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EVALUATION OF COMPRESSIVE STRENGTH AND RADIOPACITY OF DENOVO SYNTHESIZED CALCIUM SILICATE CEMENT CONTAINING ZINC OXIDE NANOPARTICLES VERSUS COMMERCIAL MATERIALS

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ABSTRACT

This in-vitro study evaluated the compressive strength and radiopacity of denovo synthesized calcium silicate cement containing zinc oxide nanoparticles versus commercial materials. A total of 100 specimens were prepared for this study, 25 of them were prepared for each of the 4 materials group: Synthesized Calcium Silicate Cement (SYNT), Nano Zinc Oxide added to the synthesized calcium silicate cement (NANO), Angelus White Mineral Trioxide Aggregate (MTA) and Theracal (THCL). The 25 specimens of each group was then distributed as follows: 10 were tested for compressive strength (MPa) on day 10, 10 were tested for compressive strength (MPa) on day 30; the last 5 specimens were tested for radiopacity. Data was then recorded, tabulated and statistically analyzed. The mean MPa results on day 10 recorded the highest by THCL-10 (55.35 ± 9.82), while the lowest value was recorded for NANO-10 (4.90 ± 1.61). The mean MPa on day 30 recorded by the NANO-30 (52.66 ± 19.30) was the highest, while the lowest value was recorded for SYNT-30 (21.70 ± 2.55). All subgroups on day 10 compared to those on day 30 showed significant statistical difference at $p<0.05$; Where the mean MPa of SYNT-30 was less than that of SYNT-10, the same was observed for the THCL subgroups. As for the mean MPa of NANO-30 was higher than that NANO-10, the MTA subgroups expressed the same results. On the other hand, the radiopacity results showed that the highest mean radiopacity value was recorded for THCL (9.43 ± 0.60), followed by MTA (9.38 ± 0.63), then NANO (5.06 ± 0.54), while the lowest value was recorded for SYNT (1.26 ± 0.24). In conclusion, the incorporation of zinc oxide nanoparticles in calcium silicate based enhances the physicomechanical properties of the cement expressed in terms of compressive strength and radiopacity in comparison to commercially available materials such as MTA and theracal.

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INTRODUCTION

Nowadays, we are in the era of nanotechnology. The evolution of nanotechnology is attributed to the fact that decreasing the particle size while increasing surface area to volume ratio at the nanoscale level resulting in unique phenomena which enables novel applications [1]. Metal oxide nanoparticles have high potential and are widely used because of their unusual physical, chemical and biological properties, represented by their high chemical stability and surface area, in addition to their improved reactivity. Zinc oxide nanoparticles are characterized by their multifunctional physical and chemical properties and simple production, which distinguish them from other metal oxides and enables them to be the preferred nanostructured materials [2]. Presently, Zinc oxide nanoparticles are used extensively in multidisciplinary field including dentistry as it enhances the physical and biological properties of the dental materials, and medical science as a cancer treatment, in addition to the production of cosmetics, batteries, rubber, plastics, ceramics, glass and fire retardant [3].

Calcium silicate based materials have wide range of applications in dentistry; they can be used as cement liners, pulp capping materials and root canal filling materials. The calcium silicate materials have different available commercial forms such as mineral trioxide aggregate (MTA) and TheraCal LC. Thanks to its distinguished biological and physicochemical properties, MTA was developed over the past three decades and became a common alternative material to calcium hydroxide. MTA is used as pulp capping, pulpotomy, sealing of radicular perforations and root-end filling in endodontics [4] [5] [6].

TheraCal LC is a recently introduced resin modified calcium silicate based material. It has different ingredients in its composition; they are tricalcium silicate particles, barium zirconate, and polyethylene-glycol dimethacrylate monomers. Theracal has the ability to release calcium which stimulates the formation of apatite and secondary dentin; in addition, it has high sealing capabilities with easy handling, application and enhanced flowability compared to MTA, which permits this material to be used in case of pulp capping. Also, after placement and light curing of theracal, it shows highly physical properties and lower solubility that helps in the immediate placement of the final restoration. Many investigations have focused on the mechanical properties of different cement materials containing nanoparticles.

