

Modification of Silicone Elastomers Using Silicone Comonomers Containing Hydrophilic Surface Active Endgroups

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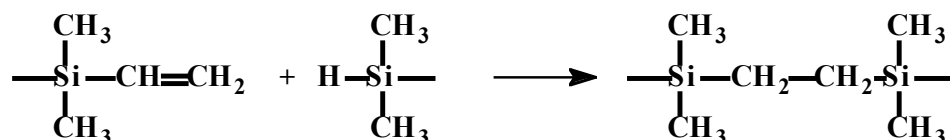
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ABSTRACT

A facile technique was developed for a long-term increase in silicone elastomer surface hydrophilicity, eliminating the need for post-cure surface treatment (e.g. oxygen plasma or surface grafting). Well-defined silicones (1-4 kDa) with a central vinyl functionality and discrete PEG₂, PEG₃ and tetrahydrofurfuryl (THF) pendant endgroups were synthesized, characterized and used as comonomers in addition-cure, platinum catalyzed 2-part silicone elastomer formulations. The modified silicone elastomers were optically clear and maintained the mechanical performance characteristic of this class of material with up to 20 wt.% comonomer in the 2-part formulation. Contact angle measurements of deionized water on the silicone elastomer surface showed improved wettability with comonomer content. The elastomer surface shifted from hydrophobic (contact angle ~120°) to hydrophilic (contact angle < 90°) at ~5 wt.% comonomer loadings for extended time frames (> 5 months). Coefficient of friction measurements of the modified silicone elastomers revealed an increase in surface lubricity with comonomer loadings.

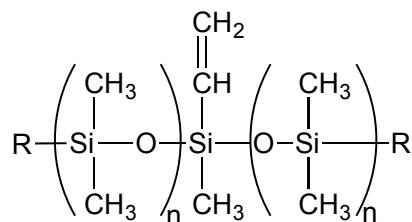
INTRODUCTION

Silicone elastomers have a myriad of uses in medical applications and microfluidics. The untreated surface of a silicone elastomer, however, is hydrophobic, with water contact angles reported in the 105-120° range.^{1,2} Long-term surface modification of silicones to improve wettability and reduce protein adsorption is desirable. Silicone elastomers are low T_g, low modulus materials with no secondary forces and negligible water adsorption and are often considered to be a paradigm for soft hydrophobic materials. The elastomers are formed by crosslinking highly flexible polymeric silicone fluids. The majority of elastomeric silicone products utilized in medical devices and microfluidics are based on the crosslinking of reactive silicones that possess vinyl and hydride substitution and typically incorporate inorganic fillers or resinous products for improved mechanical properties.¹⁻³ Commercially available addition-cure, platinum catalyzed silicone RTVs undergo a crosslinking hydrosilylation reaction yielding silicone elastomers. Typically in an addition cure 2-part RTV formulation, a Part A 'Base' of a vinyl functional silicone, filler and catalyst is mixed with a Part B hydride functional silicone 'Activator' in specific proportions and subsequently heated for cure. The stoichiometry of reactive functional groups in the formulation is set for an excess of hydride to ensure the quantitative consumption of vinyl groups and compensate for side reactions involving hydride functionality during the elastomer cure.²



Treatment of the silicone elastomer surface with O₂ plasma improves the surface wettability due to formation of hydrophilic groups, however, generation of hydrophobic cyclics and oligomers in the bulk elastomer also occurs. These low molecular weight hydrophobic species can diffuse from the bulk elastomer leading to an increase in extractables and hydrophobic recovery of the elastomer surface.⁴ Continual reapplication of an oxidative surface treatment is required to retain hydrophilic surface performance of the elastomer. Alternative surface modifying approaches include the incorporation of an unreactive hydrophilic additive (e.g. commercially available polyethylene glycol (PEG)-PDMS copolymer surfactants) into a 2-part silicone elastomer formulation, which leads to a loss of optical clarity, increase in undesirable extractables and deterioration of mechanical properties in the cured elastomer product.

Evaluation of the limitations of current elastomer surface modification approaches has led to a focus on hybrid functional silicones.² Most commercially available functional silicones are derived from the acid/base catalyzed chain growth polymerization of cyclic siloxanes.^{1,2} This approach yields a functional silicone with a telechelic structure and a broad molecular weight distribution with limited options for incorporation of hydrophilic groups. Living anionic ring opening polymerization of cyclic siloxanes is a more precise polymerization technique that allows for control of polymer architecture, endgroup moiety and chain length while maintaining a narrow molecular weight distribution.^{5,6} Advancements in living anionic ring opening polymerization techniques have made it possible to synthesize a monodisperse symmetric hybrid silicone with discrete hydrophilic endgroups and a single functional group that can participate in the hydrosilylation crosslinking chemistry of silicone elastomer formulations.^{7,8}



Herein the development of symmetric silicone elastomer comonomers containing surface active pendants and a central vinyl functionality is reported. These silicone elastomer comonomers were evaluated as additives in commercially available 2-part silicone elastomer formulations utilized in microfluidics and medical plastics. The pendant hydrophilic groups of the comonomer orient on the surface of the bulk silicone elastomer and can interact with water at the solid-liquid interface, leading to improved surface wettability and a lower coefficient of friction.

