HEALTHCARE - HCR
CASE STUDY

Thinking outside the conventional silicone box

INTRODUCTION

Studies estimate the highest growth in the silicone elastomers market over the next five years will be due to the growing consumption of cutting-edge materials in medical devices, medical implants, aerospace and other industries.[1]

As a result of this growth, some device manufacturers and other silicone end users face difficulties finding commercially available silicones that satisfy very specific requirements. They need silicone elastomers such as high consistency silicone rubbers (HCRs), with the right combination of mechanical properties and highly specific performance requirements for extreme conditions such as broad temperature range, as well as exposure to solvents, living tissue or biologically active substances.

There are device manufacturers who need to tailor silicone material properties to broader operating temperatures than can be supported by standard polydimethylsiloxane (PDMS) silicones, which typically can be used only down to about -40°C or -50°C.[2] One device manufacturer worked with NuSil® brand silicones from Avantor® to custom develop an HCR for an extremely low-temperature application.

WORKING WITH SPECIALTY SILICONE PROVIDERS

When manufacturers consider specialty silicones, they seek traditional elastomer properties, such as tensile strength, elongation and durometer, as well as more complex capabilities and support, to achieve specific — and often more rigorous — material performance characteristics.

Most silicone manufacturers can formulate a wide variety of silicones into a range of end products, from adhesives to elastomers, gels and fluids. NuSil manufactures these materials, but also synthesizes monomers and polymers to enable more complete control of customization steps such as creating low-temperature HCRs.

Choosing the right type, shape and size of filler/reinforcement, using the right filler surface treatment and choosing appropriate additives and customized packaging allow suppliers to optimize product performance in the customers' hands.[3]

It is important for the suppliers to work in close collaboration with customers throughout the entire process for efficient product commercialization (see Figure 1).

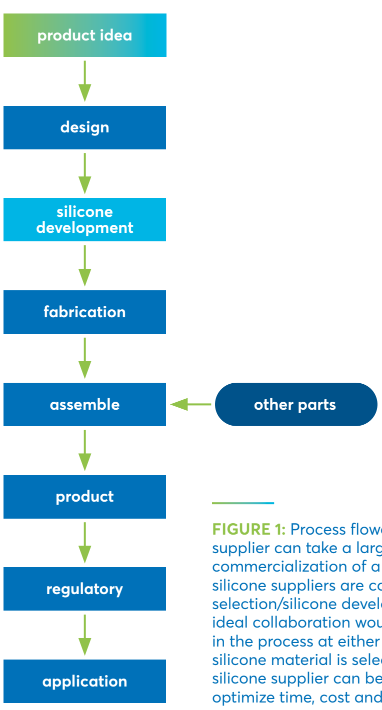


FIGURE 1: Process flowchart showing how a specialty silicone supplier can take a larger responsibility in contributing to the commercialization of a novel, silicone-based product. Traditionally, silicone suppliers are contacted to support customers in the product selection/silicone development step in the process. However, the ideal collaboration would involve the silicone supplier much earlier in the process at either product idea or design to ensure the best silicone material is selected. Collaboration and contribution by the silicone supplier can be essential throughout the entire process to optimize time, cost and performance of the end product.

DEVELOPMENT OF EXTREMELY LOW-TEMPERATURE PERFORMING HCR

The device manufacturer had an extremely low-temperature medical application, where standard HCR silicone chemistry, at the temperatures required by the customer, turns brittle and loses its elasticity — a critical property required for the medical application.

The device manufacturer also had processing parameters, requiring a particular cure profile that was similar to another product they were familiar with extruding. In addition, the manufacturer requested the HCR to comply with specific material properties (Table 1). While many of these parameters are typical for this type of extrudable HCR, the temperature range was the most significant challenge.

Critical to Performance	Desired	Achieved
Tensile	1,000 psi	1,400 psi
Elongation	500%	600%
Tear	180 ppi	230 ppi
Durometer	50	50
Processability	2 roll mill/extrusion	Yes
Cure profile	Like other HCR	Yes
Industry-specific regulatory	Compliance	Compliant
Extreme temp. performance	Not brittle at ~ -80°C	Not brittle at -90°C
Worktime	2h	~2.5h

TABLE 1: Performance characteristics of sought specialty silicone.

