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Thiol-Ene functionalized siloxanes for use as elastomeric dental impression materials

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Abstract

Objectives—Thiol- and allyl-functionalized siloxane oligomers are synthesized and evaluated for use as a radical-mediated, rapid set elastomeric dental impression material. Thiol-ene siloxane formulations are crosslinked using a redox-initiated polymerization scheme, and the mechanical properties of the thiol-ene network are manipulated through the incorporation of varying degrees of plasticizer and kaolin filler. Formulations with medium and light body consistencies are further evaluated for their ability to accurately replicate features on both the gross and microscopic levels. We hypothesize that thiol-ene functionalized siloxane systems will exhibit faster setting times and greater detail reproduction than commercially available polyvinylsiloxane (PVS) materials of comparable consistencies.

Methods—Thiol-ene functionalized siloxane mixtures formulated with varying levels of redox initiators, plasticizer, and kaolin filler are made and evaluated for their polymerization speed (FTIR), consistency (ISO4823.9.2), and surface energy (goniometer). Feature replication is evaluated quantitatively by SEM. The T_g , storage modulus, and creep behavior are determined by DMA.

Results—Increasing redox initiation rate increases the polymerization rate but at high levels also limits working time. Combining 0.86 wt% oxidizing agent with up to 5 wt% plasticizer gave a working time of 3 min and a setting time of 2 min. The selected medium and light body thiol-ene formulations also achieved greater qualitative detail reproduction than the commercial material and reproduced micrometer patterns with 98% accuracy.

Significance—Improving detail reproduction and setting speed is a primary focus of dental impression material design and synthesis. Radical-mediated polymerizations, particularly thiol-ene reactions, are recognized for their speed, reduced shrinkage, and ‘click’ nature.

Keywords

Impression material; Thiol-ene; Siloxane; Redox polymerization; Free radical

1. Introduction

Synthetic elastomeric impression materials are widely used in clinical dentistry to obtain negative replicas of hard and soft intraoral tissues from which positive gypsum casts can be prepared. Since the casts serve as templates for the fabrication of dentures, crowns, and various orthodontic appliances, precise and transferrable detail reproduction is demanded of the impression. To achieve a high degree of detail reproducibility, the impression material must possess sufficient hydrophilicity to coat moist oral surfaces and adequate fluidity to surround small features [1]. Furthermore, the impression material should be biocompatible, have reasonable working and setting times, resist permanent deformation upon removal from the mouth, and maintain dimensional stability after setting for multiple casts to be poured [2].

Towards these objectives, four classes of synthetic elastomeric dental impression materials are currently available: polysulfide, condensation silicone, addition silicone, and polyether. Although most impression materials on the market today are recognized for providing acceptable detail reproduction [3], they remain limited by their long setting times and susceptibility to dimensional instabilities [4,5]. Average setting times range from 6 min (addition silicon) to 13 min (polysulfide), with each second within the mouth serving as a source of motion-induced distortion by the patient [2]. Moreover, each class of impression material has the potential to diminish in accuracy over time. Polysulfide and condensation silicones release liquid by-products as they set, while the addition silicones (or polyvinyl siloxanes, PVS) release gas by-products. Consequently, polysulfide and condensation silicone impressions may shrink upon evaporation of water or ethanol, respectively [6,7]. Meanwhile, casts poured from PVS impressions may contain pits or voids if adequate time is not provided between full set and positive rendition [8]. Lastly, the hydrophilic nature of the polyether class of materials makes the impressions subject to swelling through absorption of moisture from the surrounding environment [9].

Clearly, the setting mechanisms employed by the current classes of materials do not offer an optimal route for a quick-setting, dimensionally stable material. Free radical-mediated polymerizations, on the other hand, are known to occur rapidly while remaining amenable to various modes of initiation including light, heat, and chemical processes [10]. Of particular interest for an impression material application is the radical-mediated thiol-ene polymerization. The thiol-ene ‘click’ reaction is well documented in the literature as proceeding at rapid rates while remaining uninhibited by oxygen, releasing no by-products, and requiring no solvents to attain quantitative conversions [11,12]. Moreover, the thiol-ene reaction mechanism proceeds through a series of alternating propagation and chain transfer events prior to termination that makes the reaction a step growth rather than a chain growth process (Fig. 1) [13]. As a result, networks formed *via* thiol-ene reactions exhibit delayed gelation and are quite homogenous. The delay in gelation is of particular importance for an impression material application since the preservation of the liquid state will allow the

working time to be extended without compromising the reaction rate. Furthermore, the limited bond capacity of sulfur leads to less volumetric shrinkage in the thiol-ene polymerization than would be seen in a comparable vinyl-based system, such as that seen in the PVS class of materials [14].

