

The use of Polyurethane to strengthen silicone aesthetic prostheses

Nicholas Zacharias,¹ Rodrigo Umanzor,¹ Eduardo Enriquez,¹ Vincent Belsito,¹ Piper Rawding,² Laurie McKenna²

¹Department of Biomedical Engineering, University of Wisconsin-Madison

²Department of Material Science and Engineering, University of Wisconsin-Madison

Abstract

Study Design: A series of mechanical tests were conducted on silicone, polyurethane, and polyurethane-coated silicone samples. From these tests, the peel strength, tear strength, coefficient of friction, and UV degradation rate were determined.

Background: Silicone is widely used in the aesthetic prosthetic industry due to its high levels of customizability, which allow for the reproduction of lifelike appendages. Silicone, however, has unsatisfactory mechanical properties, which prevent prostheses from providing patients with a cost effective life-in-service time. By coating the silicone with polyurethane, conventional silicone prostheses can exhibit improved mechanical properties and increased lifespans.

Objectives: To test the hypothesis that a polyurethane coating on a silicone aesthetic prosthesis would improve its overall mechanical properties, without affecting aesthetic qualities.

Methods: To quantify the mechanical properties and dynamic performance of the polyurethane-silicone composite, a series of tests and statistical analyses were conducted.

Results: Testing showed that polyurethane-silicone composites have the ability to enhance tear strength over silicone prosthetics, can form an interfacial bond strength greater than 1.4 N/mm, and decrease UV degradation rate. Mixed results were observed in the adhesive strength and coefficient of friction testing. A polyurethane-silicone composite is expected to improve the mechanical properties of aesthetic prostheses.

Clinical Relevance

This study aids to understand the different materials that can be combined when creating aesthetic prostheses to improve quality of life for patients who have experienced amputations or disfigurement.

Background

Individuals who undergo amputations or have disfigurements often experience severe psychological trauma due to their physical appearances that can hinder them from feeling integrated into society [1]. Aesthetic prostheses were introduced to help people with disfigurements go unnoticed in modern society via aesthetic restoration. Finger prostheses are common devices for those who have lost a finger, and while they are passive, they can indirectly improve function of the hand by covering the affected area and allowing for patients to use their hands without fear of others noticing their deformities. As a result, the patient often experiences both psychological and physical improvements, which results in an overall enhanced rehabilitation process [2]. Current aesthetic prostheses are primarily composed of silicone due to its high level of customizability, which allow for the recreation of life-like appendages; these prostheses, however, commonly fail and have a reduced life-in-service due to mechanical deformations or mold and fungal build up [3,4]. In order to increase the overall durability of aesthetic prostheses, binding polyurethane (PU) onto silicone to create a composite has been

considered [3]. Limitations with the current methodology of binding PU to silicone include an incompatibility with three-dimensional structures, such as finger prostheses, and a propensity for failure at the adhesive interface between the two materials [3]. It is proposed that these methods could be improved by utilizing a primer to bind silicone to PU. Preliminary work has indicated the ability to achieve a stronger adhesive bond than the silicone matrix [4]. Overall, it is hypothesized that developing a PU coating on silicone aesthetic prostheses will improve the prostheses' mechanical properties, without affecting the aesthetic qualities.

Methods

Sample Preparation: All samples for subsequent tests were prepared in 37.5 or 60 mm diameter petri dishes. Two fabrication methods were performed, the first using a single-cylinder, oil-less piston compressor to power an airbrush to deliver PU (SC-92 PU diluted 3:7 diH₂O:PU v/v) into the petri dish. Following 5 layers of PU application, the average PU thickness was 0.39 mm (SD = 0.12 mm). Given the petri dish area of 1943.91 mm², an average of 758.12 mm³ of PU added to each dish. Between each layering, the dish was placed onto a hot plate at 70°C for two minutes to allow for partial curing of the PU. The samples were then allowed to fully cure over 24 hours at 23.5°C. 100 µL of Sofreliner T primer (Tokuyama-US) was spread onto the PU using a small paintbrush, and allowed to react with the PU surface for

