

Silicone Elastomers with Intrinsic Control of Surface Hydrophilicity

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Introduction: Addition-cure, platinum catalyzed silicone RTVs undergo a crosslinking reaction yielding silicone elastomers.¹ Silicone elastomers have myriad uses in medical applications due to their biocompatibility. The hydrophobic surface of silicone elastomers is a well documented disadvantage in many applications. Long-term surface modification of silicones to improve wettability and reduce protein adsorption is desirable. Oxidative surface treatment of silicone elastomers to improve surface wettability has been reported, however, the surface recovers hydrophobic character over time.² As a result, oxidative surface treatments need to be continually reapplied to the silicone elastomer to retain hydrophilic surface performance. Addition of a hydrophilic additive such as polyethylene glycol (PEG) to silicone RTV formulations is another approach to modifying the surface of silicone elastomers. These unbound hydrophilic additives in silicone elastomers lead to loss of optical clarity, increased presence of undesirable extractables and degradation of mechanical properties. This paper reports the development of silicone elastomer comonomers containing surface active pendants with discrete discrete polyether or tetrahydrofurfuryl (THF) substitution and a central vinyl functionality that can react into RTV formulations. Copolymerization leads to optically clear silicone elastomers with good mechanical properties and no increase in extractables. The pendant hydrophilic groups orient on the surface of the bulk silicone elastomer, providing long-term improvement of surface wettability and reduced protein adsorption.

Methods: Vinyl terminated polydimethylsiloxane (DMS-V31), methylhydrosiloxane- dimethylsiloxane copolymer (HMS-301), platinum-divinyltetramethyldisiloxane catalyst (Karstedt catalyst, 2.2 wt% Pt⁰) and PP2-RG01 were obtained from Gelest and used as received. A series of well-defined symmetric silicones (1,000 g mol⁻¹ – 10,000 g mol⁻¹) with a central vinyl functionality and PEG₂ (MCS-VX214), PEG₃ (MCS-VX314) and THF (MCS-VF14) end-groups were synthesized using previously reported procedures (Figure 1).^{3,4} Silicon elastomers were generated by mixing DMS-V31 and HMS-301 with varying amounts of hydrophilic additive in a 1.5mol hydride:1mol vinyl ratio and heating the mixture to 80°C in the presence of 10ppm Pt⁰ catalyst for 8 hours. PP2-RG01 samples were prepared by blending Part A with additive and mixing with Part B in a 10:1 ratio and heating at 80°C for 4 hours. **Instrumentation-** A Viscotek GPC Max VE2001 with a TDA 301 detector was used for gel permeation chromatography (GPC) analysis. 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 silicone elastomers were measured using a Shore A Durometer and Instron Model 3345.

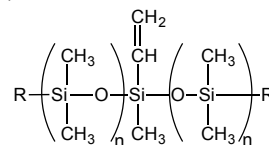


Figure 1. MCS-VX214 (R=PEG₂), MCS-VX314 (R=PEG₃) and MCS-VF14 (R=tetrahydrofurfuryl)

Results: The reactive hydrophilic silicone comonomers were blended into RTV formulations in different concentrations and cured to form optically clear silicone elastomers. Contact angle measurements of deionized water on the silicone elastomer surface showed improved wettability with comonomer content (Figure 2). Durometer measurements of PP2-RG01 showed no decrease in surface hardness (~50) in samples containing up to 20 wt.% comonomer.

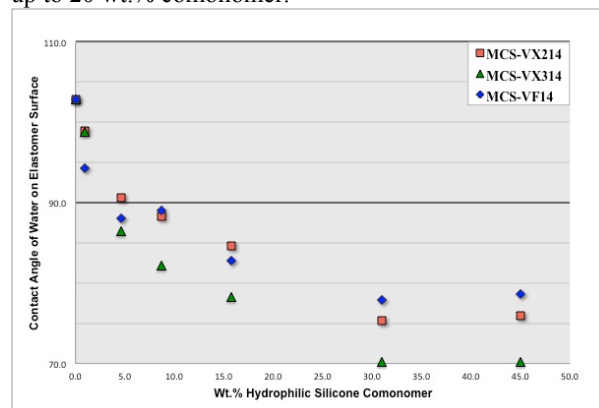


Figure 2. Contact angle of deionized water on silicone elastomers as a function of comonomer concentration

Conclusions: Contact measurements of deionized water on the silicone elastomers revealed an increase in surface wettability with increasing comonomer concentration, with MCS-VX314 providing the largest reduction in contact angle. The silicone elastomer surface became hydrophilic (contact angle < 90°) at ~5-10 wt.% additive loading for extended periods of time (> 1 month). A key advantage of this approach to surface modification of silicone elastomers is the ability to mix the comonomer with existing RTV formulations to improve wettability without compromising mechanical properties or clarity. Future studies will include differentiating protein adsorption and evaluating long term *in vivo* stability.

References:

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