While these advantages of thiol-ene reactions have led to a significant increase in its implementation and the general reference to it as one of the most prominent of the click reactions, there are some drawbacks to the thiol-ene reaction under some circumstances as well, all of which were circumvented here by a careful selection of monomers and conditions. Odor is often cited as a significant potential issue with any thiol-containing resin; however, here, the use of higher molecular weight, purified monomers eliminates the low molecular weight impurities and compounds that cause the odor. Careful selection of the ene is also necessary to eliminate the homopolymerization reaction as has been done here. Further, others have noted that the thiol-ene reaction is not well-suited for polymer-polymer conjugation and other reactions that involve dilute concentrations of functional groups, particularly when large concentrations of photoinitiator are used [15]. Under these dilute functional group conditions, side reactions such as chain transfer to oxygen and radical-radical termination that are unimportant in bulk polymerizations such as those used here become relatively much more important.

Thiol-ene chemistry could potentially be incorporated into a wide range of monomer species; however, impression materials must be elastomeric at room temperature with adequate strength to resist tearing when removed from the mouth or significantly compressing under the weight of casting agents. Consequently, siloxanes are a fitting material selection for implementation with a thiol-ene-based setting/polymerization reaction given their noted flexibility, mechanical integrity, and biocompatibility [16]. Siloxanes are also highly amenable to functionalization, and multifunctional polymers can be readily synthesized through the condensation of pendant $-Cl$, $-OH$, or $-OR$ groups by a variety of catalytic species [17]. Hence, the primary objective of this study is to evaluate the use of thiol- and ene-functionalized siloxanes as a viable alternative to current impression materials. Specifically, a single thiol-ene functionalized siloxane formulation was synthesized, its polymerization kinetics monitored, and its network properties compared with a leading brand of PVS impression material. We hypothesize that the use of thiol-ene chemistry will produce a material with improved setting time and detail reproduction without statistically significant alteration in mechanical properties relative to a PVS impression material of similar consistency.

2. Materials and methods

2.1. Materials

3-aminopropyl(methyl) diethoxysilane ($SiNH_2$, 95%), 3-mercaptopropyl(methyl) dimethoxysilane ($SiSH$, 96%), diphenyl dimethoxysilane ($SiDP$, 98%), di-*n*-octyl dimethoxysilane ($SiDO$), and trimethylmethoxysilane ($SiMe$) were purchased from Gelest, Inc. (Morrisville, PA) and used without further purification. Allylchloroformate (97%), triethylamine (99%), *N,N*-bis(2-hydroxyethyl)-*p*-toluidine (DHEPT, 97%), benzoyl peroxide (BPO, 97%), monomethyl ether hydroquinone (MEHQ, 98%), and kaolin were

purchased from Sigma Aldrich (St. Louis, MO) and used as received. Aquasil Ultra Smart Wetting Impression Material Monophase (lot no. 091202) and LV (lot no. 091119, Dentsply, Tulsa, OK) was provided by Septodont.

3-(aminopropylmethyl)diethoxy silane was combined with allylchloroformate according to a method described in the literature to produce an allyl-functionalized silane monomer (82%) with hydrogen bonding capabilities [18]. Thiol- and allyl-functionalized siloxane oligomers were then synthesized *via* the acid-catalyzed condensation of alkoxy silane monomers, and their structural characteristics were reported previously [18]. The condensation process yielded a thiol-functionalized oligomer (99%, SiSH DP, Fig. 2a) with 7:3 SH:DP and an allyl-functionalized oligomer (99%, SiNHC=C DP DO, Fig. 2b) with 5:4:1 C=C:DP:DO.

2.2. Methods

Polymerization conversion studies were performed on formulated thiol-ene mixtures in the near IR (Nicolet Magna-IR 750 series II FTIR spectrometer) using glass slides separated by a 300 μm spacer as the sample holders. Real-time kinetics of samples containing no kaolin filler were collected at a resolution of 4 cm^{-1} and at a rate of 5 scans every 2 seconds at both room temperature (23 $^{\circ}\text{C}$) and oral temperature (35 $^{\circ}\text{C}$). The final conversions of thiol and allyl functionalities were calculated as one minus the ratio of final to initial peak areas centered at 2570 cm^{-1} (SiSH DP, S-H stretch) and 4490 cm^{-1} (SiNHC=C DP DO, C=C stretch), respectively. All measurements were completed in triplicate (i.e., $n = 3$). All samples were stored at ambient conditions (temperature and humidity) and not otherwise pretreated prior to their use in subsequent experiments.

