Clwyd Compounders Ltd

Since 1979

Over 40 years experience

Low temperature materials used in critical sealing applications

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RIEG Rubber in Engineering Group

www.clwydcompounders.com

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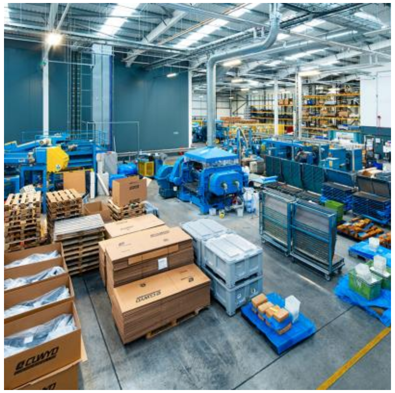

Clwyd Compounders Ltd is a family owned compounder based in North Wales founded in 1979 supplying customers across 5 continents.

In 2018 we moved to a new purpose-built facility expanding our factory capacity by 40% and the laboratory by 60% with a separate clean room facility for the compounding of Silicone (VMQ) and Perfluoroelastomers (FFKM).

Low temperature materials used in critical sealing applications

Outline

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- Low Temperature Applications
- Why Does Low Temperature Need Careful Consideration?
- Low Temperature Requirements in Specific Industries
- Low Temperature Polymer Grades in Oil and Gas
    - Improvements that can be made to compounds by adjusting compounding ingredients
- Low Temperature Polymer Grades in Aerospace

Low temperature materials used in critical sealing applications

Introduction

The low temperature performance of elastomer sealing compounds can be critical in the applications within the following industries:

Aerospace

Oil & Gas

Food & Dairy

Pharmaceutical/medical

Petrochemical applications

When elastomers are presented with low temperatures, they lose their flexibility and ability to respond to a reaction force, making it essential that the compound is formulated in a way to ensure longevity and optimum performance of the end part.

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Low Temperature Conditions

AN AIRLINER OR JET OUTSIDE TEMPERATURE CAN BE -55°C

COLDEST RECORDED ON EARTH WAS VOSTOK STATION IN THE ANTARCTIC -89°C

SOUTHERN SEA TEMPERATURES - 2°C

AVERAGE TEMPERATURE IN OUTER SPACE ORBIT AROUND THE EARTH IS 10.17°C OR 53.2°F WITH EXTREMES OF HOT AND VERY COLD

TYPICAL FRIDGE TEMPERATURE = BELOW 5°C

TYPICAL FREEZER TEMPERATURE -18°C

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Low Temperature Testing Methods

The following test methods are the most commonly used as a way to assess the suitability of a compound in low temperature applications:

- Brittleness point ISO 812:2017
- Low temperature compression set ISO 815-2:2019
- Low temperature stiffening Gehman test ISO 1432:2013
- Temperature retraction TR-10 test ISO 2921:2011
- Increase in hardness ISO 3387:2020
- Determination of crystallisation under compression ISO 6471:1994
- Dynamic Mechanical Analysis ISO 4664-1:2011

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TR-10

TR-10 is the temperature at which the material loses its resilience and transitions from rubber like behaviour to a soft plastic. This test is considered the industry standard for low temperature testing.

The test simply stretches the material 50% in a temperature controlled chamber and it is lowered to a temperature where the material can not recover from (freezing point).

Gradually the temperature of the chamber is increased until the material regains its flexibility/resilience and begins to retract.

*The temperature at which the specimen retracts 10% of its elongated length is defined as **TR-10 temperature***

In the O ring industry application experience says the elastomer will seal statically 10 degrees below the TR-10 value and dynamically O rings perform at or above the TR-10.

