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Ultra-high Elongation Silicone Elastomers

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Ultra-high elongation silicone elastomers

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Silicone elastomers with elongations approaching 5,000%, nearly four times greater than any other commercial elastomer, are now available. These new elastomers utilize a cure mechanism that generates elastomeric properties by driving linear polymers to extremely high molecular weights with concomi-

tant formation of intra- and inter-chain entanglements, rather than covalent crosslinking (ref. 1). When elastomers have elongations significantly above 1,500%, they exhibit behavior that is readily differentiated from conventional elastomers. These new silicone elastomers are able to undergo extreme multi-axial distortion and return to their original shape in what may be described as pseudo-shape memory behavior. Tear propagation mechanisms are altered, and tear failure occurs at radically greater elongations. Recovery from penetration is also improved. Below the failure limits, these new silicones exhibit surprising pseudo-self-healing recovery from narrow gauge object penetration. Table 1 compares the elongations of typical commercial grades of elastomers. The last column shows the highest reported elongations for different classes of elastomers. Table 2 provides a summary of the properties of the first two commercial grades of ultra-high elongation silicone elastomers: ExSil 100, an industrial grade, and Gelest RG-09, a precision reprographic grade. Figure 1 depicts a test bar of the high elongation elastomer before and after extension to 2,500% (50% of ultimate elongation). Noteworthy is the decrease in size in the cross-section during extension and the recovery to original dimensions

Both grades of ultra-high elongation silicones are supplied as two-component 100:1 kits. Gelest ExSil 100 is intended for mold-making and encapsulation applications. Gelest RG-09 was originally introduced for microfluidics and semiconductor applications, but is now being considered for a variety of implantable medical devices. Both grades can be utilized in LIM (liquid injection molding) applications if the molding equipment has the capability of processing at 100:1 ratios. The same features that differentiate silicones from organic elastomers are apparent in the physical properties of the ultra-high elongation materials, including elastomeric performance over a wide tem-

Table 1 - elongations of commercial elastomers

<i>Rubber</i>	<i>Elongation at break (%) commercial grades</i>	<i>Elongation at break (%) highest reported</i>
Ethylene propylene diene monomer (EPDM)	100-600	-
Epichlorohydrin rubber (ECO)	200-800	-
Polybutadiene (BR)	300-450	850
Styrene butadiene rubber (SBR)	450-600	-
Acrylonitrile butadiene rubber (NBR)	400-600	-
Natural rubber		
cis-1,4-polyisoprene (NR)	500-850	1,300
Butyl rubber	300-400	-
Styrene/butadiene/styrene (SBS)	1,000-1,500	1,750
Thermoplastic copolyester elastomers (TPC-ET)	350-650	-
Thermoplastic urethane (TPU)	400-700	1,400
Conventional polysiloxanes	100-1,000	1,200

Table 2 - mechanical and physical properties of ultra-high elongation silicone elastomers

<i>Cured property</i>	<i>Method</i>	<i>Unit</i>	<i>Gelest ExSil 100</i>	<i>Gelest RG-09</i>
Elongation	D412	%	5,000	4,600
Tensile strength	D412	MPa	8-9	9-10
Tear strength	D624	kN/m	-	40-42
Elongation at tear failure	-	%	-	2,000
Durometer	Durometer A	-	15	15
Compression set, 22 hours at 23°C	-	%	5	5
Rebound resistance	-	%	30	30
Specific gravity	-	-	1.12	1.12
Linear shrinkage, 110° cure	-	%	<0.05	<0.03
Volatiles, 150°C/4 hours	-	%	<0.5	<0.1
Refractive index	-	-	1.41	1.41
Contact angle, water	-	°	105-110	105-110
Extractables	-	%	0.5	0.2

