International Journal of Adhesion & Adhesives 54 (2014) 206–213

Contents lists available at ScienceDirect

International Journal of Adhesion & Adhesives

journal homepage: www.elsevier.com/locate/ijadhadh

Bonding of facial silicon with nanoparticles to an acrylic resin substrate

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ARTICLE INFO

Article history:
Accepted 6 June 2014
Available online 7 July 2014

Keywords:
Acrylic resin
Silicone elastomer
Nanoparticles
Maxillofacial prostheses
Aging

ABSTRACT

The aim of this study was to evaluate the influence of different adhesive techniques and accelerated aging on the bonding of maxillofacial biomedical silicone to an acrylic resin substrate. 960 acrylic resin samples (PMMA) were manufactured and bonded to the silicone with or without oil painting and/or opacifier. Both materials were bonded through mechanical retentions and/or application of primers (DC 1205 primer and Sofreliner primer S) and adhesive (Silastic Medical Adhesive Type A) or not (control group). The samples dimension were 75-mm length, 10-mm width and 6-mm thickness.The samples were divided in 4 groups ($n=240$) for the pigmentation variable, and 12 subgroups ($n=20$) accordingly to the bonding technique. Half of the samples of each group underwent the peel test at baseline and the fracture pattern was measured through direct observation and SEM and then classified into adhesive, cohesive and both failure. The remaining samples were submitted to accelerated aging (8 hours – ultraviolet light irradiance was at a temperature of 60 ± 3 °C and 4 h – a dark condensation period was at a temperature of 45 ± 3 °C) during 1008 hours and the peel test, direct observation and SEM were performed. The peel value needed to separate the resin from silicone (PS) was statistically analyzed with the ANOVA variance test and the Tukey test ($p < 0.05$). The failure pattern was assessed statistically through the qui square test and the fisher exact test. The bond strength test results indicated a statically significance ($p < 0.05$) for all factors. These values raised after the aging period, and the oil painting group presented the higher mean value (PS=3.53 N/mm). Groups with were applied the Sofreliner Primer presented higher bond strength values than other subgroups for both periods of evaluation. The factors time and technique influenced significantly in failure pattern, the most common failure was mixed failure ($n=671=69.9\%$) and the least common was the cohesive one ($n=109$). Greater PS values were presented by the subgroups pigmented with oil painting, without scratches and that received the sofreliner primer after the accelerated aging period. The sofreliner primer promotes a higher adherence between acrylic resin and facial silicone and the incidence rate of both failure augmented after the aging period.

1. Introduction

The facial rehabilitation through implant retained prostheses is a valid treatment to re-establish esthetics, function and quality of life to many patients who suffered facial mutilation due to cancer, trauma or burns [1]. Silicon is widely used to manufacture facial prostheses for its unique characteristics such as biocompatibility, texture similar to skin and for being easy to pigment [2,3].

Facial prostheses made of silicon that are retained by dental implants require a retention matrix, made of acrylic resin, where clips and/or magnets are installed. The silicone is positioned over the matrix, so it is very important to have enough adherence at the interface so the patient can use the prostheses in a secure and comfortable way [4].

These maxillofacial prostheses may undergo color change and delamination during its usage [5–7].

The pigmentation with oil painting in addition to opacifiers is a valid solution to the imminent chromatic changes, but the loss of bond between the matrix and the silicone remains a problem. Clinical and experimental studies suggest several techniques to position the acrylic matrix like the association with a fiber glass structure, utilization of different primers and adhesives that can be

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http://dx.doi.org/10.1016/j.ijadhadh.2014.06.011
0143-7496/

applied in many ways associated or not with mechanic retention [4]. But this is still a treatment limitation, it is not rare for patients rehabilitated with implant retained prostheses to report looseness or tear up of the prostheses esthetic portion during its removal [4,8,9].

Tests developed to evaluate the adhesive bond strength of materials include peel, tensile, shear, fatigue, creep, impact, and cleavage tests. The most commonly used methods to measure the bond strength of resilient lining materials to acrylic materials have been peel, tensile, and shear tests. The peel test is believed to simulate the horizontal component of forces that causes lateral displacement of the prosthesis. The tensile test gives information on the strength of the bond in comparison to the tensile strength of the material. In shear testing, the stresses are unevenly distributed. At the edges the stresses are much greater [10].

The bond strength test was used as an evaluation method (peel test) which simulates the prostheses removal act through a mechanical test and interface adhesion analysis that can present different failure patterns classified as adhesive (only the detachment of the surfaces happen), cohesive (when only tears happen), and mixed (when both types of failure are presented) [3,4,11].

The samples were submitted to artificial aging [12] for 1008 hours [13,14] in which the they were submitted to different temperatures, darkness and ultraviolet light cycles, simulating one year of clinical use of the prostheses [15,16].

The aim of this study was to evaluate the influence of nanopalticles (oil painting or barium sulfate), of different bonding techniques and of the accelerated aging for 1008 hours on the bonding of facial silicone to an acrylic resin substrate. The hypothesis of this study is that by adding the nanoparticles no difference will be perceived on the bond strength values or the failure patterns; that the association between mechanical imbrications and primer application provides higher bond strength values, that the accelerated aging influences negatively the silicone-resin adhesion and that failure pattern most commonly found is the one that presents both kinds of failure.

2. Materials and methods

2.1. Specimens fabrication

Each sample consisted of two bars of autopolymerized acrylic resin [17,18] (Orto cor, VIPI, Pirassununga, SP, Brazil) and facial silicone (Silastic MDX 4-4210, Dow Corning Corporation, Midland, MI, USA). A metallic matrix with ten rectangular spaces with 75-mm length, 10-mm width and 3-mm thickness [4] was used to fabricate the acrylic resin bars.