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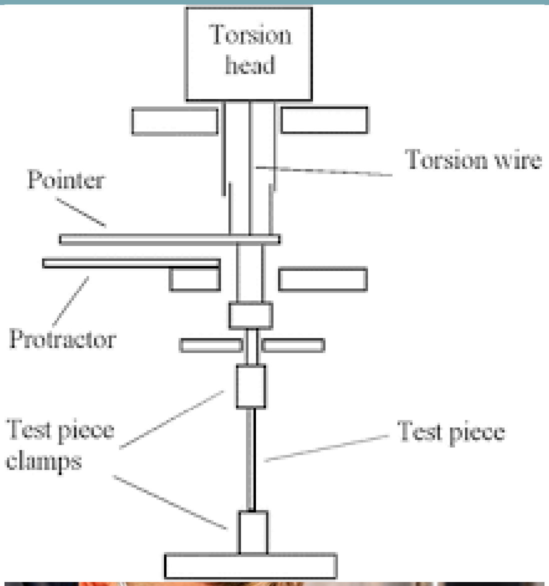
Gehman Test

Also known as the low temperature stiffening test, this test method measures the relative stiffness (modulus) of the rubber at a range of temperatures.

The concept of this method is that a piece of vulcanised rubber strip is twisted to a certain angle in a cold liquid bath.

The relative stiffness of the material is recorded first at room temperature before the material is then cooled down to the low temperature desired. The bath temperature is lowered by 1°C/min with the stiffness measured every minute to produce a graph of the relative modulus of the material against temperature.



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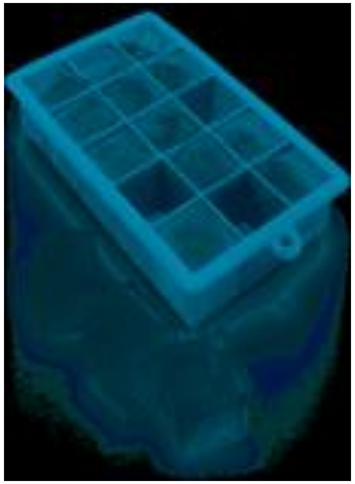
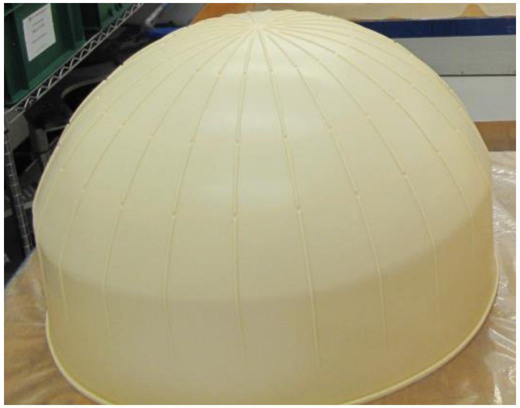
Rubber Applications at Low Temperatures

- Moon landing boot sole of Neil Armstrong
- Ice Cube Trays
- Critical O rings in aviation
- Bladders in outer space satellite systems





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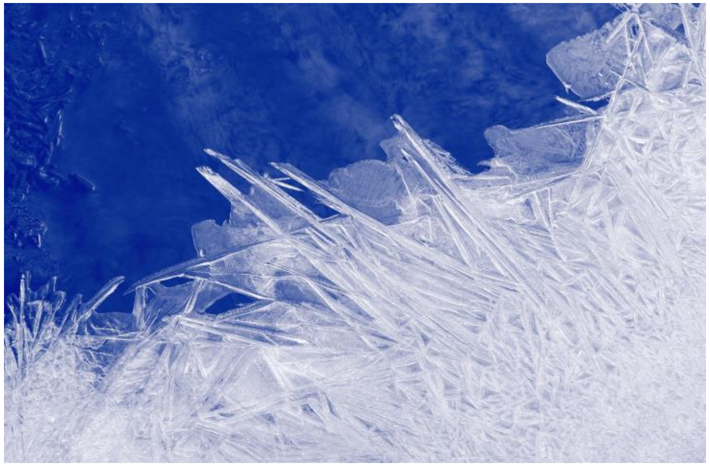
Why do materials fail at low temperatures?

The choice of elastomer is critical to its success or failure at low temperature in application.

