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SURFACE COATING OF SILICON ELASTOMER WITH TITANIUM-DIOXIDE NANOPARTICLES (In Vitro study)

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ABSTRACT

INTRODUCTION: Maxillofacial prostheses made of medical grade silicone elastomers are routinely used to replace facial parts lost through disease or trauma. The most serious problems encountered with silicone include: discoloration of the prosthesis; deterioration of its physical and mechanical properties; difficulties related to the repair process; and a relatively short service life of the prosthesis. Fillers are nanosized particles added to the silicone elastomer to improve the physical properties, mechanical properties and viscosities of silicone elastomers. The fillers fulfill the task of supporting the cross-linked matrix by diffusing to the matrix. Recent studies have shown that nanoparticles can be extrinsically coated on the surface of silicone elastomer.

To assess the bond between the maxillofacial silicone elastomer and the surface coated nanoparticles with fourier transform infrared spectroscopy.

MATERIAL AND METHODS: The silicone elastomer was mixed and polymerized. It was divided into two groups; group I with no titanium dioxide nanoparticles and group II with extrinsically coated titanium dioxide nanoparticles. As for group II, the elastomer was subjected to oxygen plasma treatment, afterwards it was dipped into 10% APTES solution. 30% Zein solution was prepared for the dispersion of 2.5% titanium dioxide nanoparticles. The polymerized elastomer was then dipped into the Zein/titanium dioxide nanoparticles solution for 48 hours.

Bond evaluation was carried out through Fourier Transform Infrared Spectroscopy.

RESULTS: FTIR graph analysis showed the same peaks for group I and group II.

CONCLUSION: An incomplete chemical bond between the silicone elastomer surface and the titanium dioxide nanoparticles.

KEYWORDS: A-2186 silicone elastomer, extrinsic coating, FTIR.

RUNNING TITLE: Surface Coating Of Silicone Elastomer.

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INTRODUCTION

Maxillofacial prostheses made of medical grade silicone elastomers are mainly used to restore defects occurring as a result of disease or trauma.(1) The prosthesis needs to be biocompatible to enable wound healing and the restoration of healthy tissue; as well as, appearing esthetically pleasing.(2) Research has indicated an ideal maxillofacial silicone elastomer with high values of tensile strength, elongation percentage, tear resistance, but low values of hardness.(3, 4)

Listing silicone elastomer drawbacks include: prosthesis color degradation; deterioration of its physical and mechanical properties; a high cost and a hard repair process; and a relatively short life span of the prosthesis, which depends on different patient's habits, and different environmental conditions.(4, 5)

Regards the social and psychological effects on patients, it is necessary to decrease the effect of bacterial contamination, the deterioration of color and enhance the overall properties of elastomers used for facial prosthesis.(6)

One of the most usable materials is the A-2186 silicone elastomer (Factor II inc. USA), which despite its preferable clinical use, suffers durability.(7) Rates of failure for the prostheses are about 5%, which can get higher with patients undergoing radiotherapy.[8] Hence, extending years of service for the silicone elastomer is clinically desirable. Silicone elastomers used for maxillofacial prosthesis are far from ideal and preferably be replaced every 6 to 12 months owing to patients' dissatisfaction.[9]

One of the crucial technicalities perceived by patients is deterioration of color. Color stability is the key factor for the assessment of the success of a maxillofacial silicone prosthesis. Color stability is dependent on many variables such as weathering, environmental conditions, climate change and the patients' habits.[10] [11] Color of the maxillofacial prosthesis can be enhanced by the addition of intrinsic or extrinsic coloring pigments which help the prosthesis being more satisfactory to the patient. The application of these pigments adds to the color stability of such an elastomer.[12] However, external coloring pigments are more vulnerable to color instability in relation to internal coloring pigments.[13]

The use of nanomaterials with antimicrobial properties, photocatalytic activities in conjunction with silicone elastomer prostheses may offer an improvement. Nanomaterials have found applications in many areas of medicine including drug delivery, vaccine development, medical imaging, diagnostics, and medical implants.[14] Nanoparticles are defined as systems for which all three dimensions are roughly 1–100 nm . Fillers are used to modify silicone elastomers in terms of color stability, mechanical properties, and viscosities of silicone elastomers. This occurs as the nanosized particles support the cross-linked matrix of silicone elastomers.[15]

