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Development of a 3D printable maxillofacial silicone. Part II: Optimization of moderator and thixotropic agent

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Facial prostheses can restore a patient's quality of life by disguising facial disfigurements caused by disease, trauma, or congenital deformity. Facial prosthetic fabrication is a labor-intensive process that relies on the artistic skill of maxillofacial technicians and their subjective judgements about color, fit, and texture. Digital manufacturing technologies, including 3-dimensional (3D) printing, are used by some craniofacial centers to make prostheses and remove some variability from the process.[1,2] Under those circumstances, either the prostheses are printed using hard materials that are used to make a 2-part mold, or the mold is printed directly. Subsequently, pigmented silicone is hand packed into the mold to fabricate the definitive prosthesis.[3]

Commonly available 3D printing technologies using thermoplastic materials have achieved good resolution, and some, using ink jet printing, have achieved good color fidelity. However, techniques are currently lacking for the high-quality, color-matched

ABSTRACT

Statement of problem. Conventionally, maxillofacial prostheses are fabricated by hand carving the missing anatomic defect in wax and creating a mold into which pigmented silicone elastomer is placed. Digital technologies such as computer numerical control milling and 3-dimensional (3D) printing have been used to prepare molds, directly or indirectly, into which a biocompatible pigmented silicone elastomer can be placed.

Purpose. The purpose of this in vitro study was to develop a silicone elastomer that could be 3D printed directly without a mold to create facial or body prostheses by varying its composition.

Material and methods. The room temperature vulcanizing silicone composition was divided into 2 components which were mixed 1:1 to initiate polymerization in the printer before printing began. Different types of moderators and thixotropic agents were used, and the base composition was varied to obtain 11 formulations. The specimens were printed and polymerized from these formulations and tested for tear and tensile strength and hardness. Ten readings of the specimens were recorded for tear and tensile strength and 6 for hardness. Results were analyzed using ANOVA (α=.05). Visual assessment of uncured printed specimens was undertaken for 5 formulations to assess any differences in their ability to hold their shape after printing.

Results. The tear and tensile strength of the 11 formulations with varying moderators, thixotropic agents, and base compositions were statistically similar to each other (P>.05). Five of 11 formulations were chosen for the visual assessment as they had sufficient thixotropic agent to avoid slumping while printing. The specimens showed varied slumping behavior until they polymerized. The filler content was increased in the selected formulation, and the tear and tensile strength of the formulation was increased to 6.138 kNm^{-1} and 3.836 MPa; these increases were comparable to those of commercial silicones currently used for the fabrication of facial prostheses.

Conclusions. The optimum combination of mechanical properties implies the use of one of the formulations as a suitable material for the 3D printing of facial prostheses. (J Prosthet Dent 2017;■:■-■)

printing of 2-component silicones with elastomeric properties suitable for facial prostheses. To overcome one of the challenges of the digital production of facial prostheses, it was first necessary to develop a new material that could be printed, that was suitable

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Table 1. Composition of 2 components of RTV silicone

Part A	Part B
95 g base	90 g base
5 g RTV catalyst	10 g cross-linker
Moderator	Moderator
Thixotropic agent	Thixotropic agent

RTV, room temperature vulcanizing.

for prostheses, and that exhibited controllable mechanical properties.

The chosen 3D printing method for this research was similar to the fused deposition modelling scheme but without the heated nozzle and print bed.[4] A silicone elastomer was extruded through a room-temperature deposition nozzle onto an unheated substrate in a controlled, layer-by-layer pattern. For successful printing, the silicone must flow at a controlled rate through the deposition head with modest pressure, retain the extruded shape without significant slumping, polymerize at a controlled rate, and have mechanical properties comparable to those of existing clinical silicones. Room-temperature vulcanizing (RTV) silicone systems using an unmasked platinum catalyst that polymerizes silicone without the application of heat are preferred. Although 1-component RTV silicones can be 3D printed, 2-component RTV silicones are preferable because of their biocompatibility and are therefore more suitable for prostheses in contact with the patient's tissues.[5]