When an elastomer is exposed to low temperatures, it becomes less flexible and therefore less elastic and starts to become brittle, until it reaches its glass transition (Tg) point, at which there will be a phase change from a soft and pliable material to one that is now hard and brittle.



Under low temperature conditions, the rubber will contract as it is cooled which can lead to deformation in the part.

When you add this to the fact that stresses induced at higher temperatures may be unable to relax out at cooler temperatures, a process referred to as ‘cold set’ will occur and this can present issues in leakage and seal failure becomes likely.

Low temperature materials used in critical sealing applications

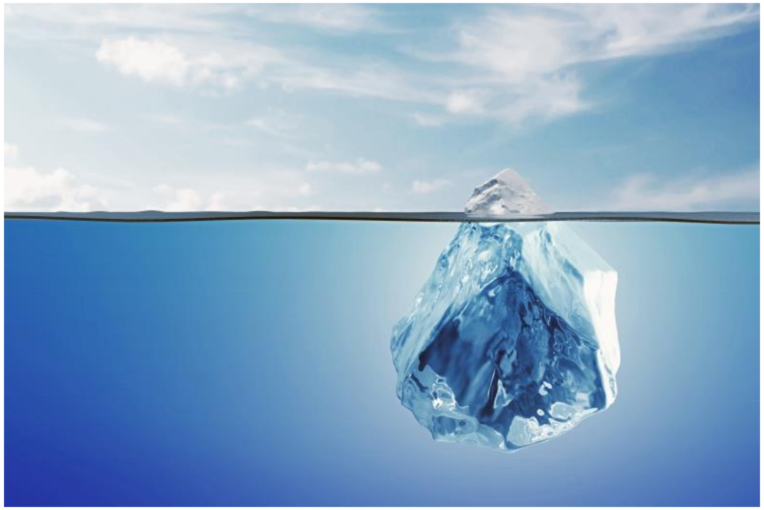
Choosing a suitable elastomer for low temperatures

Choosing the right polymer is essential to enabling the part will withstand low temperatures.

The challenge that we are often faced with, is that low temperature performance is often not the only requirement for the final part, especially with specific Oil and Gas or Aerospace standards in which other requirements are often required as well, such as:

- Physical/mechanical properties
- Resistance to chemicals
- Pressure capability
- Compliance with industry standards

We generally find we are left in a position where a compromise is needed to ensure a polymer grade is chosen that meets a range of application requirements.



Low temperature materials used in critical sealing applications

Selecting the elastomer for the application – Oil & Gas

The choice of elastomers used in industry applications will often be dictated by the related specification as the application environment will limit which elastomers are suitable.

Oil and Gas

In Oil and Gas, the elastomer selected will often be required to be resistant to some of the most aggressive chemical mixtures (hydrocarbons) whilst also being able to operate at extreme temperatures and very high pressures (HPHT). The elastomers are often chosen for:

- Explosive Decompression (ED) Resistance
- Sour Gas H_2S Resistance
- Extreme Temperatures
- Aggressive Chemicals (Drilling fluids)

Low temperature materials used in critical sealing applications

Selecting the elastomer for the application – Oil & Gas

The more exotic elastomers are often required to provide the necessary compromise between chemical resistance and good/excellent low temperature performance required for arctic environments.

- The well itself will be very hot.
- Surface conditions in Arctic areas will be sub zero.
- Tools are often tested at the surface before descending down-hole.
- If the conditions are cold enough, standard FKM materials may fail.
- Additionally, cold tools may be thermally shocked as they are lowered into the well. Seals must remain flexible during thermal shock cycle – cold tool introduced into a warm fluid.

Clwyd offer a range of low temperature elastomers designed to meet Oil and Gas standards such as NORSOK M710, ISO 23936-2, ISO 10423 (API 6A) & NACE TM0297.