To achieve the desired low-temperature performance and retain the necessary flexibility, NuSil modified the molecular structure to tune the level of crystallinity and refractive index in the solid cured material. Once these specialized building blocks are incorporated into the polymer backbone, the cross-linked polymer network will not go through crystallization, resulting in an HCR that will perform more consistently across a broader temperature range retaining elastomeric properties.[4] An added benefit of this modification is that the HCR is changed from translucent to transparent. This was not a requirement requested by the device manufacturer; however, transparency can be useful to allow users to observe and follow processes or material flow within the device.

NuSil performed several tests to confirm the targeted broad operating change was achieved. This process of testing and validation is a standard approach in NuSil's custom silicone development. To learn more about the testing validation completed for this material, see the Quantitative Testing and Analysis section at the end of the document.

RESULTS

To successfully create this extreme low-temperature performing HCR, silicone experts from NuSil worked with the medical device manufacturer to quantify, test and eliminate the potential for low-temperature brittleness in the custom HCR, as compared to that of a standard HCR. This low-temperature performance was achieved while not losing focus on more traditional critical to quality (CTQ) parameters such as mechanical performance, processability, work time and biological compatibility requirements.

Close collaboration between component manufacturers, finished product manufacturers and specialty silicone manufacturers throughout the whole development process is critical to the success of products in cutting-edge and highly regulated industries.

Having the specialty silicone manufacturer collaborating on further downstream processes, such as device assembly, is also crucial to make sure materials from different parts in the device are compatible. Silicone suppliers can recommend optimized adhesives, primers, lubricants or coatings for assembly. In the final stages, silicone manufacturers can provide guidance and regulatory support for faster and smoother commercialization and more successful final end use.

APPENDIX: QUANTITATIVE TESTING AND ANALYSIS

As part of the process for developing the low-temperature HCR, NuSil conducted several quantitative tests to confirm that the properties for the new material were on target.

The differential scanning calorimetry (DSC) curves in Figure 2 clearly show the complete lack of crystallization at around -50°C in the custom HCR, while an endotherm peak shows this transition in the standard HCR. The glass transition temperature (Tg) of both samples can be found close to -120°C (with a different character), which is the expected range for standard HCR silicones.[5]

The mechanical performance was also studied at sub-zero temperatures to confirm consistent performance and retention of flexibility at desired temperatures down to around -80°C. The dynamic mechanical analysis (DMA) curves in Figure 3 show the storage and loss moduli of both HCRs tested, demonstrating how they change when the temperature is ramped at 2°C/min.

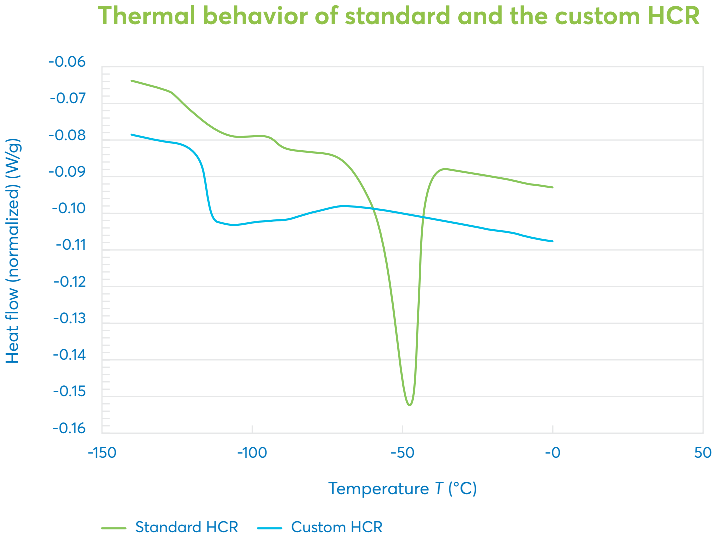


FIGURE 2: Second heating scan of DSC of standard and custom HCR with 5°C/min ramp.