EXPERIMENT

Materials

Hexamethylcyclotrisiloxane (D₃, 98%), vinylmethyldichlorosilane (97%), 2-(allyloxymethyl)tetrahydrofuran (95%), allyloxy(diethylene oxide)-methyl ether (95%), allyloxy(triethylene oxide)-methyl ether (95%), platinum-divinyltetramethyldisiloxane complex (Karstedt Catalyst, 2.2 wt% Pt⁰), vinyl terminated polydimethylsiloxane (DMS-V31), methylhydrosiloxane-dimethylsiloxane copolymer (HMS-301) and 2-part addition cure 10:1 RTV silicone elastomer kit (PP2-RG01) were obtained from Gelest and used as received. Methyllithium (3.0 M in diethoxymethane) was purchased from Rockwood Lithium and was used without further purification.

Synthesis of Silicone Elastomer Comonomers

An exemplary synthesis of a 2,000 g mol⁻¹ methoxy(diethylene oxide)propyl terminated, monovinyl functional symmetric polydimethylsiloxane (PDMS-PEG₂ 2k) is provided. Molecular weight of the symmetric silicone comonomer can be adjusted by changing the monomer to initiator ratio in the reaction mixture. For methoxy(triethylene oxide) (PEG₃) and tetrahydrofurfuryl (THF) comonomer termination, the appropriate allyl functional starting material is used during the *in situ* initiator formation step. Methoxy(diethylene oxide)propyl dimethylsilyllithium silanolate (112g, 0.46mol) in diethoxymethane (117g) was synthesized using previously reported procedures.⁹ D₃ (463g, 2.1mol) in hexanes (309g) was added to the reaction mixture, followed by addition of DMF (76g). The polymerization mixture was stirred at room temperature for 2 h. A stoichiometric amount of vinylmethyldichlorosilane (32g, 0.23mol) was added dropwise to the stirring reaction mixture. The reaction mixture was stirred for 3 h and washed with deionized water (500mL). The organic layer was dried with MgSO₄ and concentrated under vacuum at 100°C.

Preparation of Modified Silicone Elastomers

Unfilled modified silicone elastomers were prepared by blending DMS-V31 and HMS-301 with different loadings of vinyl functional silicone elastomer comonomer (1-45 wt%). Formulations were based on a targeted 1.5mol hydride:1mol vinyl ratio of functional groups. In a 10 wt% PDMS-PEG₂ unfilled silicone elastomer formulation, DMS-V31 (10g), HMS-301 (0.5g) and PDMS-PEG₂ 2k (1g) were mixed together at room temperature with 5ppm of Pt⁰ catalyst. The mixture was heated at 80°C for 8 h, resulting in a cured, optically clear elastomer.

Silicone elastomer comonomers were added to commercially available 2-part RTV formulations (PP2-RG01). Different concentrations of silicone elastomer comonomers (5-30 wt%) were added to the PP2-RG01 Part A (base). The modified PP2-RG01 Part A (10g) was blended with PP2-RG01 Part B (activator, 1g) in a 10:1 ratio and cured at 80°C for 4 h. An optically clear elastomer was recovered.

Instrumentation

Comonomer viscosities were measured using a Brookfield Viscometer Model DV-II+ at 25°C. Gel permeation chromatography (GPC) analyses of silicone comonomers were performed on a Viscotek GPC Max VE2001 with a TDA 301 detector. Contact angle measurements of deionized water on the silicone elastomer surfaces were performed on a Rame-Hart Model

100-00 goniometer. Mechanical properties of the modified silicone elastomers were measured using an Instron Model 3345 and a Shore A Durometer.

Coefficient of friction (CoF) measurements of the modified PP2-RG01 elastomers were carried out using a 31.8 mm CoF fixture geometry with a polished stainless steel ring on a TA AR-G2 rheometer. The silicone elastomers were immersed in water at 37°C and placed in contact with the CoF fixture at a 1.0 N normal force. Coefficient of friction measurements were taken at two different velocities (0.1 and 1.0 rad/s).

