

Silicone Elastomers with Exceptional Elongation

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ABSTRACT

Polysiloxanes elastomers formed by the step-growth of heterobifunctional macromers achieve high molecular weights and show elastomeric behavior. There is no apparent mechanism for crosslinking and advanced NMR and DSC techniques as well as rheological studies support the fact that, within the limits of detection, the step-growth elastomers are linear. When formed into nanocomposites by the incorporation of surface passivated fumed silica, they exhibit elongations exceeding 5000%. At extensions comparable to conventional silicone elastomers, they show similar elastic recovery. At greater extensions, recovery is reduced marginally. These materials are readily manufacturable and can be compounded and processed similar to conventional two-component platinum cure silicone RTVs. We have adopted the designation of xPDMS for these materials, a modified acronym for “high eXtension PolyDiMethylSiloxanes”. The synthesis, characterization, and mechanical properties of the first example of an xPDMS suitable for commercial production is presented.

INTRODUCTION

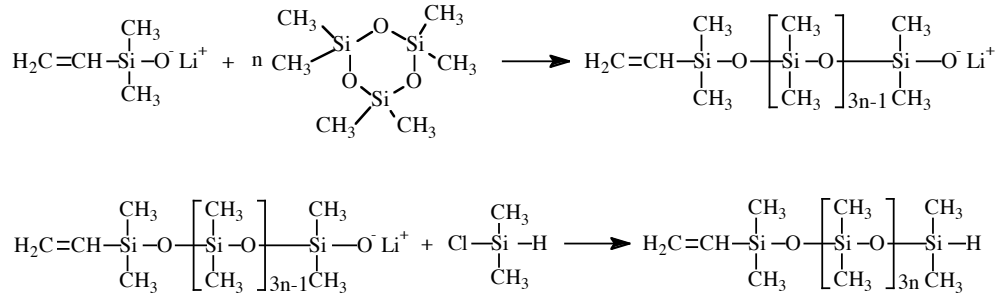
In most commercial applications, single component silicone elastomers are conventionally prepared by either the crosslinking of a polysiloxane component in a silica reinforced base by a peroxide (HCR, *high consistency rubber*) or by a moisture-cure mechanism (condensation RTVs, *room temperature vulcanizates*)¹. Another more flexible approach for commercial fabrication of silicone elastomers is to use two polysiloxane components in which

one polysiloxane component is generally of higher molecular weight and can be thought of the matrix polymer, and the second polysiloxane component, which is generally of lower molecular weight and can be thought of as a crosslinker.

These two components react with each other, most often in a platinum-catalyzed reaction (LSR, *liquid silicone rubber* or 2-component RTVs). Regardless of the cure mechanism, the polysiloxane components can be described as polydisperse and the silicone elastomers formed have similar tensile strengths, 500-1000psi, and elongations, 200-800%. The siloxane polymers that comprise the polysiloxane components are typically prepared by equilibrium ring-opening polymerization, which results in polymers with broad molecular weight distributions (PDI >2.5).²

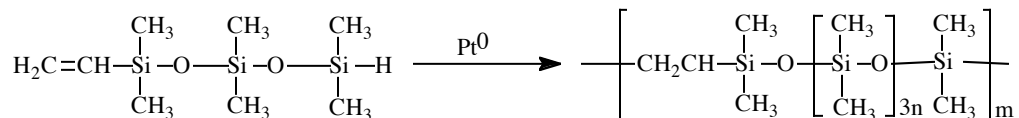
An alternative polymerization technology is “living” anionic ring-opening polymerization (AROP), which is an established method of prepare narrow molecular weight distribution polymers (PDI <1.4).³ This technique has typically been used to prepare siloxane macromers with a single functional group. These siloxane macromers are asymmetric with a single functional group which afford many desirable properties, in particular, the ability to form copolymers with organic monomers, but 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.⁴ Reported here are alpha-vinyl, omega-hydride terminated siloxanes, synthesized according to the following reactions:



The macromers are monodisperse (PDI <1.3) and contain a vinyl group and a hydride group at the opposite ends of the siloxane, which were confirmed to be in a substantially 1:1 stoichiometric ratio using NMR.

They can then be formulated into elastomer bases by compounding with fillers, pigments and reinforcing agents such as silica. Subsequently the formulated bases can be converted to silicone elastomers of high molecular weight by a platinum-cure mechanism.⁵



The silicone elastomers formed in this manner have exceptionally high elongations, exceeding 5000%. Other differentiating features are low-levels of extractables, improved dimensional stability on aging and improved thermal stability when compared to silicone elastomers fabricated by conventional technology.

