

RESEARCH AND EDUCATION

Influence of adding nanoparticles on the hardness, tear strength, and permanent deformation of facial silicone subjected to accelerated aging



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Maxillofacial prostheses, beyond protecting areas containing tissues that are exposed and bloody because of surgical resections, traumas, tumors, or congenital problems represent a noninvasive and risk-free treatment for esthetic recovery. They especially help improve self-esteem and quality of life and reintegration of the patient into society.¹⁻³

Silicone is the material used most in the fabrication of maxillofacial prostheses⁴⁻⁷ because its flexibility provides the patient with both wellbeing and comfort. It also possesses a texture similar to that of human skin, is stable when exposed to heat, and repels water, blood, and organic materials, thereby eliminating bacterial colonization.^{1,8,9} In addition, it is resistant to the action of cleaning and is the best commercially available material.^{1,8,9}

However, silicone is limited in that early material deterioration may occur. For example, it may exhibit modified texture, poorly fitting edges because of shape

ABSTRACT

Statement of problem. The efficiency of adding nanoparticles to silicone protection has proven to prevent color degradation. However, reports of other physical property changes in facial silicone are scarce.

Purpose. The purpose of this in vitro study was to evaluate the influence of adding nanoparticles on the hardness, tear strength, and permanent deformation of a facial silicone.

Material and methods. Specimens were made for each test, with 140 for the hardness test, 140 for the permanent deformation test, but 280 for the rupture test. This higher number was due to the fact that the first 140 specimens were ruptured and unusable after the initial reading. ZnO, BaSO₄, and TiO₂ nanoparticles at concentrations of 1% and 2% of silicone were used, as well as specimens without nanoparticles that consisted of only oil paint and of only silicone. Outcomes were measured before and after 1008 hours of accelerated aging. Data were analyzed by nested analysis of variance (ANOVA) and Tukey honest significant differences test ($\alpha=.05$).

Results. Results showed that the presence of nanoparticles influenced the properties of the assessed groups. The nanoparticles decreased hardness values. The highest values of tear strength were observed for the groups with addition of BaSO₄. The 1% ZnO group without oil paint showed the lowest values of permanent deformation.

Conclusions. Based on the findings of this in vitro study, the use of ZnO nanoparticles is recommended, since they did not negatively affect the properties of the materials evaluated. (*J Prosthet Dent* 2016;116:623-629)

changes, reduced tear strength, and material discoloration after only 3 months of use.⁹⁻¹² These changes are directly related to patient care during handling and hygiene and the type of exposure that the prosthesis undergoes (air pollution, ultraviolet [UV] rays, temperature fluctuations).⁹⁻¹³

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Clinical Implications

Nanoparticles are used to prevent silicone discoloration. Therefore, the use of ZnO nanoparticles may be a viable method of avoiding facial silicone discoloration, as they do not negatively affect the material hardness, tear strength, or permanent deformation.

Different methods have been tested to prevent the intrinsic and extrinsic discoloration of the material. One of these methods is addition of nanoparticles, which are opacifiers such as zinc oxide (ZnO), barium sulfate (BaSO₄), and titanium dioxide (TiO₂).³ They are used in the manufacture of sunscreens to protect human skin against UV rays because they have a high refractive index.^{14,15} As the nanoparticles are smaller than the UV light wavelength, their electrons vibrate when they hit by such radiation, thereby dissipating one portion of the light while absorbing another. Thus, the smaller the nanoparticles, the better the shielding against solar radiation.¹⁶

Several studies have confirmed the effectiveness of nanoparticles in protecting silicone against color deterioration, since nanoparticles block the ultraviolet rays and so increase its durability.^{3,5,6,16-22} However, to increase material durability, other important properties should also be evaluated.^{23,24} The hardness of silicone determines its flexibility and enables the prosthesis to mimic the skin texture as closely as possible, promoting greater comfort for the patient.^{10,25-28} Its tear strength should be adequate to allow the edge of the prosthesis to have good marginal adaptation^{10,28,29} and endurance during its removal, even though it is very thin.^{23,30} Its elastic recovery ability, evaluated through the permanent deformation test, ensures a good fit of the prosthesis without the material changing its shape when subjected to different types of forces during its daily handling.^{31,32}

Although some studies³³⁻³⁶ assert that nanoparticles may provide benefits, including the improvement of the physical properties of polymers, the number of published studies is scarce related to changes in hardness, tear strength, and permanent deformation when nanoparticles are added to facial silicone. The purpose of this *in vitro* study was to evaluate the influence of the addition of nanoparticles on the hardness, tear strength, and permanent deformation of a facial silicone under the influence of accelerated aging. The null hypothesis was that the addition of nanoparticles and accelerated aging would not influence these properties of the studied silicone.