DISCUSSION

The macromolecular design approach of the silicone elastomer comonomer had three important requirements: 1) ability to react into addition cure silicone elastomer formulations; 2) provide a long-term improvement in surface wettability; and 3) preserve the mechanical properties of the elastomer. The general concept of the silicone comonomer design is to have endgroup polarity that can modify the silicone elastomer surface. Vinyl functionality was chosen for the silicone comonomers to take advantage of the molar excess of hydride present in most 2-part silicone elastomer formulations. To increase the molar concentration of end groups per vinyl group, a symmetric architecture was developed for the silicone comonomers instead of traditional asymmetric silicone macromer architectures. The central functionality reacts into the crosslinked elastomer network and the flexible PDMS chains allow the surface active hydrophilic endgroups to orient on the surface and improve surface wettability.

Three requirements for successful hydrophilic modification of silicone elastomers are durability of the modification in an aqueous environment, little or no introduction of extractables and maintenance of optical clarity by the elastomer. Linear polyethers were the first hydrophilic moiety explored as a surface-active endgroup. The manufacturing process of the commercially available PEG-PDMS copolymers results in excess PEG (> 5 wt%) present in the bulk material. Stability is an issue with PEG-PDMS copolymers as oxidative and hydrolytic effects degrade the copolymers over time. The release of low molecular degradation products is a concern from the viewpoint of extractables present in an elastomer. To limit degradation, extractables and opacity issues, low molecular discrete polyether groups (PEG₂ and PEG₃) were chosen for evaluation as hydrophilic endgroups. An aprotic cyclic ether surface modifying hydrophilic endgroup (THF) was also explored.¹⁰ The aprotic cyclic ether structure of THF does not undergo the oxidative and hydrolytic degradation processes that results in chain scission of linear polyethers. The structures of the three symmetric silicone comonomers with surface active endgroups studied are shown in **Figure 1**.

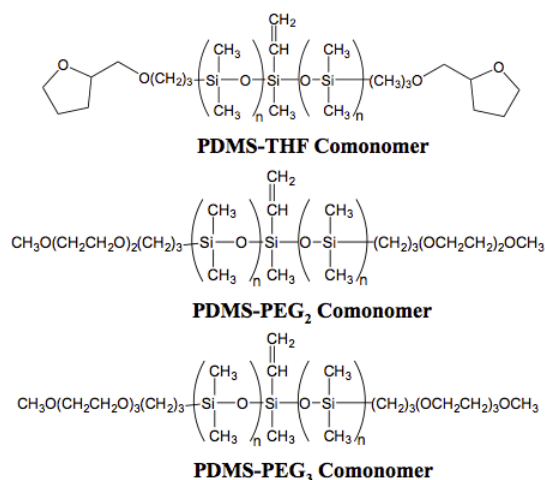


Figure 1. Symmetric silicone comonomers with a central vinyl functionality and surface modifying endgroups.

Table 1 shows the characterization data for the series of silicone comonomers synthesized via living anionic ring opening techniques. Comonomers with a targeted molecular weight of $2,000 \text{ g mol}^{-1}$ were synthesized for each surface active endgroup to study the effect of endgroup moiety on surface wettability as a function of comonomer concentration. The molecular weight of the PDMS-PEG₃ comonomer was varied between $1,000\text{-}4,000 \text{ g mol}^{-1}$ to study the effect of PDMS block length on the surface modification. GPC results compared favorably to the targeted molecular weights, with low molecular weight monomodal distributions (PDI) indicating a well-defined symmetric architecture of the comonomer and no low molecular weight species.

Composition of Comonomer	Target MW	GPC M_n	PDI	Viscosity (cSt)
PDMS-THF 2k	2,500	2,400	1.2	39
PDMS-PEG ₂ 2k	2,500	2,500	1.2	37
PDMS-PEG ₃ 1k	1,600	1,500	1.3	27
PDMS-PEG ₃ 2k	2,600	2,300	1.2	38
PDMS-PEG ₃ 4k	4,600	4,800	1.3	75

Table 1. Characterization data of silicone comonomers.

The silicone comonomers were blended into unfilled silicone elastomer formulations (DMS-V31 and HMS-301) and commercially available 2-part RTV kits (PP2-RG01). Contact angle measurements of water on the elastomer surface were used to study the effect of the comonomer on the surface wettability of the modified elastomers (**Figure 2**). Universally, contact angles decreased with increased comonomer loadings in both systems. In unfilled elastomer systems $\sim 5\text{wt}\%$ comonomer loadings brought the elastomer surface into the wettability region (contact angle $< 90^\circ$). The PDMS-PEG₃ (2k) effected the largest reduction in contact angle with comonomer concentration. The PDMS-THF and PDMS-PEG₂ comonomers showed a similar performance in the unfilled elastomer systems. Similar trends were observed in the PP2-RG01 system, except the reductions in contact angle with comonomer concentration were not as drastic- likely due to the reinforcing agents influencing the ability of the surface

active pendants to orient on the elastomer surface. The measured contact angles of water on the elastomer surface were stable over extended periods of time (> 5months).