EXPERIMENTAL

Siloxane Synthesis. The synthesis has been reported previously. A specific example is provided;

Monovinyl-Monohydride terminated Polydimethylsiloxane (DP=50)

A 5L 4 neck flask equipped with an overhead stirrer, pot thermometer, reflux condenser, water bath, and addition funnel was blanketed with nitrogen and charged with 39.6g (0.15 moles) of trivinyltrimethylcyclotrisiloxane and 100g of hexane, and then sparged with nitrogen for 1/2 hour. Methyl lithium (140 ml of 3.22M in diethoxymethane solution) was added to the reaction mixture via an addition funnel over 15 minutes. After an exotherm of 5°C was observed, a cooling bath was used to maintain temperature below 40°C during the methyl lithium addition. The mixture was stirred for 1 hour, during which time the consumption of greater than 95% of the trivinyltrimethylcyclotrisiloxane was observed. At the end of this period, the cooling bath was allowed to warm, and the temperature of the reaction mixture was allowed to return to 25°C. Then, a solution of 1671g (7.5 moles) of hexamethylcyclotrisiloxane in 1025g of hexane was added, followed by the rapid addition of 186g of dimethylformamide (DMF). A slight exotherm was observed, pot temperature rose from 24° to 33°C, and the mixture was stirred for 1 hour. The capping reaction was accomplished by the addition of 45g (0.47moles) of dimethylchlorosilane over fifteen minutes. An exotherm was observed. The mixture changed from clear to cloudy and was stirred for an additional 17 hours. Water (500g) was added to the reaction mixture with stirring and agitated for 90 minutes. The contents of the flask were separated into aqueous and non-aqueous layers in a separatory funnel. The aqueous layer was discarded. The organic phase was washed 1 time with deionized water, 1 time with 5% sodium bicarbonate solution and 1 more time

with deionized water. The last water wash contacting the organic phase remained neutral (pH: 7-8). The organic layer was dried over anhydrous sodium sulfate, filtered, transferred to a rotary evaporator, and stripped under 5mm Hg vacuum to a maximum pot temperature of 100°C. The resulting oil (1732g) had a density of 0.960 and a viscosity of 49 cSt. GPC data (polystyrene st'd without correlation)- Mn: 4370, Mw/Mn: 1.20.

Formulation and Compounding

Compounding and Sample Fabrication:

In reinforced systems, 30 wt% of hexamethyldisilazane-treated silica nanoparticles (20 nm) was compounded into the heterofunctional macromer using a FlackTek DAC 600.1 VAC programmable speedmixer at 2200 rpm for 5 min.

Step-Growth Polymerization of Formulated Heterobifunctional Macromers:

Two protocols were utilized.

A. To prepare cured samples and platinum-divinyltetramethyldisiloxane catalyst was added to compounded mixture and dispersed using a FlackTek speed mixer.

The mixture was poured into a mold and heat cured in an oven at 80°C for 1 hour.

B. In order to minimize issues associated with weighing and dispersing the relatively small amounts of catalyst, the following protocol was adopted. Two additional monodisperse DP=50 telechelic polymers, one vinyl terminated and one hydride terminated, were prepared. One weight percent of the hydride terminated telechelic replaced the heterobifunctional base polymer in the compounded base. Separately the platinum catalyst was mixed with an

equivalent weight of the vinyl terminated telechelic. This allowed more accurate introduction of the platinum catalyst as what may be considered a 2-component 100:1 kit. The component that contains the platinum is referred to as the activator component. The cure was activated by manually mixing the two components as described above.

Mechanical Property Measurements: Tensile and elongation testing of the samples was conducted at 20-22°C, a minimum of 24 hours after cure, according to ASTM D-412-80 test method using dumbbell configured specimens according to ASTM D-638 Type V (width: 3.18mm; length: 9.53mm; thickness: 2mm) at a crosshead speed of 500mm/min using an Instron Universal Testing Machine model 3345.

RESULTS and DISCUSSION

While the monovinyl-monohydride terminated polydimethylsiloxane can be catalyzed directly to form an elastomeric product, from a manufacturing technology perspective it is more practical to process the mixture as a two component RTV system. A Karstedt platinum catalyst is diluted in a monodisperse vinyl-terminated siloxane which is offset by adding an equivalent amount of monodisperse hydride-terminated silicone to the compounded base. A 100:1 ratio was chosen to facilitate mixing without compromising properties (Figure 1).