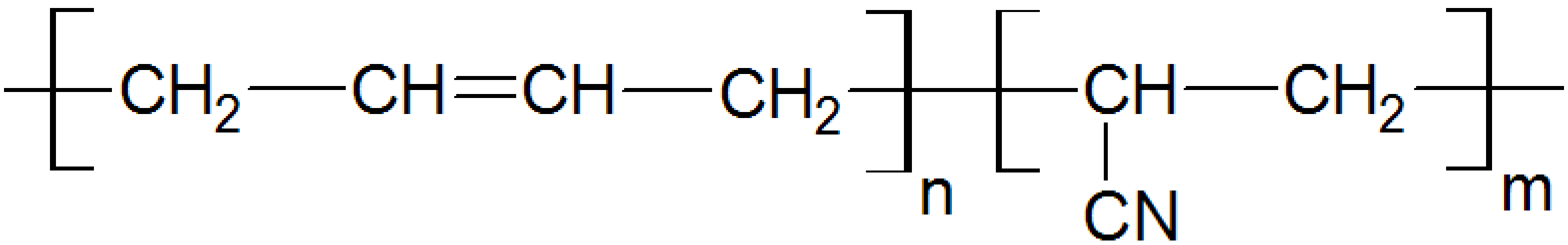
Low temperature materials used in critical sealing applications

NBR – Oil & Gas

Nitrile rubber (NBR) is considered the workhorse of the Oil and Gas industry for its excellent all-round property performance and hydrocarbon resistance.

The low temperature performance of NBR is down to its acrylonitrile (ACN) content with certain grades as low as 17% ACN. This is a double-edged sword as the ACN content drops so does the oil / chemical resistance. It is very important to understand the compromise.

Clwyd tries to ascertain as much information as possible, utilising clever and novel compounding techniques, using some specialist plasticisers etc we can often settle on a good compromise to achieve the balance required.



Low temperature materials used in critical sealing applications

HNBR – Oil & Gas

Hydrogenated NBR (HNBR) elastomers are often used in the Oil and Gas industry as they provide many desirable features which makes them suitable for some of the most inhospitable of environments around the world.

HNBR elastomers follow the same convention as NBR, with lower ACN contents enhancing the low temperature performance. HNBR has the added benefit of the polymer being hydrogenated and this enhances weathering, chemical and heat resistance, and they are very tough.

With wells getting deeper and therefore inevitably hotter, elastomers are required to be resistant to oil, extreme temperatures, H_2S, amine corrosion inhibitors, steam and explosive decompression. HNBR materials provide many of these desirable properties including:

- Temperature Resistance -40°C to +160°C
- Oil and fuel resistance
- High physical strength and performance

Low temperature materials used in critical sealing applications

HNBR LT – Oil & Gas

Clwyd has developed materials with low temperature performance and explosive decompression (ED) resistance that can occur in these severe oil well environments.

Certain tests such as Norsok M710 , API 6A chemical testing have been performed on materials in conjunction with the customer.