Nanomaterials used in conjunction with the silicone elastomers have been proved to significantly affect the color degradation and the physical properties of the prosthesis. Many studies have illustrated the use of the nanoparticles as an incorporation of the nanosized filler like Titanium Dioxide in the silicone elastomer during the mixing procedure.[16] These studies have found satisfactory results by incorporating nanoparticles into polymeric materials (mainly silicone elastomers used for facial prostheses), in terms of protecting such materials from degradation.[12] The use of Titanium Dioxide nanoparticles has been widely accepted to contribute to the color stability of many materials.[17]

Recent research have shown that nanoparticles could be surface coated on a maxillofacial silicone elastomer. Meran et al have illustrated an experiment where silver nanoparticles were surface coated on a cured silicone elastomer . The surface coating was shown to be successful using scanning electron microscopy. Theses nano coatings hindered the growth of infection on the cultured fibroblasts.[18]

Further studies are still needed to develop the ideal maxillofacial silicone material which will solve the issues of color instability, mechanical properties, ease of repair and lifespan of the prosthesis.

The null hypothesis states that titanium dioxide nanoparticles will not adhere to the silicone elastomer surface.

MATERIAL AND METHODS

Study setting:

Sample preparation, treatment, experimentation and testing took place at the laboratory of City of Scientific Research and Technological Applications.

Study design(figure 1):

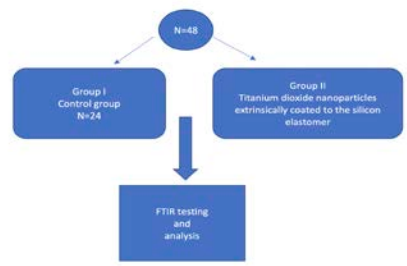

Figure 1 representing an illustrative diagram of the in vitro study.

An experimental in vitro study was conducted to test the presence of a bond between a maxillofacial silicone elastomer after the application of Titanium Dioxide nanoparticles.

Sample size calculation:

The minimal sample size calculation was based on a study aimed to evaluate the effect of incorporation of two compositions of nano-oxides on color stability of intrinsically colored maxillofacial silicone elastomer subjected to outdoor weathering.[18, 19]

Methods

A total of 48 specimens (n=48) are divided to two groups as follows:

Twenty four (n=24) control specimens without the addition of the nanoparticles.

Twenty four (n=24) specimens extrinsically coated with the nanoparticles.

Preparation of the control group. Group I (n=24)

A-2186 maxillofacial silicone elastomer specimens mixed 10:1 by weight following the instructions of the manufacturer. The intrinsic pigment application was added after the mixing procedure using wooden tongue blades, where the mix was poured into Teflon molds (20*3 mm) in diameter. The mixed elastomer was left in the vacuum chamber for 30 minutes to eliminate any formed air bubbles.

Preparation of the specimens extrinsically coated with titanium dioxide nanoparticles. Group II (n=24)

Twenty four blank silicone elastomer specimens were prepared. A plasma enhanced chemical vapor deposition reactor was used to oxidize the specimens at 13.56 MHz radiofrequency where oxygen was the inlet gas under 230 mTorr pressure. The process was carried out for 60 seconds with a 55 W power source.(20) After which, the surface treated silicone specimens were treated with 10% 3 amino isopropyl triethoxy silane, followed by adding 2.5% Glutaraldehyde to act as a crosslinker. Silanization of the polydimethyl siloxane (PDMS) surface with amino isopropyl triethoxy silane (APTES) enables the formation of self-assembled monolayers of molecules with reactive functional groups amide group (–NH_2) or carboxyl group (–COOH) and specific covalent binding with proteins.[21] [22]Among the different proteins which can serve as carriers are Cellulose, Collagen and Zein. They are selected primarily for their biodegradability, biocompatibility without being toxic.[22, 23] Hence, a 30% Zein solution prepared 80:20% by volume absolute ethyl alcohol : water respectively, where titanium dioxide nanoparticles were added to the solution[24] with a concentration of 2.5% by volume. The mix was carried out initially at 50° temperature using a magnetic stirrer for 1 hour then the temperature was dropped down to room temperature and left to stir for 24 hours. After mixing the titanium dioxide nanoparticles with the zein solution, the surface treated silicone specimens were dip coated in the solution and left for 48 hours.