Figure 1 - ExSil 100 before (left), during (center) and after (right) extension

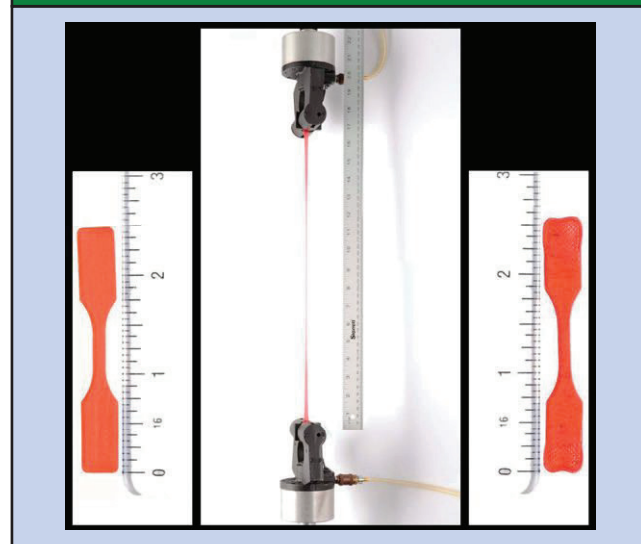
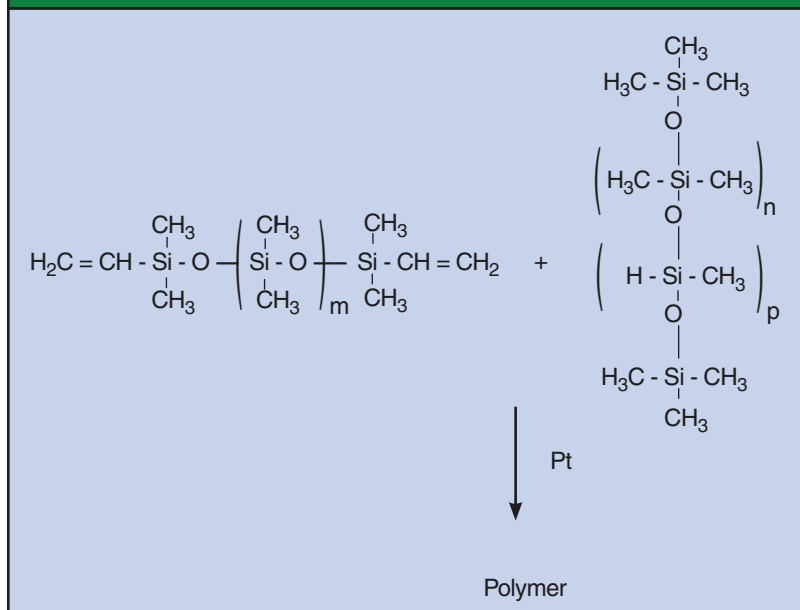


Figure 2 - cure mechanism for conventional LSR silicones



perature range, high temperature stability and low surface energy. The differentiator from traditional silicones is the extreme elongation, both at ultimate failure and, perhaps more significantly, resistance to tear-induced failure.

Background (polymer theory and chemistry)

It is well understood that for a polymer to exhibit elastomeric behavior, it must have a high molecular weight flexible backbone and a recovery mechanism. Typically, the mechanism for recovery is through crosslinking, as exemplified by vulcanized rubber and heat-cured silicone rubber, or an entropy driven reversal of strain-induced crystallization, as exemplified by thermoplastic urethane (TPU) and thermoplastic styrene-ethylene/butadiene-styrene (SEBS) block polymers. Single-component, high consistency silicone rubber (HCR) is traditionally cured by the peroxide initiated crosslinking of a polysiloxane component in a silica-reinforced base. A moisture-induced room-temperature cure mechanism is favored in applications where silicones are field applied as RTV (room temperature vulcanizing) caulks and sealants. Another more flexible approach for

commercial fabrication of silicone elastomers is to use two polysiloxane components. One polysiloxane component is generally of higher molecular weight and may be thought of as the matrix polymer, and the second polysiloxane component, which is generally of lower molecular weight and may be thought of as a crosslinker. These two components react with each other in a platinum-catalyzed reaction which forms the basis for LSR (liquid silicone rubber) and two-component RTVs. The reaction is depicted in figure 2.

Regardless of the cure mechanism, the polysiloxane components can be described as polydisperse, and the silicone elastomers formed from them typically have tensile strengths of 500-1,000 psi, with elongations of 100-1,000%. The polysiloxane components of silicone elastomers are usually prepared by equilibrium ring-opening polymerization, which results in polymers with broad molecular weight distributions or high polydispersity indexes (PDI > 2.5).

An alternative polymerization technology is “living” anionic ring-opening polymerization (living AROP) (ref. 2), which is an established method of preparing narrow molecular weight distribution polymers (PDI < 1.3). This technique can be used to prepare asymmetric siloxane macromers with a single functional group. These siloxane macromers afford many desirable properties, in particular the ability to form copolymers with organic monomers; but until now they have not offered any substantial benefits in the fabrication of silicones, and have strong economic disadvantages.

