Silicone Colour Stability: The TiO2 and ZnO Nanoparticle Showdown

Dr. Diksha Verma[1]; Dr. Rajesh Kumar[2]; Dr. Sunil Kumar M.V.[3]; Dr. Krishan Kumar[4]
Jaipur Dental College, Maharaj Vinayak Global University

Abstract:-

- ***Statement of Problem:-***

The limited service life of maxillofacial prostheses is a significant disadvantage, mostly because of deterioration and uneven surface coloration. Though several modifications among the materials and techniques used in the creation of silicone maxillofacial prosthesis have been introduced, Unwanted colour changes over time continue to be a problem. It has been reported that silicone elastomers can be given an ultraviolet shielding property by ZnO and TiO2 nano-oxides. This study compares and evaluates the effectiveness of TiO2 and ZnO nano-oxide particles with skin pigments on the consistency of colour in maxillofacial silicone elastomers.

- ***Purpose:-***

This in vitro investigation aimed to assess the impact of ZnO and TiO2 nanoparticles present on the colour stability in a room-temperature RTV silicone elastomer during artificial ageing.

- ***Methodology:-***

Sixty disks (10 x 2 mm) were made using RTV silicone. Three groups (Group 1: TiO2, Group 2: ZnO nanoparticles, and Group 3: CONTROL with skin pigments and silicone) were created for the specimens. Using a computerised device, specimens were subjected to 120 days of accelerated ageing. Before and after ageing, CIELab colour coordinates and the total colour difference (DE*) values were ascertained. The groups' DE* values were compared.

- ***Result:-***

Nano-TiO2 will make the maximum color stability after artificial ageing than Nano-ZnO, and it was the least stable in the control group. With the study, it can be concluded that the Control group had a more significant color change than other groups.

- ***Conclusion:-***

Nano-TiO2 will help stabilize color after ageing under various environmental conditions, so it can be incorporated into silicone for further use.

Keywords:- *RTV* - *Room Temperature Vulcanizing Silicone, Nanoparticles, Artificial Aging, Digital Incubator, Spectrophotometer, Color Stability, BYR – Blue, Yellow, Red. CIE Colour Coordinates.*

I. INTRODUCTION

Prosthetic restoration and replacement of missing structures in the maxillofacial region of the head and neck are the focus of maxillofacial prosthetics [1]. Masking maxillofacial abnormalities dates back centuries, to Egypt and China, when their use of wax and resins, respectively, allowed them to rebuild missing parts of the head and neck region. The search for the perfect material began in 1500 A.D., when French surgeon Ambrose Pare described facial prostheses in 1575. Since then, prostheses have evolved from earlier versions made of gold, silver, paper, cloth, leather, wrought iron, metals, ceramics, vulcanite, and acrylic to latex, polyvinyl chloride and copolymers, polyurethane elastomers, medical-grade silicones, and polyphosphazines. [2].

Although silicones were initially developed in 1946, Barnhart (1960) used them for the first time in an extra-oral prosthesis and found that they worked better than other materials.[2].

Materials for Maxillofacial prosthesis come in a wide variety of chemical configurations, and their physical characteristics range from stiff, hard alloys and polymers to flexible, soft polymers and elastomers. Latexes, silicone rubber materials, poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC), and polyurethanes were among these materials [2,3]. Silicone is the most popular and beneficial material due to its biocompatibility, low viscosity, simplicity of manipulation, and patient accomodation qualities (i.e., non-toxic, lightweight, and easily cleaned). Additionally, they exhibit good dimensional stability, high elongation, and high tensile strength. [2,4]. As silicone material deteriorates over time, maintaining the colour stability of maxillofacial prosthetic silicone elastomers (MFPSE) has remained a basic problem.. This could be influenced by Ultraviolet (UV), environmental factors that may include light, heat, moisture, pollutants, chemicals used in cleaning, and various methods affecting silicone's colour and mechanical characteristics. [4]

Nano-oxides are inorganic particles with a white colour. When integrated into organic polymers, their small size, large specific area, resilient interface, and quantum impact improve the polymer's mechanical and optical properties. Therefore, artificial weathering is helpful, quick, and efficient for understanding out how stable a material's colour is for oral applications. A variety of variables, including temperature, UV radiation, water, and humidity, are tested for materials by means of automated weathering instruments. [5]

Skin color is among the most commonly observed colors in our everyday life and has a rather significant part in numerous interdisciplinary uses. In all of these applications, it is pertinent to find an accurate method of measuring the color of skin in a quantitative manner. [6,7].

Since CIE (Commission Internationale de l'Eclairage) colorimeters were designed to substitute for human color vision, there have been successful attempts to measure skin color using spectrophotometers and tele-spectroradiometers in terms of CIELAB values [8,9].

The implications of this study extend beyond maxillofacial prosthetics. Improved color stability in silicone can benefit other medical devices, consumer electronics, and automotive components. Additionally, the enhanced biocompatibility and antimicrobial properties of nanoparticle-infused silicone can lead to safer and more durable medical applications, ultimately contributing to better patient outcomes and reduced healthcare costs.[17]

II. MATERIAL AND METHODOLOGY

The in vitro investigation was carried out within the Department of Prosthodontics of Jaipur Dental College, Jaipur. This study evaluated the effectiveness of TiO2 and ZnO nanoparticles with skin pigments regarding the maxillofacial silicone elastomers' colour stability.

➢ *Inclusion Criteria*

- The substance needs to be biocompatible.
- Durable to withstand wear and tear.
- Allow for the minimization of color degradation due to environmental factors.
- Aging machine should have controlled setting to replicate environmental factors.
- Specific size range (1-100nm) for nanoparticles
- Skin pigments should be able to provide even coverage without blotching or streaking.

➢ *Exclusion Criteria*

- Silicone material that does not withstand mechanical damage.
- Material that reacts adversely with pigments, resulting in early discoloration and degradation.
- Aggregation and clumping of nanoparticles and pigments are not considered.
- Samples with voids.

In order to assess the impact of ZnO and TiO2 nano-oxide particles on the colour stability of maxillofacial silicone elastomers during artificial ageing in a digital incubator, 60 samples in total were created. This allowed for the evaluation of the post-aging impacts of ageing under ideal conditions.