Assessment of the bond:

Assessment of the bonding between the maxillofacial silicone elastomer and the surface coated nanoparticles was carried out through Fourier transform infrared spectroscopy.

RESULTS

FTIR analysis for group I and group II was demonstrated in figures 3 and 4 respectively. Figure 1 shows the peaks in the untreated silicone elastomer group. Clearly, it can be seen that peaks are present at different wavelengths 460, 691, 784, 861, 1005, 1254, 1406, 2902, 2957. On the other hand, figure 2 shows the analysis for the surface coated titanium dioxide nanoparticles with nearly the same absorbance spectrum except for a new band at 2846.

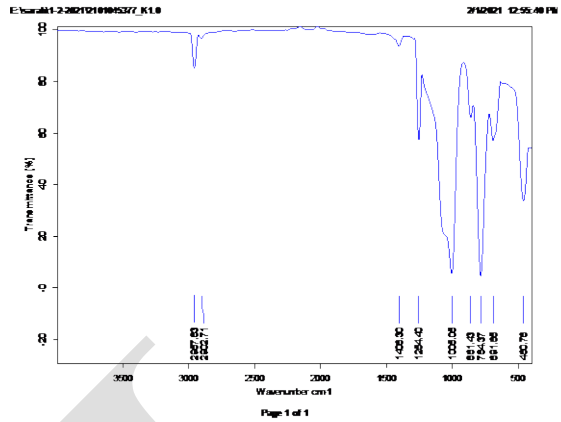

Figure 3: FTIR sample for the untreated silicon elastomer specimens.

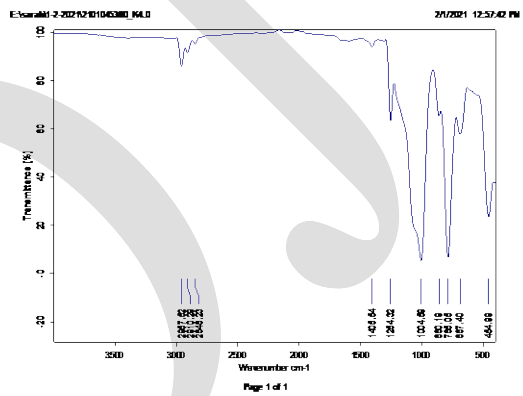

Figure 4: FTIR sample for the surface coated silicon elastomer with titanium dioxide nanoparticl

DISCUSSION

Silicone elastomers undergo significant changes regarding physical and mechanical properties which in turn decrease the patients' satisfaction with the prostheses after long term usage.[1] Thus, enhancing silicone elastomers with organic and inorganic fillers took place to overcome such drawbacks including lack of tensile and elongation strengths, as well as, color degradation.[6, 16, 25, 26] With the availability of the materials that enhance silicone elastomers at a nanoscale, research trials were carried out to test the effect of such materials on the overall properties of the newly formed composites. Specifically, titanium dioxide nanoparticles were incorporated within the matrix of the silicone elastomers to improve its mechanical properties[25], as well as, decreasing its color deterioration when being subjected to different environmental conditions.[26]

An alternative way to add nanomaterials to the silicone elastomer was to surface coat the polymerized elastomer [18, 27]which is thought to yield better results in comparison to incorporating such materials within the matrix. Hence, this study was conducted to evaluate the adherence of the added nanomaterial to the elastomer surface. Before adding titanium dioxide, silicone elastomer surface has to be functionalized as its surface is chemically inert. Functionalization of the silicone elastomer was carried out through oxygen plasma treatment as it relies on the use of an ionized gas to functionalize the outer surface, and is by far the most commonly utilized technique for the surface modification of polydimethylsiloxane polymer.[20] Followed by the addition of the APTES which in turn would render the elastomer surface hydrophilic to promote the binding with nanoparticles.[21] The composite was ready to be dipped into the Zein/titanium dioxide solution as Zein serves as one of the carries proteins to bind with substrates.[22] [23]