MATERIAL AND METHODS

For specimen fabrication, a facial silicone (Silastic MDX4-4210; Dow Corning Corp Medical Products), 3 types of

Table 1. Material used for specimen fabrication

Trade or Generic Name	Manufacturer
Silicone silastic MDX4-4210	Dow Corning Corp Medical Products
Zinc oxide	Apothicário
Barium sulfate	Apothicário
Titanium dioxide	Apothicário
Oil paint	Acrixex

nanoparticles, and a brown oil paint (Table 1) were selected. A total of 560 facial silicone specimens were fabricated. Only 280 specimens were used in the hardness and permanent deformation tests (140 for each test). The other 280 specimens were prepared for the tear strength test, with half for the initial test (ruptured and lost) and the other half for the final test. For each test, the specimens were divided into 14 groups (n=10) according to nanoparticle type and concentration. Ten specimens were made for each nanoparticle type (ZnO, BaSO₄, or TiO₂). Thirty specimens were made for each nanoparticle concentration (1% or 2%).¹⁶ Sixty specimens were made with pigmented silicone with oil paint and 60 without pigmentation. Twenty specimens were created without nanoparticles for each test; 10 with oil paint and 10 without oil paint.

The silicone and pigments were weighed on a digital precision scale (Adventurer; Ohaus Corp), and the nanoparticles¹⁶ and oil paint were added according to the proposed group.^{5,36}

For specimen fabrication for the hardness test, a metal matrix was obtained containing 10 circular compartments with dimensions of 30×2 mm in its interior.^{26,37} For the tear strength test, a metal matrix was obtained containing 6 compartments with dimensions of 75×25×0.5 mm.³⁸ For the permanent deformation test, a metal matrix with 10 cylindrical compartments with dimensions of 20×12.5 mm was used.³⁹

The silicone was handled according to the manufacturer's specifications at a controlled temperature of 23 ±2°C. Each nanoparticle and/or pigment was mixed with silicone on a glass slab with a stainless steel spatula until a homogeneous mass was obtained. The average diameter of each nanoparticle was 390 nm for ZnO, 250 nm for TiO₂, and 670 nm for BaSO₄ (Figs. 1-3). The silicone mixture was then inserted into the matrix, its surface was flattened with a spatula, and its thickness was standardized. The matrix was placed in a polymerization device with 0.96 kPa of pressure to avoid bubble formation in the silicone. Specimens remained confined within the matrix under controlled temperature with the surface exposed for 72 hours to complete polymerization of the material with release of the byproduct (formaldehyde). After silicone polymerization, each specimen was carefully separated from the metallic matrix.

The hardness test evaluation (Shore A) was performed using a digital durometer (GDS 709; Teclock) according to American Society for Testing Materials

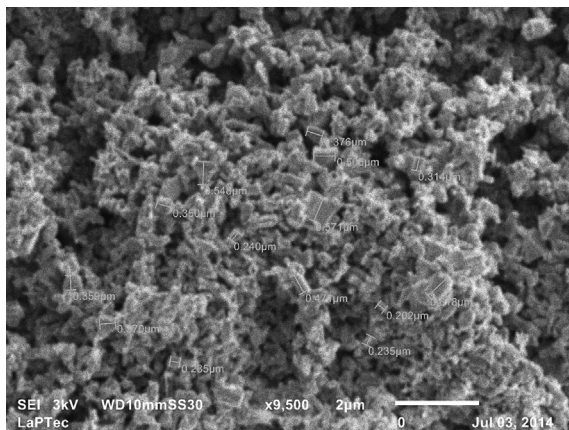


Figure 1. Scanning electron microscopy analysis of zinc oxide nanoparticles with medium diameter of 390 nm (original magnification $\times 9500$).