Recently, living polymerization methods have been developed that result in heterobifunctional macromers (refs. 3-5). Alpha-vinyl, omega-hydride terminated siloxanes are synthesized according to the reactions depicted in figure 3.

These macromers are monodisperse (PDI < 1.3) and contain a vinyl group and a hydride group at the opposite ends of the siloxane, which are confirmed to be in a substantially 1:1 stoichiometric ratio using NMR. The heterobifunctional macromers for the first commercial grades of ultra-high elongation elastomers have degrees of polymerization, or DPs, of 50-200.

These macromers are formulated into elastomer bases by compounding with fillers, pigments and reinforcing agents

Figure 3 - the synthesis of heterobifunctional siloxane macromers

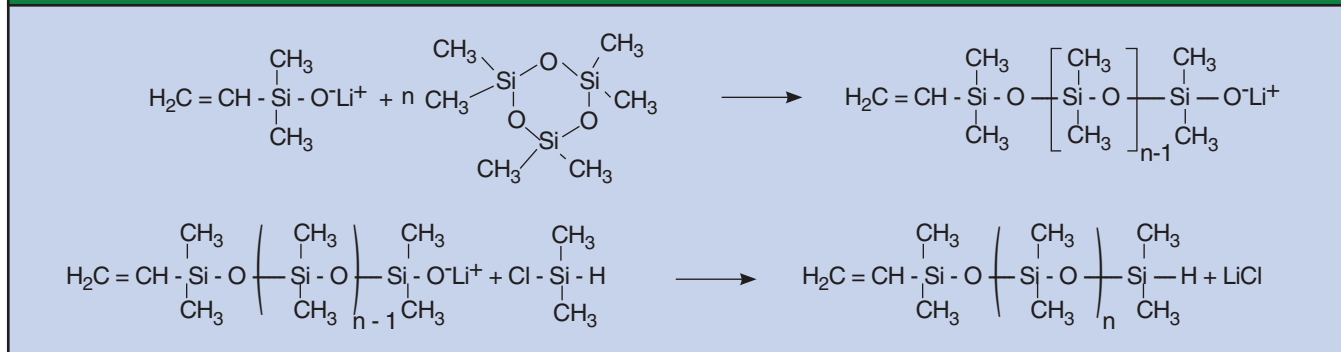
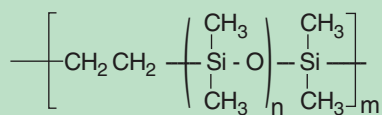


Figure 4 - chemical structure of fully polymerized (cured) ultra-high elongation elastomers



such as fumed silica. The formulated bases can be converted to silicone elastomers of high molecular weight by addition of a platinum-based catalyst. For industrial grades of high elongation elastomers, the platinum-based catalyst is dispersed in an inert silicone. For low volatility and low extractable grades, the platinum-based catalyst is dispersed in a reactive silicone. The cure mechanism is actually a step-growth polymerization that results in linear polymers of exceptionally high molecular weight with no evidence of covalent crosslinking to the limits of detection. Figure 4 depicts the cured polymer structure of the ultra-high elongation elastomers.

During the polymerization, the extremely flexible growing polymer chains become entangled not only with each other, but within themselves. It is the intra-chain or self-knotting of the polymers that is considered by the authors to be essential for achieving extreme elongations. Depicted in figure 5 is an atomistic model of a 50,000 MW segment of a cured elastomer with a molecular weight estimated to be in excess of 3×10^6 . The segment shows multiple knots. The probability of forming even a single knot in organic polymers of similar molecular weight is <1 , a consequence of both lower flexibility on a molecular level and higher free molal volume.

It is the difference between the apparent length of the coiled and loosely knotted segment and its actual end-to-end length when pulled straight with concomitant knot tightening that provides the mechanism for high extension. The return to coils and knot-loosening is enabled by vibrational modes of the polymer backbone, and is driven by entropic recovery. The silicone elastomers formed in this manner have exceptionally high elongations, approaching 5,000%. Further support for an intra-chain contribution to elongation and recovery is the observation that when solution polymerization, rather than bulk polymerization, is utilized to cure these materials, the elongation increases by nearly 20%, while tensile properties are maintained.