Sixty circular disks (Ø10×2mm) measured using vernier caliper (SKADIOO) were made for RTV silicone in stainless steel custom-made mould). Silicone RTV (VEDAYUKT INDIA PVT. LTD) was mixed, and nanoparticles TiO2 and ZnO (VEDAYUKT INDIA PVT. LTD) in the group were added to a concentration of 1:16 and skin pigments (CHEMZEST TECHNOPRODUCTS PVT. LTD), a single drop of each colour is used with the help of the dropper (BOROSIL) and mixed vigourously, after that poured to the mould with glass slide kept as a base, and other glass slide over it to have a even thickness of the sample, which was kept for 24hrs to have a complete set. The samples were divided into three groups.

- GROUP 1 is RTV Silicone and skin pigments (BYR) with TiO_2 nanoparticles,
- GROUP 2 is RTV Silicone and skin pigments (BYR) with ZnO nanoparticles,
- GROUP 3 is RTV Silicone and skin pigments (BYR).
- (BYR: Blue, Yellow, Red), (RTV: Room Temperature Vulcanizing)

Fig 1: Measurement of Inner Diameter and Width

International Journal of Innovative Science and Research Technology
https://doi.org/10.38124/ijisrt/IJISRT24NOV803

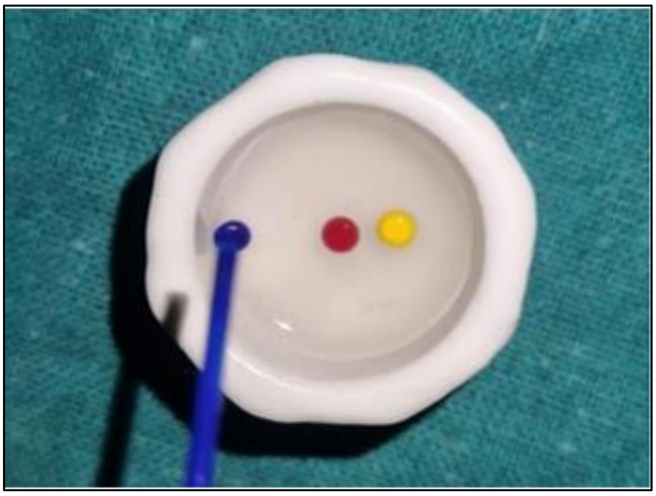


Fig 2: Adding Pigments to Silicone

Fig 3: Adding Nanoparticles to Silicone

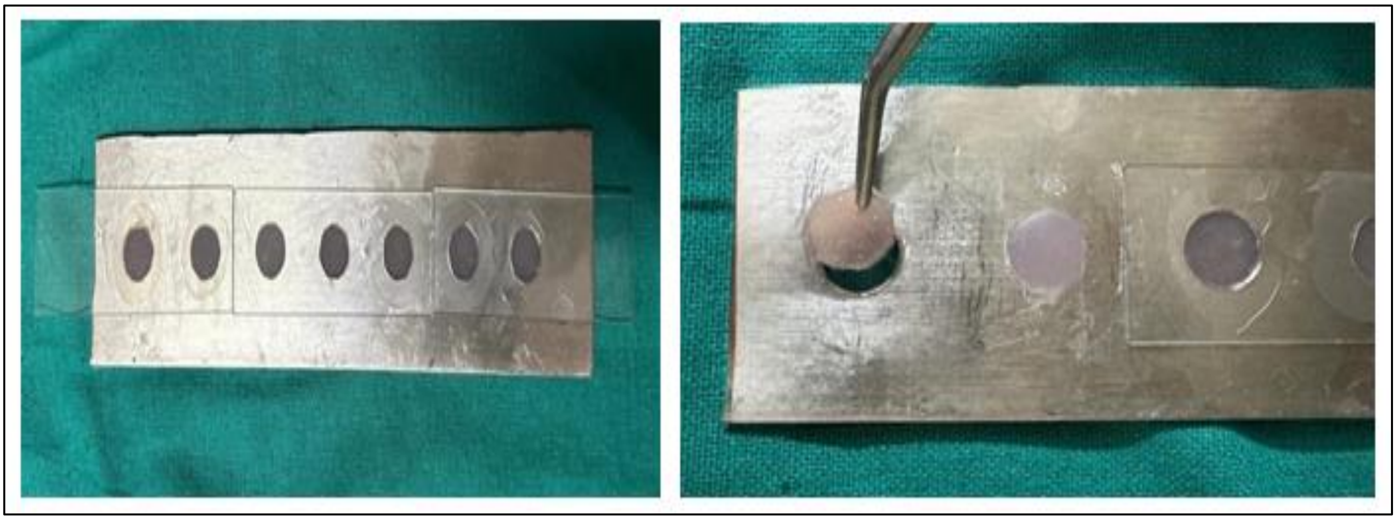


Fig 4: Sample Preparation

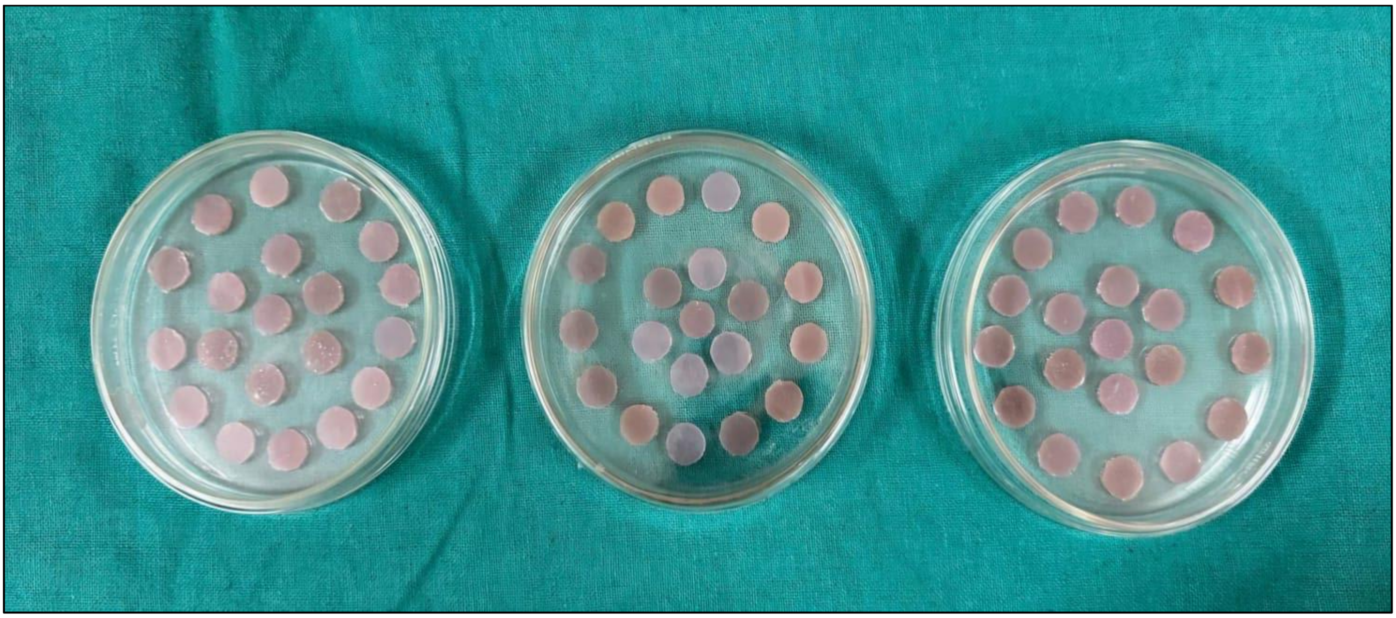


Fig 5: Pre-Sample Preparation = 20*3 = 60 no's

Fig 6: Digital Incubator

Fig 7: Sample Color Testing

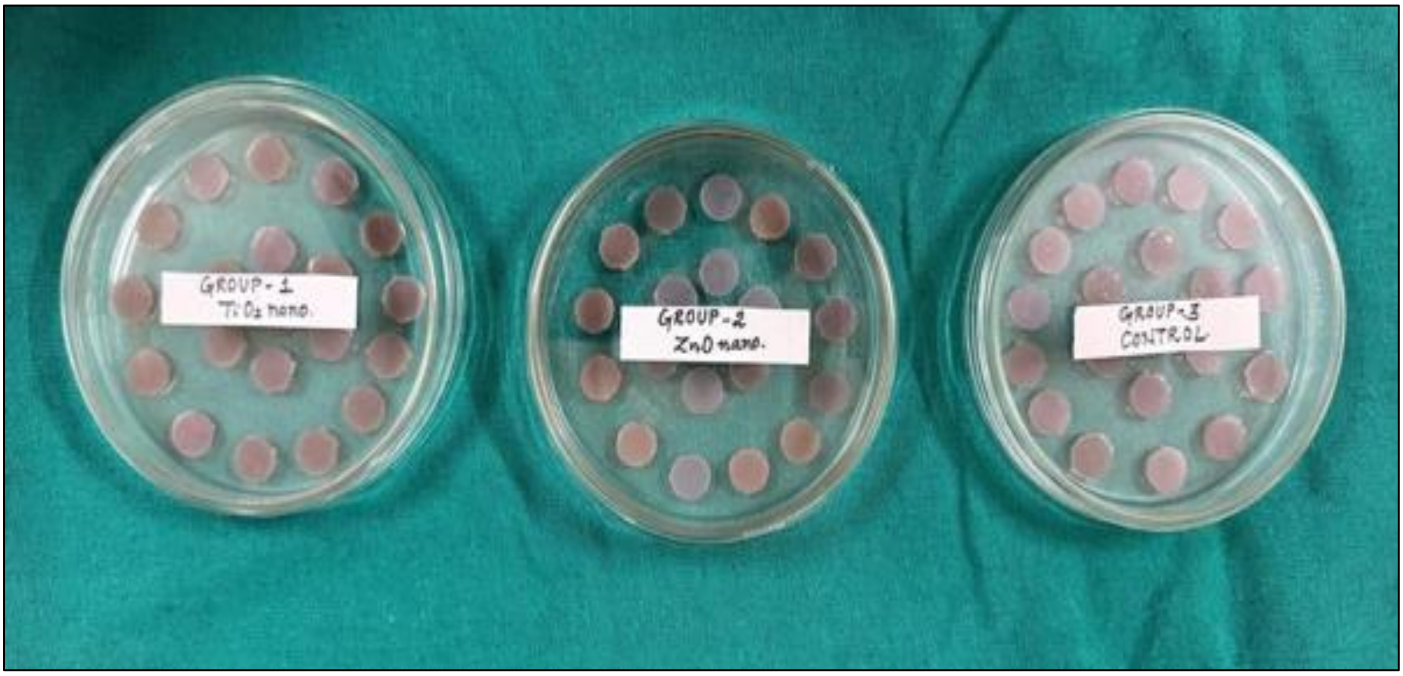


Fig 8: Post-Sample After Ageing = 20*3 = 60 no's

20 samples of each group and each sample were tested on a CM-5 Spectrophotometer (KONICA MINOLTA) based on CIElab color system, which analyse samples to investigate the various silicone, colourants, and opacifiers utilised in the computation of total colour difference (DE*) values both prior to and following ageing.

Samples were then put onto three Petri dishes of GROUP A (TiO2), GROUP B (ZnO), and CONTROL and placed in the digital incubator (M.C Dalal & Co.) to provide optimum conditions, including a temperature of 100 degrees Celsius and 67% humidity. They were kept continuously for 120 days. The samples were then retested to evaluate whether the nanoparticles could stabilize the color.