In this regard, literatures investigating the properties of different cement materials containing nanoparticles with little attention to the mechanical and physical properties of nano zinc oxide particles in comparison to other calcium silicate materials [7,8].

So, the aim of this study was to evaluate the compressive strength and radiopacity of denovo synthesized calcium silicate cement containing zinc oxide nanoparticles versus commercial materials.

MATERIALS AND METHODS

Synthesized Calcium Silicate Cement (SYNT), Nano Zinc Oxide added to the synthesized calcium silicate cement (NANO), Angelus White Mineral Trioxide Aggregate (MTA) and Theracal LC (THCL) were used for this study. Their descriptions and compositions were shown in table 1.

Preparation of Calcium Chloride Solution

10 gram of calcium chloride powder was added to 90 ml distilled water to prepare the calcium chloride solution.

Preparation of Synthetic Calcium Silicate Cement

Calcium silicate cement was synthesized from pure oxides as that of Sinai white Portland cement: Calcium Oxide (69.74% wt), Silicon oxide (25.21%wt), Aluminum Oxide (2.58%wt), Iron Oxide (0.21%wt), Calcium Fluoride (0.30%wt). Then 5 weight % sieved natural gypsum

($CaSO_4.2H_2O$) and limestone were added to the calcium silicate based powder to control the setting time of the cement.

Then specimens of the newly formulated calcium silicate based cements were prepared by mixing 1 scoop of cement powder and 1 drop of solution.

Preparation of Nano Zinc Oxide Added to the Synthesized Calcium Silicate Cement

20% of zinc oxide nanoparticles and 80% of synthetic calcium Silicate cement were mixed together using mortar and pestle for one hour each day for 3 days to insure homogenous mix.

Compressive Strength (MPa) Measurement

Compressive strength of the tested materials was determined according to the method recommended by the ISO 9917-1.

A sectional Teflon mold, 4x6 (4mm in diameter and 6mm in thickness), was used to prepare the specimens from each material to ensure uniform condensation with minimum porosity. After finishing condensation of the mix into the mold, the mold and glass slides were covered with slightly wet cloth to help in setting to avoid glass slides fracture then screwed tightly and carefully. The complete assembly was transferred to an incubator and maintained at 37ºC for 12 hours to ensure complete setting of samples before removing from mold. Then specimens were removed from molds and checked for the presence of air voids and any defective specimens were discarded.

Then 20 acceptable samples from each of the 4 groups were prepared and stored in distilled water; ten per group were tested on day 10 and ten per group were tested on day 30. A total of 80 specimens were prepared.

Then, each specimen was mounted vertically on a computer controlled materials testing machine with a load cell of 5KN. Using computer software (Bluehill Lite software Instron instruments), the maximum failure load was recorded in Newton and converted into mega Pascal (MPa). After which, the compressive strength was calculated from the recorded peak load divided by sample surface according to the following equation:

$$\text{Compressive strength} = 4 \times P/d^2$$

Where (P) is the load at the fracture point, and (d) is the diameter in mm of the cylindrical specimen.

Radiopacity Measurement:

A sectional Teflon mold, 8x2 (8 mm in diameter and 2 mm in thickness), was used to prepare the specimens for the radiopacity measurement. A total of twenty specimens were prepared to be tested for radiopacity, five specimens from each of the 4 cement groups. Each material was condensed using an amalgam condenser inside the mold. In the time being, two glass slides, one under the mold and the other over the mold were placed to allow easy application of the materials and to ensure uniform sample with minimum air voids or porosities. Then the samples were put in an incubator at 37ºC for 48 hours to ensure setting of the cements. After that specimens were removed from the mold and positioned on dental radiographic film. Aluminum step wedge with a thickness between 0.5 mm to 5 mm in equally and uniformly spaced steps each of 0.5 mm was put alongside and used as a reference.