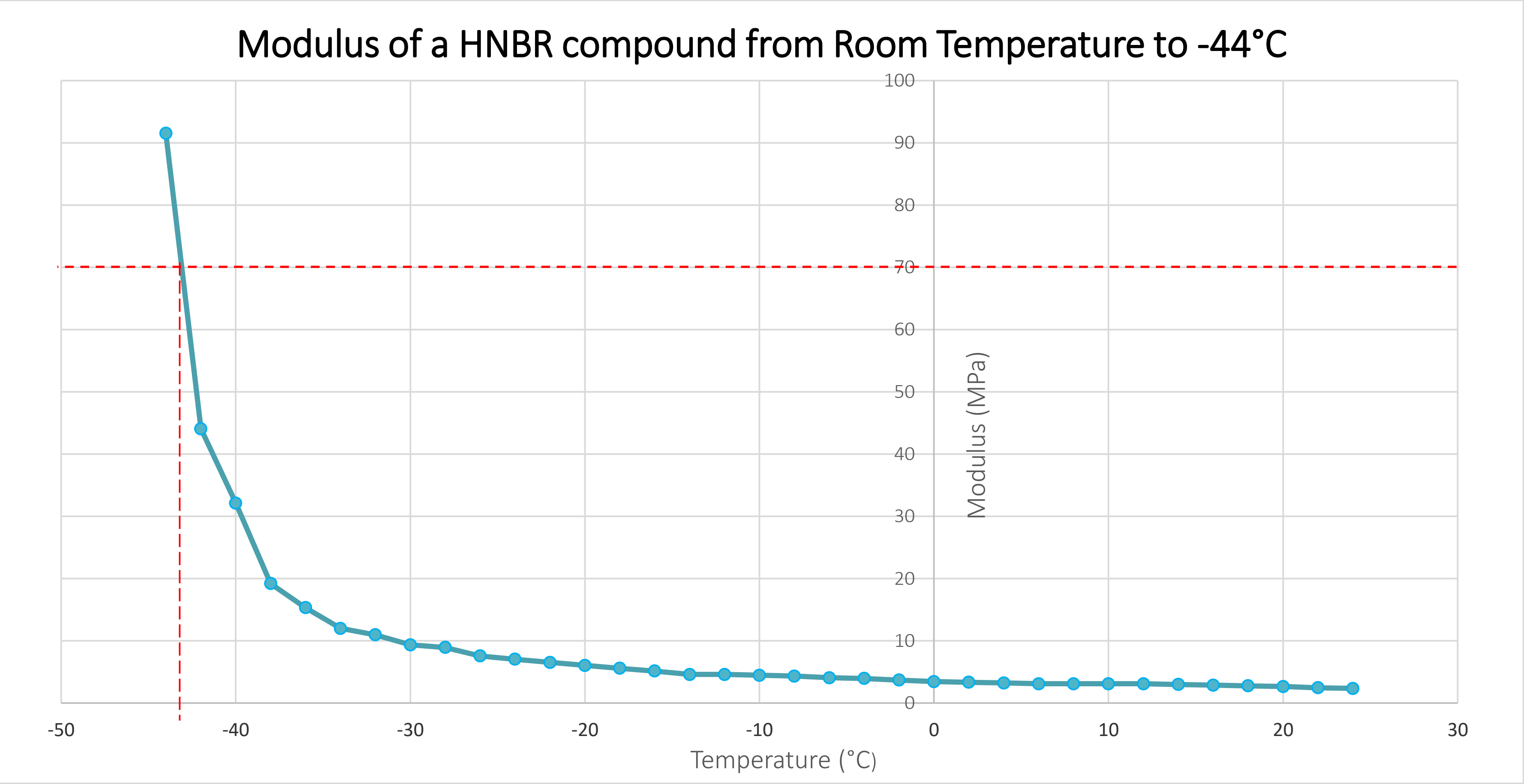
Typical co-polymer HNBR grades have Tg's of approx. -30°C whilst there are some special terpolymer grades which offer Tg's of approx. -40°C.

A compromise in chemical resistance is often required with these low temperature grades.

These LT grades can also be enhanced for sub-artic conditions with the addition of specific LT plasticisers

Low temperature materials used in critical sealing applications

HNBR LT – Oil & Gas



Low temperature materials used in critical sealing applications

Compounding NBR/HNBR for LT – Oil & Gas

Rubber compounds can vary in their construction, but the base polymer choice is key and will often drive how well the material performs at low temperature.

With elastomers such as NBR and HNBR, materials such as plasticisers can be incorporated to enhance the low temperature performance.

The incorporation of low temperature plasticisers provides the rubber compound with improved flexibility and resistance to cracking at low temperatures.

The specialist low temperature plasticisers are the aliphatic diesters:

$ROOC\text{-}(CH_2)_n\text{-}COOR$ Adipic $=n_6$, Azelaic n_9 , Sebacic n_{10}

These can be used in NBR, NBR/PVC, HNBR, PCR, CSM, ECO, ACM and AEM, these can help with the low temperature performance.