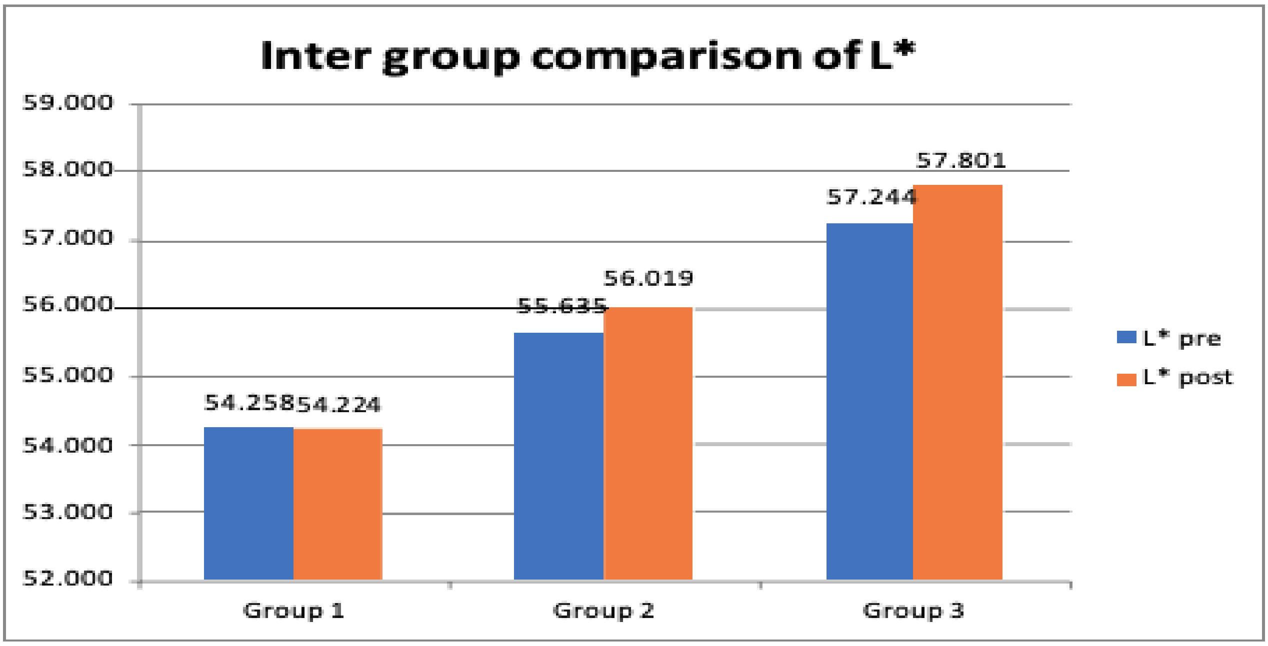
III. RESULTS

Table 1: The Statistical Analysis in this Study Utilized the Chi-Square Test, Kruskal-Wallis Test and Mann-Whitney U Test.

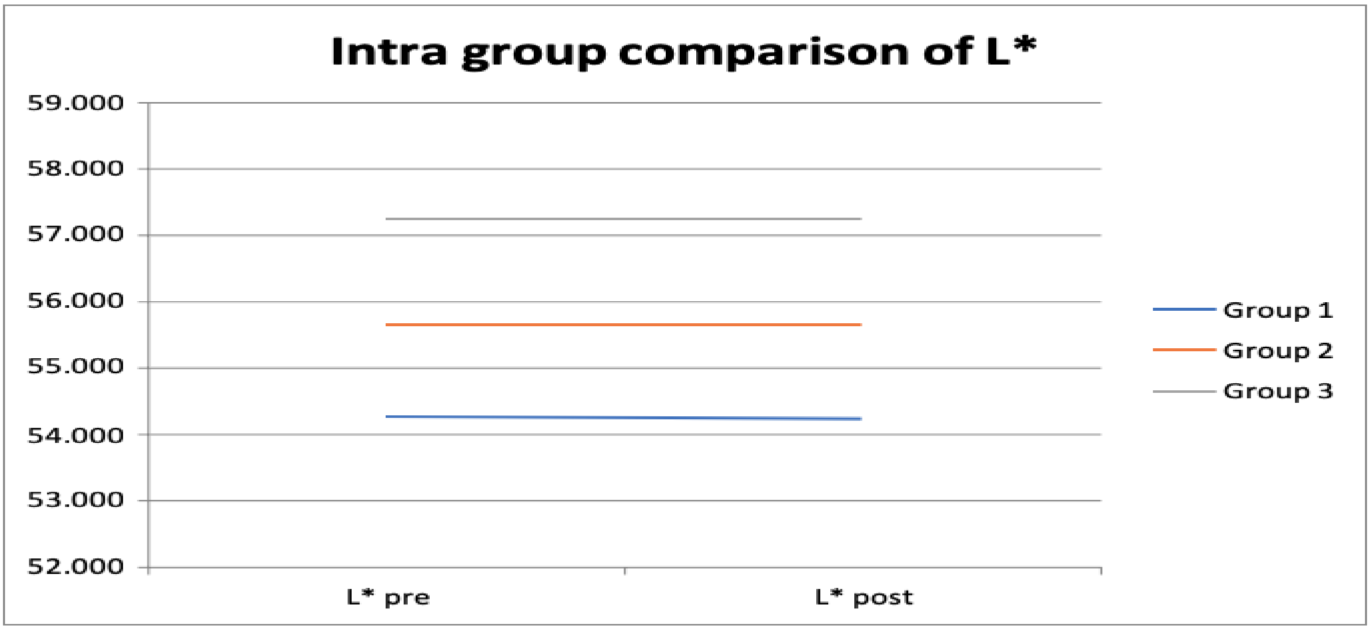
	Group	N	Mean	Std. Deviation	Median	Mean rank	Chi square value	p value of Kruskal-Wallis Test
L* pre	1	20	54.2580	1.49096	54.080	16.15	23.351	0.000**
	2	20	55.6350	1.26727	55.695	32.83		
	3	20	57.2435	2.17112	57.585	42.53		
a* pre	1	20	1.9890	.12135	2.000	38.83	6.856	0.032*
	2	20	1.8915	.23858	1.900	25.95		
	3	20	1.8100	.27743	1.935	26.73		
b* pre	1	20	.0650	.03635	0.065	18.03	22.188	0.000**
	2	20	.1100	.07834	0.090	29.58		
	3	20	.1625	.07913	0.150	43.90		
L* post	1	20	54.2235	.43188	54.155	12.90	34.446	0.000**
	2	20	56.0185	1.34615	56.025	33.80		
	3	20	57.8005	2.28855	57.065	44.80		
a* post	1	20	1.5265	.10080	1.555	11.55	36.111	0.000**
	2	20	1.8210	.18367	1.790	37.63		
	3	20	1.9165	.25897	1.830	42.33		
b* post	1	20	.5080	.05944	0.505	10.65	39.570	0.000**
	2	20	.9030	.08247	0.905	38.08		
	3	20	.9110	.12358	0.965	42.78		
dE	1	20	.9365	.15705	0.925	12.58	40.629	0.000**
	2	20	1.5120	.44100	1.535	31.18		
	3	20	2.4305	.67474	2.335	47.75		