50 minutes before adding RTV-4420, VST-30, or A-2186F silicone (Factor II). At least 24 hours were allowed to pass before testing the final sample. The outline for this procedure is depicted in Figure 1A. The second method, conversely, involves the forming and priming of the silicone layer first, before applying layers of PU. The second method will allow the anaplastologist to create a fully functional silicone prosthetic as is currently done in industry before adding a layer of PU to add durability to the prosthetic.

Peel Strength: Peel strength was quantified by the resistance of the PU and silicone (RTV-4420, VST-30, or A-2186F) layers to peel from one another under a constant crosshead speed [4-6]. Given material restrictions, sample geometry was limited. This test requires free, unadhered ends in order to peel the layers apart. Thus, pieces of tape were placed on the edge of the sample prior to the addition of the second material. Samples were cut into rectangular segments with dimensions of approximately 43x 7 mm² with a thickness of about 3 mm in the silicone layer, and 0.2 mm in the PU layer. The silicone and PU layers were loaded into the top and bottom clamps, respectively, of a MTS machine as shown in Figure 1B and separated at a crosshead speed of 25.4 mm/min until either separation of the adhesive bond or failure of the silicone or PU component. The MTS machine output force, displacement, and time data, that was plotted and analyzed in MATLAB. Peak values were extracted from the loading profiles to represent the peak peel strength unnormalized and normalized to width of the sample. The mean peel strength required to propagate peeling following the initial peak [4-6] was obtained by determining the average load during the peeling process following the peak.

Tear Strength: The tear strength quantifies the resistance of materials to applied shear stresses [7-11]. RTV-4420 silicone samples were prepared in 37.5 mm diameter petri dishes with variable thicknesses (0.503-0.991 mm). PU samples were prepared in 49.75 mm petri dishes at 5, 10, and 15 layers to create variable thickness samples (0.21884-0.86106mm). An initial tear was made through two-thirds of the sample. The peak load required to propagate the tearing perpendicular to the circular plane was acquired at a crosshead speed of 20 mm/min on an MTS machine, as shown in Figure 1C [10]. The loads were normalized to sample thickness to acquire tear strength after verifying a linear relationship between tear load and sample thickness [7,8].

Coefficient of Friction (CoF): Two sets of samples were made using Silicone RTV-4420 and SI-2186, yielding a total of six samples. These samples were cut into 32 mm diameter circles to match the size of the Nano-tribometer mounting platform. Three sets of experiments were carried out at different normal loads (10, 20, and 50 mN), and repeated three times. For each experiment, a 2 mm diameter probe with a gliding range of 250 μm was used and the InstrumX software was set to carryout 180 iterations (3 minute testing period) at a 400 Hz acquisition frequency while sampling data for each cycle. Surface images using a 4X objective microscope were captured before and after each test. Using a MATLAB script the peak values were obtained and averaged to obtain the CoF for each sample. The first 20 seconds of data collection were excluded to account for the time required for the normal load to stabilize upon contact initiation.