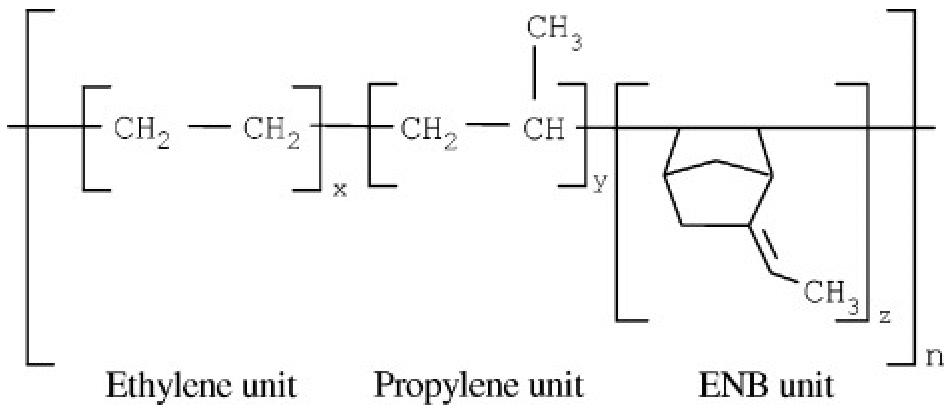
Low temperature materials used in critical sealing applications

EPDM (Geothermal)- Oil & Gas

EPDM is a polymer that is made up of Ethylene / Propylene with a diene modification (this helps the cure chemistry)

Lower Ethylene means a more amorphous polymer and therefore better low temperature performance.

EPDM can be used here because there is no hydrocarbon resistance required, just a large temperature range -55°C to +180°C, this is achieved by careful ingredient selection.



Low temperature materials used in critical sealing applications

FKM – Oil & Gas

The Fluorocarbon (FKM) elastomer family are often selected for their renowned resistance to a wide range of chemicals at a broad range of temperatures (-50°C to +230°C). As a result, they are often selected for harsh demanding environments. The FKM family has this broad range as each member has a different monomer make up.

Experience is needed here to select the correct FKM for the application. There are now 6 Types of FKM classified (copolymers through to tetra polymers) some specifically designed with amine resistance in mind.

Each grade has its own specific attributes, but in general, the higher the fluorine content the higher the chemical resistance but the poorer the low temperature performance. But with new polymer architecture (MOVE technology) this can be challenged. See below Table:

	Monomers	Fluorine Content (%)	TR-10 Rating
Typical co-polymer	VDF, HFP	66	-18°C
Typical ter-polymer	VDF, HFP, TFE	67 – 70	-15°C to -5°C
LT ter-polymer	VDF, TFE, PMVE	65 – 67	-30°C to -24°C
VLT ter-polymer	VDF, TFE, MOVE	65 – 67	-45°C to -30°C

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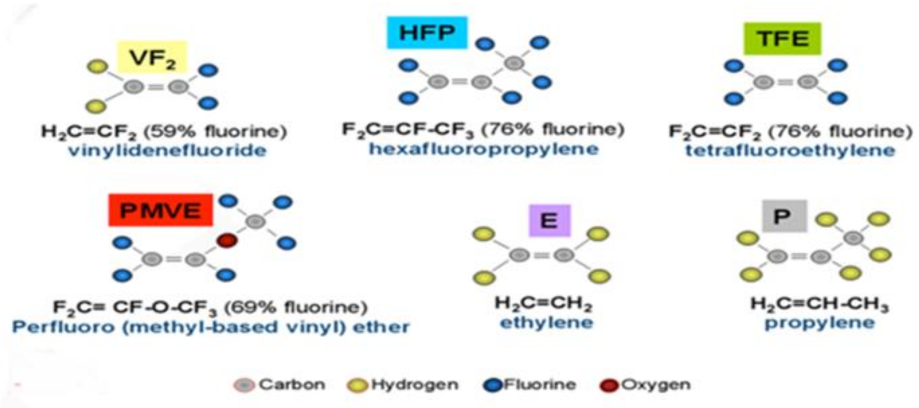
FKM Building Blocks – Oil & Gas



The PMVE is the monomer responsible for the improved low temperature performance of the FKM and this can be replaced with the novel monomer technology which improves this performance without compromising the fluorine content and therefore the chemical resistance.