(ASTM) standard D-2240.⁴⁰⁻⁴³ This method is based on needle penetration of the material surface under a constant load of 10 N.

The tear strength test was performed according to the standards outlined by ASTM standard D 1938-67.³⁸⁻⁴⁴ In order to facilitate the tension distribution on the specimen during the test, 3 points were marked with a scalpel. A spot was marked between the larger edges, centered and 50 mm distant from the first edge, while the other 2 points were marked 25 mm and 15 mm from this edge.

The larger edges of the specimen were secured in a universal testing machine (EMIC; São José dos Pinhais). The machine was operated at a constant speed of 25 mm/min and load of 166.7 N. Maximum resistance values were recorded. Half of the specimens from each group were tested at this time, whereas the other half was tested after accelerated aging.

The permanent deformation test was performed according to International Standards Organization (ISO) specification 4823:2000.³⁹ Deformation measurements were performed through a zeroed dial indicator. This device has an analog marker graduated in increments of 0.01 mm. The specimens were subjected to a compressive load of 9.8 N applied for 1 minute, enabling the reading of the initial deformation of each specimen (A). After charge removal and specimen stabilization, a re-read was performed, indicating the elastic recovery rate (B). The difference between the A and B values divided by the original length of the specimen and multiplied by 100 was regarded as the permanent deformation of the specimen.⁴⁴

After the initial readings of the test result, the specimens were subjected to the accelerated aging test (aging chamber for nonmetallic specimens with UVB/condensation; Equilam)⁴⁵ and subjected to alternating periods of UV light and distilled water condensation saturated with

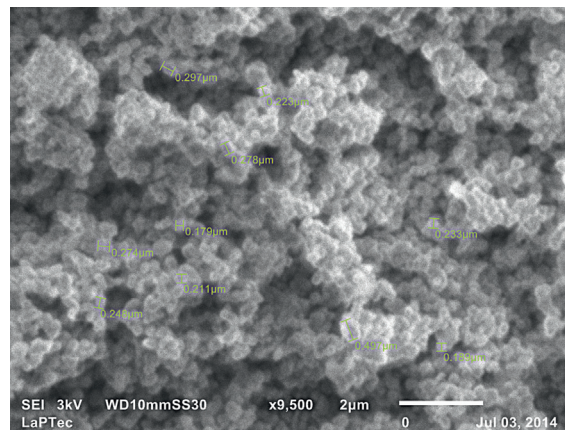


Figure 2. Scanning electron microscopy analysis of barium sulfate nanoparticles with medium diameter of 670 nm (original magnification $\times 9500$).

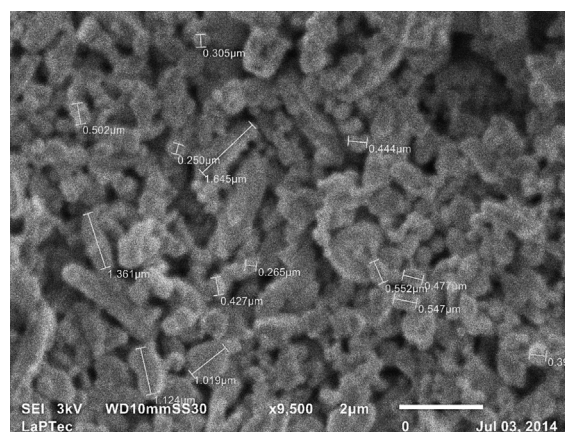


Figure 3. Scanning electron microscopy analysis of titanium dioxide nanoparticles with medium diameter of 250 nm (original magnification $\times 9500$).

oxygen under conditions of heat and 100% humidity. Each aging period was carried out for 12 hours. Silicone was exposed to UV light at $60 \pm 3^\circ\text{C}$ for the first 8 hours. In the remaining 4 hours, the water condensation procedure occurred without light at $45 \pm 3^\circ\text{C}$. This test was performed for 1008 hours,^{5,6,8,9,11,17,26} simulating the deterioration caused by rain, moisture, and the UV rays of the sun. The tear strength specimens were ruptured and lost after the initial reading. Therefore, their duplicates were aged for this test.