Investigations into the initial development of a biocompatible silicone elastomer suitable for facial prostheses have been described.[6] The formulation of base A (70% long, 20% medium, and 10% short polydimethylsiloxane [PDMS] chains) with 2.5% catalyst and 5% cross-linker was chosen from among the 20 formulations investigated with varying amounts of long-, medium-, and short-chained PDMS and 5 concentrations of cross-linker. In this study, the silicone formulation was divided into 2 parts before printing through a customized 3D printer. The heat-activated catalyst used in the previous work was replaced by an RTV catalyst to develop a printable 2-component RTV silicone. The purpose of this study was to determine whether a 2-component silicone elastomer could be developed to print facial or body prostheses by optimizing the mechanical properties and composition.

MATERIAL AND METHODS

The 2 components (part A and part B) of the silicone were mixed in equal quantities of 1:1 during the printing process to form/print the polymerized silicone (Table 1). Part A incorporated 5% catalyst whereas part B included 10% cross-linker. The base A from the previous study was used, which was formed of 70% long, 20% medium, and 10% short PDMS chains, each with 20% w/w surface treated silica filler.[6] Base E was developed with 80% long, 15% medium, and 5% short PDMS chains, each with 20% w/w surface-treated silica filler to further increase the amount of long-chain PDMS.

Moderator was added to inhibit the polymerization rate while a thixotropic agent was used to increase the viscosity of the silicone. Moderators including 0.5-g moderator 1 (Cyclotetra siloxane inhibitor; Silanes and Silicones Ltd) and 0.15-g moderator 2 (PT 188 moderator; Wacker Chemie AG) were used to make up 100 g for the various formulations. The addition of a thixotropic agent increased the viscosity of silicone by changing the spatial distribution, increasing interparticle attractions and increasing the entanglement density of the chains.[7,8] The thixotropic agents, thixotropic agent 1 (silanol-terminated fluid; Silanes and Silicones Ltd) and thixotropic agent 2 (chain extender additive; Technovent Ltd) were used at various concentrations for different formulations. However, the concentrations of moderator and thixotropic agent were the same in both parts of the silicone. The RTV catalyst was platinum divinyltetramethyldisiloxane complex (Gelest Inc).

The silicone was printed using a customized 3D printer developed for printing 2-component RTV silicones.[9] The silicone components were housed in separate syringes and held affixed to the z-axis of the printer in controllable syringe pumps. Hence, the 2 components were pumped at a controlled volumetric flow rate and directed to a mixing device just before extrusion and deposition. The active mixer had a mixed volume of approximately 90 nL. Although this volume is small, it is sufficient to permit the active flow and simultaneous mixing of 2-component silicone for printing. The deposition nozzle was a 2-mm-long stainless steel capillary tube with an inside diameter of 0.5 mm. The linear print speed was 10 mm·s^{-1} as the printer traced the predefined patterns in the x-y-z space. This machine has a precision of 0.01 μm in the x-y plane and a precision of 0.1 to 1 μm in the z plane.

The print patterns consisted of multiple layers of silicone deposition lines printed in parallel in the x-y plane to produce the geometry desired within a layer. After printing a layer in the x-y plane, the z height was increased to build the next layer onto it and hence

complete the 3D geometry. The parallel lines within a layer and the z spacing were adjusted such that the deposited filaments overlapped sufficiently to avoid entrapment of air that could reduce the strength of the specimens. Two contours were drawn initially and filled with a series of strokes of silicone called raster infill.[4] The raster infill pattern for the subsequent layers was designed at alternating angles of 45 or 135 degrees. Ten air-free specimens were prepared for the tensile and tear testing of various formulations and were printed into standardized molds to assure identical specimen dimensions. Hardness specimens were printed without the use of molds.

The 2 components of silicone (parts A and B) were individually loaded into 10-mL Luer syringes, speed-mixed (Speedmixer DAC 150FVZ-K; Synergy Devices Ltd) to remove entrapped air, and transferred to 5-mL syringes of the customized 3D printer. The formulations with thixotropic agent were speed-mixed at 2700 rpm for 7 minutes, whereas the formulations without thixotropic agent were speed-mixed at 2700 rpm for 5 minutes.