The consistency of fully formulated siloxane samples with adequate working time was measured in accordance with ISO 4823, section 9.2 dental standards. Briefly, 0.5 mL of unset siloxane material was injected between two glass slides (7" $\times$ 5") and compressed for 5 sec with 14.7 N of force. Following the designated 15 min polymerization period, the major and minor diameters were measured, and the average of the two lengths was recorded ($n = 3$ for each sample).

Surface energy was quantified by measuring the static contact angle (DROPimage Advanced, v.2.0.10) of DI water atop a film of each crosslinked network with a goniometer (Ramé-Hart Instruments, Model 500 Advanced). Samples were prepared by injecting uncured formulations between two glass slides separated by plastic spacers (300 μm thick). Complete conversion of each experimental siloxane sample was confirmed by FTIR; the commercial PVS samples were allowed to set for the manufacturer-instructed timeframe prior to testing.

Dynamic mechanical analysis (DMA) was performed in triplicate on crosslinked thiol-ene siloxane networks and on set PVS light and medium body samples (300 μm thickness) in tension using a TA Instruments Q800 scanning at 1 $^{\circ}\text{C}/\text{min}$ from -40 to 40 $^{\circ}\text{C}$ at a frequency of 1 Hz and a strain of 0.1%. The glass transition temperature (T_g) was defined as the temperature corresponding to the maximum in the $\tan \delta$ curve. Creep recovery and stress relaxation of the medium and light bodied thiol-ene functionalized siloxanes and commercial PVS materials were also measured in tension by DMA. Creep recovery was

performed by extending samples under a constant load of 0.1 MPa for 10 min followed by 20 min recovery. Stress relaxation was conducted with an initial strain of 15% with 10 min recovery. Both test methods were run in triplicate on 600 μm thick samples at 35 $^{\circ}\text{C}$.

Feature replication was evaluated qualitatively on a centimeter size scale and quantitatively by scanning electron microscopy (SEM, JEOL JSM 7401F) on a nanometer size scale. Centimeter size scale features were constructed of rectangular solids, four-sided pyramids, and elliptical half domes in three sizes: (blocks, length $\times$ width $\times$ height) $3 \times 3 \times 6$ cm, $4 \times 3 \times 8$ cm, $5 \times 3 \times 10$ cm; (pyramids, length $\times$ width $\times$ height) $3 \times 3 \times 6$ cm, $4 \times 4 \times 8$ cm, $5 \times 5 \times 10$ cm; (domes, diameter_{major} $\times$ diameter_{minor}) 3×6 cm, 4×8 cm, 5×10 cm. The rectangular solid features were spaced 75 μm from the pyramidal features, which were separated by 50 μm from the half dome features. Replication of patterns with nanometer periodicities on silica wafers was quantified by SEM image analysis. ImageJ public domain software [19] (NIH) was used to enhance contrast and smooth images, as well as to provide initial estimates of dimensions. MATLAB software (The MathWorks, Inc.) was then used to calculate the Fast Fourier Transform of the image, which allowed the periodicity of the sample to be measured. Feature replication was quantified as the absolute percent difference between sample and substrate periodicities.

2.3. Statistical Analysis

The Student's t-test ($n = 3$, $\alpha = 0.05$) was used to compare the difference of means between PVS and thiol-ene siloxane samples at two consistency levels (light body and medium body) for the material properties under investigation. In particular, statistical analysis was performed on storage modulus, creep recovery, stress relaxation, and contact angle data sets.