Evaluation was carried out through fourier transform infrared spectroscopy. FTIR testing services help as a great first step in a product analysis. This technique helps identify and characterize the main ingredients within a sample. The absorbance spectrum created is analyzed to identify which chemical family a sample's components fit within. Upon examination, figure 3 demonstrates the graph analysis for an untreated silicone elastomer sample with no titanium dioxide particles. As illustrated, each peak marked on the graph is correspondent to a specific chemical family.[28] 784 cm−1 methyl group ($-CH_3$) rocking and Silicon Carbon (S-C) stretching in tetramethyl silane (Si–CH3), 1005 cm−1 siloxane group stretching(Si–O–Si), 1254 cm−1 methyl (CH3) deformation in tetramethyl silane group (Si–CH3), and 2957cm−1 asymmetric methyl group (CH3) stretching in tetramethyl silane (Si–CH3).[29] Moreover, figure 4 represents the FTIR analysis for the surface coated titanium dioxide nanoparticles. The main concern regarding this analysis is the absence of stretching at 3335 cm−1 or bending at 1634 cm−1. This bending or stretching corresponds to the amine group (-NH).[29] This specific group is fundamental after functionalizing silicone elastomer surface with APTES.[28, 29] Accordingly, its absence indicates an incomplete chemical binding between the silicone elastomer and the surface coated titanium dioxide nanoparticles. This finding contradicts the study conducted by Bishal et al. [27] As for rocking found at 2846.23, this supports the presence of asymmetric methyl group which may be the result of the plasma oxygen treatment.

CONCLUSION

1- Oxygen plasma treatment was able to promote surface changes as observed in the FTIR graph analysis.
2- An incomplete chemical bond between the silicone elastomer surface and the titanium dioxide nanoparticles.
3- The newly formed elastomer with surface coated titanium dioxide is not the most favorable material to protect against mechanical or physical deterioration of facial prostheses.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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REFERENCES

1. Chang T-L, Garrett N, Roumanas E, Beumer III J. Treatment satisfaction with facial prostheses. J Prosthet Dent. 2005;94:275-280.
2. Sanchez RA, Moore DJ, Cruz DL, Chappell R. Comparison of the physical properties of two types of polydimethyl siloxane for fabrication of facial prostheses. J Prosthet Dent. 1992;67:679-682.
3. Polyzois GL. Color stability of facial silicone prosthetic polymers after outdoor weathering. The Journal of prosthetic dentistry. 1999;82:447-50; Nemli SK, Aydin C, Yilmaz H, Bal BT, Arici YK. Quality of life of patients with implant-retained maxillofacial prostheses: a prospective and retrospective study. J Prosthet Dent. 2013;109:44-52.
4. Gary JJ, Smith CT. Pigments and their application in maxillofacial elastomers: a literature review. J Prosthet Dent. 1998;80:204-208.
5. Hu X, Pan X, Johnston WM. Effects of pigments on dynamic mechanical properties of a maxillofacial prosthetic elastomer. J Prosthet Dent. 2014;112:1298-1303.
6. Han Y, Kiat-amnuay S, Powers JM, Zhao Y. Effect of nano-oxide concentration on the mechanical properties of a maxillofacial silicone elastomer. J Prosthet Dent. 2008;100:465-473.
7. Montgomery PC, Kiat-Amnuay S. Survey of currently used materials for fabrication of extraoral maxillofacial prostheses in North America, Europe, Asia, and Australia. J Prosthodont. 2010;19:482-490.
8. Chrcanovic BR, Nilsson J, Thor A. Survival and complications of implants to support craniofacial prosthesis: A systematic review. J Craniomaxillofac Surg. 2016;44:1536-1552.