The powder and liquid of the autopolymerized acrylic resin were manipulated in a ratio of 3:1, according to the manufacturer's instructions, and was poured into the metallic matrix. The matrix was closed and a 17.78 PSI of pressure was applied during 10 min with a hydraulic press (Midas Dental Products Ltd, Araraquara, SP, Brazil).

Afterwards, the matrix was placed in a curing resin device (Metalvander, Piracicaba, São Paulo, Brazil) during 20 min under hydrostatic pressure of 25 PSI. The matrix was opened and the acrylic resin bars removed. P220 sandpaper (Tigre, Rio Claro, SP, Brazil) was used as a finishing procedure [4].

A total of 960 acrylic resin bars were obtained, and 480 bar did not receive any mechanical retention (scratches), and the remaining bars were scratched with a number 2135 diamond bur (KG Sorensen, Barueri, SP, Brazil). The bur was placed in a high-speed hand piece, and the long axis of the bur was parallel to the bar and tilted 45° in relation to the horizontal axis during the scratches fabrication. Each scratch presented the same diameter of the bur and it was performed 25 mm in length of the bar in the bond area between the acrylic resin and silicone. The distance of each scratch had the same diameter of the bur [19].

Another metallic matrix was used to fabricate the facial silicone bar and to bond the acrylic resin bar to the facial silicone bar. This matrix had ten rectangular spaces with 75 mm in length, 10 mm in width and 6 mm in thickness [4].

Initially, the acrylic resin bars were cleaned with gauze and acetone and then placed into the matrix. An adhesive tape was positioned covering 50 mm in length of the acrylic resin bar (unbonded portion), and the remaining 25 mm length were used to bond the silicone to the acrylic resin [4]. Bars were divided into 4 groups, according the pigmentation, and 12 groups according to the adhesive system used and the presence of surface scratches (Fig. 1) [3,8,20,21].

The application of primer on the acrylic resin surface was used to enhance the adhesive penetration. Therefore, a 30-min period was allowed after Dow Corning 1205 Prime (Dow Corning Corporation, Midland, MI, USA) or Sofreliner Prime S (Tokuyama Corp., Taitou-ku, Tokyo, Japan) application so that the prime reacts with the resin surface.

Before placing the silicone mixture into the matrix, some groups (Fig. 1) received a thin layer of Silastic Medical Adhesive Type A (Dow Corning Corporation, Midland, MI, USA) [3,20] applied directly on the primed acrylic resin surface.

Afterwards, the MDX 4-4210 facial silicone was weighted in a digital precision scale (BEL Equipamentos Analíticos, Piracicaba, SP, Brazil) and manipulated according to manufacturer's instructions, mixing one part of curing agent with 10 parts by weight of the base elastomer, under controlled temperature (23 ± 2 °C) and humidity (50 ± 10%), in order to obtain a homogeneous mixture. Groups 2, 3 and 4 (Fig. 1) was pigmented with nanoparticles (oil pigment and/or barium sulfate opacifier). Pigments were weighed with a precision digital scale, equivalent to 0.2% by weight 3, 4, 16, 29 of the necessary silicone to fill up the space of the metallic flask [15,16,22].

The silicone mixture was then used to overfill the matrix and its surface was flattened with a steeling steel spatula and its thickness was standardized. The matrix was placed in a curing resin device with 25 PSI of pressure to avoid bubbles formation into the silicone. A total of 72 hours under room temperature were allowed so the silicone polymerizes and the formaldehyde releases, following manufacturer's instructions [15,16,22]. After silicone polymerization, the specimens were separated from the matrix, and the adhesive tape, used to create the unbonded area of 50 mm in length and to allow the placement of the specimens in the universal testing machine, was removed [4].

Half of the specimens ($n=480$) were subjected to the bond test 24 h after their fabrication, and the other 480 specimens were subjected to artificial aging test.

2.2. Bond test (T-peel test)

An universal testing machine (Emic DL-3000, EMIC, São José dos Pinhais, PR, Brazil) was used to conduct the bond test at a crosshead speed of 10 mm/min [4,23].

The applied load and the limit load were recorded for each specimen. The T-peel strength for each specimen was determined using the average load divided by specimen width, as described in ASTM Standard D 1876-72 [23] according to the following formula:

$$PS=\frac{F}{W}\cdot\left(\frac{1+\lambda}{2}+1\right)$$

where F is the maximum force recorded (N), W is the width of the specimens (mm), and · is the extension ratio of the silicone elastomer (the ratio of stretched to unstretched length).

Group/ Pigmentation	Subgroup	Samples	Scratches	Prime	Adhesive
1 Colorless	1	20	No	Não	No
	2	20	No	Não	Yes
	3	20	No	DC 1205	No
	4	20	No	DC 1205	Yes
	5	20	No	Sofreliner	No
	6	20	No	Sofreliner	Yes
	7	20	Yes	Não	No
	8	20	Yes	Não	Yes
	9	20	Yes	DC 1205	No
	10	20	Yes	DC 1205	Yes
	11	20	Yes	Sofreliner	No
	12	20	Yes	Sofreliner	Yes
2 Oil	1	20	No	Não	No
	2	20	No	Não	Yes
	3	20	No	DC 1205	No
	4	20	No	DC 1205	Yes
	5	20	No	Sofreliner	No
	6	20	No	Sofreliner	Yes
	7	20	Yes	Não	No
	8	20	Yes	Não	Yes
	9	20	Yes	DC 1205	No
	10	20	Yes	DC 1205	Yes
	11	20	Yes	Sofreliner	No
	12	20	Yes	Sofreliner	Yes
3 Opacifier	1	20	No	Não	No
	2	20	No	Não	Yes
	3	20	No	DC 1205	No
	4	20	No	DC 1205	Yes
	5	20	No	Sofreliner	No
	6	20	No	Sofreliner	Yes
	7	20	Yes	Não	No
	8	20	Yes	Não	Yes
	9	20	Yes	DC 1205	No
	10	20	Yes	DC 1205	Yes
	11	20	Yes	Sofreliner	No
	12	20	Yes	Sofreliner	Yes
4 Oil + Opacifier	1	20	No	Não	No
	2	20	No	Não	Yes
	3	20	No	DC 1205	No
	4	20	No	DC 1205	Yes
	5	20	No	Sofreliner	No
	6	20	No	Sofreliner	Yes
	7	20	Yes	Não	No
	8	20	Yes	Não	Yes
	9	20	Yes	DC 1205	No
	10	20	Yes	DC 1205	Yes
	11	20	Yes	Sofreliner	No
	12	20	Yes	Sofreliner	Yes

Fig. 1. Groups division according to the presence or not of pigment, scratches, primer and adhesive.

