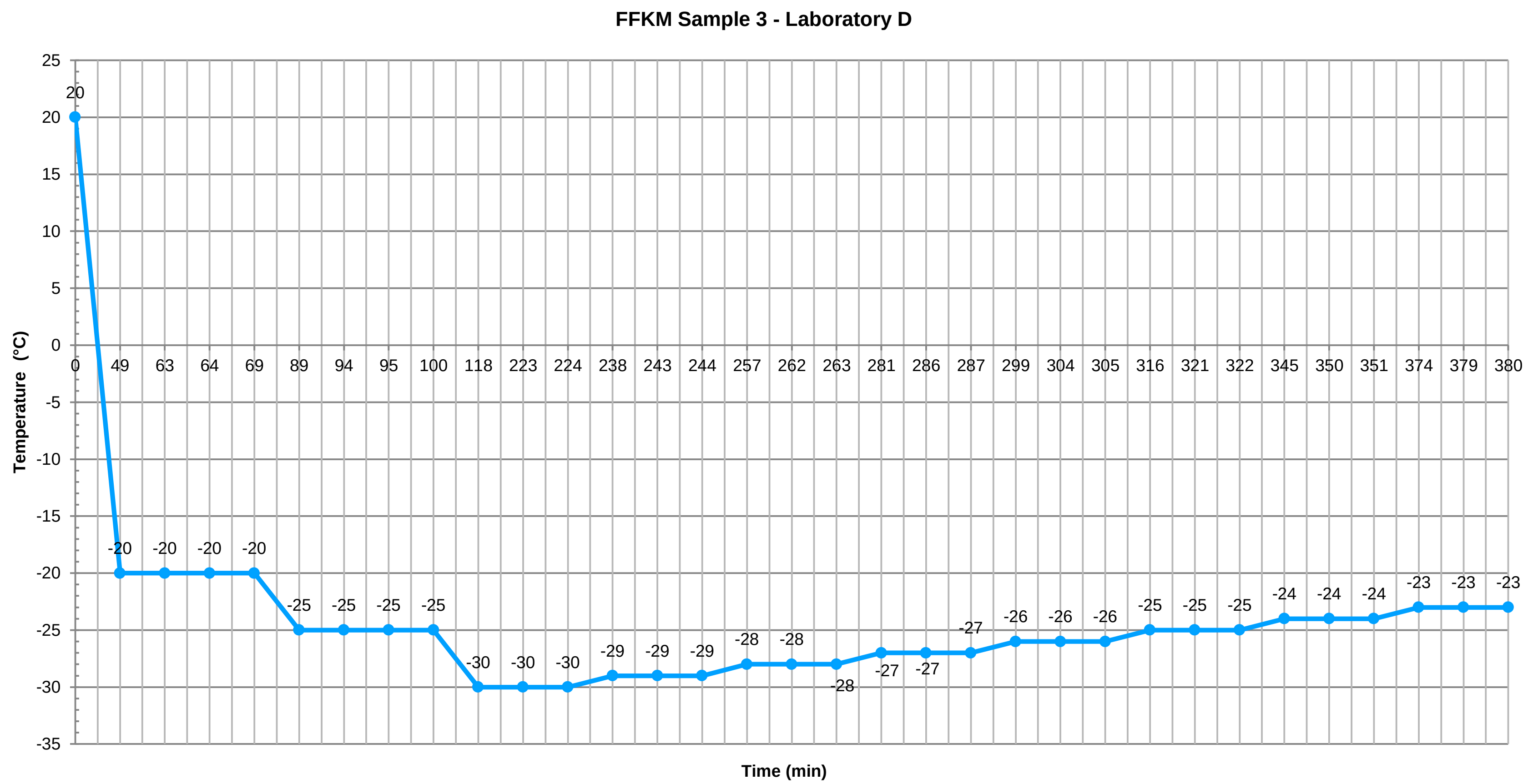
All the work presented focuses on an FFKM material with a T_g of -19ºC as found by DSC.