- A statistically significant difference was observed between the groups ($p<0.01$) for the following:
- L* pre with higher values in group, b* pre with higher values in group,
- L* post with higher values in group, a* post with higher values in group, b* post with higher values in group, dE with higher values in group 3.
- There was a statistically significant difference in the values across the groups ($p<0.05$), with group 1 exhibiting higher values for a* pre.

ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/IJISRT24NOV803



(a)

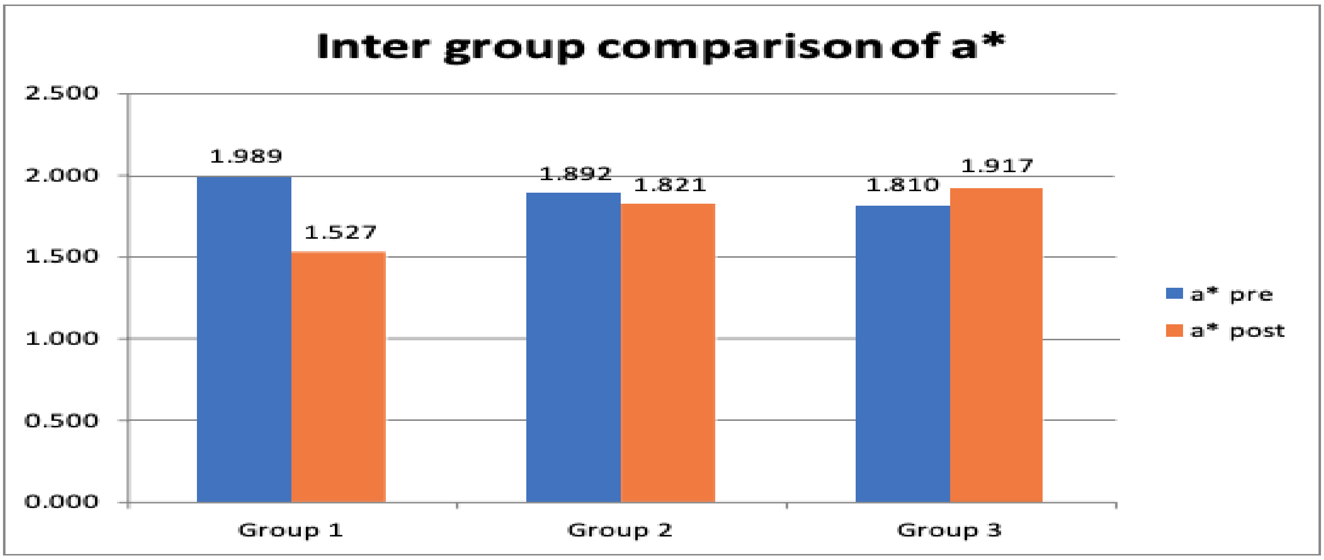


(b)

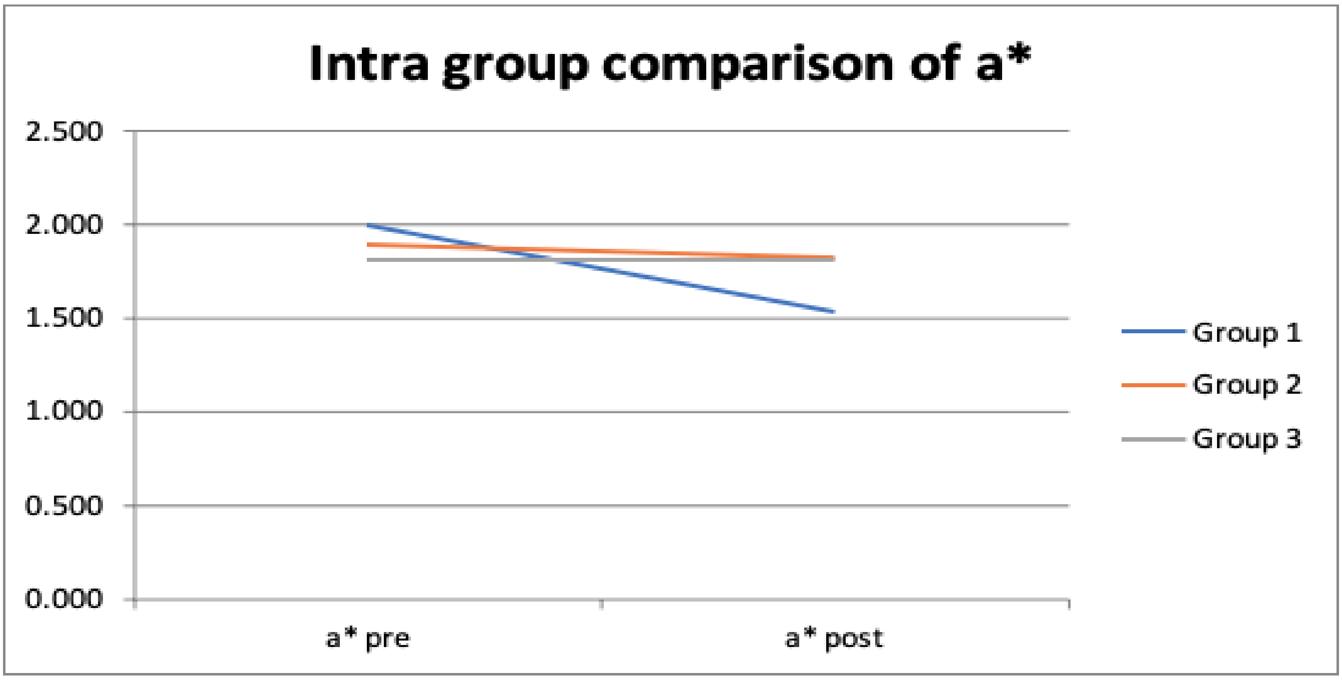
Graph 1: a) Inter Group Comparison of L*
b) Intra Group Comparison of L*

Table 2: Comparing group 3 to Groups 1 and 2, the Difference Between Pre and Post was Statistically Significant.