The specimens were then irradiated at an exposure time of 2 seconds, X-ray tube voltage euals to 64 kV, target film distance of 30cm, using standard X-ray machine on self-processing film and a digital image of radiograph was then obtained. The mean grey radiographic density values of the different cement materials were then converted into radiopacity values expressed as the equivalent thickness of aluminum step wedge using DIGORA 2.7 Windows software. This procedure allowed comparison between the radiographic density of the cements and helped in comparing between different radiographic densities of cements and that if the radiopacity of different aluminum step wedge thickens.

Data was analyzed using Statistical Package for Social Science software computer program version 23 (SPSS, Inc., Chicago, IL, USA). Data were presented in mean and standard deviation. One way Analysis of variance (ANOVA) and tukey were used for comparing data. Two way ANOVA followed by post-hoc Bonferroni was used to detect the effect of different materials and time periods on Compressive Stress (MPa). P-value less than 0.05 was considered statistically significant.

TABLE (1) Material specifications, manufacturers and compositions

Material	Manufacturer	Description & Ingredients
Synthesized Calcium Silicate Cement	Synthesized	Calcium Oxide (69.74% wt), Silicon oxide (25.21%wt), Aluminum Oxide (2.58%wt), Iron Oxide (0.21%wt), Calcium Fluoride (0.30%wt), natural gypsum-$CaSO_4.2H_2O$ (5%wt), Limestone
Calcium Chloride	El Salam for Chemical Industries	$CaCl_2$
Zinc Oxide Nanoparticles (NT-ZONP)	NanoTech Egypt for Photo-Electronics, Giza, Egypt	Average particle size: 20 ± 5 nm Prepared through the hydrolysis and condensation of zinc acetate dihydrate by potassium hydroxide in alcoholic medium at low temperature condition.
Angelus White Mineral Trioxide Aggregate	Angelus Industria de Produtos Odontologicos S/A Londrina-Brasil	Silicon Oxide (SiO_2) (25.21%wt), Potassium Oxide (K_2O) (%wt), Aluminum Oxide (Al_2O_3) (2.58%wt), Sodium Oxide (Na_2O) (%wt), Iron Oxide (Fe_2O_3) (0.21%wt), Sulphate (SO_3), Calcium Oxide (CaO) (69.74%wt), Bismuth Oxide (Bi_2O_3), Magnesium Oxide (MgO)
TheraCal™ LC	BISCO Dental Products, Illinois, U.S.A.	Resin modified Tricalcium Silicate particles in hydrophilic monomer
Bluephase N MC LED Light curing unit	Ivoclar Vivadent AG, Liechtenstein, Switzerland	Light intensity = 800 mW/cm^2

TABLE (2) Variables used in this Study

Groups	Description	After 10 Days Subgroups	After 30 Days Subgroup
SYNT	Synthesized Calcium Silicate Cement	SYNT-10	SYNT-30
NANO	Nano zinc oxide added to the synthesized calcium silicate cement	NANO-10	NANO-30
MTA	Angelus White Mineral Trioxide Aggregate	MTA-10	MTA-30
THCL	TheraCal	THCL-10	THCL-30

RESULTS

Compressive Strengths (MPa) Results

Table 3 and Figure 1 showed descriptive statistics of compressive strength (MPa) results for each group.

The results of different groups on day 10 showed that the highest mean compressive strength value was recorded for theracal subgroup (55.35 ± 9.82), while the lowest value was recorded for nano zinc oxide added to the synthesized calcium silicate cement subgroup (4.90 ± 1.61). The second highest mean compressive strength value was recorded for synthesized calcium silicate cement subgroup (33.29 ± 2.43), followed by the results of angelus white mineral trioxide aggregate subgroup (14.48 ± 2.40). There was statistical significant difference found between nano zinc oxide added to the synthesized calcium silicate cement subgroup and the other three subgroups. There was statistical significant difference found between theracal subgroup and the subgroups: synthesized calcium silicate cement and angelus white mineral trioxide aggregate at $p<0.05$. There was statistical significant difference found between synthesized calcium silicate cement and angelus white mineral trioxide aggregate subgroups at $p<0.05$.