Low Temperature Results

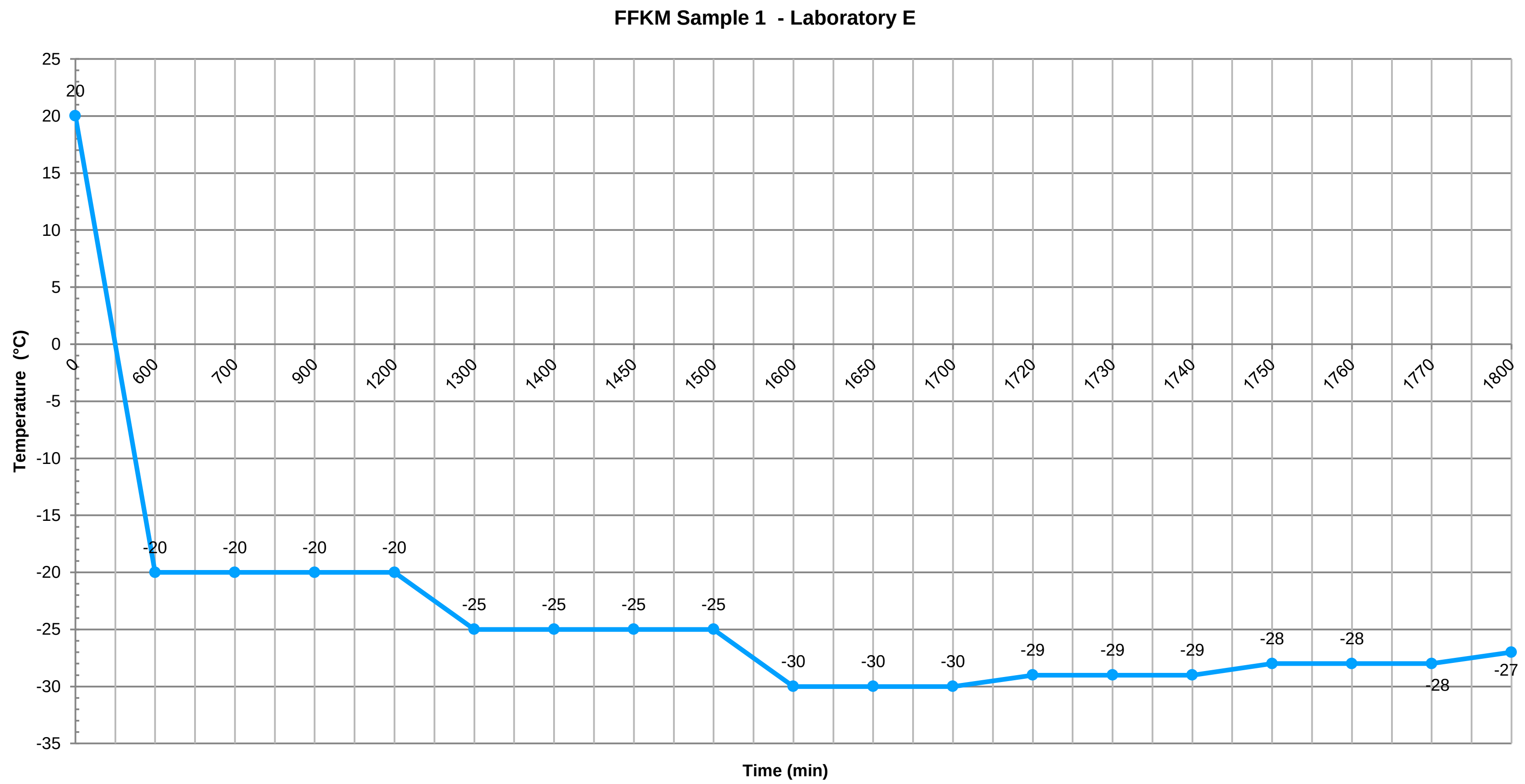


Low Temperature Results

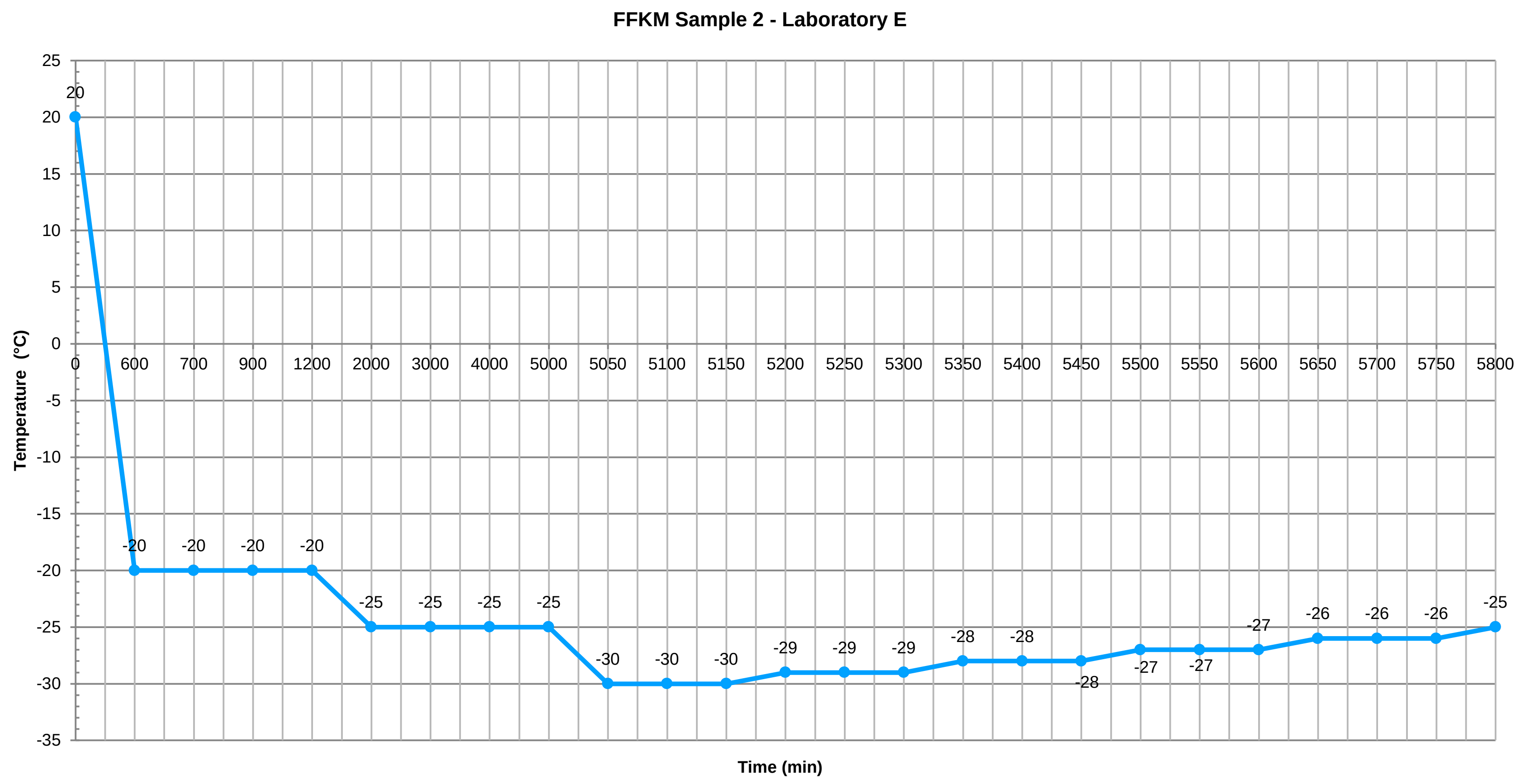


IVS INDUSTRIALVALVESUMMIT | VALVE campus THE VALVE INDUSTRY THINK TANK

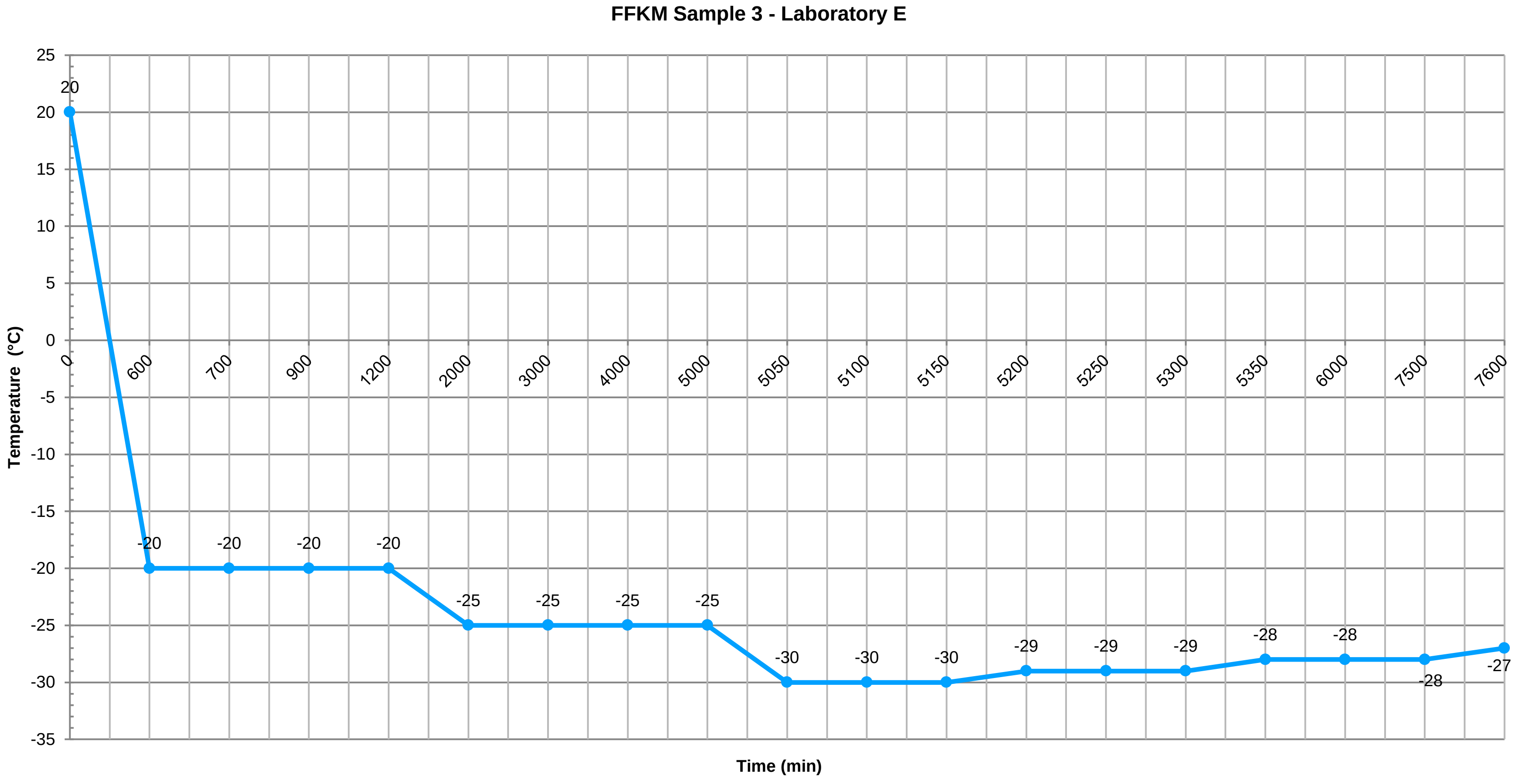
Low Temperature Results



Low Temperature Results



Low Temperature Results



Low Temperature Results

- Within each lab results were consistent.
- Some variation between laboratories
- The rate of cooling has altered the minimum sealing temperature achieved.
- Temperature reduction rate needs to be fully defined in any standard.

Low Temperature – Pressure Applied First

- Given pressure was applied.
- Temperature was dropped until failure occurred.
- No re-sealing temperature was determined.

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

ESA E&PSD Proposed method

- The ESA EPSD believe that the above results demonstrate that it is possible to define a test method that is more closely related to ‘real world’ low temp. capability than existing laboratory methods.

- A second method could be developed which covers the situation in which the system is already energised. Together the two minimum sealing temperatures would well define the seal capability.

ESA E&PSD Proposed method

- 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.

Conclusions

- Existing testing methods can provide a useful comparison between materials.

- There is no substitute for real world testing.

- What is required is that a test program is defined, often in collaboration between seal manufacturer and OEM, to give the end user enough confidence in a proposed sealing solution to be adopted in a given critical application.

- ESA has produced a Position Statement on Low Temperature sealing https://www.europeansealing.com/wp-content/uploads/2018/07/180301_Low_Temperature_Sealing_-_Statement_Final_Amd.pdf

Thank you!

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Do you have questions?

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