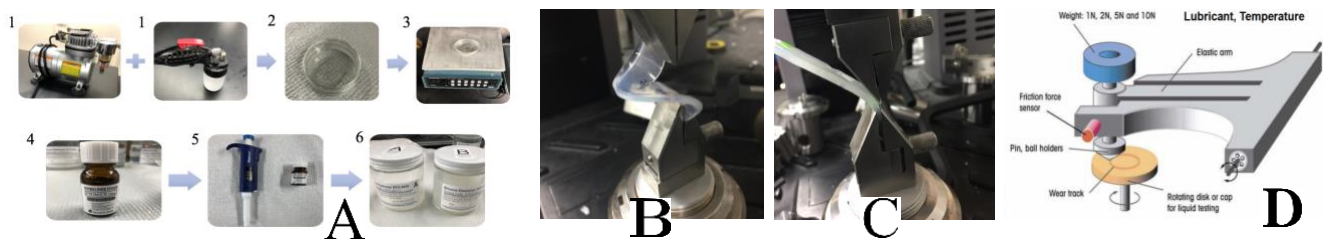


Figure 1: A. Sequence of steps for sample fabrication. 1. Load PU into the airbrush. 2-3. Airbrush multiple layers into a petri dish, while heating after adding each layer, and allow curing overnight. 4-5. Add Sofreliner T primer via pipette. 6. Mix silicone parts A and B 1:1 and add to primed PU surface. B. A sample loaded in the MTS machine prior to the bond strength testing. C. Silicone sample loaded in the MTS grips prior to tear. D. Schematic of the main components of the nano-tribometer.

UV Degradation: A sample of silicone and PU-coated silicone were created and tested according to ASTM D1148. [1-3,14] These samples were placed under an RSM Type 275 W, 125 V sun-lamp bulb contained in a metal housing test chamber and exposed to light for 340 hours. This setup allowed for a UV intensity of 1.05 mW/cm², which is approximately 1.4 times greater than natural sunlight intensity. The samples were imaged every 10 hours, and the degree of discoloration was determined qualitatively by rating the samples against each other. The change in color was also measured instrumentally using a light box colorimeter and the color difference (ΔL) between the samples at different time points was calculated using the following equation:

$$\Delta L = L_2 - L_1$$

Results

Peel Strength: Varying results were found in adhesive strength based on the silicone used and the fabrication method. Results are shown in Figure 2A. The highest peak peel load (15.56±1.62 N), peak peel strength (1.74±0.10 N/mm), and mean peel strength (1.46±0.11 N/mm) were observed in the A-2186F silicone when the PU was applied first, while the lowest peak peel load (1.40±0.42 N), peak peel strength (0.16±0.04 N/mm), and mean peel strength (0.12±0.03 N/mm) were observed in the A-2186F silicone when the silicone was applied first. When using the RTV-4420 silicone, in both the silicone-first and the PU-first samples, there was tearing in the silicone

before any adhesive failure was measured, so mean peel strength was not determined. Additionally, while a peak peel load and peak peel strength were measured, the actual values are likely greater given the silicone failure. Significant differences were found between the peak peel strengths of the silicone-first samples and PU-first samples using both the VST-30 silicone (p-value < 0.01) and A-2186F silicone (p-value < 0.00005). Because the peak peel strength using the RTV-4420 silicone was not fully quantified, the difference was not analyzed for significance.

Tear Strength: Thickness and peak tear load was plotted (Figure 2B). The results indicated a linear trend for RTV-4420 silicone (5.5171x-1.6844; R²: 0.9654). However, SC-92 PU exhibited less linearity (15.208x+1.8452; R²: 0.81305). SC-92 PU was shown to have 6-fold greater tear strength (19.44±3.43 N/mm) compared to RTV-4420 silicone (3.15±0.70 N/mm) with a P-value < 0.0005 between materials. This data, along with tear strength calculated for 5, 10, and 15 layers of PU, is shown in Figure 2C.

Coefficient of Friction: The average CoF for PU-coated samples was found to be lower (p-value < 0.05) than either of the two silicone variants (Table 1) and there was at least a 57% decrease and a maximum of 77% decrease in CoF observed in the specimens containing the PU layer (Figure 2D).