Figure 5 - atomistic model of a 50,000 MW segment of ultra-high elongation elastomer

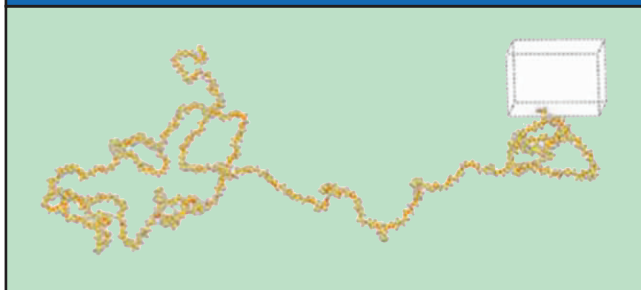
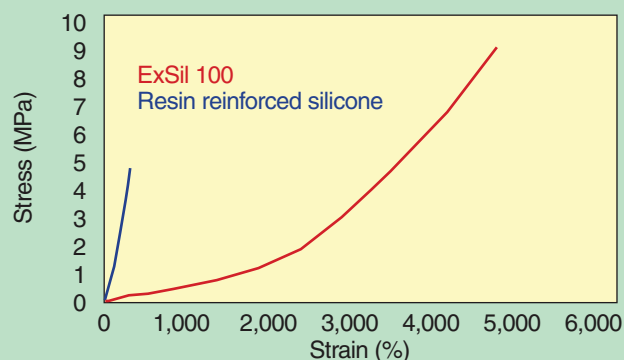


Figure 6 - stress-strain curve of ultra-high elongation elastomer compared to resin-reinforced silicone



Design properties

The primary differentiating properties of the new materials are elastic recovery as well as resistance to tear propagation failure after extreme distortion and elongation. The resistance to tear propagation failure is associated with the low levels of stress associated with strains at levels below about 40% of ultimate elongation (figure 6).

Other differentiating features of the ultra-high elongation elastomers are low levels of extractables and volatiles, improved dimensional stability on aging and improved thermal stability. These differences are directly associated with the living AROP polymerization. The primary polymerization technology for traditional silicone elastomers, regardless of the cure mechanism, relies on an equilibrium polymerization which generates a broad molecular distribution of polymeric species that contain traces of the polymerization catalyst which remain in the fabricated polymer. Not only are low molecular weight species present as an intrinsic consequence of the equilibrium polymerization, residual catalyst causes a continual re-equilibration at elevated temperature, generating low-molecular weight species and deteriorating mechanical properties. The presence of low molecular weight volatiles and extractables is an important consideration when selecting materials for electronic and medical applications. Silicones have excellent di-

Figure 7 - TGA thermogram of ExSil 100 elastomer versus conventional silicone

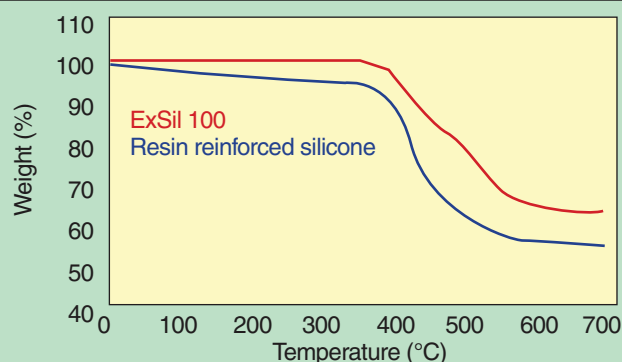


Figure 8 - elongation - thermal aging at 125°C of ExSil 100 (red) versus resin reinforced silicone (blue)

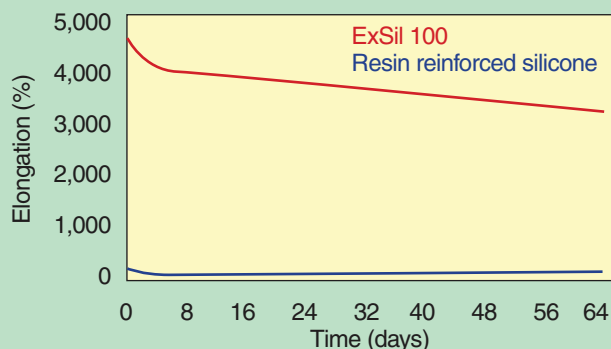


Figure 9 - tensile strength - thermal aging at 125°C of ExSil 100 (red) versus resin reinforced silicone (blue)