The results of different groups on day 30 showed that the highest mean compressive strength value was recorded for nano zinc oxide added to the synthesized calcium silicate cement subgroup (52.66 ± 19.30), while the lowest value was recorded for synthesized calcium silicate cement subgroup (21.70 ± 2.55). The second highest mean compressive strength value was recorded for angelus white mineral trioxide aggregate subgroup (50.11 ± 3.48), followed by the results of theracal subgroup (39.84 ± 8.55). There was significant statistical difference found between the synthesized calcium silicate cement subgroup and the subgroups: nano zinc oxide added to the synthesized calcium silicate cement and theracal at $p<0.05$. There was significant statistical difference between angelus white mineral trioxide aggregate subgroup and that of angelus white mineral trioxide aggregate at $p<0.05$.

All subgroups on day 10 compared to those on day 30 showed significant statistical difference at $p<0.05$. Where, the synthesized calcium silicate cement subgroup on day 30 was less than that on day 10, the same was observed for the theracal subgroups. As for the nano zinc oxide added to the synthesized calcium silicate cement subgroup on day 30 was higher than that on day 10, the angelus white mineral trioxide aggregate subgroups expressed the same results.

TABLE (3) Mean, Standard Deviation and Significance of Difference of Compressive Strength (MPa) Test on Day 10 and Day 30

Compressive Strengths (MPa)	SYNT			NANO			MTA			THCL		
Day 10	33.29	±	2.43^{ab}	4.90	±	1.61	14.48	±	2.40^{abc}	55.35	±	9.82^{a}
Day 30	21.70	±	2.55^{ab*}	52.66	±	19.30^{*}	50.11	±	3.48^{c*}	39.84	±	8.55^{*}

Data expressed as mean ± SD ***SD: standard deviation*** ***P: Probability***

Test used: One way ANOVA followed by post-hoc tukey ***a: significance vs NANO group (p <0.05),***

b: significance vs THCL group (p <0.05) , ***c: significance vs SYNT group (p <0.05)***

****: significance vs 10 days (p <0.05)***

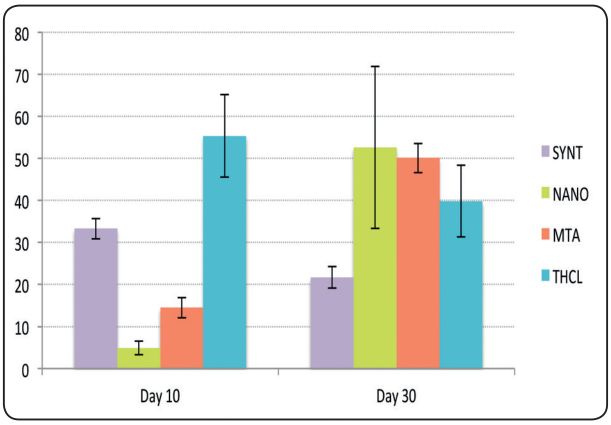

Fig. (1) Representing mean and standard deviation of compressive strength (MPa) results of tested subgroups on day 10 and day 30

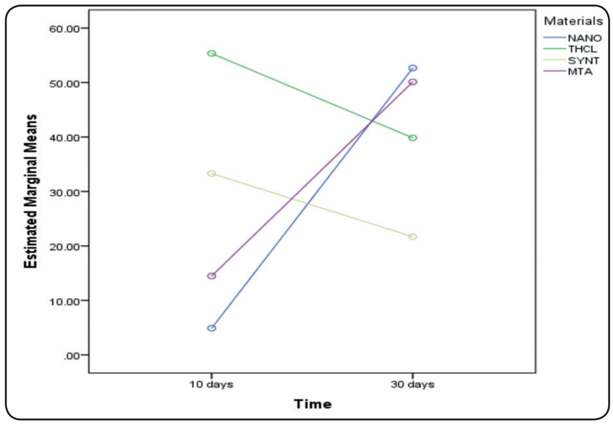

Fig (2) representing results of two way ANOVA

Table 4 and Figure 2 presented the results of two way ANOVA that showed statistical significant effect of different materials, time periods and the interaction between both of them at F-value = 50.864 on the mean compressive strength at P < 0.001. Since the interaction between different materials and time periods was significant, then the different materials and time periods are dependent upon each other.

