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Soft Tissue Compliant Silicones for Medical Devices

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Soft tissue compliant silicones for medical devices

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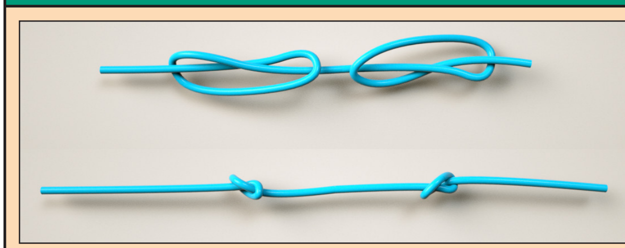
ExSil silicone nanocomposites are the first in a series of ultra-high elongation materials that achieve their unique mechanical properties via a radically different mechanism than traditional silicones. Traditional silicones rely on formation of chemically crosslinked chain networks for their elastomeric properties. ExSil nanocomposites, on the other hand, rely on mechanically interlocked polymer chains. Mechanically interlocked molecules (MIMs) include chain-linked macrocycles (catemers), as well as a variety of other topologically-linked structures, and are considered to have great potential for a new generation of "smart" soft materials (ref. 1). In the case of ExSil nanocomposite MIMs, flexible high molecular weight polydimethylsiloxane (PDMS) chains mechanically crosslink as a result of high degrees of entanglement and knot formation (figure 1).

This distinct class of silicone elastomer exhibits surprising material properties, such as up to 5,000% stretchability with elastic recovery, the ability to resist tear failure (both initiation and propagation), self-healing/sealing behavior and intrinsically low extractables. As a group, these materials demonstrate an ability to resist and recover from conditions that would normally result in the failure of other elastomers. ExSil was commercially introduced in 2016 as a two-component 100:1 kit formulated for maximum mechanical properties (ref. 2). New grades of ExSil have since been introduced, with ranges of hardness and modulus which meet the requirements for soft-tissue implants and extracorporeal device applications.

Background

The base polymer in ExSil nanocomposites is a heterobifunctional polydimethylsiloxane with α-vinyl, ω-hydride functionality (figure 2) (ref. 3). The synthesis employs living anionic ring opening polymerization techniques, yielding monodisperse polydispersity index (PDI < 1.1) polymers with an extremely low level of impurities and a precise 1:1 stoichiometric ratio of the vinyl and hydride endgroups, attributes that cannot be achieved using traditional acid/base catalyzed polymerization of silicones.

Figure 1 - polymer knots, both inter- and intra-molecular, provide a mechanism for high elongation; the tightening of simple knots shown here gives a sense of the elongation; relaxation of the knots, induced by molecular vibration and polymer reptation, allows the polymer to recover from extension



The heterobifunctional PDMS macromonomer is the base resin that undergoes a hydrosilylation-driven polymerization between the vinyl and hydride groups in the presence of platinum catalyst and heat. The extremely flexible reactive PDMS chains serve as A-B step growth monomers, increasing in molecular weight and entanglements until they form a transparent, solid, mechanically interlocked material with no evident chemical crosslinking and elastomeric properties (figure 3). This 'curing' process contrasts with that used in conventional two-part room temperature vulcanized silicones (RTVs), which depends on two distinct silicone resins that chemically crosslink. Figure 3 shows the repeat unit structure of the MIM silicone.

Compounding reinforcing agents such as fumed silica into the ExSil base polymer increases the tensile strength of the cured material to match that of conventional resin reinforced silicones and, surprisingly, increases the recoverable elongation to levels not previously reported. These properties, along with other newly observed behaviors (e.g., tear resistance, self-healing, self-sealing), are discussed below.

Design properties

ExSil nanocomposities have been formulated into two-part kits, in which part A is the reinforced heterobifunctional PDMS base polymer and part B is a platinum-based catalyst. Two commercial grades of the nanocomposites have been introduced: ExSil 50 and ExSil 100. ExSil 50 is an ultra-high elongation medical grade silicone elastomer that has been formulated to match the properties of soft tissue. ExSil 100 is an ultra-high elongation industrial molding grade silicone elastomer that has been formulated to maximize mechanical properties. The relative difference in hardness between these two elastomers is shown in figure 4. These kits are mixed in a part A to part B ratio of 100:1, and the elastomers are then fabricated via a cast molding process or high-speed LIM (liquid injection molding). Both ExSil 50 and 100 elastomers are naturally translucent, but can be pigmented or dyed.