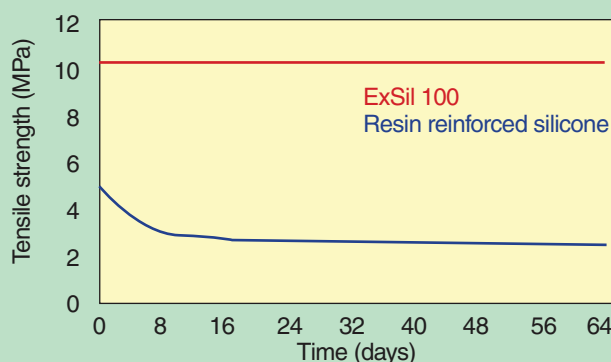


Table 3 - elastic recovery and stress decay of ExSil 100 versus silicone elastomer

Silicone elastomer	Test elongation %	Elastic recovery % (1 cycle)	Stress decay, % (1 cycle)	Elastic recovery, % (10 cycles)
ExSil 100	50	100	1.3	Not tested
Resin reinforced silicone	50	100	1.3	Not tested
ExSil 100	150	98	6.2	97
Resin reinforced silicone	150	99	8.5	96
ExSil 100	1,500	93	7.0	-
Resin reinforced silicone	1,500	Failed	Failed	Failed
ExSil 100	4,000	89	17	82
Resin reinforced silicone	4,000	Failed	Failed	Failed

Table 4 - processing properties for ultra-high elongation elastomers

Uncured property	Unit	ExSil 100	Gelest RG-09
A:B ratio		100:1 (nominal)	100:1 (critical)
Viscosity A	cSt	12,000-14,000	12,000-14,000
Viscosity B	cSt	900-1,100	900-1,100
Cure time, 80°C	-	1 hour	1 hour
Cure time, 170°C	-	<30 seconds	<30 seconds
Post-cure, 125°C	Hours	4-6	4-6
Work time, 25°C	Hours	8	8

electric properties, but migration of volatile low molecular weight species can result in insulating films in active circuitry components. Extractable species are of obvious concern in any medical device. Figures 7-9 show room temperature volatiles, TGA (thermogravimetric analysis) and aging studies.

There are no precedents for applications in which elongations in the range of 5,000% are critical for device performance. In external contact medical devices, there is demand for installation and overlay on stretchable areas of skin. Maximum elongations of skin (over 150%) are reported in the finger-joint and elbow areas, nominally within the limits of most elastomers. With installation extensions of up to 3x and a design safety of 2x, the desired maximum elongations for medical applications are in the range of 1,000%. The additional requirement that the device should be able to withstand tear propagation failure at maximum elongation eliminates virtually all materials except the ultra-high elongation silicone elastomers. Intraocular lenses that are folded, rolled or distorted in a syringe-like insertion device for cataract replacement surgery are an example of minimally invasive implantable devices. More complex architectures associated with sensors, nerve stimulation and *in situ* physiological analysis or drug delivery have greater demands for recovery from distortion during the im-

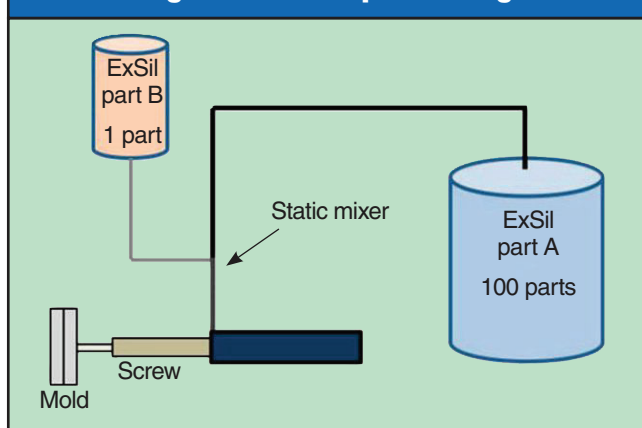
plantation process.

Fatigue, recovery and other mechanical properties of these new elastomers are comparable to other silicones in the low elongation range, but differ at higher elongations (table 3). Resistance to tear and recovery from punctures are greater for ultra-high elongation silicones than all other silicones. While high-temperature stability in terms of chemical degradation exceeds conventional silicones, certain mechanical properties, in particular compression set and creep, are inferior at elevated temperatures. The differences can be attributed to the fact that the ultra-high elongation elastomers can be thought of as non-Newtonian liquids that rely on a variety of entanglement mechanisms to provide cohesion and resilience. The materials are capable of shape recovery at extreme distortions beyond those previously reported for any material.