3. Results

Commercial impression materials have a standard formulation that consists of reactive monomer(s), an initiating species, and an inorganic filler. Additional components such as plasticizer or surfactant can be incorporated to adjust the mechanical properties or ability to coat moist surfaces, respectively. Consequently, establishment of a novel impression material must undergo systematic variation in each of the components to determine what quantity will produce the best material. In this study, formulations of SiNHC=C DP DO/ SiSH DP with varying levels of redox initiators, plasticizer, and kaolin filler were created and evaluated to identify formulations that resulted in adequate working time, rapid setting time, and robust network properties. Polymerization kinetics of the neat SiNHC=C DP DO/ SiSH DP systems (i.e., 0 wt% DIDP and 0 wt% kaolin) are shown in Fig. 3 for varying concentrations of BPO. All formulations contained an equal molar quantity of DHEPT and BPO and a low inhibitor (i.e., MEHQ) level, 200:7 BPO:MEHQ. Clearly, polymerization rate increases directly with initiator concentration, but this appealing decrease in setting time is countered by a decrease in working time since the inhibitor fraction was held constant with respect to BPO. Therefore, an intermediate BPO fraction was selected for further evaluation with three levels of plasticizer (DIDP, 0 wt%, 1 wt% and 5 wt%). The results of the real-time FTIR testing are provided in Fig. 4. For plasticizer levels greater than zero, samples were tested at both ambient and oral temperatures, but only the kinetic profiles of samples tested under oral conditions are shown. Addition of the plasticizer increases the

working time, a feature noted by the lower conversion of allyl functionalities in the 5 wt% DIDP samples relative to the 1 wt% and 0 wt% DIDP samples. Still, at oral temperatures the final fractional conversion of all mixtures is over 80%.

Moving forward with the selected redox and plasticizer concentrations, the thermomechanical properties of crosslinked networks in both filled and neat systems were determined by DMA. The results are given in Table 1. Kaolin clay was chosen as the inorganic filler component owing to the ease with which it dispersed in the oligosiloxanes to yield highly uniform pastes. As seen in Fig. 5, the addition of plasticizer dramatically reduces the glass transition temperature but leads to a simultaneous drop in crosslink density. However, with the addition of 15 wt% kaolin filler, the decline in storage modulus is recovered while the glass transition region remains lower than seen when no plasticizer is present.

Consistency testing and contact angle studies were also performed on the fully formulated oligosiloxane systems. Consistency measurements revealed that one system fell into the ‘medium body’ category, and the remainder met the requirements for a ‘light body’ impression material (Table 1). As such, the surface energy of each crosslinked siloxane network was compared against that of a medium and a light body commercial PVS impression material (Table 1). Prior to polymerization, the experimental siloxanes proved to be more hydrophilic than the commercial material. Furthermore, at the 95% confidence level the thiol-ene networks were significantly more hydrophobic after set than the commercial PVS samples, which rapidly transitioned from a hydrophobic to a hydrophilic surface upon contact with water. Among the thiol-ene siloxane systems, the 1 wt% DIDP/10 wt% kaolin formulation showed the greatest hydrophobicity upon set and the 5 wt% DIDP/5 wt% kaolin formulation the least. None of the experimental siloxane surfaces allowed for complete water dispersion when fully crosslinked as the commercial PVS materials did.

The viscoelastic properties of the medium body thiol-ene functionalized siloxane (1 wt% DIDP/10 wt% kaolin) and the light body thiol-ene functionalized siloxane with the greatest storage modulus at intraoral temperature (5 wt% DIDP/15 wt% kaolin) were collected for comparison with the commercial medium and light body PVS impression materials. From the creep recovery experiments, the percent strain recovery ($\%\epsilon_{\text{rec}}$) was measured and is reported for all four systems in Table 2. The maximum stress (σ_{max}) induced in the test samples during stress-relaxation experiments was also determined, as was the percent stress reduction ($\%\sigma_{\text{rec}}$) following 10 min recovery. These experimental values are documented in Table 2. No statistical difference in means ($\alpha=0.05$) was observed between the PVS and thiol-ene samples in strain recovery during the creep experiments or stress reduction during the stress-relaxation experiments regardless of consistency. However, a statistical difference in means did exist for the maximum stress attained in the stress-relaxation test samples; the PVS light and medium body specimen accrued significantly higher stress during testing than the crosslinked thiol-ene functionalized siloxane specimen.

Replication of large and microscopic features was evaluated on qualitative and quantitative levels, respectively. On the visible scale, the thiol-ene functionalized siloxane systems displayed greater flow tendencies, filling the 75 μm and 50 μm spaces completely, while the

light and medium body commercial materials failed to produce distinct walls (Fig. 6). However, limited mechanical integrity of these thin films formed via the thiol-ene formulations caused the set material to tear easily upon removal from the mold. The precision of thiol-ene functionalized siloxane replication was quantified by SEM. Using patterned silica wafers as reference substrates, the percent difference in periodicity was found to be 2.5% and 1.2% for the medium and light body formulations, respectively. In other words, the formulations were able to replicate micrometer-scaled features with up to 99% accuracy. Accuracy here refers to the absolute proximity of the sample periodicity to that of the substrate without distinguishing how the deviations arose (i.e., increased periodicity between sample and substrate were treated identically to equivalent magnitudes of decreased periodicity between sample and substrate).