For the tensile test, 10 dumbbell-shaped specimens were printed for each formulation and tested according to International Organization for Standardization (ISO) 37.[10-13] The thickness of the dumbbell-shaped specimens were 2 mm. Ten trouser-shaped tear test specimens were printed for each formula (100×15×2 mm) and tested according to ISO 34.[10-12,14] A cut in the test specimen was made at the center of the width of the test piece (40 mm long). Tensile and tear specimens were tested at a strain rate of 100 mm·min^{-1} with a universal testing machine (Model 5569A; Instron). Three hardness test specimens (40×25×8 mm) were printed with each specimen measured twice using a Shore A durometer (HBA 100-0; Sauter GmbH). The hardness test used in this study was based on the measurements of indentation of a rigid ball into the test specimen under specified conditions and conducted according to ISO 868.[15] Commercially available silicone specimens (M511; Technovent Ltd) were molded and used as the acceptable standard in the study.

Material rheology was characterized by testing on a rheometer (AR2000; TA Instruments) with a 40-mm-diameter, steel plate peltier. Flow experiments were conducted by using a logarithmic sweep of shear rates (0.1 to 10 001 s^{-1}). All experiments were performed under ambient conditions, with a gap height of 1000 μm and preliminary soak time of 60 seconds. Parts A and B of formulations were tested separately, and the effect of shear rate on viscosity was studied.

A visual assessment was made to indicate the ability of a formulation to hold its shape with increasing height. The tubes were printed with an internal diameter of 6 mm and an external diameter of 10 mm with 30 layers. This shape was selected to print a high object with a low volume of silicone because the material holders had a capacity of only 5 mL.

Filler content affected the tear strength and tensile strength of the resulting polymer, so the content was increased to enhance these properties. Base A was composed of long, medium, and short PDMS chains with 20% filler. Additional filler was added to the base to make up to 30% w/w. This base was then used to prepare silicone part A and B for printing.

Data for mechanical tests were analyzed using software (Stata v14.1; Stata Corp LP) (α=.05). The normality of residuals, an assumption for a valid analysis of variance (ANOVA), was tested graphically using normal probability plots in conjunction with the procedure described by Cox.[16] The Šidák method was used to adjust for multiple comparisons between different formulations.[16]

RESULTS

The 2-component RTV silicone specimens were printed with various formulations of moderator and thixotropic agent, and the mechanical properties observed are listed in Table 2. The hardness test was undertaken with formulations III, VI, VII, X, and XI, which could be printed without molds or any support material and had a minimum of 3 g moderator 1 or 0.5 g moderator 2 per 100 g of formulation (Table 2).

The rheology was tested for both parts of formulations I, III, V, VII, IX, and X. Figure 1 shows the part A and part B of formulation I and III, which only differ in the content of thixotropic agent. Formulation III had 3 g of thixotropic agent 1 while formulation I did not, and its viscosity was lower than formulation III at all shear rates. With increasing shear rates, the silicone was showing shear thinning effect and viscosity was decreasing. The shear rate of the printing with an 0.5-mm tip at 10 mm·s^{-1} was 40 s^{-1}.
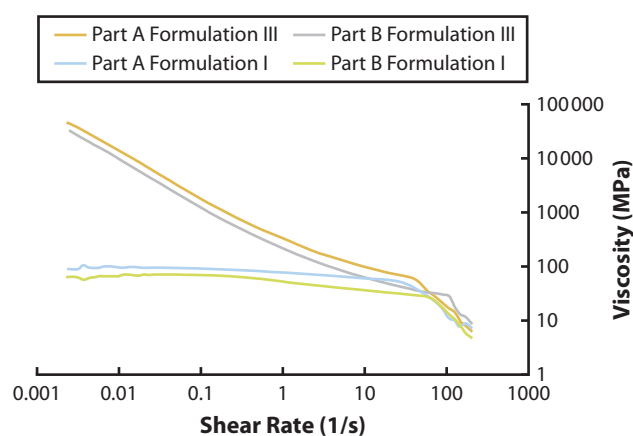
The tubes printed with formulations III, VI, VII, X, and XI are shown in Figure 2. The tubes printed well and slumped over time while polymerizing. Visually, formulation III provided the optimum result as the tube maintained its shape. This formula was therefore selected over others for the next experiment of increased filler concentration.