Data were evaluated using 4-way nested ANOVA. Nested effects can be used when constraints prevent crossing every level of 1 factor with every level of the other factor.³⁵ ANOVA was used to evaluate the effects of oil paint treatment, nanoparticle concentration, nanoparticle type, period (before and after accelerated aging) on the hardness, tear strength, and permanent deformation values of facial silicone. The ANOVA was performed by nesting the nanoparticle factor to

Table 2. Mean (\pm SD) hardness (Shore A) for all groups in initial and final periods

Oil Paint/ Concentration/Nanoparticle	Period	
	Initial	Final
No		
–	27.23 (\pm 1.82) ^{Aa}	31.93 (\pm 1.86) ^{Ab}
1%		
ZnO	23.57 (\pm 1.01) ^{Ba}	28.43 (\pm 1.28) ^{Bcb}
BaSO ₄	22.07 (\pm 1.98) ^{Bca}	28.47 (\pm 1.84) ^{Bcb}
TiO ₂	18.23 (\pm 2.07) ^{DEa}	23.80 (\pm 0.94) ^{DEb}
2%		
ZnO	25.97 (\pm 0.74) ^{Abba}	29.33 (\pm 1.04) ^{Bb}
BaSO ₄	25.50 (\pm 1.51) ^{Abba}	28.80 (\pm 0.98) ^{Bb}
TiO ₂	25.13 (\pm 2.15) ^{Abba}	27.63 (\pm 1.10) ^{Bca}
Yes		
–	26.70 (\pm 1.22) ^{Aa}	29.80 (\pm 1.01) ^{Abb}
1%		
ZnO	22.10 (\pm 1.50) ^{Bca}	28.93 (\pm 1.64) ^{Bb}
BaSO ₄	19.80 (\pm 1.32) ^{Ca}	25.97 (\pm 1.02) ^{Eb}
TiO ₂	18.90 (\pm 2.99) ^{DEa}	21.47 (\pm 1.11) ^{Db}
2%		
ZnO	25.63 (\pm 1.99) ^{Abba}	29.90 (\pm 1.00) ^{Abb}
BaSO ₄	24.80 (\pm 1.26) ^{Abba}	28.67 (\pm 1.78) ^{Bb}
TiO ₂	19.13 (\pm 1.60) ^{DEa}	22.27 (\pm 0.86) ^{Bb}

Groups statistically different from each other by Tukey test ($P < .05$) are indicated by different superscript uppercase letters (within column) and lowercase letters (within row).

the concentration factor because the levels of the nanoparticle factor were not the same for the levels of the concentration factor. Statistical software (Software R v.3.2.3.; The R Foundation) was used for descriptive and statistical analyses. If the ANOVA test showed a significant difference, then the Tukey HSD post hoc test was applied ($\alpha = .05$).

RESULTS

Nanoparticle presence influenced hardness, tear strength, and permanent deformation (Tables 2-4). The ANOVA for hardness values showed statistically significant differences ($P = .012$) in the interaction among the factors oil paint, nanoparticle (concentration), and period (Supplemental Table 1).

In the initial period, the presence of nanoparticles decreased hardness values (Table 2). A statistically significant increase ($P < .001$) in hardness values was verified after aging (final period), except for the 2% TiO₂ group without oil paint ($P = .080$). However, even with this increase, the groups with the addition of TiO₂ nanoparticles showed the lowest hardness values in the final period. The addition of oil paint did not influence the hardness values, except for the 2% TiO₂ group in the initial period.

Statistically significant differences ($P < .05$) in tear strength were observed in the interaction between oil paint and nanoparticle (concentration); period and

Table 3. Average values of tear strength (MPa) for all groups, regardless of addition of oil paint

Concentration/Nanoparticle	Period	
	Initial	Final
	1.89 ^{Aa}	2.46 ^{Ab}
1%		
ZnO	1.92 ^{Aa}	2.30 ^{Aa}
BaSO ₄	2.10 ^{Aa}	3.11 ^{Bb}
TiO ₂	1.83 ^{Aa}	2.39 ^{Ab}
2%		
ZnO	2.32 ^{Aa}	2.39 ^{Aa}
BaSO ₄	2.10 ^{Aa}	2.48 ^{Aa}
TiO ₂	2.11 ^{Aa}	2.45 ^{Aa}

Groups statistically different from each other by Tukey test ($P < .05$) are indicated by different superscript uppercase letters (within column) and lowercase letters (within row).