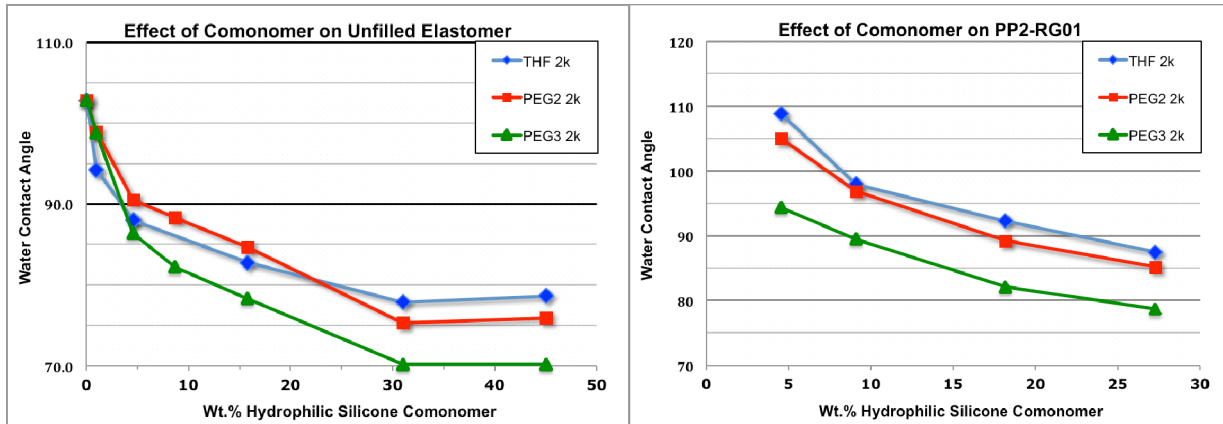


Figure 2. Surface wettability of silicone comonomer modified elastomer systems.

The mechanical properties of the comonomer modified PP2-RG01 elastomer were evaluated (**Table 2**). The standard 2-part silicone elastomer kit has a tensile strength of 700 psi, an elongation of 160% and a Shore A hardness of 50. The modified PP2-RG01 elastomers retained their mechanical properties and optical clarity with comonomer loading up to 15wt%.

	RG01	RG01 (10wt% PEG ₂)	RG01 (10wt% PEG ₃)	RG01 (15wt% PEG ₃)
Tensile Strength (psi)	700	730	710	680
% Elongation	160	190	185	197
Durometer, Shore A	50	53	54	51

Table 2. Mechanical properties of comonomer modified PP2-RG01.

Coefficient of friction measurements of the modified PP2-RG01 elastomers in water at physiological temperature were recorded (**Figure 3**). Consistent with silicone rubbers, unmodified PP2-RG01 had a CoF > 1, indicating that that the force required to slide an object along the elastomer surface is greater than the applied normal force. The surface lubricity of the modified PP2-RG01 increased with comonomer loading. PDMS-THF and PDMS-PEG₂ showed similar reductions in CoF, while the PDMS-PEG₃ dropped the CoF of the modified elastomer substantially below 1.

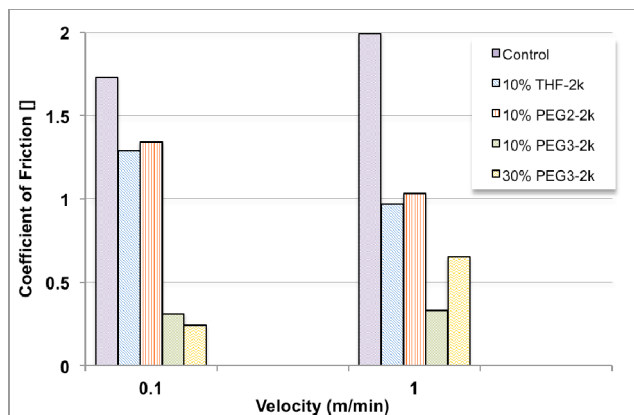


Figure 3. Effect of comonomer concentration on Coefficient of Friction in an aqueous environment of PP2-RG01 modified elastomers.

CONCLUSIONS

This paper reports the development of silicone elastomer comonomers containing surface active pendants with discrete polyether or tetrahydrofurfuryl (THF) endgroups and a central vinyl functionality that can react into 2-part silicone elastomer formulations. Copolymerization leads to optically clear silicone elastomers with good mechanical properties. The pendant hydrophilic groups orient on the surface of the bulk silicone elastomer, providing long-term improvement of surface wettability and lubricity.

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