The filler content of the formulation was increased to 30%, and the results of the mechanical tests are shown in Table 2 for formulations XII and XIII. They show a significant increase in tear and tensile strength and are comparable with commercial silicone M511 (Technovent Ltd).[5] The tubes printed with formulation XIII (with thixotropic agent 1) retained their shape whereas the tubes of formulation XII did not. The results of the ANOVA showed a significant difference between the formulations for tear and tensile strength (Table 3). The

Table 2. Tear and tensile strength of printed formulations

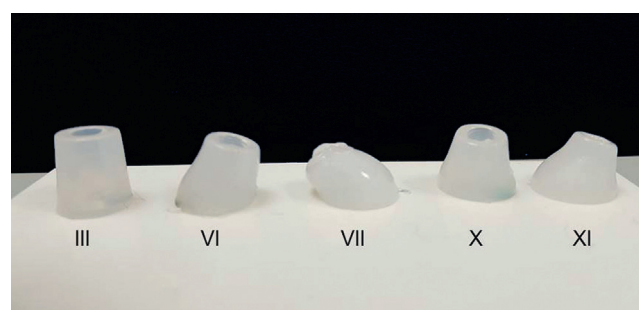| Formulation	Base	Moderator	Thixotropic Agent	Tear Strength ±SD (kN m⁻¹)	Tensile Strength ±SD (MPa)	Hardness ±SD (Shore A)
I	A	1	0	3.076 ±0.75	1.634 ±0.2	
II	A	1	1.5 g thixotropic agent 1	1.804 ±0.34	1.217 ±0.15	
III	A	1	3 g thixotropic agent 1	1.587 ±0.11	1.26 ±0.2	20.2 ±0.41
IV	A	2	0	2.464 ±0.61	1.694 ±0.3	
V	A	2	0.25 g thixotropic agent 2	2.737 ±0.6	1.6 ±0.13	
VI	A	2	0.5 g thixotropic agent 2	2.344 ±0.4	1.573 ±0.11	19.7 ±0.52
VII	A	2	0.75 g thixotropic agent 2	2.501 ±0.39	1.702 ±0.18	20.2 ±0.41
VIII	E	2	0	2.811 ±0.7	1.62 ±0.2	
IX	E	1	0	2.712 ±0.76	1.54 ±0.17	
X	E	1	0.5 g thixotropic agent 2	2.277 ±0.3	1.571 ±0.05	21.5 ±0.55
XI	E	1	0.75 g thixotropic agent 2	2.198 ±0.44	1.592 ±0.23	21.2 ±0.75
XII	A-30	1	0	7.057 ±0.98	4.297 ±0.22	
XIII	A-30	1	3 g thixotropic agent 1	6.138 ±1.28	3.836 ±0.3	22.2 ±0.9
M511				8.002 ±0.56	3.804 ±0.36	18.7 ±0.47

Mean (±SD) g of thixotropic agent show amount in 100 g of each formulation.

Figure 1. Change in viscosity with increasing shear rate.

Figure 2. Tubes printed using formulations III, VI, VII, X, and XI.

Table 3. ANOVA for 13 formulations

	Sum of Squares	df	Mean Square	F	P
Tear strength					
Between formulations	320.17	12	26.68	58.13	.001
Within samples	53.71	117	0.46		
Total	373.87	129	2.89		
Tensile strength					
Between formulations	111.11	12	9.26	227.95	.001
Within samples	4.75	117	0.04		
Total	115.86	129	0.89		

Šidák analysis showed that formulations sharing letters in groups were not significantly different at the 5% level (Table 4).

DISCUSSION

The research demonstrated that 3D printing of 2-component silicone elastomers with appropriate mechanical properties could be used to fabricate facial or body prostheses. The process of 3D printing involves printing layers of the material one on top of the other to create a complete object. Therefore, while the silicone is being printed, the layers must retain their extruded shape without significant slumping to support the layers being built above. Additionally, the polymerization rate must be controllable, and the mechanical properties must be comparable with existing clinical silicones. The RTV silicone for printing had to be divided into 2 parts as the catalyst needed to be kept separate from the cross-linker to avoid initiation of the polymerizing reaction. The 2 parts were created such that equal volumes were needed

for polymerization. Part A was made up of 95% base and 5% catalyst, while part B consisted of 90% base and 10% cross-linker. Equal amounts of moderator and thixotropic agent were added into parts A and B of different formulations.