2.3. *Type of failure analysis through direct observation and SEM*

To assess the failure pattern [3,4,24] found in the interface silicone-resin, the samples were analyzed visually and through SEM. Initially the specimens were cut in order to reduce their length so that the only part left was the adhesion interface of the silicone and resin, then were fixated to a metallic submitted to an ultrasonic bath for three minutes, so that contaminants would not interfere with the SEM observation [25].

Then the samples were metallized with gold and taken to the Scanning Electron Microscope (JSM 5600LV, JEOL, Tokyo, Japan) where they were analyzed [25]. The failure pattern was characterized as adhesive, when occurred a complete separation of the two bars; cohesive when the silicone tear, and mixed, when areas of detachment and tear areas of silicon were observed [3,24].

2.4. *Artificial aging*

For the artificial aging, 480 specimens were positioned in the artificial aging chamber (Equilam, Diadem, SP, Brazil) and submitted to alternated periods of ultraviolet light and darkness with condensation of distilled water saturated in oxygen. Each aging cycle was accomplished in 12 h.

In the first 8 h, ultraviolet light irradiance was at a temperature of 60 ± 3 °C. In the following 4 h, a dark condensation period was at a temperature of 45 ± 3 °C [13–16,22]. In this way, 1008 artificial aging hours were accomplished simulating deterioration caused by rain, dew, and UV light (both direct and indirect sunlight irradiance).

After this period another bond test was carried out and the failure pattern analysis was performed once again as describe previously.

2.5. *Statistical analysis*

The T-peel strength data were recorded. Data were submitted to the three-way Analysis of Variance (ANOVA), and Tukey test was used as a post-hoc technique when necessary ($p < 0.05$).

For failure pattern analysis the qui-square test was used, which is useful to assess the association between the type of failure and the variable specified (time, pigment or bonding technique) followed by the Fisher exact test.

3. Results and discussion

The results are presented in Table 1–4 and Figs. 2–4.

In order to promote adhesion between the acrylic resin and the facial silicone different bonding techniques were applied, and we noticed that all factors evaluated, whether associated or not, influenced significantly ($p < 0.05$) all the bond strength values acquired (Table 1). The failure pattern most frequent was the one with both kinds of failures, the nanoparticles addition didn't interfere with the failure pattern, but the bonding technique and the accelerated aging did, therefore the study hypothesis was partially accepted.

The bond between different materials can occur in three ways: mechanical bond, micromechanical or molecular adherence. The mechanical bond happens due to small surface irregularities. The micromechanical happens when a bonding agent is used on an irregular surface creating an effective micromechanical bond that is resistant to tension. The molecular adherence is a process in which physical and chemical forces bond the molecules of different substances [26]. The bond between silicone and resin is influenced by the chemical affinity of primers and silicones [4], so it is mainly related to the composition of such materials.

Accordingly to the manufacturer, the autopolymerising acrylic resin OrtoCor presents itself in a liquid powder set, in which the powder composition is polymethylmethacrylate and benzoyl peroxide; and the liquid part is methylmethacrylate, EDMA

Table 1
Three-way analysis of variance (ANOVA) of the bond strength test.

Variables	DF	SQ	MS	F Value	*P* value
Nanoparticles	3	56,735	18,912	23,625	< 0.0001*
Bonding Technique	11	2,523,199	229,382	286,549	< 0.0001*
Period	1	453,795	453,795	566,890	< 0.0001*
Nanoparticles × Bonding Technique	33	419,585	12,715	15,883	< 0.0001*
Nanoparticles × Period	3	42,241	14,080	17,590	< 0.0001*
Bonding Technique × Period	11	728,040	66,185	82,680	< 0.0001*
Nanoparticles × Bonding Technique × Period	33	742,291	22,494	28,100	< 0.0001*
Error	864	691,631	0.800		
Total	959	5657,518			

* $p < 0.05$ – Statistically significant difference.

Table 2
Mean values of bond strength and standard deviation (SD) between acrylic resins and Facial Silicone for each nanoparticle and each period, regardless of bonding technique.

Nanoparticles	Period	
	Baseline (N/mm)	After accelerated Aging (N/mm)
Colorless	1.36 (0,35) Aa	2,68 (0.77) Ab
Oil painting	1.46 (0,30)Aa	3,53 (1,11) Bb
Opacifier	1.46 (0,43) Aa	2,53 (0,66) Ab
Oil painting and opacifier	1.34 (0,46) Aa	2,37 (0,74) Ab

Mean values with equal letters show there are no differences between them at 5% significance level ($p < 0.05$) according to the Tukey test.

Table 3
Mean values of bond strength and standard deviation (SD) between acrylic resins and Facial Silicone bonding technique and period, regardless of the pigmentation technique used.