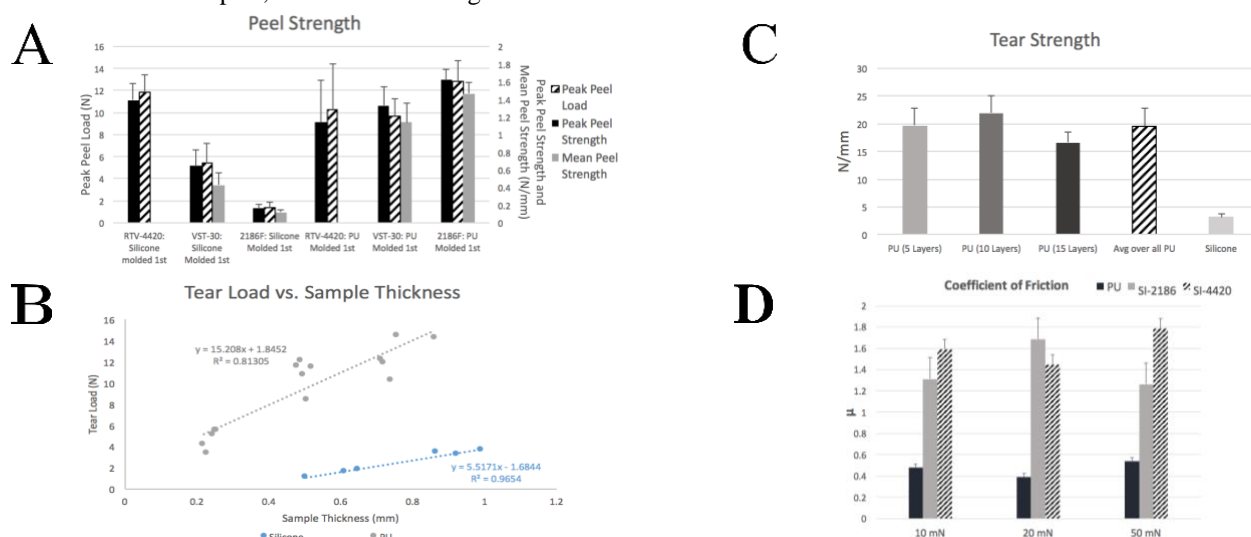


Figure 2: **A.** Comparison of peel strength between different silicones and fabrication methods. **B:** Load necessary to propagate an initial tear in a sample plotted against the thickness of the sample and fitted with a linear trend. **C:** Tear strength for samples prepared at 5, 10, and 15 layers for PU and variable thickness along a similar range for silicone. **D:** Average CoF values for all three samples at 10, 20, and 50 mN normal loads.

Table 1: Coefficient of friction data showing values for PU and silicone samples.

Coefficient of Friction of PU and Silicone			
Normal Load	PU	SI-2186	RTV-4420
10 mN	0.478	1.312	1.590
20 mN	0.390	1.687	1.449
50 mN	0.540	1.263	1.787

UV Degradation: Following completion of UV testing, the initial and final images from the two samples were compared (Figure 3). The control silicone sample showed approximately a 50% darkening in color, and significant degradation. The PU coated silicone sample, on the other hand, showed approximately a 20% darkening in color, and minimal degradation, centralized to the sides of the sample where the PU was weakly bound to the silicone. Using a colorimeter, data was collected, and the color difference was determined (Table 2). The data showed that silicone experienced twice as much darkening from UV exposure as opposed to PU coated silicone.

Table 2: Colorimeter data showing color value for silicone and PU coated silicone samples.

Time Point (hr)	Sample Coloration Value (L)	
	Silicone (Control)	PU coated Si
0	213	213
340	103	162
ΔL	-110	-51

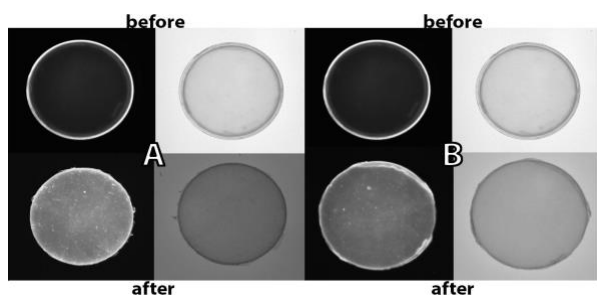


Figure 3: Images showing A: silicone control sample and B: PU coated silicone before and after 340 hours of UV degradation