In addition to ultra-high elongation with elastic recovery and tunable hardness, ExSil elastomers have exceptional tear resistance, high elongations at tear failure and

Figure 2 - chemical structure of ExSil base polymer

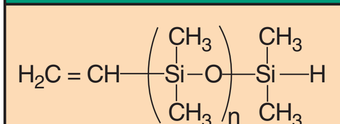


Figure 3 - chemical structure of fully polymerized ultra-high elongation silicone elastomer

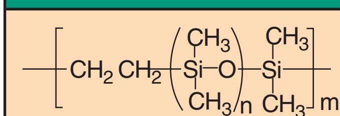


Figure 4 - relative hardness comparison of ExSil grades to other materials

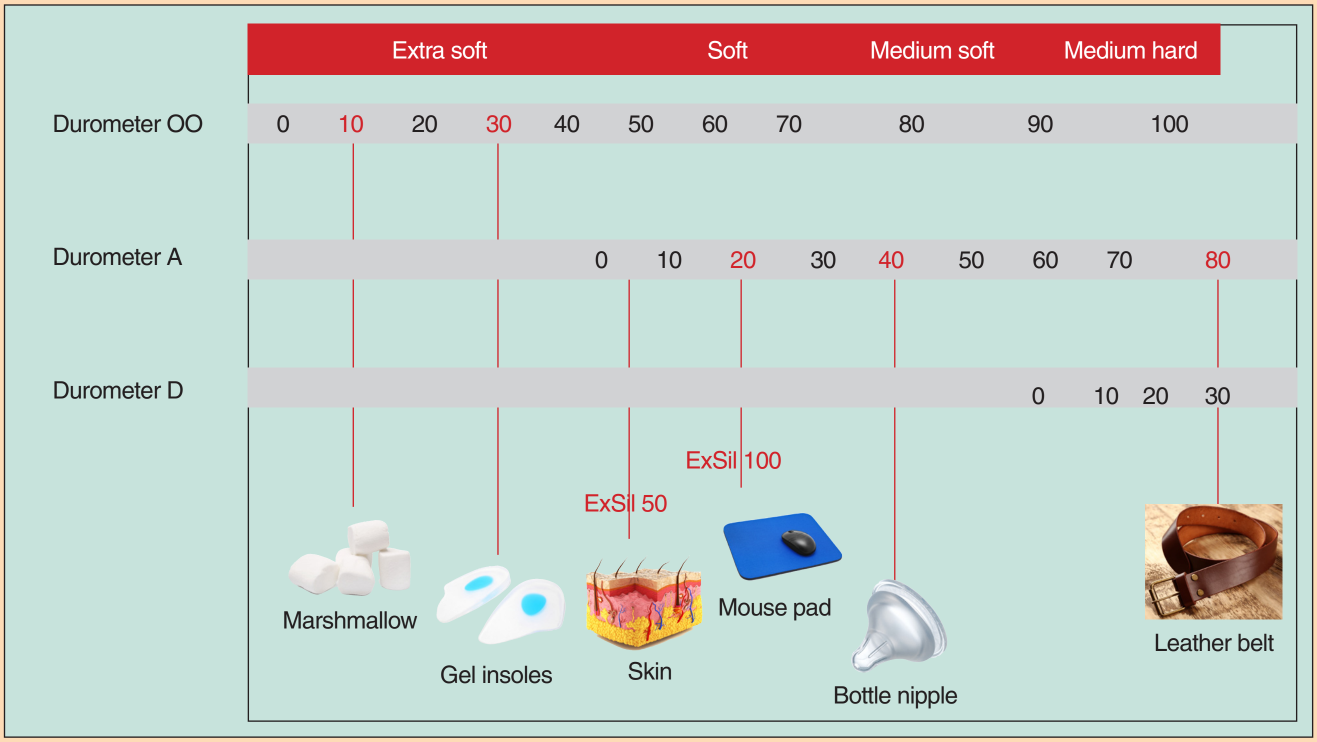


Table 1 - mechanical and physical properties of ExSil grades compared to resin reinforced silicone