Fabrication (casting, molding, bonding)

Ultra-high elongation silicone elastomers can be fabricated by a casting process analogous to silicone mold-making or by high-speed LIM (liquid injection molding). The elastomers are liquid materials of intermediate viscosity. While the ratio of part A to part B at 100:1 is nominal for ExSil 100, this ratio is critical for Gelest RG-09 to achieve maximum product perfor-

Figure 10 - LIM processing



mance (table 4). Both standard grades are clear to translucent. Dyes or pigments can be incorporated, depending on whether transparency or opacity is desired.

For casting or conventional molding applications, it is preferred to de-gas the elastomer after adding the catalyst. If a high-speed accentric mixer (for example a Flacktek Speed-mixer) is utilized, degassing is usually not critical. Liquid injection molding can be performed on any machine that has the capability of 100:1 proportional metering (figure 10). If available equipment is not capable of 100:1 proportions, a Graco multi-stream proportioner pump can generally be adapted to the equipment. Post-cure is not critical if 48 hours are allowed before component service.

Clean, freshly molded parts can be readily bonded to each other by exposure to a low-level oxygen plasma followed by heating at 100-125°C for 30 minutes. Application of light uniform pressure to ensure contact is recommended. Parts that have been exposed to ambient atmospheres adsorb contaminants on the surfaces and must be physically cleaned, followed by a quick alcohol wipe before the bonding process.

Figure 11 shows a microfluidic device with a single serpen-

Figure 11 - microfluidic device in tortuous extension

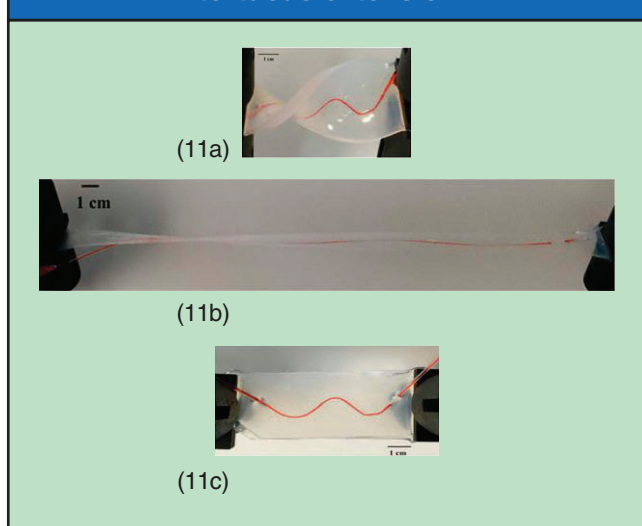


Figure 12 - a solid 1 meter x 9 mm diameter section of ExSil 100 at 0% (12a and 12b) and ~ 2,000% elongation (12c)

(12a and 12b)



(12c)



tine channel with a fluid (red) passing through it fabricated from Gelest RG-09. It is shown twisted (11a), subjected to tortuous extension (11b) and in its original configuration (11c).

Figure 12 shows a macro-scale example of ExSil 100 with a rope attached between a concrete barrier block and a truck.

Conclusion

Ultra-high elongation silicone elastomers have been made possible by a new synthetic pathway. The new materials are formally linear polymeric liquids that exhibit elastomeric properties with elongations in the range of 5,000%. This development has been enabled by a living polymerization that results in

heterobifunctional macromers of intermediate molecular weight, which in a distinct platinum catalyzed step-growth polymerization are converted to elastomers with high molecular weight. In addition to ultimate elongation, resistance to tear propagation failure and recovery from penetration are substantially improved compared to conventional elastomers. In other respects, the new silicone elastomers have properties similar to other high performance silicone elastomers. The first two commercial grades, Gelest ExSil 100 and Gelest RG-09, are expected to enable engineers to design new devices for medical and industrial applications.

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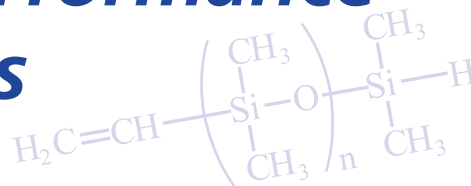
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