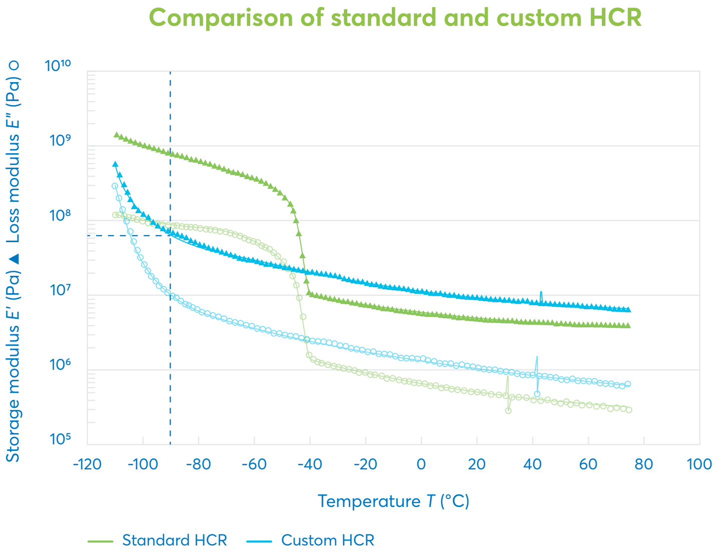


FIGURE 3: DMA scan of standard and custom HCR with 2°C/min cooling rates (▲: storage modulus; O: loss modulus).

This measurement illustrates the viscous response of a material[6] and clearly shows that the custom HCR performs in a stable and consistent manner to about -90°C. Meanwhile, the standard HCR had a major transition around -50°C to -40°C, which we know from the DSC is a crystalline transition of the structure and, thus, loss of elasticity.

When this happens to a standard HCR, the modulus increases from ~10 MPa to ~800 MPa — an approximately 80-fold increase by the time the operating temperature of -80°C to -90°C is reached. In contrast, at the operating temperature of -80°C or -90°C, the custom HCR showed only some minor chain mobility limitations compared to room temperature. This testing shows the custom HCR clearly remains more flexible at extreme low temperatures of -80°C or -90°C.

To mimic flexibility of HCRs at -90°C, samples were exposed to a cyclic tensile strain with elongations beyond their respective linear viscoelastic regions (Figure 4). Although measurements are outside the linear viscoelastic region, the nature of the material's response can be investigated. The elastic and viscous responses of the custom HCR stayed respectively the same throughout the 5,000 cycles of the testing; thus its viscoelastic behavior has not changed throughout the cycles, clearly demonstrating that the custom HCR is less or not brittle at all at -90°C while the standard HCR is more brittle and becomes even more brittle with multiple cycles of tensile strain.

LONG-TERM SUPPORT FOR CUSTOMIZED SILICONES

NuSil continues to collaborate and provide support for our customers in applicable phases of the commercialization process. This is critical if the final part or device undergoes further processing that may potentially affect the silicone performance characteristics.

Often these interactions are not addressed at the design phase of the product because they can be carried out by contract manufacturers or end users. For this custom broad operating temperature range HCR, additional data collection was performed for identifying and quantifying extractables and leachables to support the end user.

The data collection process mimicked the post-manufacturing treatment that the device is expected to undergo to understand

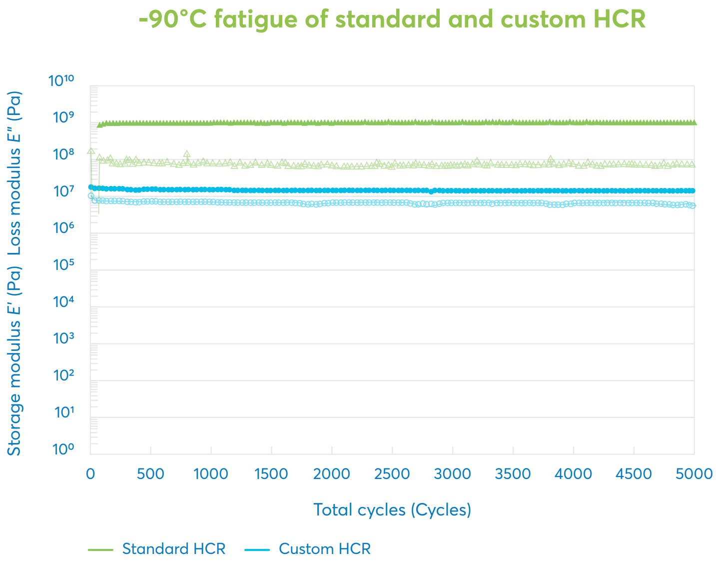


FIGURE 4.1: Mimicking a low-temperature fatigue test at -90°C for both standard and custom HCRs (filled symbols: elastic response, hollow symbols: viscous response).