Cured property	*Method*	*Unit*	*ExSil 100 (molding grade)*	*ExSil 50 (medical grade)*	*Resin reinforced silicone*
Elongation	D412	%	5,000	6,000	100
Tensile strength	D412	MPa	8	3	6
Tear strength	D624 (type B)	kN/m	42	5-7	2
Elongation at tear failure	D624 (type B)	%	2,000	1,000-1,500	30
Durometer	A	-	15	5	50
Specific gravity		-	1.06	1.06	1.04
Refractive index		-	1.41	1.41	1.41
Volatiles (150°C for 4 hours)		wt.%	<0.1	<0.1	>2

low volatiles/extractables content. Table 1 provides an overview of the properties of ExSil elastomers. Figure 5 shows the different ASTM test specimens used to generate the mechanical property and tear resistance data reported in this article.

Ultra-high elongation and elastic recovery are the properties that most obviously differentiate ExSil from other silicone elastomers. Both grades of ExSil have elongations that exceed 5,000%, a significant step change in elongation compared to the reported elongations of commercial elastomers. Figure 6 shows the stress-strain curves of both ultra-high elongation ExSil elastomers compared to a conventional resin reinforced silicone elastomer. Resistance to tear propagation failure during extreme distortion and elongation is, in many cases, more important than ultimate elongation. This property is associated with the absence of significant yield stress typically linked to strains at levels below about 40% of ultimate elongation. The ability of ExSil materials to achieve great extensions with low applied forces is a benefit in medical applications, since the behavior allows compliance with soft tissues.

Thermal analysis of ExSil nanocomposites reveals extremely low levels of low molecular weight/volatile impurities associated with extractables and elastomer shrinkage. A thermogram of ExSil 50 and 100 compared to a resin reinforced silicone is shown in figure 7. Weight loss below 400°C is typically associated with these low molecular weight/volatile species, while weight loss above 450°C results from the thermal and oxidative degradation of PDMS chains. The resin reinforced silicone shows >10 wt. % loss at 400°C, whereas both ExSil grades show no weight loss up to that point. In most silicone elastomers, catalysts associated with polymerization of the base polymer and radical (peroxide)-cure are the source of impurities. ExSil base polymers and cure processes do not rely on these catalysts, resulting in high purity elastomers with good dimensional stability.

While their extreme elongations obviously set ExSil materials apart, the new designs enabled by other unique ExSil properties, particularly resistance and recovery from device insults (incidental damage) and defects, are of even greater practical impact. Devices should be able to withstand failures caused by

Figure 5 - ASTM Instron dies: D638V (left); D412C (center); D624B (right)

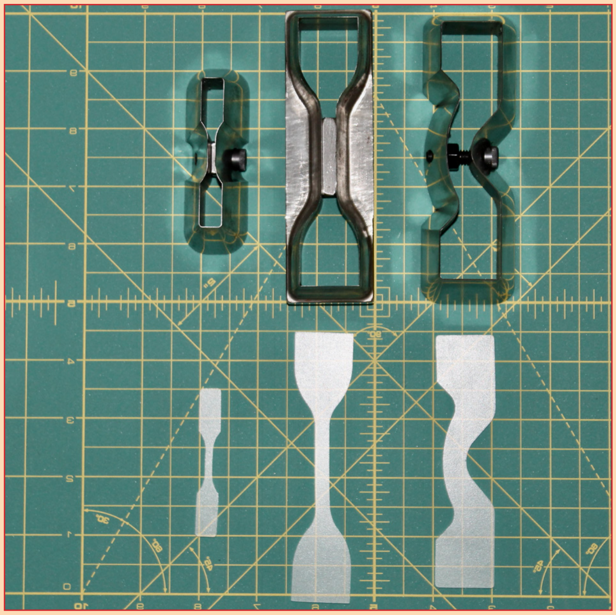
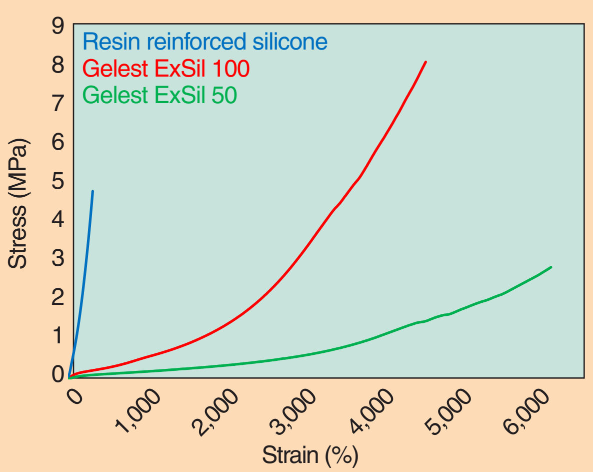
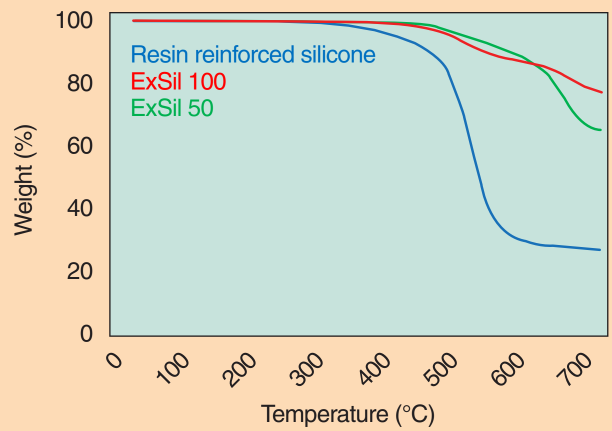