Bonding technique	Period	
Subgroups	Baseline (N/mm)	After accelerated aging (N/mm)
1	0.29 (0.08) Aa	0.33 (0.11) Aa
2	0.11 (0.04) Aa	1.04 (0.53) Bb
3	0.64 (0.24) Aba	0.40 (0.12) Aba
4	0.14 (0.15) Aa	1.99 (0.75) Cb
5	4.21 (1.12) Ba	3.35 (1.12) Db
6	1.77 (0.47) Ca	6.58 (1.65) Eb
7	0.21 (0.05) Aa	0.87 (0.24) ABb
8	1.32 (0.44) Ca	3.84 (1.21) Db
9	0.22 (0.05) Aa	1.09 (0.34) Bb
10	0.32 (0.09) Aa	3.94 (1.24) Db
11	4.46 (1.18) Ba	3.68 (1.17) Db
12	3.13 (0.86) Da	6.24 (1.57) Eb

Mean values with equal letters show there are no differences between them at 5% significance level ($p < 0.05$) according to the Tukey test.

(Crosslink) and an inhibitor. Silastic MDX4-4210 is provided in two materials, an elastomeric component and a curing agent. The elastomeric component has in its composition a dimethylsiloxane polymer, reinforced by silica and platinum catalyst. The curing agent is composed by a dimethylsiloxane polymer, inhibitor and siloxane crosslinking agent [3].

As the materials composition is so different, the bond strength within the specimens with no primer or adhesive application wasn't high (subgroups 1 and 7 – Tables 3 and 4).

As for the pigmentation, the specimens pigmented exclusively with oil painting exhibited (after the accelerated aging) the higher bond mean values (PS=3.53 N/mm-Table 2).

According to the manufacturer the oil painting has in its formulae grinded pigments mixed with linseed oil, but the type of pigment wasn't specified. Some authors [20] state that the linseed oil produces a film which envelops the pigment particles. Ergo it is assumable that the pigment unites to the primer, adhesive and/or silicone polymeric chain in a way they cannot be unleashed from the polymerized structure, in addition of being protected from superficial deterioration caused by the accelerated aging process [22]. If this was not so, micropores would form turning the specimens susceptible to physical and chemical alterations as well as bonding failure between the resin and silicone [14,15,27].

The bond values increased significantly after the accelerated aging process (Table 2). According to the manufacturer, the pigment take a long period to dry completely, even with the addition of specific cobalt based dryer. So the silicone polymerization process may have been delayed at baseline by the oil painting addition. Which could explain the higher values after the accelerated aging since after the process the silicone polymerization was completed [20].

Some studies [15,16,22,27] imply that the aging process induces the facial silicone to its ultimate curing value, since this material undergoes a constant polymerization. The greatest formaldehyde release occurs at the first 72 h, but after that the substrate release persists indefinitely. In addition to this process the accelerated aging promotes an increase in hardness, which increases the tear strength [16,22].

Comparing the bond technique in each subgroup (Tables 3 and 4) we observed that the specimens which received the Sofreliner Primer, in spite of the association of scratches or adhesive application (5, 6, 11 and 12) exhibited higher bond values for both periods. Considering that acrylic resin has a different chemical composition than the facial silicone, it was needed to alter its surface in order to create union between these materials.

According to the DC 1205 primer manufacturer, their product has a solving as base, and it forms a film over plastics, painted surfaces, construction materials, wood or metal when applied, favoring the bond of these material to the silicone. Based on that we elaborated the hypothesis that better values would be obtained by the groups which received scratches and the primer DC1205 in association to the adhesive, but this hypothesis was rejected.

The Sofreliner primer is a material used to favor the conditioning and adherence between acrylic resin for dentures and silicone based resilient relining materials. It is known that this primer contains polimetilmetacrilate with polyorganosiloxane as active ingredients and methylene chloride as a solvent but its action mechanism is unknown [3]. One can assume that these components are able to provide molecular adherence between silicone and resin, once the groups which received this primer application exhibited the highest bond results.

The obtained results are in accordance with the ones from Chang et al. [3], who evaluated adherence between polyurethane and facial silicone, they had the best results when the sofreliner primer was applied. The authors [3] attributed this fact to the solving agent, whose action mechanism is unknown, and it is not

Table 4
Mean values of bond strength (PS N/mm) and standard deviation (SD) between acrylic resin and facial silicone for each nanoparticle, bonding technique and period analyzed.

Nanoparticles	Bonding technique (groups)	Period	
		PS at baseline (N/mm)	PS after 1008 h (N/mm)
Colorless	1	0.02(0.00)Aa	0.66(0.24)Aa
	2	0.11(0.04)Aa	1.94(0.56)Bb
	3	0.11(0.03)Aa	0.35(0.05)Aa
	4	0.10(0.04)Aa	1.51(0.53)Aa
	5	5.95(1.14)Ba	1.41(0.32)Ab
	6	0.79(0.26)Aa	6.22(1.75)Db
	7	0.17(0.03)Aa	0.69(0.27)Aa
	8	0.72(0.10)Aa	2.54(0.96)BCb
	9	0.30(0.04)Aa	0.97(0.36)Aa
	10	0.29(0.05)Aa	4.25(1.33)Cb
	11	3.07(1.00)Ca	4.18(1.07)Ca
	12	4.73(1.47)BCa	7.44(1.84)Db
Oil painting	1	0.34(0.09)Aa	0.36(0.11)Aa
	2	0.12(0.04)Aa	0.71(0.19)Aa
	3	0.05(0.01)Aa	0.27(0.08)Aa
	4	0.09(0.03)Aa	2.63(1.03)Bb
	5	1.32(0.12)Aa	9.67(3.59)Cb
	6	3.73(0.67)Ba	7.63(1.77)Db
	7	0.25(0.05)Aa	0.61(0.20)Aa
	8	1.09(0.25)Aa	4.94(1.56)Eb
	9	0.37(0.08)Aa	0.81(0.25)Aa
	10	0.36(0.10)Aa	3.79(1.14)BEb
	11	4.91(1.21)Ba	4.74(1.86)Ea
	12	4.87(0.98)Ba	6.26(1.49)DEa
Opacifier	1	0.03(0.01)Aa	0.16(0.06)Aa
	2	0.07(0.02)Aa	0.97(0.30)Aba
	3	2.34(0.90)Ba	0.82(0.29)Aba
	4	0.17(0.04)Aa	1.48(0.52)Aba
	5	4.29(1.51)Ca	1.96(0.45)Bb
	6	2.52(0.93)Ba	7.68(1.61)Cb
	7	0.20(0.05)Aa	1.34(0.21)Aba
	8	0.22(0.08)Aa	3.61(0.79)BDb
	9	0.09(0.03)Aa	1.52(0.50)Aba
	10	0.24(0.06)Aa	3.73(1.30)Db
	11	6.75(1.36)Da	2.05(0.59)Bb
	12	0.56(0.19)Aa	5.08(1.33)Db
Oil painting and opacifier	1	0.76(0.20)Aa	0.13(0.04)Aa
	2	0.15(0.04)Aa	0.54(0.19)Aa
	3	0.04(0.01)Aa	0.17(0.06)Aa
	4	0.22(0.10)Aa	2.36(0.92)Bb
	5	5.30(1.69)Ba	0.35(0.13)Ab
	6	0.06(0.02)Aa	4.80(1.45)Cb
	7	0.24(0.06)Aa	0.82(0.28)Aba
	8	3.26(1.34)Ca	4.27(1.51)Ca
	9	0.12(0.04)Aa	1.06(0.24)Aa
	10	0.39(0.14)Aa	4.00(1.20)BCb
	11	3.10(1.14)Ca	3.72(1.17)BCa
	12	2.37(0.78)Ca	6.17(1.63)Db