	Group 1	Group 2	Group 3
L* pre	54.258	55.635	57.244
L* post	54.224	56.019	57.801



(a)

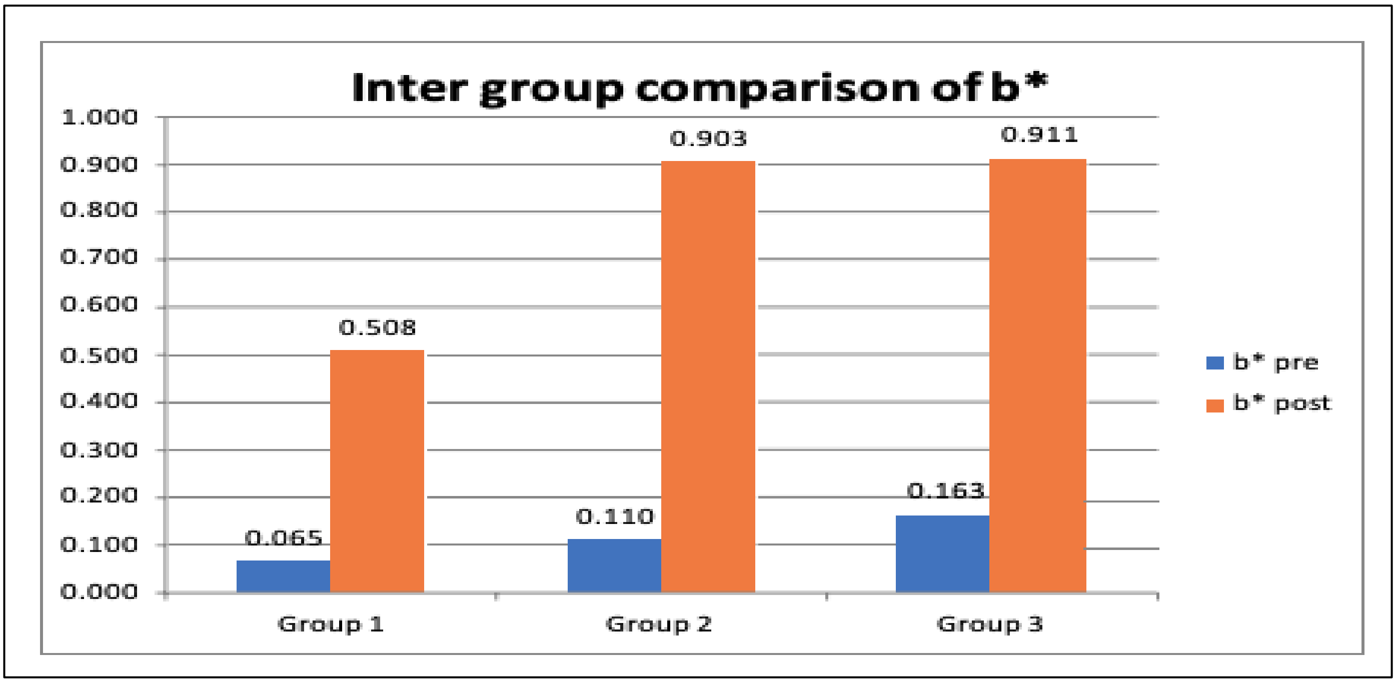


(b)

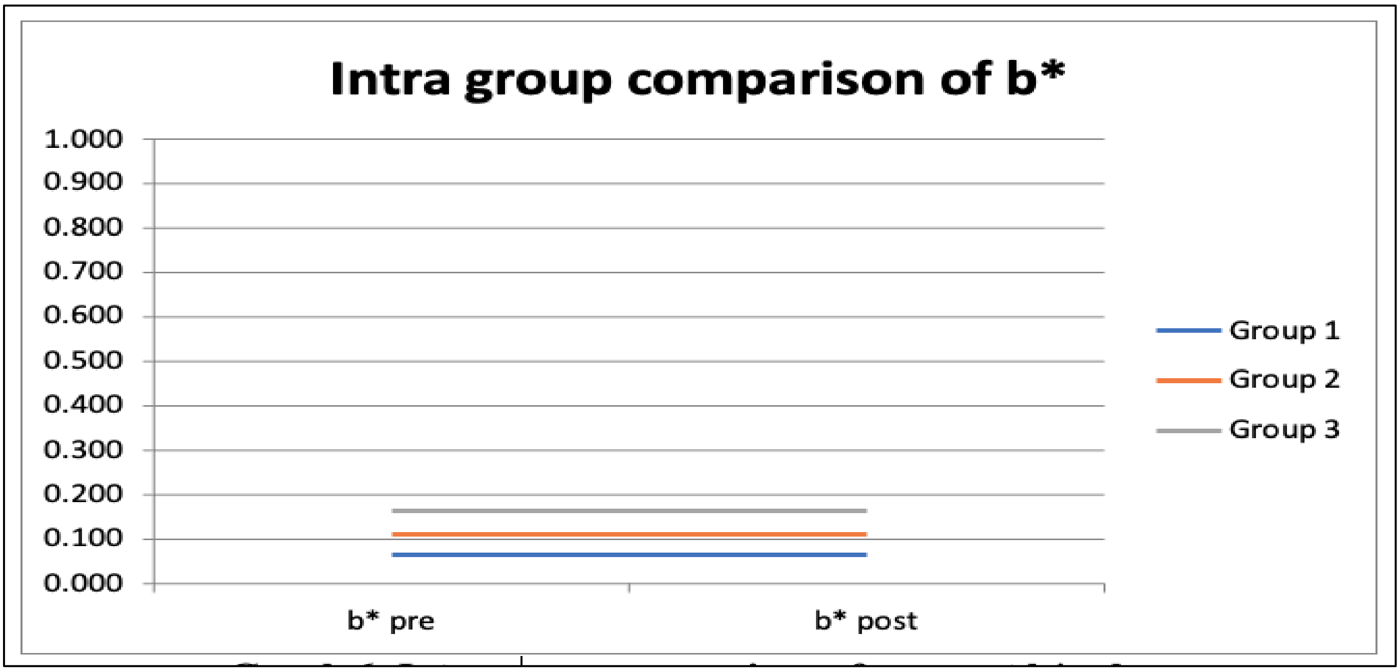
Graph 2: a) Inter Group Comparison of a*
b) Intra Group Comparison of a*