Figure 6 - stress-strain curves of ultra-high elongation elastomer compared to resin-reinforced silicone



incidental damage associated with nicks and tears that may occur during installation or operation outside of expected operating limits. In external contact medical devices, there is demand for installation and overlay on stretchable areas of skin. Table 2 provides a summary of skin properties, providing a baseline for comparison with materials considered in soft tissue applications. A variety of medical device installations overlay on stretchable areas of skin, in which maximum elongations are in the range of 150%. If installation extensions exceed 300% and there is a design safety factor of 2x, then the desired minimum elongations for the application are in the range of 1,000%. The possibility of tear failure at these extreme elongations exists for virtually all traditional materials except ExSil ultra-high

Figure 7 - TGA thermograms of ExSil compared to conventional resin reinforced silicone



elongation silicone elastomers. In this context, the examples below provide specific data on resistance and recovery behavior.

Tear resistance

ExSil polymers are resistant to tear failure at much greater elongations than conventional silicones. Figure 8 shows the stress/strain tear resistance curves of both grades of ExSil silicones compared to a conventional resin-reinforced silicone, with data generated using an ASTM D624 die B. The 'nicked' dumbbell shape of the die B specimens measures resistance to tear propagation. Failure due to tear propagation occurs at elongations exceeding 1,500% for both ExSil 50 and ExSil 100. The threshold for resistance to tear failure occurs when the energy dissipative processes of an elastomeric material are exceeded (ref. 4). For silicone elastomers, the dissipative limit is associated with the length (molecular weight) between polymer crosslinks (ref. 5). Unlike other silicone elastomers, ExSil silicones do not undergo covalent crosslinking during cure, and the higher molecular weight between topological crosslinks provides the physical basis for their greater tear resistance.

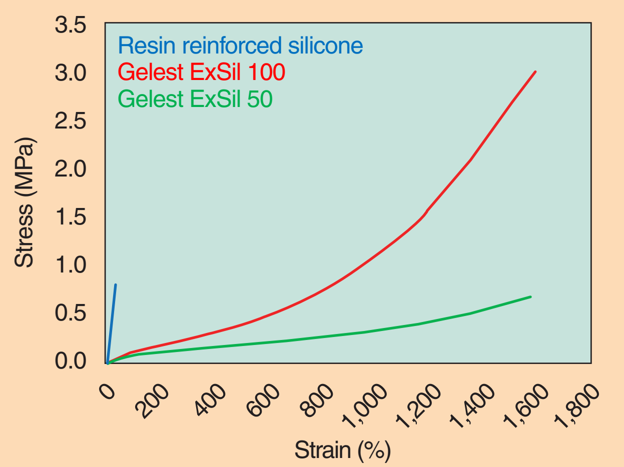
Self-bonding and pseudo-self-healing

Self-healing materials can be defined as materials that have the intrinsic ability to recover from damage. As a mechanical property, recovery from rupture, cracks, micro-cracks or tears can be compared for two separate pieces of material placed into inti-