Means followed by the same uppercase letter in the column (comparison among bonding technique for each nanoparticles) and the same lowercase letter in the line (comparison among period) does not differ to 5% level of significance ($P < 0.05$) in Tukey's test.

in the composition of the other primers (DC 1205 Primer and Silastic Medical Adhesive Type A).

Different than expected the subgroups which received scratches (1–6) didn't had their adherence improved when compared to the subgroups without scratches (7–12), and the adhesive application (subgroups 2, 4, 6, 8, 10 and 12) didn't improved significantly when compared to the subgroups without adhesive (1, 3, 5, 7, 9 e 11). These results could be explained by the incomplete polymerization of the adhesive inside the scratches.

According to the manufacturer this adhesive consists of a transduced material, composed by metil triacetoxisilano with no solving substances, and is indicated to bond the silicone to synthetic materials, metals or other silicones. A thin layer should be applied on an oil free clean surface. It is cured at environment temperature under oxygen exposure, and during this process the adhesive eliminates acetic acid as waste. During the experiment, it was observed that both adhesive and silicone didn't complete the curing process completely in the resin specimens with scratches. It is believed that this is due to the fact that such materials have less exposure to the environment, thereby reducing the release of waste products (acetic acid by the adhesive and formaldehyde by the silicone).

Udagama [20] created another protocol, which consists of the mixture of Silastic Medical Adhesive Type A with Silastic MDX 4-4210 in a 40 to 60 proportion. But there are reports of health risks to patients and operators who have contact with this material due to steam release of acetic acid, which can cause skin burns, permanent eye damage, and irritation of mucous membranes [3], when such protocol is adopted. Considering this information and with the team and patient safety in mind, Udagama protocol was disregarded and the adhesive manufactures instructions were followed.

When comparing the PS presented by each subgroup in the different periods analyzed it can be noted that the bond values raised after the 1008 h of accelerated aging, however, the samples of subgroup 5 from groups Colorless, Opacifier and Oil painting with Opacifier exhibited a significant reduction in these values (Table 4). This probably occurred after the accelerated aging process due to the fact that the adhesive Silastic Medical Adhesive Type A had not been applied and also for the change suffered by Sofreliner Primer during this process. As previously mentioned, the Sofreliner Primer contains methylene chloride in its composition. This compound has a boiling point around 40 °C [28], and evaporates when exposed to heat or climate changes, simulated during this test, leading to changes in the material properties. However, it is possible to believe that it can be used is in the clinic, since patients do not undergo changes in humidity and temperature as extreme as those performed during this laboratory test.

We also noticed that the samples pigmented exclusively with oil paint which received the application of Sofreliner Primer did not suffer the same change. This fact is explained by the possible interaction of the oil present in this pigment with this primer, since its solvent (methylene chloride) is not soluble in water, but soluble in oil [28].

Applying the results of this study to the clinical practice, it is ideal that a stable bond occur in the initial period (at the time of installation of the prosthesis). The subgroups that showed the highest bond values at baseline were, in general, those which received Sofreliner Prime application (5, 6, 11 and 12).

Regarding maxillofacial prostheses, there must be a minimum bond value to ensure its use. Goiato et al. [29] evaluated the stress distribution of three attachment systems associated with implants for facial prosthesis using photoelastic analysis. The force values required for the removal were recorded: O'ring = 20.57 N; bar-clip = 29.22 N and magnets = 13.75 N. To obtain the bond value is necessary to divide the amount of force (N) by the union area (mm). The prostheses used in the study of Goiato et al. [27] presented an union area of 314 mm. Thus, we calculate the PS value for the O'ring (20.57 N ÷ 314 mm), bar-clip (29.22 N ÷ 314 mm) and magnets (13.75 N ÷ 314 mm), and the values were, respectively, 0.07, 0.09 and 0.04 N/mm. Thus, it can be stated that clinically, the bond value between acrylic resin and facial silicone is, on average, 0.07 N/mm.

Analyzing the values at baseline (Table 4) the subgroups, 1 for Colorless group, 3 for oil painting group, 1 for Opacifier group, and 3 and 6 for Ink plus Opacifier group cannot be clinically accepted.