Discussion

Peel Strength: As mentioned, the highest peak peel load, peak peel strength, and mean peel strength was measured with the A-2186F silicone in the PU-first samples. While

this is a desirable result, the best adhesion was observed in the RTV-4420 silicone, where the silicone tore before the adhesive bond failed. This indicates that for prosthetic fabrication, it may be best to use RTV-4420 silicone whether the silicone or the PU is applied to the mold first. If A-2186F silicone were used, it would be best to apply the PU first. It is unclear why the order of application had such a large effect, but it may be related to differences in the way silicone or PU interacted with the primer when fully cured vs while curing. VST-30 silicone also displayed improved adhesive qualities when the PU was applied first. Lower adhesion strength would lead to easier separation of the materials, creating unattached pockets throughout the prosthetic that would impact its appearance and longevity.

Tear Strength: The six-fold increase in tear strength from RTV-4420 silicone to SC-92 PU shows a potential for enhanced resistance to shear deformation when PU is sufficiently bound and coated on a silicone prosthetic. The large difference in tear strength between silicone and PU samples is likely a result of differences in their respective molecular weights (MWs). In general, the stiffness and strength of a material increases with MW [13]. Liquid silicone elastomers used in the fabrication of prosthetics have repeating units with MW of 204 g/mol whereas the repeating monomer units of PU elastomers have a MW of 548.59 g/mol. Hence, the material with higher MW values is expected to have a higher tear strength when evaluated under the same mechanical conditions. Although not tested in this study, a Silicone-PU composite material would theoretically provide a higher tear strength relative to the silicone component.

The variation in tear strength between samples of different layers of PU is expected to have a limited effect on the comparison to silicone because all thicknesses showed a large improvement over silicone. It is important to note, however, that future tests should be conducted with a greater sample size and more intermediate values of thickness in the range of 5, 10, and 15 layers to fully elucidate the trend between thickness and tear load. The results also indicate a significant difference between the materials under the aforementioned testing conditions. The performance of a material during a tear test can be highly dependent on the testing arrangement, especially with regards to strain rate given the viscoelastic properties of PU and silicone [8]. These results are only meant to show a potential for shear resistance during life in service, but cannot guarantee it given variable loads, loading directions, and loading rates during prosthetic use.

Coefficient of Friction: The CoF profiles for the proposed PU coated silicone material composition were in line with predictions. At all three loading conditions, the material with PU was quantified to have a CoF at least

57% less than both of the silicone variants. This decreased CoF would reduce the likelihood of the prosthesis from catching on fabrics and other materials during everyday use. Additionally, this would help with preventing the prosthetic device from being dislodged from its attachment site as the patient's hand comes in contact with various surfaces throughout the day. A lower CoF is also indicative of an expected decrease in wear from abrasion when compared to the current silicone based models, although it does not directly translate to an increased longevity.

Wear Rate: While wear rate was tested using the Nano Tribometer, the machine was unable to cause permanent deformation on the samples and so the data was not reflective of true wear. Wear rate testing using a surface abrader must be done to determine any effects on wear rate from the PU coating.

UV Degradation: While both samples degraded due to UV exposure, the PU coated silicone sample did not change color and darken to the extent that the silicone control sample did. This signifies that the PU is effective at preserving the underlying silicone, thereby making a PU coated silicone prosthesis less prone to UV degradation. Given that a limited sample size was used for this set of tests ($n < 3$), no statistical implications can be drawn from these results.