4. Discussion

The selection criteria for choosing thiol-ene formulations capable of performing as viable dental impression materials consisted of the inhibition period (working time), polymerization speed (setting time), consistency, and network properties (T_g and E' at 35 °C). Of the neat formulations tested, the 0.86 wt% BPO system offered the best combination of working and setting times at 1.8 ± 0.2 min and 3.4 ± 0.4 min, respectively. Here, 'working time' is defined as the time period between initial contact of the thiol and ene components and the subsequent gel point. 'Setting time' is defined as the time period between the onset of gelation and 80% allyl conversion.

By the Flory-Stockmayer equation, the thiol-ene functionalized siloxane formulation used in this study (5:4:1 C=C:DP:DO with 7:3 SH:DP in a 1:1 C=C:SH mixture) should theoretically gel at 20% allyl conversion. Using this value in conjunction with the observed rate of polymerization (taken as the initial slope of the conversion vs. time plot) allows the working and setting times to be calculated. Application of this methodology to the systems formulated with DIDP shows that the addition of the plasticizer serves to increase the working time to 2.5 ± 0.2 min at 1 wt% and 2.8 ± 0.1 min at 5 wt% while decreasing the setting time to 2.6 ± 0.8 min and 1.7 ± 0.2 min for the 1 wt% and 5 wt% DIDP levels, respectively. Relative to the commercial PVS impression material, this represents a 50% decrease in setting time while maintaining sufficient working times.

Consistency measurements revealed that only one of the thiol-ene formulations at the 0.86 wt% BPO level met the requirements for a medium body impression material. However, multiple systems possessed sufficient flow to serve as a light body material. Thus, the selection of the light body formulation was made based on its thermomechanical properties and contact angle when set (Table 1). Since the 5 wt% DIDP/15 wt% kaolin formulation displayed the highest storage modulus at 35 °C and the strongest hydrophobic tendencies when set, it was chosen as the thiol-ene comparison to the light body PVS material. Hydrophobicity improves the ability of the set material to release from oral structures, while storage modulus implicates the overall strength of the material. Consequently, a hydrophobic elastomer with a high storage modulus should exude high strength in an impression material application.

The medium and light body thiol-ene siloxanes were compared against the medium and light body commercial PVS impression material for contact angle before and after set, glass transition temperature, storage modulus (at 35 °C), creep behavior, and feature replication. As mentioned previously, the contact angles of unset thiol-ene siloxanes were more hydrophilic than the PVS material, and the contact angles of the set thiol-ene siloxanes were more hydrophobic, regardless of consistency. Clinically this translates to a liquid material that responds better to the moist oral environment and releases more readily from oral structures once set. Moreover, the negligible statistical differences in % ϵ_{rec} and % σ_{rec} between the thiol-ene systems and the commercial systems indicate that the thiol-ene functionalized siloxanes can recover from the impact forces of removal and casting to the same degree as their commercial counterparts. However, the statistically significant lower moduli in the medium body thiol-ene formulation is indicative of its lower overall strength relative to the commercial PVS material and is therefore more susceptible to tear when removed. Such damage is realized in the large feature replication studies. Although the thiol-ene formulations displayed sharper edges from their greater flow tendencies, mechanical failure was evident. Nevertheless, SEM evaluation of micro-scale features revealed 98% accuracy by the medium and light body thiol-ene functionalized siloxanes.

5. Conclusion

The thiol-ene reaction shows excellent potential as the setting mechanism in dental impression materials. Siloxane-based systems utilizing this radical-mediated technique demonstrate faster setting times with stronger hydrophilic characteristics in the unset period and hydrophobic characteristics when set than leading polyvinylsiloxane materials. More importantly, siloxanes cured by the thiol-ene reaction displayed highly accurate detail reproduction, and in the presence of greater mechanical strength that would be achieved through variable filler loading, would prove a superior impression material in clinical dentistry.

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Fig. 1. Schematic of the thiol-ene reaction mechanism. The thiol-ene polymerization proceeds through a cyclic step growth mechanism consisting of alternating propagation/chain transfer steps following initiation and prior to termination. The reaction mechanism assumes ideal conditions in which the alternating steps proceed at the same overall rate and homopolymerization of the ene is minimized.