These subgroups presented bond values inferior than 0.07 N/mm at baseline. After 1008 h of accelerated aging these values

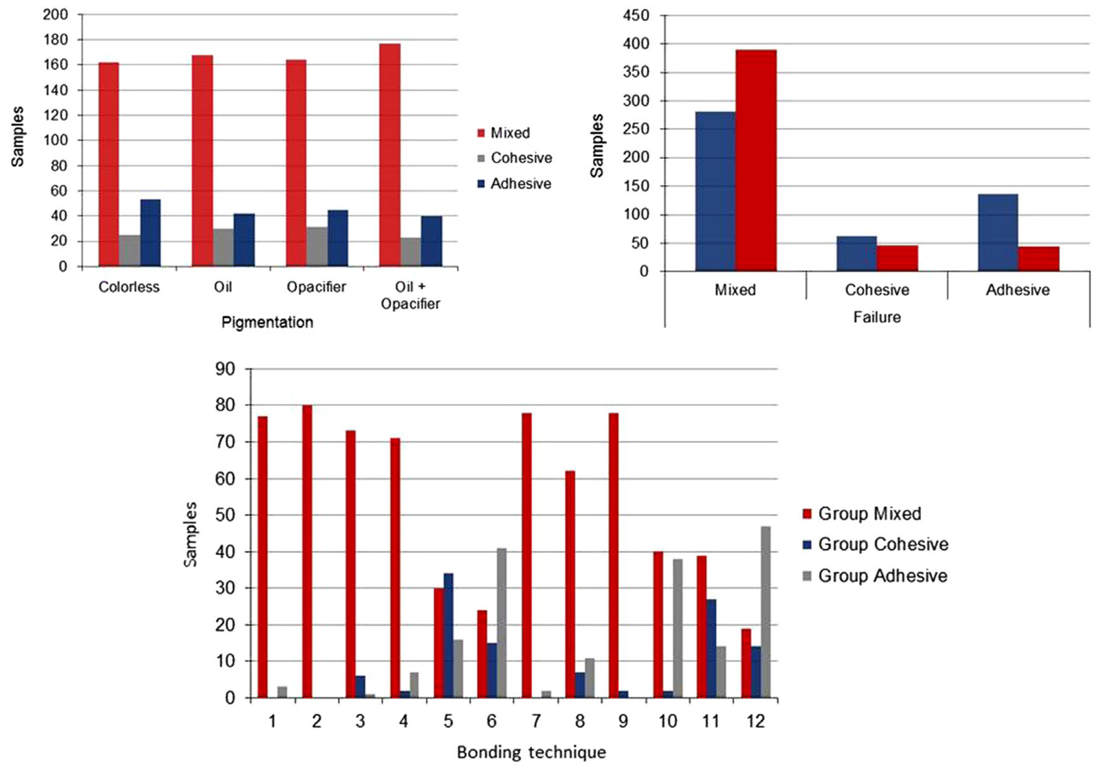

Fig. 2. Quantity of samples according to failure pattern for each variable specified (time, pigment or bonding technique). (a) Failure pattern of specimens for each nanoparticle failure, regardless of time and bonding technique. (b) Failure pattern of specimens for each period regardless of the addition or not of nanoparticles. (c) Failure pattern of specimens for each bonding technique regardless of period and the addition or not of nanoparticles.

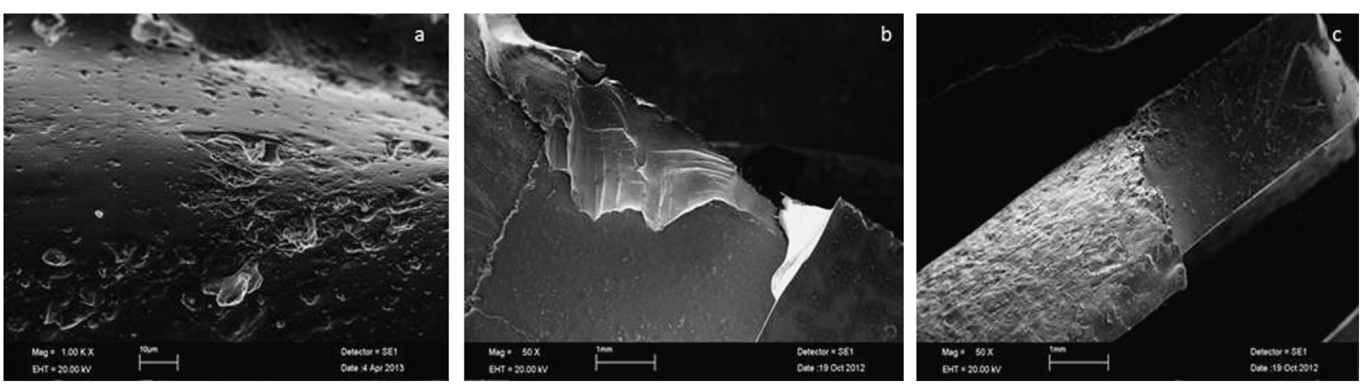

Fig. 3. SEM generated image of failure patterns: (a) adhesive failure. (b) cohesive failure. (c) mixed failure.

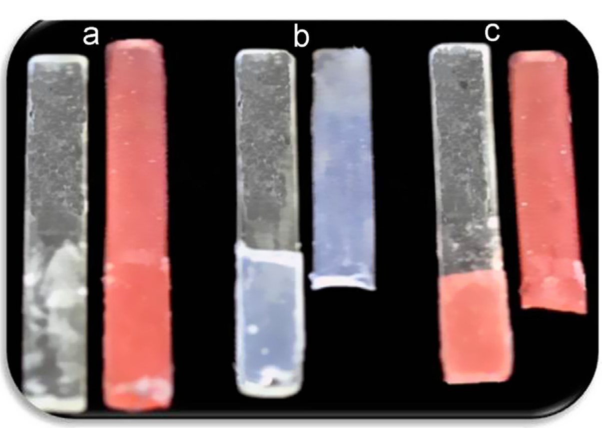

Fig. 4. Bond failures observed directly between acrylic resin and facial silicone: (a) adhesive failure; (b) cohesive failure; (c) mixed failure.

increased, but when converted to the clinical reality, if the adhesion between the acrylic component and the esthetics portion fails initially, this prosthesis would not be in use for a year as reproduced by the accelerated aging test.