9. Hatamleh MM, Haylock C, Watson J, Watts DC. Maxillofacial prosthetic rehabilitation in the UK: a survey of maxillofacial prosthetists' and technologists' attitudes and opinions. Int J Oral Maxillofac Surg. 2010;39:1186-1192.
10. 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.
11. Goiato MC, Pesqueira AA, Ramos da Silva C, Gennari Filho H, Micheline Dos Santos D. Patient satisfaction with maxillofacial prosthesis. Literature review. J Plast Reconstr Aesthet Surg. 2009;62:175-180.
12. Andreotti AM, Goiato MC, Moreno A, Nobrega AS, Pesqueira AA, dos Santos DM. Influence of nanoparticles on color stability, microhardness, and flexural strength of acrylic resins specific for ocular prosthesis. Int J Nanomedicine. 2014;9:5779-5787.
13. Hu X, Pan X, Johnston WM. Effects of pigments on dynamic mechanical properties of a maxillofacial prosthetic elastomer. J Prosthet Dent. 2014;112:1298-1303.
14. Fadeel B, Garcia-Bennett AE. Better safe than sorry: Understanding the toxicological properties of inorganic nanoparticles manufactured for biomedical applications. Adv Drug Deliv Rev. 2010;62:362-374.
15. Han Y, Zhao Y, Xie C, Powers JM, Kiat-amnuay S. Color stability of pigmented maxillofacial silicone elastomer: effects of nano-oxides as opacifiers. J Dent. 2010;38 Suppl 2:100-105.
16. Cevik P, Eraslan O. Effects of the Addition of Titanium Dioxide and Silaned Silica Nanoparticles on the Mechanical Properties of Maxillofacial Silicones. J Prosthodont. 2017;26:611-615.
17. Kiat-Amnuay S, Mekayarajjananonth T, Powers JM, Chambers MS, Lemon JC. Interactions of pigments and opacifiers on color stability of MDX4-4210/type A maxillofacial elastomers subjected to artificial aging. J Prosthet Dent. 2006;95:249-257.
18. Meran Z, Besinis A, De Peralta T, Handy RD. Antifungal properties and biocompatibility of silver nanoparticle coatings on silicone maxillofacial prostheses in vitro. J Biomed Mater Res B Appl Biomater. 2018;106:1038-1051.
19. Akash R, Guttal SS. Effect of incorporation of nano-oxides on color stability of maxillofacial silicone elastomer subjected to outdoor weathering. J Prosthodont. 2015;24:569-75; Killeen PR. An alternative to null-hypothesis significance tests. Psychological science. 2005;16:345-353.
20. Gokaltun A, Yarmush ML, Asatekin A, Usta OB. Recent advances in nonbiofouling PDMS surface modification strategies applicable to microfluidic technology. Technology (Singap World Sci). 2017;5:1-12.
21. Yuan H, Mullett WM, Pawliszyn J. Biological sample analysis with immunoaffinity solid-phase microextraction. Analyst. 2001;126:1456-61; Wang ZH, Jin G. Covalent immobilization of proteins for the biosensor based on imaging ellipsometry. J Immunol Methods. 2004;285:237-243.
22. Kumar M, Kong X, Behera AK, Hellermann GR, Lockey RF, Mohapatra SS. Chitosan IFN-γ-pDNA nanoparticle (CIN) therapy for allergic asthma. Genetic Vaccines and Therapy. 2003;1:1-10.
23. Nascimento A, Laranjeira M, Favere V, Josue A. Impregnation and release of aspirin from chitosan/poly (acrylic acid) graft copolymer microspheres. J Microencapsul. 2001;18:679-684.
24. Plath AMS, Facchi SP, Souza PR, Sabino RM, Corradini E, Muniz EC, et al. Zein supports scaffolding capacity toward mammalian cells and bactericidal and antiadhesive properties on poly(ε-caprolactone)/zein electrospun fibers. Materials Today Chemistry. 2021;20:100465.
25. Zayed SM, Alshimy AM, Fahmy AE. Effect of Surface Treated Silicon Dioxide Nanoparticles on Some Mechanical Properties of Maxillofacial Silicone Elastomer. Int J of Biomater. 2014;2014:750398.
26. Nada H. E, Ahmad M. A, Moustafa N. A. Evaluation of intrinsic color stability of facial silicone elastomer reinforced with different nanoparticles. Alex Dent J. 2016;41:50-54.
27. Bishal AK, Wee AG, Barão VAR, Yuan JC-C, Landers R, Sukotjo C, et al. Color stability of maxillofacial prosthetic silicone functionalized with oxide nanocoating. J Prosthet Dent. 2019;121:538-543.
28. Le T-N, Lee C-K. Surface Functionalization of Poly(N-Vinylpyrrolidone) onto Poly(Dimethylsiloxane) for Anti-Biofilm Application. Applied Biochemistry and Biotechnology. 2020;191.29-44.
29. Antônio Belinelli Silva F, Chagas Silva F, Florenzano F, Pissetti F. Poly(dimethylsiloxane) and Poly[vinyltrimethoxysilane- co -2-(dimethylamino) ethyl methacrylate] Based Cross-Linked Organic-Inorganic Hybrid Adsorbent for Copper(II) Removal from Aqueous Solutions. J. Braz. Chem. Soc.. 2016;27.2181-2191.