Table 2 - summary of skin properties

Density	1.2 g/cc
Modulus, 22°, 82% RH	0.5-1 x 10^6 N/m^2
Hardness, durometer A	3-15 (fingertips 9-15)
Electrical conductivity, epidermis	8.01 S/m
Thermal conductivity, epidermis	0.23 W/m °C
Specific heat, epidermis	3,590 J/kg °C
Coefficient of friction, dynamic	0.2 (average) (forehead: 0.34, abdomen: 0.12)
Contact angle, water (cleaned, degreased):	>100°

Figure 8 - resistance to tear propagation (ASTM D624 die B) of ExSil compared to resin reinforced silicone



mate contact, which assume the same properties as the bulk material. ExSil and silicone polymers are generally utilized at temperatures above their thermodynamic melt-points. Because ExSil polymers are not covalently crosslinked, molecular diffusion, polymer reptation and topological interactions are all potential mechanisms for apparent or pseudo-self-healing. As with other composites, however, ExSil's recovery of mechanical properties is limited by the strength of the base polymer.

To demonstrate the pseudo-self-healing capability of ExSil silicone nanocomposites, D638V dumbbells were bisected using a razor. The clean, cut surfaces were pressed together and heated at 100°C for 24 hours, resulting in intact test specimens with the original dimensions and geometry (figure 9).

The stress-strain curves of the healed ExSil specimens are shown in figure 10. Although the samples only exhibit ~5% of their original tensile strengths, elongations approaching (ExSil 50) or exceeding 1,000% (ExSil 100) were observed (table 3). Conventional resin reinforced silicones do not possess pseudo-self-healing behavior. Self-bonding can be achieved when clean ExSil surfaces are pressed together for one hour at 100°C, or for 24 hours at room temperature.

Figure 9 - pseudo-self-healing demonstation of bisected D638V ExSil dumbbell

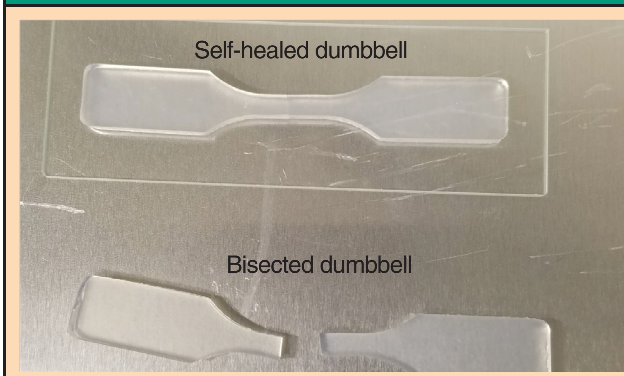
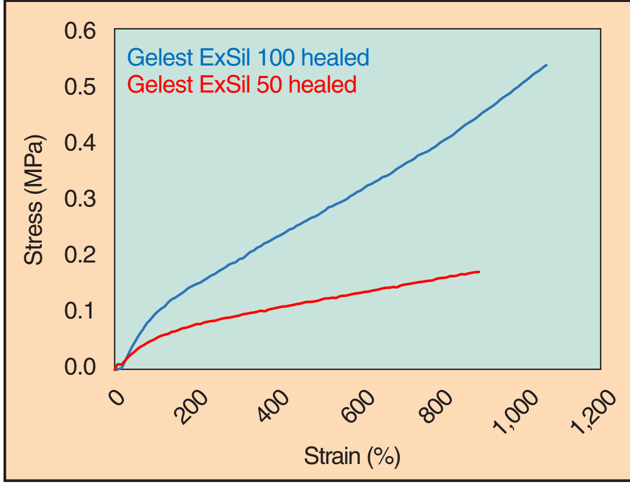


Figure 10 - stress-strain curves of healed ExSil test specimens



Self-sealing

Self-sealing behavior is desirable in many applications in which penetration or cannulation of a polymeric material is essential for the assembly, use or protection of devices. For example, electronic and optical connections often require hermetic seals to prevent device failure in operating environments. In medical and drug applications, self-sealing can be essential for protection against microbial and other sources of contamination, and resistance to the repeated puncture of septum closures used for pharmaceutical packaging and surgical access ports has obvious benefits. Self-sealing typically relies on a combination of two mechanisms: recovery of cohesive properties and maintenance of mechanical strength. A material's ability to regain cohesive strength can be associated with self-bonding and self-healing behavior. Unlike in single-use septums, in multiple-use septums, both self-sealing mechanisms are critical for performance.