Such values reinforce the need of association between the silicone and acrylic resin, since the silicone isolated is not strong enough to be removed without tearing up, besides this it is important to instruct the patient on hoe to remove the prosthesis, by holding it from the thickest part.

When combining the findings of this study to the literature and to clinical experience it can be assumed that the Sofreliner Primer application on acrylic resin devices used in implant retained maxillofacial prosthesis can promote a safe bond between these materials, and was the most indicated bonding method under these conditions.

There was a statistically significant association ($P < 0.0001$, chi-square test) between failure and time, regardless of the addition of nanoparticles and the bonding technique. As seen in Fig. 2, at baseline the mixed type of failure were the most common (281), followed by adhesive failure (136) and cohesive (63). These findings are in agreement with clinical observations, since it is not uncommon for patients rehabilitated with implant retained maxillofacial prostheses seek treatment for the esthetic portion of the prosthesis to be affixed to the acrylic resin device [9,17], partially or completely. Which is favorable since it is much easier and faster to perform new glue than to repair tears that occur in facial silicone, and can be explained by the elasticity and tear resistance characteristic of facial silicone. It is known, however, that these properties can be changed by varying the thickness of the evaluated structure and the exposure of the material to changes in temperature and humidity [3].

As for the final period, the mixed type of failure still prevail (390), followed by cohesive (46) and adhesive failure (44). Thus, it can be seen that the rate of mixed failures increased after the period of accelerated aging (Fig. 2). It is known that elastomeric materials present a continuous polymerization, in the silicone case, with the release of formaldehyde as waste [15,20,24]. Besides, most polymers present molecular chains in the aromatic ring and C=C bonds, capable of absorbing ultraviolet light during accelerated aging process [22,26]. So, when a polymer molecule absorbs ultraviolet light, this energy promotes instability in the molecular structure.

The excess energy can be transmitted through the transfer of excitation to another molecule, allowing the first to regain stability [26]. Affected groups can return to its original state, through the remission of the excess energy into longer wave lengths, such as visible light or heat. If an excited molecule produce this excess energy, it will undergo photochemical degradation [22,26]. These factors contribute to the surface deterioration of the materials, evidenced by changes in color and brightness, loss of opacity, cracks formation and increase in hardness [16,26]. This stiffening of the material can be identified as responsible for the reduction of adhesive and cohesive type failures observed in the final period (Fig. 2).

Comparing the different types of pigmentation, independent of time and bonding technique, no statistically significant association ($p=0.595$, chi-square test) was observed with the type of failure therefore, the distribution of failure is independent of the pigmentation used (Fig. 2), and the most common type of failure was the mixed type followed by adhesive and cohesive types.

Finally it can be verified a statistically significant association ($p<0.0001$, Fisher's exact test) between failure and bonding technique. Comparing the different adhesive systems used, it may be noted that all subgroups presented specimens with the both types of failure. The same did not occur with other failure patterns, since the subgroups which received Sofreliner Primer application (5, 6, 11 and 12) presented the highest rates of cohesive failures (Fig. 2).

Thus, it can be stated that the Sofreliner Primer promotes a great bond strength between acrylic resin and silicone facial; force that is superior to the tear resistance of the silicone [19]. As previously mentioned, adhesive failure is more favorable clinically than the cohesive one because it is easier to repair, however, it is worth remembering that the maxillofacial is not completely as thin as the specimens used (3 mm). Therefore the patient should be instructed to remove the prosthesis holding its thickest portion (corresponding to the portion where the bond between acrylic resin and facial silicone occurs), preventing thereby the tear of the esthetic component.

The Greater adhesion promoted by Sofreliner Primer is probably due to its chemical composition. It is known that this primer contains polymethylmethacrylate with polyorganosiloxane as active ingredients, and methylene chloride as a solvent for which the precise mechanism of action remains unknown [3,19].

Fig. 3 show SEM images of a specimen failure patterns, and Fig. 4 show images of direct observation of failure patterns. The direct visual [4,19,24] and photographic [3] assessment are the most used techniques to assess bonding failure patterns, but the microscopic observation provides details impossible to be seen by those [25] for providing images in large increases, which suggests caution when interpreting articles that only use direct view or photographic analysis as a methodology.

Regarding the limitations of an in vitro study, one of the many factors that could affect the tear up resistance of elastomers is the material thickness. In this study, all samples presented the same thickness through all its length, accordingly to the protocol previously established. Differing from the clinical reality, where the facial prostheses present different thickness measurements of esthetical material in order to obtain the ideal anatomical properties. Other limitation is regarding the damages caused by the accelerated heating procedure. This essay seeks to reproduce, in a controlled environment, the material exposure to different climatic conditions, however it is impossible to reproduce such conditions exactly as it would be during the prostheses use. The exposure of each individual to the sun and rain is variable, as well as the environment temperature, which is different in every location on the planet.

4. Conclusions

Considering the limitations of an in vitro study, it can be concluded that the best bond between autopolymerized acrylic resin and facial silicone were presented when the silicone was pigmented exclusively with oil pigment, without scratches in acrylic resin and with Sofreliner Primer application with or without the adhesive.

Acknowledgments

This study was supported by the Sao Paulo Research Foundation (FAPESP), Brazil.