Fig. 2.
 Silane oligomers used in this study: a) SiSH DP (SH:DP 7:3), b) SiNHC=C DP DO
 (C=C:DP:DO 5:4:1).

Fig. 3.

Conversion versus time for the oligosiloxane system formulated with three weight fractions of BPO ($\square$ 1.0 wt%, $\triangle$ 0.75 wt%, and $\circ$ 0.5 wt%). All systems contained 1:1 BPO:DHEPT and 200:7 BPO:MEHQ. Studies were performed in triplicate, and the presented data represent the averages and error bars the standard deviations. For clarity, not all data points are shown.

Fig. 4. Conversion versus time for the oligosiloxane system formulated with 0.86 wt% BPO and three levels of DIDP ($\circ$ 0 wt%, $\blacktriangle$ 1 wt%, and $\square$ 5 wt%). The systems containing DIDP were tested at oral (35 °C) temperature. All systems contained 1:1 BPO:DHEPT and 200:7 BPO:MEHQ. Data is presented as avg $\pm$ st. dev. For clarity, not all data points are shown.

Fig. 5.

Storage modulus versus temperature plot of the crosslinked oligosiloxane system in four formulations: △ 0 wt% DIDP/0 wt% kaolin, □ 5 wt% DIDP/0 wt% kaolin, ▽ 1 wt% DIDP/15 wt% kaolin, and ○ 5 wt% DIDP/15 wt% kaolin. All samples were polymerized with 0.86 wt% BPO (1:1 BPO:DHEPT, 200:7 BPO:MEHQ). Samples were collected in triplicate (avg ± st dev). For clarity, not all data points are shown.

Fig. 6.

Replication analysis of (A) centimeter and (B) micrometer scaled features: A1) centimeter-scale mold, A2) light body PVS, A3) medium body PVS, A4) medium body thiol-ene, B1) micrometer-scale mold, B2) light body thiol-ene, B3) micrometer-scale mold, B4) medium body thiol-ene.

Table 1

Summary of selection criteria used to identify viable light and medium body thiol-ene functionalized impression materials.

Siloxane system (DIDP/kaolin fraction in thiol-ene formulations)	Final allyl conversion [%]	T _g (°C)	E' (MPa) ^a	Post-set contact angle	Consistency ^b (mm)
0 wt%/0 wt%	82 (2)	3.2 (1.5)	2.8 (0.1)	80 (1)	–
1 wt%/7.5 wt%	83 (6)	–3.6 (1.7)	2.2 (0.1)	74 (1)	–
1 wt%/10 wt%	79 (4)	–5.8 (1.0)	1.5 (0.4)	82 (1)	41 (1), M
1 wt%/15 wt%	78 (5)	–4.8 (0.9)	2.4 (0.1)	81 (1)	52 (4), L
5 wt%/0 wt%	89 (2)	–8.5 (1.1)	1.1 (0.3)	80 (4)	–
5 wt%/5 wt%	77 (6)	–6.5 (0.7)	2.0 (0.2)	70 (1)	63 (4), L
5 wt%/10 wt%	79 (1)	–5.8 (1.5)	1.8 (0.4)	71 (1)	53 (1), L
5 wt%/15 wt%	79 (2)	–2.8 (0.6)	3.5 (0.6)	79 (5)	54 (0), L
Aqualil Ultra Monophase	–	–45 (0)	4.0 (0.8)	31 (7)	–, M
Aqualil Ultra LV	–	–32 (1)	3.1 (0.5)	0 (0)	–, L

^aReported at T = 35 °C.

^bConsistency measurements are denoted 'M' for medium body and 'L' for light body.

Table 2

Comparison of light and medium body thiol-ene siloxane networks with commercial PVS networks.

Siloxane system (DIDP/kaolin fraction in thiol-ene formulations)	Pre-set contact angle	% ϵ_{rec}	% σ_{rec}	σ_{max} (MPa)	Reproduction ^a
1 wt%/10 wt%	59	94 (2)	12 (7)	0.17 (0.01)	2.5%
5 wt%/15 wt%	53	94 (1)	18 (10)	0.24 (0.04)	1.2%
Aquasil Ultra Monophase	72	97 (2)	21 (8)	0.40 (0.08)	–
Aquasil Ultra LV	68	97 (2)	18 (9)	0.61 (0.01)	–

^aReproduction represented as % difference in periodicity between sample and substrate.