Uncured Properties	ASTM	Value	Unit
Base Viscosity	D1084	12,000 to 14,000	cSt
Activator Viscosity	D1084	800 to 1000	cSt
Catalyzed Mix Viscosity	D1084	12,000 to 14,000	cSt

Figure 1. xPDMS Uncured Component Properties

The salient feature which distinguishes xPDMS elastomers from not only other silicone elastomers, but elastomers in general is the dramatic difference in stress-strain behavior. In their unreinforced state, elongations exceed 500%. The silica-reinforced versions exhibit elongations of 5000% or more. At equivalent stress levels the strain of the xPDMS is significantly greater. The ultimate tensile strength is comparable to that of high performance HCR and LSR rubbers, but ultimate elongation exceeds them by a factor of five to ten. A typical stress-strain curve is depicted in Figure 2 and compared to a conventional 2-component silicone RTV elastomer.

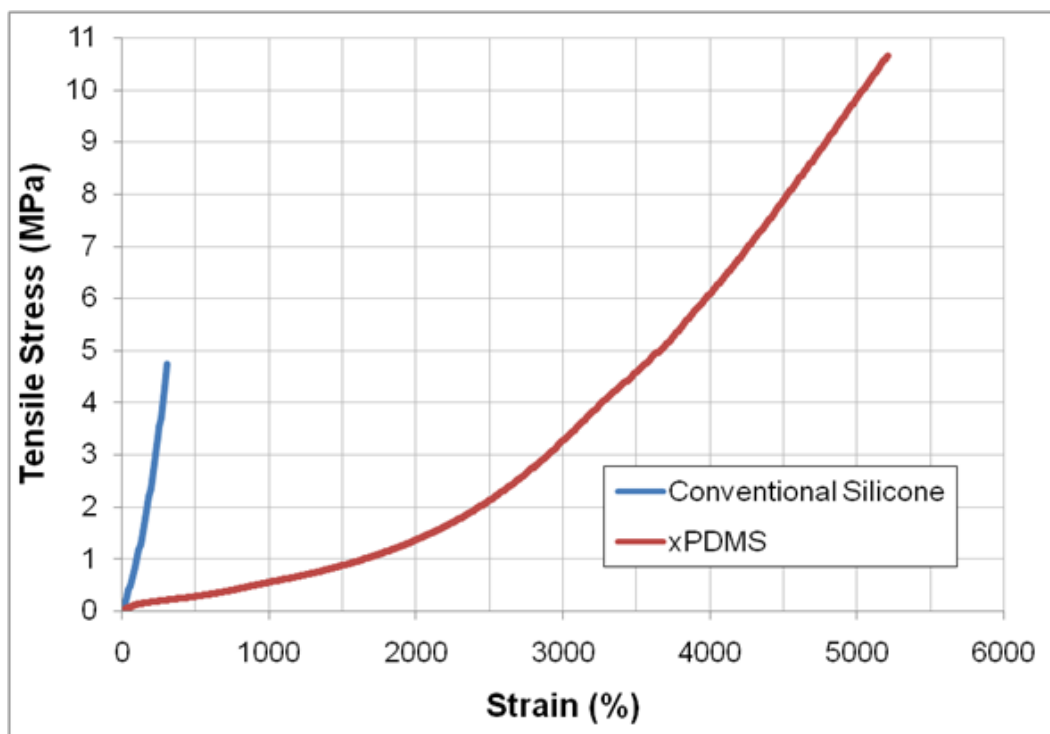


Figure 2. Comparative stress-strain behavior of xPDMS and a silicone RTV.

The inherent physical properties associated with silicones, such as release and wetting characteristics are maintained by the xPDMS elastomers. Of note is extremely low volatile content, <0.1 wt%, compared to 2-4 wt% for conventional silicone elastomers, suggesting potential applications in electronic and medical devices where migration of low molecular weight species is undesirable. A property profile is tabulated in Figure 3. A comparison of extractables is provided in Figure 4.