References

[1] Goiato MC, dos Santos DM, Dekon SFC, Pellizzer EP, Santiago Jr JF, Moreno A. Craniofacial implants success in facial rehabilitation. J Craniofac Surg 2011;22:241–2.
[2] Hatamleh MM, Watts DC. Effects of bond primers on bending strength and bonding of glass fibers in fiber-embedded maxillofacial silicone prostheses. J Prosthodont 2011;20:113–9.
[3] Chang PP, Hansen NA, Phoenix RD, Schneid TR. The effects of primers and surface bonding characteristics on the adhesion of polyurethane to two commonly used silicone elastomers. J Prosthodont 2009;18:23–31.
[4] Hatamleh MM, Watts DC. Bonding of maxillofacial silicone elastomers to an acrylic substrate. Dent Mater 2010;26:387–95.
[5] Hooper SM, Westcott T, Evans PL, Bocca AP, Jagger DC. Implant-supported facial prostheses provided by a maxillofacial unit in a U.K. regional hospital: longevity and patient opinions. J Prosthodont 2005;14:32–8.
[6] Polyzois GL, Frangou MJ. Bonding of silicone prosthetic elastomers to three different denture resins. Int J Prosthodont 2002;15:535–8.
[7] Frangou MJ, Polyzois GL, Tarantili PA, Andreopoulos AG. Bonding of silicone extra-oral elastomers to acrylic resin: the effect of primer composition. Eur J Prosthodont Restor Dent 2003;11:115–8.
[8] Goiato MC, Garcia-Júnior IR, Magro-Filho O, dos Santos DM, Pellizzer EP. Implant-retained thumb prosthesis with anti-rotational attachment for a geriatric patient Gerodontology 2010;27:243–7.
[9] Goiato MC, Delben JA, Monteiro DR, dos Santos DM. Retention systems to implant-supported craniofacial prostheses. J Craniofac Surg 2009;20:889–91.
[10] Al-Athel MS, Jagger RG. Effect of test method on the bond strength of a silicone resilient denture lining material. J Prosthet Dent 1996;76:535–40.
[11] McCabe JF, Carrick TE, Kamohara H. Adhesive bond strength and compliance for denture soft lining materials. Biomaterials 2002;23:1347–52.
[12] Santos RM, Botelho GL, Cramez C, Machado AV. Outdoor and accelerated weathering of acrylonitrile-butadiene-styrene: a correlation study. Polym Degrad Stab 2013;98:2111–5.

[13] Mancuso DN, Goiato MC, Dekon SF, Gennari-Filho H. Visual evaluation of color stability after accelerated aging of pigmented and nonpigmented silicones to be used in facial prostheses. Indian J Dent Res 2009;20:77–80.

[14] Haddad MF, Goiato MC, Dos Santos DM, Pesqueira AA, Moreno A, Pellizzer EP. Influence of pigment and opacifier on dimensional stability and detail reproduction of maxillofacial silicone elastomer. J Craniofac Surg 2011;22:1612–6.

[15] Filié Haddad M, Coelho Goiato M, Micheline Dos Santos D, Moreno A, Filipe D'almeida N, Alves Pesqueira A. Color stability of maxillofacial silicone with nanoparticle pigment and opacifier submitted to disinfection and artificial aging. J Biomed Opt 2011;16:095004.

[16] Goiato MC, Pesqueira AA, Moreno A, dos Santos DM, Haddad MF, Bannwart LC. Effects of pigment, disinfection, and accelerated aging on the hardness and deterioration of a facial silicone elastomer. Polym Degrad Stab 2012;97:1577–80.

[17] Aydin C, Karakoca S, Yilmaz H. Implant-retained digital prostheses with custom-designed attachments: a clinical report. J Prosthet Dent 2007;97:191–5.

[18] Gion GG. Surgical versus prosthetic reconstruction of microtia: the case for prosthetic reconstruction. J Oral Maxillofac Surg 2006;64:1639–54.

[19] Haddad MF, Goiato MC, Santos DM, Crepaldi Nde M, Pesqueira AA, Bannwart LC. Bond strength between acrylic resin and maxillofacial silicone. J Appl Oral Sci 2012;20:649–54.

[20] Udagama A. Urethane-lined silicone facial prostheses. J Prosthet Dent 1987;58 (3):351–4.

[21] Lemon JC, Chambers MS. Locking retentive attachment for an implant-retained auricular prosthesis. J Prosthet Dent 2002;87:336–8.

[22] dos Santos DM, Goiato MC, Moreno A, Pesqueira AA, Dekon SFC, Guiotti AM. Effect of addition of pigments and opacifier on the hardness, absorption, solubility and surface degradation of facial silicone after artificial ageing. Polym Degrad Stab 2012;97:1249–53.

[23] American Society for Testing Materials: Standard test for peel resistence, D1876, West Conshohocken, PA, ASTM; 2001.

[24] Hatamleh MM, Watts DC. Effects of accelerated artificial daylight aging on bending strength and bonding of glass fibers in fiber-embedded maxillofacial silicone prostheses. J Prosthodont 2010;19:357–63.

[25] Guiotti AM, Goiato MC, dos Santos DM. Marginal deterioration of the silicone for facial prosthesis with pigments after effect of storage period and chemical disinfection. J Craniofac Surg 2010;21:142–5.

[26] Anusavice KJ. Phillips science of dental materials. 11th ed. St. Louis, Chicago: Saunders; 2003 p. 135–60.

[27] Goiato MC, Haddad MF, dos Santos DM, Pesqueira AA, Moreno A. Hardness evaluation of prosthetic silicones containing opacifiers following chemical disinfection and accelerated aging. Braz Oral Res 2010;24:303–8.

[28] Agency for toxic substances and disease registry (ATSDR). Toxicological Profile for methylene chloride; 2000.

[29] Goiato MC, Ribeiro Pdo P, Pellizzer EP, Garcia Júnior IR, Pesqueira AA, Haddad MF. Photoelastic analysis of stress distribution in different retention systems for facial prosthesis. J Craniofac Surg 2009;20:757–61.