The RTV was a rapid-acting catalyst, and polymerization occurred during the mixing of the 2 components in less than 1 minute. Hence, the silicone was polymerizing in the mixing chamber, and thus, extrusion of the silicone was prevented. Consequently, a moderator which inhibited and slowed the hydroxylation cross-linking reaction at the vinyl end groups of PDMS chains was added to both parts to inhibit the polymerizing rate. As a result, the working time was increased to 30 minutes.

Table 4. Šidák analysis of differences between formulations

Formulation	Tear Strength (kN·m⁻¹)		Tensile Strength (MPa)	
	Mean Values	Šidák Groups	Mean Values	Šidák Groups
I	1.587	C	1.26	BC
II	1.805	AC	1.217	C
III	3.076	B	1.634	A
IV	2.465	ABC	1.601	A
V	2.737	AB	1.573	A
VI	2.344	ABC	1.702	AB
VII	2.502	ABC	1.62	A
VIII	2.811	AB	1.54	A
IX	2.713	AB	1.57	AB
X	2.277	ABC	1.571	AB
XI	2.199	ABC	1.592	A
XII	7.057	D	4.297	
XIII	6.138	D	3.836	

The layers of the printed silicone did not maintain their shape, and the subsequent layers to be printed did not have a stable base. This behavior hindered printing as the layers above did not have a stable base to print on. This resulted in uneven printing and entrapment of air. The problem was resolved by adding a thixotropic agent to both parts of the silicone elastomer. Varying amounts of thixotropic agent were added to silicone to increase its viscosity and their effect on printed specimens was observed. The addition of a thixotropic agent made the silicone slightly translucent yet suitable for printing, as the silicone specimens could hold their shape thereafter. The thixotropic agent was responsible for increasing the viscosity of silicone by changing the spatial distribution, increasing interparticle attractions, and increasing the entanglement density of the chains.[7,8]

In a previous paper,[6] it was shown that base A with 2.5% catalyst and 5% cross-linker had a tensile and tear strength of 3.524 MPa and 8.484 kNm⁻¹ which decreased to 1.634 MPa and 3.076 kNm s⁻¹, respectively with addition of moderator (Table 2, Formulation I). It further decreased to 1.26 MPa and 1.587 kNm⁻¹ with the addition of 3% thixotropic agent (Table 2, Formulation III). Thus, the addition of moderator and thixotropic agent decreased the tear and tensile strength of silicone.

The tear strength of formulations I to VII were lower than that of the commercial silicone M511 (8.002 kN·m⁻¹). Formulations I, III, IV, and VI were also polymerized under pressure by hand packing and polymerizing. Because the polymerization reaction does not require air, the specimens polymerized. The hand-packed specimens showed higher tear and tensile strength than printed specimens polymerized without pressure. This explains the decreased strength of printed formulations.

Moderator 1 at 0.25% was used for printing with the working time of 15 minutes, but the printing was disturbed and often led to blocked print head channels.

Therefore, 0.5% moderator 1 was chosen with a working time of 30 minutes. This working time was suitable for printing. Moderator 2 was concentrated, and 0.15 g was sufficient to achieve a working time of 30 minutes. Different concentrations of thixotropic agents were added to find the most suitable for printing. The specimens with 1.5 g thixotropic agent 1 did not retain their shape, so 3 g of thixotropic agent 1 was tested. These specimens retained their shape, and further additions of the thixotropic agent were not required.