Table 3: Compared to Groups 2 and 3, Group 1 Showed a Significantly Significant Difference Between Pre- and Post-Test Results

	Group 1	Group 2	Group 3
a* pre	1.989	1.892	1.810
a* post	1.527	1.821	1.917



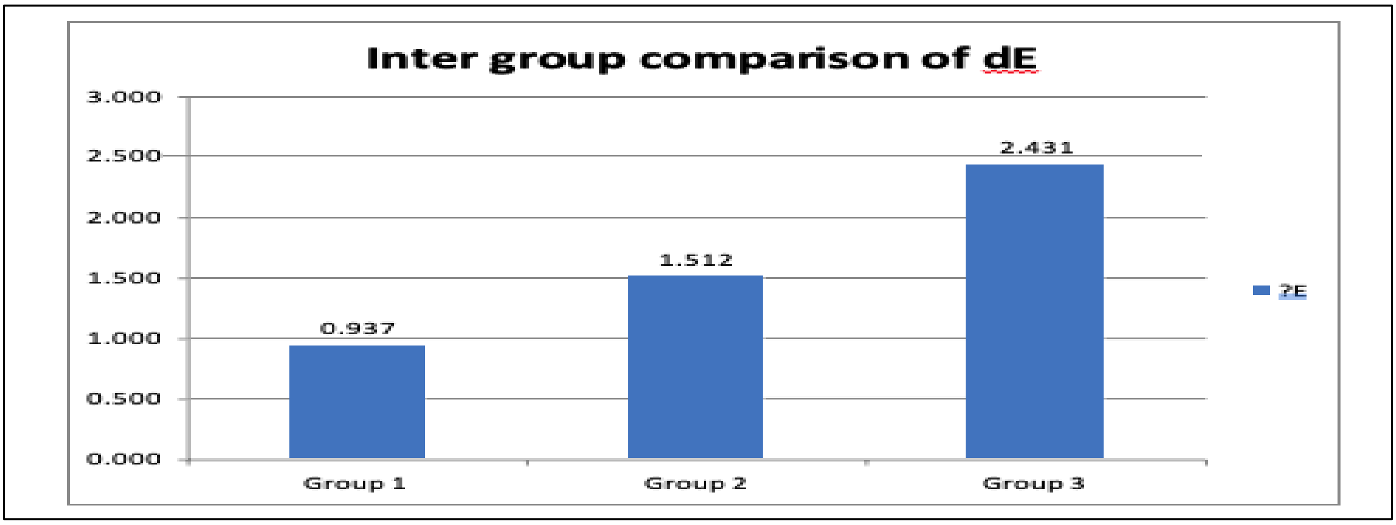
(a)



Graph 3: a) Inter group comparison of b*
b) Intra group comparison of b*

Table 4: Comparing group 3 to groups 1 and 2, the difference between pre and post was statistically significant.

	Group 1	Group 2	Group 3
b* pre	0.065	0.110	0.163
b* post	0.508	0.903	0.911



Graph 4: Inter Group Comparison of dE.
Comparing Group 3 to Groups 1 and 2, the Difference between Pre and Post was Statistically Significant

IV. DISCUSSION

The materials employed for this purpose are silicone elastomers, which have been used to make facial prosthetics for more than 50 years [10,11]. However, colour degradation is one of the primary causes of facial prosthesis refabrication [12,13]. It frequently restricts the availability of face prosthetics and causes patients' cosmetic concerns. The fading of the colour of a facial prosthesis is typically associated with particular environmental factors such as humidity, water, temperature, and radiation [14].

The mechanical and optical properties of silicone material have been demonstrated to be enhanced by the addition of nano-oxide materials, such as ZnO and TiO2, to polymers. [15]

This study's objective was to evaluate an RTV silicone elastomer's colour stability under accelerated ageing conditions by including TiO2 and ZnO nanoparticles. Three sets of 20 specimens each were created from the samples. The CIELAB colour space is used in this study to represent colour using three parameters: L* for visual brightness and a* and b* for the four basic colours that humans perceive red, green, blue, and yellow.

An instrument used in laboratories to incubate samples under certain conditions—such as humidity, air temperature, and other factors like artificial aging is called a digital incubator.

Incubators are designed to provide consistent temperature control, tailored to different models. This exceptional performance is achieved through a precise microprocessor controller and an innovative warm air jacket design. The triple wall construction enables heated air to circulate in an open plenum between the inner chamber and outer walls. [16]

Inter group comparison of dE, Group 1= 0.937, Group 2= 1.512, Group 3= 2.431 showed that Group 3 is highly significant as compared to other groups (as lower the dE signifies least color change) (Graph 4).

This explains that Group 1 (TiO_2) will make maximum color stable after artificial aging of 120 days than Group 2 (ZnO) and it was least stable in the control group.So, as observed the Control group was having highly significant color change than other groups.

Group 3> Group 2> Group 1 (color change)

A comprehensive review was carried out by Nithin Kumar Sonnahalli et al. to evaluate the effects of adding different nanoparticles pertaining to the maxillofacial silicone elastomer's mechanical, biological, and colour stability. Furthermore, they asserted that the prosthetic material made from silicone elastomers may benefit from the influence of nanoparticles at various concentrations in terms of its mechanical, physical, and colour stability features. [17].

