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Peel strength and interfacial characterization of maxillofacial silicone elastomers bonded to titanium

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ABSTRACT

Objectives. To investigate the effect of three adhesive primers on the morphology, chemistry and peel bond strength of two maxillofacial silicone elastomers with commercially pure titanium (cpTi).

Methods. The effect of three primers (PR2:A-304 Primer/A-320 Bonding Enhancer, PR3:Super Bond, and PR4:Super Glue) on cpTi morphology and chemistry were studied by reflected light polarized microscopy (RPOLM) and reflection Fourier-transform infrared microspectroscopy (RFTIRM). For testing the bond strength between two elastomers (EL1:MDX4-4210, EL2:A-2006) and primed cpTi surfaces, a 90° T peel test was performed (PBS), using as reference EL1, EL2 specimens bonded to heat-cured poly(methyl methacrylate) resin (PMMA) primed with A-330G primer (PR1). Failure modes were analyzed under a stereomicroscope, and the percentage of remaining silicone (RS%) on cpTi and PMMA were calculated by image analysis. Scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDX) was used to investigate representative failure patterns on cpTi. Data were analyzed with Weibull analysis, ANOVA plus post hoc tests, and Pearson correlation coefficient ($a = 0.05$).

Results. Thick-irregular (PR2), thin-smooth (PR3), and uniform-porous (PR4) films were identified on cpTi by RPOLM. RFTIRM revealed: a strong peak of Si–O–Si with a distribution following the outline of the image (PR2); COO-M groups developed, but unevenly distributed (PR3); and reduction in C=C groups due to in situ polymerization (PR4). Following PBS, the ranking of the statistical significant differences in Weibull scale parameter (σ_0) of the EL1 group was PMMA_PR1 > cpTi_PR2,cpTi_PR3 > cpTi_PR4, whereas for the EL2 group cpTi_PR2 > PMMA_PR1 > cpTi_PR4,cpTi_PR3. For RS%, the ranking in the EL1 group was: PMMA_PR1 > cpTi_PR2 > cpTi_PR3 > cpTi_PR4, and in the EL2 cpTi_PR2 > cpTi_PR3 > cpTi_PR4,PMMA_PR1. There was no statistically significant correlation

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between PBS and RS%, with the exception of EL1_PMMA_PR1. In all groups mixed failure modes were found by SEM/EDX.

Significance. Although there is evidence of bonding with cpTi, there are important differences among the primer/elastomer combination that may affect the clinical performance of these materials.

1. Introduction

A variety of materials is currently used in maxillofacial prostheses including poly(methyl methacrylate) or urethane-backed, medical grade silicone. Room temperature-vulcanizing (RTV) addition silicones are probably the most widely used materials for facial restoration, with MDX4-4210 (Dow Corning, Midland, MI, USA) shown to be the most popular among clinicians [1,2]. These prostheses are retained with adhesives, tissue undercuts, magnets or in some cases extraoral osseointegrated implants [3–5]. The success of the prostheses is strongly related to their retention.

The fabrication of effective bone-anchored extraoral prostheses, made possible by the introduction of magnets and osseointgrated implants, greatly improved the treatment outcome. Several attachment systems have been used to retain facial prostheses, such as bar-clips, commercially pure titanium (cpTi) encapsulated magnets, and O-ring types. In case of bar-clip systems and O-ring type attachments, a clear heat-cured poly(methyl methacrylate) resin (PMMA) substructure is housing the retentive elements [6–8]. The substructure should extend into the body of the silicone and possess sufficient surface area for efficient bonding [4,9]. In case of magnetic retention, magnetic attachments are positioned and secured in the body of the silicone prosthesis, especially in small defects where space is limited [10]. Encapsulation of samarium-cobalt (Co_5Sm) magnets with tin or cpTi, improved their biocompatibility, minimizing corrosion and cytotoxicity [11].

A strong bond between the silicone and the PMMA substructure of the prosthesis or the cpTi encapsulated magnets is important for sufficient retention and stability, so that the junction will not fail during insertion or removal of the prosthesis. The bonding capacity of facial elastomers to acrylic resin substructures has been the subject of many studies. Several surface treatments have been proposed to improve bonding of PMMA and various facial elastomers [12–17]. However, there is only a single report on the bond strength between silicone materials and cpTi, as mediated by different primers [18].

The purpose of this study was to investigate the effect of three primers on the adhesion of two addition silicone maxillofacial elastomers to cpTi. The experimental methodology included assessment of the primers contribution to the morphological and chemical alterations induced on cpTi surfaces and to the interfacial strength of silicones bonded to cpTi. The null hypothesis was that there are no differences among the primer induced effects on cpTi surfaces including morphological, chemical and bond strength issues.

2. Materials and methods

The products used in the present study are listed in Table 1.

2.1. *Effect of primers on cpTi surface morphology and chemistry*

Specimens made of cpTi (length = 120 mm, width = 5 mm, thickness = 3 mm, $n = 5$) were ground with 600-grit size silicon carbide papers and polished with a colloidal silica suspension (OP-S, Struers, Ballerup, Denmark) containing 30% H_2O_2 with a 0.4 μm polishing cloth (MD-Chem, Struers) in a grinding/polishing machine (DAP-V, Struers) and then cleaned in an ethanol ultrasound bath for 10 min. On these surfaces, the priming treatments (PR2, PR3, PR4) were performed following the manufacturers' instructions. The specimens were then stored at 37 °C for the maximum setting times given in Table 1, air dried and then studied by reflected light polarized microscopy (RPOLM) and reflection Fourier-transform infrared microspectroscopy (RFTIRM). For RPOLM a microscope (ME 600 Eclipse, Nikon Kogaku, Tokyo, Japan) was used in bright-field mode and 40× magnification. RFTIRM analysis was performed by an FTIR microscope (AutoImage, Perkin-Elmer, Beaconsfield, Bacon, UK) attached to an FTIR spectrometer (Spectrum GX, Perkin-Elmer) operated under the following conditions: Liquid N_2-cooled mercury–cadmium telluride (MCT) detector, 4000–650 cm^{-1} wave number range, 4 cm^{-1} resolution, 100 μm × 100 μm aperture, 400 μm × 300 μm scan size for mapping and 100 scans co-addition per site. All spectra were subjected to Kramers–Kroning and baseline corrections.

2.2. *Effect of primers on bond strength*

For testing the bond strength between silicone elastomers and cpTi, a peel bond strength test (PBS) was performed based on the procedure described in ASTM D3167 standard (90° T peel test) [19]. Specimens of cpTi (length = 120 mm, width = 5 mm, thickness = 3 mm, $n = 36$) were prepared as previously described, whereas PMMA specimens (same dimensions, $n = 12$) were prepared by conventional flasking heat-cured procedures and polished according to the manufacturer's recommendations. On each of the specimens prepared as above, rectangular wax base plate patterns with dimensions (length = 120 mm, width = 5 mm, thickness = 3 mm) were attached. Half the wax pattern length was in contact with the metal or polymer surfaces and half in contact with a thin layer of a tin foil separating medium. All specimens, were invested in dental stone, preheated to remove wax, and the areas without the separating medium