Table 4. Mean percentages of permanent deformation for all groups, regardless of addition of oil paint

Concentration/Nanoparticle	Period	
	Initial	Final
	1.03 ^{ACa}	0.83 ^{Ab}
1%		
ZnO	0.81 ^{DEa}	0.70 ^{Aa}
BaSO ₄	1.13 ^{ABCa}	0.81 ^{Ab}
TiO ₂	0.98 ^{CEa}	0.69 ^{Ab}
2%		
ZnO	0.91 ^{ACDa}	0.77 ^{Aa}
BaSO ₄	1.24 ^{Ba}	0.86 ^{Ab}
TiO ₂	0.77 ^{Da}	1.21 ^{Bb}

Groups statistically different from each other by Tukey test ($P < .05$) are indicated by different superscript uppercase letters (within column) and lowercase letters (within row).

nanoparticle (concentration); and oil paint, concentration, and period factors (Supplemental Table 2). Higher values of tear strength after aging (final period) could be observed, with a statistically significant difference ($P < .05$) for the groups with 1% BaSO₄ and 1% TiO₂ nanoparticle addition (Table 3). Moreover, the highest values of tear strength were observed for the groups with BaSO₄ addition in the final period, with a statistically significant difference ($P = .01$) in the group with 1% concentration. ANOVA for permanent deformation values exhibited statistically significant differences ($P < .05$) in the interaction between period and concentration and between period and nanoparticle (concentration) (Supplemental Table 3).

In relation to permanent deformation, accelerated aging (final period) showed decreased values, except for the 2% TiO₂ group, which showed higher values with a statistically significant difference ($P < .05$) compared with the other groups (Table 4). The 1% ZnO group without oil paint showed the lowest values of permanent deformation, with a statistically significant difference ($P < .05$) compared with the other groups without oil paint and compared with the 1% ZnO group with oil paint (Table 5).

Table 5. Mean percentages of permanent deformation for all groups, regardless of period

Concentration/Nanoparticle	Oil Paint	
	No	Yes
	0.89 ^{Aca}	0.98 ^{ABa}
1%		
ZnO	0.65 ^{Ba}	0.86 ^{ABb}
BaSO ₄	0.95 ^{Aca}	0.98 ^{ABa}
TiO ₂	0.84 ^{Aa}	0.83 ^{Aa}
2%		
ZnO	0.80 ^{Aa}	0.82 ^{Aa}
BaSO ₄	1.06 ^{Ca}	1.04 ^{Ba}
TiO ₂	0.98 ^{Aca}	1.00 ^{ABa}

Groups statistically different from each other by Tukey test ($P < .05$) are indicated by different superscript uppercase letters (within column) and lowercase letters (within row).

DISCUSSION

The null hypothesis was rejected because the addition of nanoparticles and accelerated aging influenced the physical properties evaluated. The addition of nanoparticles in the initial period decreased the hardness values (Table 1). This may be due to nanoparticle incorporation into the silicone matrix, which may hinder the intertwining of the polymer chains, reducing the material polymerization rate. However, the hardness values increased after aging, independently of the addition of the nanoparticles. Several studies^{22,26,27,43} have indicated that accelerated aging increases the degree of polymerization of facial silicone, because this material polymerizes continuously. The greatest release of formaldehyde occurs in the first 72 hours. However, the release of the byproduct after this period continues indefinitely^{6,43} and could be related to the main changes in the structure of the silicone.³⁰ Therefore, the nanoparticles decreased the hardness values, but they could not hinder the continuous polymerization degree of silicone.