Conclusions

In this study, the binding of PU and silicone was investigated for aesthetic prosthesis purposes. It was determined that the use of Sofreliner-T Primer allowed for the creation of a composite polymer prosthesis that does not fail at the materials interface. Furthermore, the PU coating was found to reduce the CoF, thereby decreasing the generation of friction forces during use. In addition, due to the increased mechanical properties of PU, the risk of failure at thin areas, such as the locations that engage with the digit residuum, is decreased. While PU significantly increases the mechanical properties of the aesthetic prosthesis, the two currently used adhesion methods do not seem capable of creating a aesthetic prosthesis without severe detrimental effects to the appearance. On account of this, the adhesion method must be developed further to ensure no negative impact on esthetic appeal and at this point the composite prosthesis cannot be recommended as a replacement of the normal silicone prosthesis manufacturing method.

Acknowledgments

The authors would like to thank Mr. Gregory Gion, Dr.

Tracy Puccinelli, Mr. Russ Haas, and Mr. Ahmet Deniz Usta.

Declaration of conflicting interests

The authors declared no potential conflicts of interest with regard to the research and authorship of this manuscript.

Funding

All funding for this manuscript was supplied by Mr. Gregory Gion.

References

1. J. Pillet and A. Didierjean-Pillet, "Aesthetic Hand Prosthesis: Gadget or Therapy? Presentation of a New Classification," *Journal of Hand Surgery*, vol. 26, no. 6, pp. 523–528, 2001.
2. Bowker, John H., and John W. Michael. *Atlas of limb prosthetics: surgical, prosthetic, and rehabilitation principles*. 2nd ed., Mosby Year Book, 2002.
3. A. Udagama, "URETHANE-LINED SILICONE FACIAL PROSTHESES," *Journal of Prosthetic Dentistry*, vol. 58, no. 3, pp. 351-354, Sep 1987.
4. P. P. Chang, N. A. Hansen, R. D. Phoenix, and T. R. Schneid, "The Effects of Primers and Surface Bonding Characteristics on the Adhesion of PU to Two Commonly Used Silicone Elastomers," *Journal of Prosthodontics*, vol. 18, no. 1, pp. 23–31, 200
5. G. L. Polyzois, A. Hensten-Pettersen, and A. Kullmann, "An assessment of the physical properties and biocompatibility of three silicone elastomers," *The Journal of Prosthetic Dentistry*, vol. 71, no. 5, pp. 500–504, 1994.
6. American Society for Testing and Materials: Standard test for peel resistance, D1876, West Conshohocken, PA, ASTM, 2001.
7. T. Aziz, M. Waters, and R. Jagger, "Analysis of the properties of silicone rubber maxillofacial prosthetic materials," *Journal of Dentistry*, vol. 31, no. 1, pp. 67–74, 2003.
8. "ASTM D624 - 00(2012) Standard Test Method for Tear of Conventional Vulcanized Rubber and Thermoplastic Elastomers," ASTM International, 2012. [Online].
9. "Standard Test Method for Tear-Propagation Resistance (Trouser Tear) of Plastic Film and Thin Sheet by a Single-Tear Method," *ASTM Compass*. [Online].
10. R. A. Sanchez, D. J. Moore, D. L. Cruz, and R. Chappell, "Comparison of the physical properties of two types of polydimethyl siloxane for fabrication of facial prostheses," *The Journal of Prosthetic Dentistry*, vol. 67, no. 5, pp. 679–682, 1992.
11. G. L. Polyzois, A. Hensten-Pettersen, and A. Kullmann, "An assessment of the physical properties and biocompatibility of three silicone elastomers," *The Journal of Prosthetic Dentistry*, vol. 71, no. 5, pp. 500–

504, 1994.

12. AZoNano.com. (2017). *Tribometer for Tribology of Polymers*. [online]

13. T. Osswald and G. Menges, *Material science of polymers for engineers*, 3rd ed. Munich [Germany]: Hanser Publishers, 2012, pp. 50-80.

14. "ASTM 1148-95(2011) Standard Test Method for Rubber Deterioration-Heat and Ultraviolet Light Discoloration for Light-Colored Surfaces," ASTM International, 2011. [Online].