Anjali et al. studied the influence of adding nano oxides on maxillofacial silicone elastomer exposed to outside weathering, they identified a statistically significant change in the mean hardness and mean tear strength of the silicone elastomer having 1.5% zirconium silicate. This work shows that the incorporation of zirconium silicate nanoparticles in medical-grade maxillofacial silicone elastomer can help it maintain acceptable ISO criteria for hardness and tear strength even after being exposed to the effects of natural weathering [18].

V. CONCLUSION

Nanoparticles are very useful for controlling and preserving colour in a variety of applications, such as improved UV protection, because of their special qualities. Paints and varnishes frequently contain nanoparticles to give UV protection, such as zinc oxide (ZnO) and titanium dioxide (TiO2). Over time, colour stability is preserved by these

ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/IJISRT24NOV803

nanoparticles because they scatter and absorb UV light, which would otherwise degrade the pigments and dyes [19].

It increases the uniformity of nanoparticle dispersion, which is possible as compared to larger particles in a given medium. Consistent colour is achieved and problems such as streaking or uneven colouration are avoided with this homogeneous dispersion [20]. Because of their small size, nanoparticles have a high surface area to volume ratio, which helps to increase surface area. In addition to improving the colourants' stability and preventing them from settling or aggregating, this enables improved interaction with the surrounding media [20].

Nanoparticles enhances the chemical stability of colorants as incorporating nanoparticles into polymers can make the material more resistant to chemical reactions that might otherwise alter its color [21]. Nanoparticles can form a barrier that protects the underlying material from environmental factors such as moisture, oxygen, and pollutants. This barrier effect helps in preserving the original color of the material [21].

Optical Properties Certain nanoparticles can be engineered to have specific optical properties that enhance the brightness and vibrancy of colors. For instance, gold and silver nanoparticles can be used to create vivid colors through plasmonic effects [19].

In conclusion, nanoparticles play a crucial role in maintaining colour stability and control across various applications.

REFERENCES

[1]. Zarrati S, Safi M, Mohammad Rezaei SM, Shadan L. Effect of nano-oxides on the color stability of maxillofacial silicone elastomers. The Journal of Prosthetic Dentistry. 2020 Dec;127(2).

[2]. Mitra A. Maxillofacial Prosthetic Materials- An Inclination Towards Silicones. JOURNAL OF CLINICAL AND DIAGNOSTIC RESEARCH. 2014;8(12).

[3]. Hatamleh MM, Polyzois GL, Nuseir A, Hatamleh K, Alnazzawi A. Mechanical Properties and Simulated Aging of Silicone Maxillofacial Elastomers: Advancements in the Past 45 Years. Journal of Prosthodontics. 2016 Jan 24;25(5):418–26.

[4]. Rashid Farah, Barman Aparna, Factors affecting color stability of maxillofacial prosthetic silicone elastomer: A systematic review and meta-analysis, Journal Of Elastomers & Plastics, 2020 Aug Vol. 53, Issue 6.

[5]. Han Y, Zhao Y, Xie C, Powers JM, Kiat-amnuay S. Color stability of pigmented maxillofacial silicone elastomer: Effects of nano-oxides as opacifiers. Journal of Dentistry. 2010 Jan;38:e100–5.

[6]. He R, Xiao K, Pointer M. Development of an image-based Measurement System for Human Facial Skin Colour. Wiley online library.

[7]. 3D representations of the L*a*b* gamut, Bruce Lindbloom. 2024 Sep 25. http://www.brucelindbloom.com/index.html?LabGamutDisplay.html

[8]. CIE Colorimetry 15 (Third ed.). CIE. 2004. ISBN 3-901-906-33-9.

[9]. The CIELAB L*a*b* System – the Method to Quantify Colors of Coatings, by Jochum Beetsma September 11, 2020.

[10]. Aziz T, Waters M, Jagger R. Analysis of the properties of silicone rubber maxillofacial prosthetic materials. Journal of Dentistry 2003;31:67–74.

[11]. Gary JJ, Huget EF, Powell LD. Accelerated color change in a maxillofacial elastomer with and without pigmentation. Journal of Prosthetic Dentistry 2001;85:614–20.

[12]. Polyzois GL. Color stability of facial silicone prosthetic polymers after outdoor weathering. Journal of Prosthetic Dentistry 1999;82:447–50.

[13]. RN Akash, Guttal SS. Effect of incorporation of nano-oxides on color stability of maxillofacial silicone elastomer subjected to outdoor weathering. J Prosthodont 2015;24(7):569-75.

[14]. Abdullah HA. Evaluation of some mechanical properties of a new silicone elastomer for maxillofacial prostheses after addition of intrinsic pigments. M. Sc. Thesis University of Baghdad 2018.

[15]. Nobrega AS, Andreotti AM, Moreno A, et al. Influence of adding nanoparticles on the hardness, tear strength, and permanent deformation of facial silicone subjected to accelerated aging. J Prosthet Dent 2016;116(4):623-9.

[16]. Microbiology Incubator - Haes Brothers.. 2024 Sep 26. https://www.haes.co.id/instrument/microbiology-incubator.

[17]. Sonnahalli N, Chowdhary R. Effect of nanoparticles on color stability and mechanical and biological properties of maxillofacial silicone elastomer: A systematic review. The Journal of Indian Prosthodontic Society. 2020;20(3):244.

[18]. Anjali Anjali, Hegde Chethan. Effects of incorporation of nano particles on the mechanical properties of maxillofacial silicone elastomer subjected to outdoor weathering. Heliyon. 2024 Feb 1;10(3):e25039–9.

[19]. Mourdikoudis S, Pallares RM, Thanh NTK. Characterization techniques for nanoparticles: comparison and complementarity upon studying nanoparticle properties. Nanoscale [Internet]. 2018;10(27):12871–934.

[20]. Razi M, Contreras-Mateus M, Kotaybah Hashlamoun, Nassar NN. Nanoparticles: Preparation, Stabilization, and Control Over Particle Size. Springer eBooks. 2021 Jan 1;1–40.

[21]. Goiato MC, Andreotti AM, Moreno A, Nóbrega AS, Pesqueira AA, dos Santos DM. Influence of nanoparticles on color stability, microhardness, and flexural strength of acrylic resins specific for ocular prosthesis. International Journal of Nanomedicine. 2014 Dec;5779.