Since the advances in monomer architecture (MOVE technology) – there are now special grades with TR10 ranging from -35°C , -40°C and now even -45°C!

Low temperature materials used in critical sealing applications

FKM LT – Oil & Gas

Clwyd over the years have developed a range of FKM LT / FFKM LT based materials that meet the balance of all round properties in these arctic and other environments by good collaboration with all concerned (suppliers, customers and end users), in this sector feedback is very important in order to meet these challenging demands.

It is very important that the product is fully consolidated after moulding for the part to be able to function correctly.

Part/material failures can look dramatic and can cause downtime and loss of expensive equipment, so it is important to get the choice right.

Low temperature materials used in critical sealing applications

FKM Datasheet – Oil & Gas

CLWYD COMPOUNDERS LTD — Compound Data Sheet

FKM 90 VLT (ED)

Press Cure	10 minutes @ 180 °C
Post Cure	16 hours @ 220 °C
Service Temperature Range	- 40 °C to + 200 °C
Peak Working Temperature	+ 250 °C

Original Properties
ISO 48-2:2018

	Units	Typical Result
Hardness	Shore A	90

ISO 37:2017	Units	Typical Result
Tensile strength	MPa	14.8
M50	MPa	7.6
Elongation to Break	%	93

Low temperature materials used in critical sealing applications

FFKM LT – Oil & Gas

The family of Perfluoroelastomers (FFKM) elastomers provides the ultimate performance with excellent resistance to almost every chemical required, whilst also providing excellent heat resistance (>300°C) for the most demanding applications.

The low temperature performance of this elastomer range was always its limitation, but not anymore. Incorporating propriety monomer technology extends the low temperature performance of an FFKM down to – 40 °C (from approximately – 10 °C), whilst retaining typical fluid resistance.

The FFKM LT represents a breakthrough in technology

It offers outstanding sealing behaviour in the widest range of aggressive media along with excellent compression set values and best in class low temperature flexibility.

Combine this low temperature performance with its unrivalled resistance to aggressive media and the end result is an elastomer with excellent temperature performance (-40°C to 230°C) and excellent chemical resistance.

Low temperature materials used in critical sealing applications

Selecting the elastomer for the application - Aerospace

Aerospace

In Aerospace and defence, again the environment in which the elastomer is used will dictate which elastomer is selected. Due to the broad range of temperatures often experienced, silicone is a popular choice as it can perform at a wide range, typically -70°C to >200°C. Lightweight materials are also becoming important for fuel efficiency etc.

If improved fuel and oil resistance is required, an FVMQ will often be used. Clwyd offer a range of compounds which have been specifically formulated to be able to meet aviation and military specifications such as AMS/MIL, ABR and DTD.

AMS-R-25988 will require a FVMQ.
BSF-152 / BSF-153 will require VMQ based materials.
Clwyd Compounders has compounds available to meet both specifications.

Low temperature materials used in critical sealing applications

Selecting the elastomer for the application - Aerospace

LT FKM in Aerospace

For the most demanding or specialist aerospace applications, in which an improved chemical resistance or compression set is required, FKM or FFKM materials may be used to achieve specific aerospace specifications such as AMS 7276 and AMS 3216.

These materials are known for their high heat and chemical resistance, they are used in critical sealing applications within the engine and fuel systems.

Tried and trusted materials!