To understand ExSil's self-sealing capability, ExSil 100 septa were fabricated and compared to standard peroxide-cured silicone rubber septa. Bilayer septa fabricated from ExSil and standard silicones were also evaluated. The ExSil 100 and silicone rubber septa were cored with a 1 mm biopsy punch and then crimped onto 30 mL modified serum bottles filled with 10 mL of water (figure 11). A pressure of 2 psi was applied to the serum bottles, and time to failure by breakthrough was measured. The cored silicone rubber septum failed immediately, while the cored ExSil 100 septum failed after three minutes of pressurization.

The cored ExSil 100 septum was heated to 100°C for 24 hours, at which time visual inspection showed pseudo-self-

Table 3 - mechanical property recovery of healed ExSil test specimens

Cured property	*Method*	*Unit*	*Self-healed ExSil 100 (molding grade)*	*Self-healed ExSil 50 (medical grade)*
Elongation	D412	%	1,050	900
Tensile strength	D412	MPa	0.5	0.17

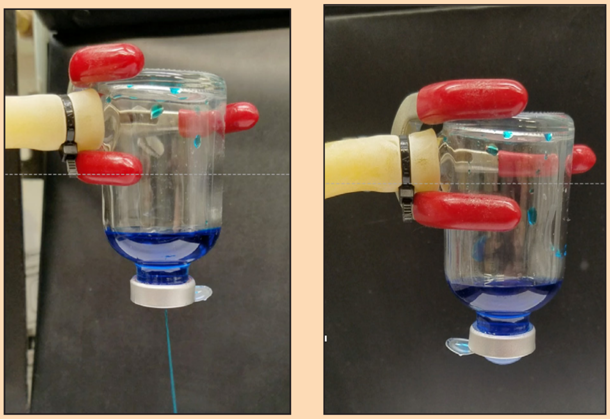


Figure 11 - cored silicone rubber septum had immediate breakthough failure at 2 psi (left); cored ExSil 100 septum breakthrough failure time at 2 psi was 3 minutes (right)

Figure 12 - silicone rubber septum with 1 mm core (left); ExSil 100 septum with healed 1 mm core (right)

healing behavior in the puncture area (figure 12). When the serum vial with the self-sealed ExSil 100 septum was pressurized to 2 psi, no breakthrough failure was observed up to 10 minutes. The conventional red silicone rubber septum leaked immediately under the same experimental conditions.

A bilayer septum was constructed from a standard silicone rubber (red) sheet bonded to ExSil 100 by curing the ExSil on the standard silicone (figure 13). The bilayer septum was then cored with a 1 mm biopsy punch and crimped onto a 30 mL serum vial. At 2 psi of pressurization, the septum leaked after one minute. At higher pressures (6 and 10 psi), the bilayer septum did not leak at all, as the applied pressure caused the soft, low modulus ExSil 100 to deform and close the defect against the bracing of the rigid red silicone rubber backing.

Figure 13 - bilayer ExSil septum structure on modified serum bottle

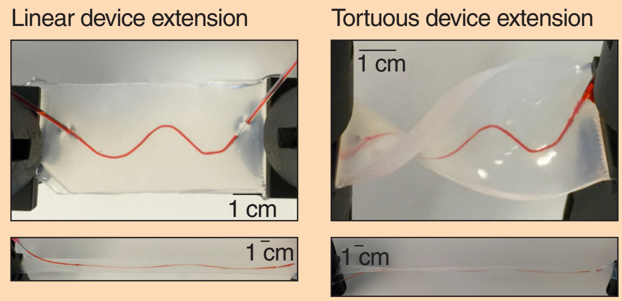


Figure 14 - microfluidic device with active filled channel was able to withstand multiaxial distortion and extension with no channel delamination or relaxed state channel distortion

Practical example of device durability and recovery during fabrication and use

The full range of benefical material properties was demonstrated with a single serpentine channel microfluidic device (figure 14). Self-bonding was utilized during device fabrication to bond an ExSil cover to a molded micropatterned ExSil. Tear resistance and self-sealing were required for the cannulation of the serpentine channel. Ultra-high elongation, recovery and tear resistance allowed the device to maintain integrity during multiaxial distortion and extension.