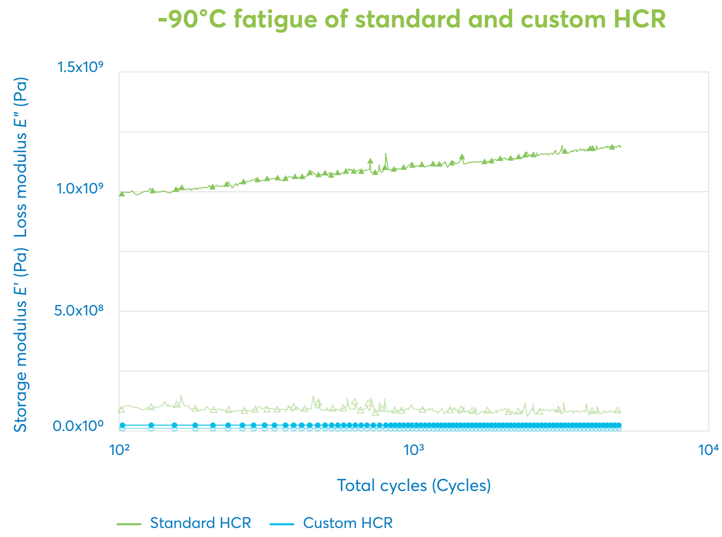
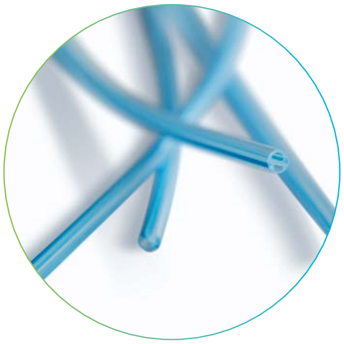


FIGURE 4.2: Mimicking a low-temperature fatigue test at -90°C for both standard and custom HCRs (filled symbols: elastic response, hollow symbols: viscous response).

downstream effects of treatment on final performance in the real-life application. This is also a point where a raw material supplier can offer additional regulatory support or certifications.

Engaging in a close collaboration with the silicone supplier about a final product's end application can help in understanding product performance characteristics or limitations.



[1] **Market Research Future.** Specialty Silicone Market Research Report — Forecast to 2023. [Online] September 2018. [Cited: September 18, 2018.] https://www.marketresearchfuture.com/reports/specialty-silicone-market-5168

[2] Polymer composition versus low-temperature characteristics of polysiloxane elastomers. **K. E. Polmanteer, M. J. Hunter.** 1, s.l.: Journal of Applied Polymer Science, 1959, Vol. 1.

[3] **Noll, W.** Chemistry and Technology of Silicones. New York: Academic Press, 1968.

[4] Monitoring of the Course of the Silanolate-Initiated Polymerization of Cyclic Siloxanes. A Mechanism for the Copolymerization of Dimethyl and Diphenyl Monomers. **Alisa Zlatanic, Dragana Radojcic, Xianmei Wan, Jamie M. Messman, and Petar R. Dvornic.** 2018, Macromolecules, pp. 895-905.

[5] **Gadda, T. M. and Weber, W. P.** Copolymers based on dimethylsiloxane and diphenylsiloxane units. Science and Technology of Silicones and Silicone-Modified Materials, ACS Symposium Series (964). s.l.: American Chemical Society, 2007.

[6] **Mezger, Thomas G.** The Rheology Handbook, 4th Edition. Hanover: Vincentz Network, 2014.

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MET37398-BB-JS

Lit. No. ZPROAVTR37398-2