When a polymer molecule absorbs UV light, this energy promotes instability in the molecular structure. The excess energy is transmitted by excitation from one molecule to another, allowing the first molecule to recover its stability. Therefore, affected groups may return to their original state by releasing energy in the form of longer wavelengths, such as visible light or heat. However, a photochemical degradation occurs when this excess energy is released, contributing to molecule deterioration. This is evidenced by changes in color and brightness, crack formation, and hardening.²⁷

Silicone hardness determines the texture, which must be similar to that of the anatomic site to be restored.^{7,26,27,29,41-43} The skin is very thin in the orbital, nasal, and ear areas of the maxilla, and bone and cartilage are very close to the surface.^{7,13} Thus, in order to mimic the texture of those sites, the silicone should exhibit hardness values of between 25 and 35 Shore A.

In this study, although hardness values increased after aging (Table 2), they decreased after the addition of nanoparticles, sometimes to below the minimum set (25 Shore A).^{7,26,27,29,41-43} Nguyen et al²³ suggested that the addition of a polyurethane liner could correct the values affected. However, TiO₂ was the nanoparticle that had the greater influence on decreasing hardness. In this case, the most likely reason for hardness reduction could be the nature of the nanoparticles. Although TiO₂ nanoparticles are very small, allowing them to penetrate between the polymer molecules, they have difficulty dispersing in organic solvents and tend to agglomerate easily.^{13,14,46} The agglomerations can reach micrometric scales larger than the polymer particles, so empty areas may arise around these agglomerations,⁴⁶ which are detrimental to the mechanical properties of the material. Therefore, the surface of this nanoparticle may require modification to reduce its clumping⁴⁶ and improve its dispersion into the silicone matrix.

The hardness values were not influenced by the addition of oil paint, except for the TiO₂ 2% group (Table 2). This exception may be directly related to higher concentration levels of nanoparticles, which lead to agglomeration formation as explained, and not to the addition of the oil paint itself. Different results regarding oil paint addition can be observed in the literature²⁷ when this pigment influenced the initial hardness values. This may be because of the difference in time between the specimen fabrication and test application.

Regarding the tear strength test, higher values were observed after accelerated aging (Table 3). As explained for hardness values, this increase may be due to continuous polymerization of silicone associated with exposure to UV rays.^{9,18-20,22,23} Higher tear strength values for groups with the addition of BaSO₄ were observed in the final period. In this study, different nanoparticles were used, which could interact with materials in different ways. Therefore, BaSO₄ nanoparticles may have associated more strongly with silicone chains,²⁶ increasing tear strength values.

Optimal tear strength values of facial silicone have been stated to be between 0.54 MPa and 1.77 MPa.^{29,47} However, the values obtained in this study, despite being above the maximum recommended value, are clinically satisfactory because a higher tensile strength is more favorable if it does not compromise other properties. Tear strength values, however, are not directly related to hardness values.²⁸ The addition of nanoparticles tends to increase the material plasticizing effect, reducing the hardness and increasing the tear strength.²⁴ Further tests, such as the elongation test, are needed to confirm these results.

Accelerated aging also influenced permanent deformation (Table 4). Aging increases material rigidity, as seen in the hardness results, resulting in decreased

permanent deformation values.^{31,48} This effect may be caused by an excessive loss of silicone plasticizer which was not compensated by water absorption,³¹ as shown by Santos et al.²⁷

Permanent deformation values were influenced by the addition of 2% TiO₂ nanoparticles after aging (Table 4). This may be associated with nanoparticle agglomeration because of the difficulty in dispersing them among the molecules of the silicone polymer chains. Furthermore, the higher the nanoparticle concentration, the higher the number and size of agglomerations.⁴⁶

The specimens of 1% ZnO without oil paint (Supplemental Table 2) showed the lowest values of permanent deformation. This may have occurred because the ZnO nanoparticles acted as a catalyst^{15,49}; this probably caused greater silicone polymerization, increasing hardness, and decreasing permanent deformation.²⁶ This can be observed in the current study, in which the highest hardness values were in groups with the ZnO addition (Table 1).

Some authors³² report that permanent deformation values of elastomeric materials above 3% are not clinically acceptable. The highest permanent deformation value found in this study was 1.33% (BaSO₄ 2% without adding oil paint). Therefore, all groups proposed in this study are within the acceptable clinical standard.

It was difficult to incorporate and dissolve the nanoparticles homogeneously into the silicone matrix during specimen confection, in particular, the addition of BaSO₄ nanoparticles, which may be because of their size (Fig. 2). This can lead to esthetic problems. Thus, future studies could be conducted with the purpose of evaluating and improving their dispersion into the silicone matrix.