Conclusion

The distinct properties of ExSil silicone elastomers enable new device designs, particularly in applications where behavior must be both compliant with soft tissues and able to withstand extreme distortion. The ability to partially recover cohesive bulk properties after tear initiation or penetration is a unique feature of this class of materials.

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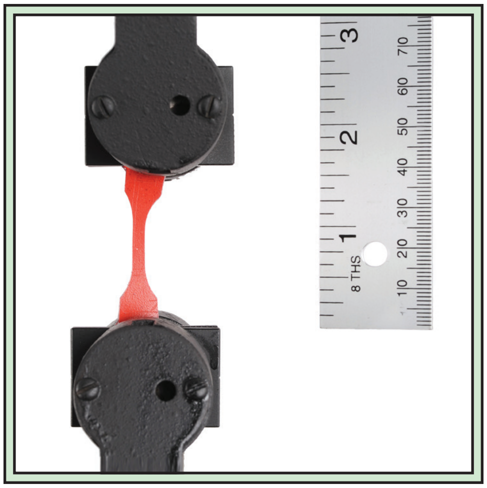
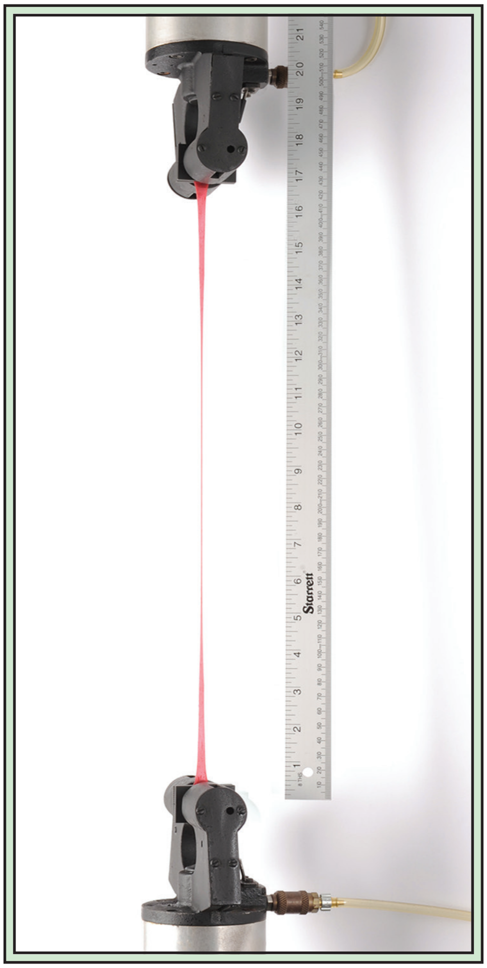
Gelest® ExSil® 50

High Elongation Elastomer – Medical Grade





Gelest® ExSil® 50 is a two-component high elongation silicone elastomer developed for medical applications.

Typical Properties

Note: The values below are typical and are not intended for use in preparing specifications. Please contact a Gelest representative when writing specifications.

Cured Properties	Units	Value
Elongation	%	6000
Tensile Strength	**MPa**	**3**
Tear Strength	**kN/m**	**5-7**
Elongation @ Tear Failure	%	1000 - 1500
Durometer	Shore A	5
Specific Gravity (Part A)	g/mL	1.06
Refractive Index (n_D^{25})		1.41
Volatiles (4 hours/150°C)	wt%	≤ 0.1
Critical Surface Tension	mN/m	23 - 24
Contact Angle, Water	°	105 - 100
Volume Resistivity	ohm*cm	2.90E+14

Features & Benefits

- Self-sealing
- High elongation
- High recovery
- Low extractables
- High tear strength
- Flowable and moldable
- High oxygen permeability
- Long-term thermal stability

Applications

- Diaphragms
- Microfluidics
- Vibration damping
- High performance seals
- Septa with easy penetration and good resealability
- Optical and electrical interconnects

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