Cured Properties	ASTM	Value	Unit
Elongation	D412	5000	%
Tensile Strength	D412	8 to 9	MPa
Tear Strength	D624		
Durometer		15	Shore A
Specific Gravity		1.12	
Refractive Index		1.41	
Volatiles (4 hours/150°C)		≤0.1	wt%
Critical Surface Tension		23 to 24	mN/m
Contact Angle, water		105 to 110	°

Figure 3. xPDMS Cured Component Properties

Sample	Extractables (%)
Conventional Silicone – Pt Cure	4.2
Conventional Silicone – Pt Cure (100°C Part A Strip)	3.2
Conventional Silicone – Pt Cure (150°C Part A Strip)	3.1
xPDMS	0.2

Figure 4. xPDMS Comparative Extractables

Strain recovery can be considered in two modalities. Within the limits of elongation for silicone elastomers (<800%), the strain recovery of xPDMS is >98%. At extreme distortion (~4000%), has a recovery of 88% for a single cycle. After a single cycle the loss for ten cycles is an additional 6% (Figure 5).

Siloxane (M_n)	Silica Nanoparticle (wt%)	Elastic Elongation (%)	Strain Recovery (1 Cycle/%)	Strain Recovery (10 Cycles/%)	Stress Decay (%)	Tensile Strength (Mpa)
14,800	30	5000	88	82	21	8 to 9

Figure 5. Elastic Recovery and Stress Decay of xPDMS.

Elevated temperature performance of xPDMS is greater than conventional silicone elastomers. The xPDMS elastomers are derived from a step-growth polymerization of macromers. Conventional silicone elastomers are derived from equilibrium polymerization, which intrinsically contain low molecular weight species, contributing to weight loss at relatively low temperatures (Figure 6). In addition, traces of equilibration catalyst in conventional silicone elastomers contribute to reversion, a term for molecular weight redistribution, on exposure to elevated temperature for extended time periods. The xPDMS elastomer contains no equilibration catalysts.

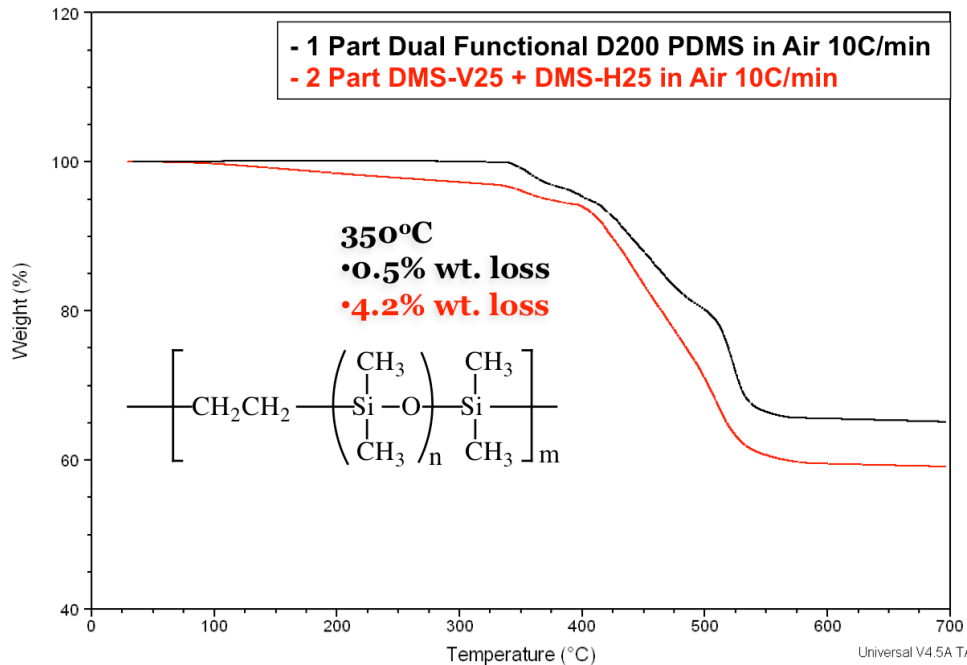


Figure 6. TGA Analysis of xPDMS Silicone Elastomer vs. Conventional Silicone

SUMMARY

The new materials reported here are specifically polysiloxanes, derived from high molecular weight uncrosslinked polymeric liquids that when formed into nanocomposites demonstrate exceptional elongations. These high extension PolyDiMethylSiloxanes have been designated “xPDMS” elastomers. While exhibiting characteristics and processing similar to conventional silicone elastomers, they exhibit unprecedented elongations up to 5000% and excellent recovery behavior. These materials are readily manufactured and satisfy the structural requirements for long-term stretchable and implantable devices with integrated fluidics and electronics in soft tissue.

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