CONCLUSIONS

Despite the limitations of an in vitro study, it was concluded that all tested nanoparticles influenced hardness, tear strength, and permanent deformation values. However, the groups with the TiO₂ nanoparticle addition exhibited hardness values lower than the clinically acceptable range, and BaSO₄ nanoparticles had the greatest difficulty dispersing in the silicone matrix. Therefore, the use of ZnO nanoparticles may be a viable method, as they do not negatively affect the material properties evaluated in this study.

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Supplemental Table 1. Results of nested ANOVA for hardness (Shore A)

Source	df	SS	SS	MS	F	P
Oil paint	1	173.38	124.82	124.82	52.92	<.001*
Concentration	2	990.58	990.58	495.29	209.98	<.001*
Nanoparticle concentration	4	947.02	947.02	236.76	100.37	<.001*
Period	1	1313.00	968.59	968.59	410.63	<.001*
Oil paint×concentration	2	9.36	9.36	4.68	1.98	.140
Oil paint×nanoparticle concentration	4	225.99	225.99	56.50	23.95	<.001*
Oil paint×period	1	0.21	2.62	2.62	1.11	.293
Period×concentration	2	61.83	61.83	30.92	13.11	<.001*
Period×nanoparticle concentration	4	33.08	33.08	8.27	3.51	.008*
Oil paint×concentration×period	2	11.20	11.20	5.60	2.37	.095
Oil paint×nanoparticle concentration×period	4	31.12	31.12	7.78	3.30	.012*
Error	252	594.41	594.41	2.36		
Total	279	4391.20				

df, degrees of freedom; MS, mean of squares; SS, sum of squares. * $P < .05$, statistically significant difference.

Supplemental Table 2. Results of nested ANOVA for tear strength (MPa)

Source	df	SS	SS	MS	F	P
Oil paint	1	0.22	0.02	0.02	0.10	.755
Concentration	2	0.56	0.56	0.28	1.24	.290
Nanoparticle concentration	4	6.61	6.61	1.65	7.36	<.001*
Period	1	15.79	13.40	13.40	59.63	<.001*
Oil paint×concentration	2	1.44	1.44	0.72	3.20	.042*
Oil paint×nanoparticle concentration	4	4.98	4.98	1.25	5.54	<.001*
Oil paint×period	1	1.03	0.03	0.03	0.11	.735
Period×concentration	2	2.33	2.33	1.16	5.18	.006*
Period×nanoparticle concentration	4	1.73	1.73	0.43	2.93	.022*
Oil paint×concentration×period	2	2.38	2.38	1.19	5.30	.006*
Oil paint×nanoparticle concentration×period	4	2.63	2.63	0.66	1.93	.106
Error	252	56.63	56.63	0.22		
Total	279	96.35				

df, degrees of freedom; MS, mean of squares; SS, sum of squares. * $P < .05$, statistically significant difference.

Supplemental Table 3. Results of nested ANOVA for permanent deformation (%)

Source	df	SS	SS	MS	F	P
Oil paint	1	0.108	0.135	0.135	4.54	.034*
Concentration	2	0.680	0.680	0.340	11.43	<.001*
Nanoparticle concentration	4	1.822	1.822	0.455	15.33	<.001*
Period	1	1.457	1.335	1.335	44.92	<.001*
Oil paint×concentration	2	0.146	0.146	0.073	2.46	.087
Oil paint×nanoparticle concentration	4	0.309	0.309	0.077	2.60	.037*
Oil paint×Period	1	0.037	0.010	0.010	0.35	.554
Period×concentration	2	0.717	0.717	0.358	12.06	<.001*
Period×nanoparticle concentration	4	3.760	3.760	0.940	31.63	<.001*
Oil paint×concentration×period	2	0.053	0.053	0.026	0.89	.412
Oil paint×nanoparticle concentration×period	4	0.196	0.196	0.049	1.65	.163
Error	252	7.489	7.489	0.030		
Total	279	16.773				

df, degrees of freedom; MS, mean of squares; SS, sum of squares. * $P < .05$, statistically significant difference.