The addition of moderator 1 and/or thixotropic agent 1 to the formulation decreased the tear and tensile strength of silicone. To enhance the tear strength, a different moderator and a thixotropic agent; moderator 2 and thixotropic agent 2 were added which had a similar mechanism of action but differing carrying agents and concentrations of active ingredients. Thixotropic agent 2 showed statistically insignificant variation on tear strength. Both of the thixotropic agents act by forming temporary hydrogen bonds with silanol groups on the surface of filler particles, and both of them act by slightly slowing the hydrosilylation process during cross-linking. It would seem that moderator 1 is too aggressive in its moderation of the reaction and in effect is permanently inhibiting cross-linking causing a reduction in tear strength. The reason for the differences seen when using the thixotropic agents is less clear. It is possible thixotropic agent 1 is also inhibiting the reaction or the effect on the filler is not being completely neutralized during polymerization thus reducing the strengthening effect of the filler.

Base A showed maximum tear strength (2.737 kN·m⁻¹) with moderator 2 and thixotropic agent 2, but to further increase the strength, the number of long-chain PDMS was increased in the formulation. Hence, the percentage of long-chain PDMS within the formula was increased from 70% to 80%. It also had 15% of medium-length and 5% of short-chain PDMS. This was named Base E. With base E, 2.5% catalyst, 5% cross-linker, moderator 1, and thixotropic agent 2 were added.

The difference in tear and tensile strength between the highest and lowest values of formulations was less than 1.2 kN·m⁻¹ and 0.5 MPa, respectively. This was practically insignificant, and the use of any particular formulation was not justified. A hardness test was undertaken to investigate possible differences between formulations. The combinations with at least 3 g thixotropic agent 1 and 0.5 g thixotropic agent 2 were printable while others were not because they could not retain their shape until the silicone had completely polymerized. Therefore, the hardness test was undertaken only for 5 formulations that could be used for further printing. The results of hardness testing showed variation between 19.7 and 21.5 Shore A for the formulations with the thixotropic agent. These differences were not statistically different. Hence further experimentation was required to

determine whether any differences existed between the formulations.

Rheology tests were performed to observe any differences between the formulations. Part A for each formulation was more viscous than part B because part B had 10% cross-linker, which was a liquid, leading to decreased viscosity of part B. Formulation I (no thixotropic agent) was shown to have nearly newtonian behavior at low shear rate (approximately $\gamma < 50 \cdot s^{-1}$), followed by shear-thinning behavior up to the maximum tested shear rate. In contrast, formulation III (containing thixotropic agent) displayed shear thinning behavior across the entire shear rate range tested. The rheology of part A and B had to be tested separately as the mixed formulation would polymerize in the rheometer. Although flow through the deposition head was achieved by all formulations, shape retention of the printed part was used to distinguish the printability of the various formulations.

The tubes were printed with the 5 formulations, and the results showed that the tube of formulation III best reproduced the designed part. The retention of good shape agrees well with the observed rheology in that high viscosity in the low shear rate regimen favors less flow after printing. This formulation was thus selected for further work.

The filler loading was increased in the chosen formulation of base A with 0.5 g of moderator 1 and 3 g of thixotropic agent 1 from 20% to 30%. Speed-mixing was insufficient to mix the filler particles into the base; therefore, a planetary mixer was used. The mixing was adequate, but air bubbles were observed trapped within the silicone. Speed-mixing was performed thereafter to remove the trapped air. The mixture had to be mixed for 5 minutes to obtain a homogenous mixture of filler. If continuous mixing for 5 minutes was applied, the lids of mixing pots were damaged inside the speedmixer and were very hot, making it necessary to open them every minute to release the generated hot air. Generally, heat generated by speed-mixing would accelerate the catalyzing reaction in RTV silicone. Because the 2 parts of silicone were kept in different pots, the silicone did not polymerize with the heat generated. The increased filler content made the formulation very viscous, but the tubes were still not printable without the thixotropic agent (Formulation XII). The tear and tensile strengths of formulation XII and XIII increased and were comparable with those of currently used commercial silicone elastomers.

CONCLUSIONS

Based on the results of this in vitro testing, the following conclusions were drawn:

1. The novel 2-component RTV silicone is printable and the hardness, tear, and tensile strength were within acceptable ranges for use as facial prostheses.
2. Addition of moderator and/or thixotropic agent decreased the tear and tensile strength of silicone, whereas increased filler content increased the tear and tensile strength.

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