Clwyd Compounders have developed materials designed to meet the tight aerospace specifications:

AMS 3216G and AMS 7276H (requires FKM to -18°C)
AMS 7379 (requires low temperature FKM to -40°C)

Low temperature materials used in critical sealing applications

Selecting the elastomer for the application - Aerospace

Speciality Aerospace Applications

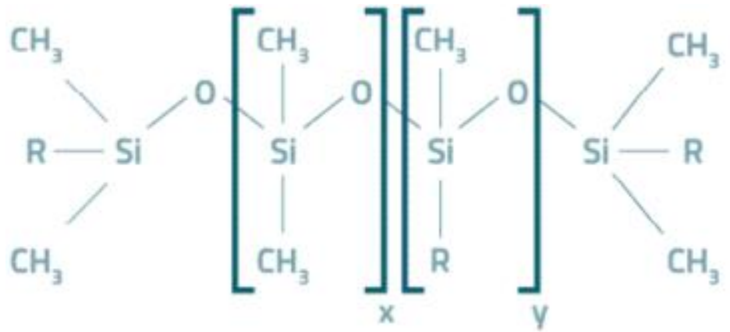
As the LT FKM/LT FFKM portfolio of materials has evolved more materials now fit the bill niche work for advanced aircraft and even more so now with ventures like Space X, Virgin Galactic and Satellite technology.

Worth noting that some special military aircraft use other materials such as Epichlorohydrin grades – very special ones contain polypropylene oxide so can be flexible down to -60°C.

Low temperature materials used in critical sealing applications

VMQ - Aerospace

One of the key features of silicone elastomers is that they have superior temperature resistance to most elastomers at both high and low temperatures. The high temperature resistance comes from the siloxane bonds that form that polymer backbone of the silicone. They are highly stable due to their high binding energy which provides them with their heat resistance. The low temperature resistance is down to the helical shape and low molecular force of the silicone molecules which provides the necessary flexibility for low temperatures.



Siloxane Backbone Structure

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VMQ - Aerospace

The low temperature performance of a general-purpose silicone is around -70°C. There are alternative options in phenyl silicone (PVMQ) and fluorosilicone (FVMQ) depending on whether you are looking for improved low temperature performance or improved chemical resistance?

Silicone Type	Polymer	ASTM D1418	Brittleness ASTM D1418	Stiffening Point ASTM D797	TR-10 ASTM D1329-60
General Purpose	Dimethyl Silicone	VMQ	-73°C	-55°C	-50°C
Low Temperature	Phenyl Silicone	PVMQ	-118°C	-115°C	-116°C
Fluorosilicone	Fluorosilicone	FVMQ	-68°C	-59°C	-57°C

With PVMQ, the methyl group with a standard silicone is replaced a phenyl group which provides significantly improved low temperature performance, reaching temperatures of -100°C. This elastomer is used to meet aerospace specifications requiring extremely low temperature performance i.e. AMS 3337F, AMS7269C etc.

Low temperature materials used in critical sealing applications

FVMQ - Aerospace

If improved chemical resistance is a requirement that you are after, then a FVMQ might be a suitable option. This elastomer is becoming more popular with aerospace specifications due to its improved chemical resistance and similar low temperature performance when compared with a standard silicone. Clwyd use FVMQ to formulate compounds to be able to meet a variety aviation and military specifications such as AMS/MIL, ABR and DTD. The improved chemical resistance results form the addition of a trifluoropropyl groups next to the methyl groups of a standard silicone.

Polymer variations exist that extend the useful range of this polymer.

Tetrafluoropropyl and phenyl chemistry replaces methyl groups along the chain.

Phenylsilicone, so named from phenyl addition, imparts extreme low temperature performance by disruption of polymer crystallization by steric hindrance.

Fluorosilicone, so named from Tetrafluoropropyl addition, improves resistance to fuels and organic oils by creating a more polar arrangement

Low temperature materials used in critical sealing applications

Conclusion

- It is important to be able to understand at what temperature an elastomer becomes brittle and glassy.
- Careful consideration is required for end applications which call for the part to be static or dynamic.
- There's a need to understand what different low temperature tests are available.
- Correct polymer selection, coupled with custom formulating and bespoke mixing are required to achieve the desired range of other properties to meet the most challenging applications.
- Clwyd Compounders have worked closely with our partners to achieve material and product performance within a range of challenging environments that we have discussed.

Thank you for listening – any questions?

Contact us today
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