TABLE (4) representing results of two way ANOVA

	F	P
Materials	16.709	<0.001*
Time	38.576	<0.001*
Materials * Time	50.864	<0.001*

Radiopacity Results

Table 5 & Figure 3 showed descriptive statistics of radiopacity results for each group. The results of radiopacity of different groups showed that the highest mean radiopacity value was recorded for TheraCal group (9.43 ± 0.60), while the lowest value was recorded for Synthesized Calcium Silicate Cement group (1.26 ± 0.24). The second highest mean radiopacity value was recorded for Angelus White Mineral Trioxide Aggregate group (9.38 ± 0.63) followed by the results of Nano zinc oxide added to the synthesized calcium silicate cement group (5.06 ± 0.54). There was significant statistical difference found between the nano zinc oxide added to the synthesized calcium silicate cement group and the other three groups at p<0.05. There was significant statistical difference between synthesized calcium silicate cement group and that of angelus white mineral trioxide aggregate group and that of theracal at p<0.05.

TABLE (5) Mean, Standard Deviation and Significance of Radiopacity Results

	SYNT			**NANO**			**MTA**			**THCL**		
Radiopacity	1.26	±	0.24[ab]	5.06	±	0.54	9.38	±	0.63[ac]	9.43	±	0.60[a]

Data expressed as mean ± SD ***SD: standard deviation*** ***P: Probability***

Test used: One way ANOVA followed by post-hoc tukey ***a: significance vs NANO group (p <0.05),***

b: significance vs THCL group (p <0.05) , ***c: significance vs SYNT group (p <0.05)***

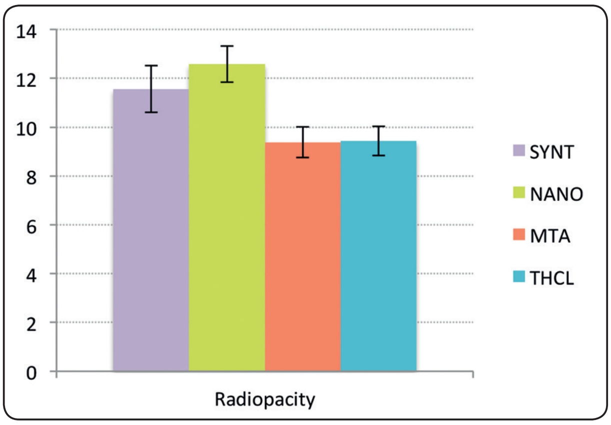

Fig. (3) Representing mean and standard deviation of radiopacity results of tested groups

DISCUSSION

This study was carried out to evaluate the compressive strength and radiopacity of denovo synthesized calcium silicate cement containing zinc oxide nanoparticles versus available commercial materials. In the present study, newly formulated cement was used, which had the same ingredients as Portland cement, but contained pure oxides without impurities in an attempt to enhance the different properties of the cement.

Nowadays, we are in the era of nanotechnology and most of the recent studies in nanomaterials had focused its use in different aspects such as medicine, dentistry, engineering…etc. Many research studied the effect of cement based materials containing nanoparticles on the mechanical and physical properties of such cement. These studies showed that incorporating nanoparticles to the cement based material have resulted in increasing the mechanical and physical properties and also resulted in a uniform and homogenous structure while hydrating the cement [9]. Moreover, nanoparticle materials were characterized by improved surface area to volume ratio at nanoscale level than that of non-nanoscale [10].

In the present study, for the preparation of Nano zinc oxide added to the synthesized calcium silicate cement, 20% of zinc oxide nanoparticles and 80% of synthetic calcium Silicate cement were mixed together. The reason behind using Zinc Oxide nanoparticles and its incorporation in the cement based material by 20% is attributed to the unique material that possesses multiple properties like high compatibility with the human cell, high selectivity and antibacterial properties [11]. Some researches had used 5%, 10% and 20% of zinc oxide nanoparticles since the nanoparticles act as filler and strengthen the calcium silicate based cement material and enhance its properties [9] [12].

Compressive strength measurement plays an important role in assessing the physical properties of water based cements during mastication. It is considered as an indirect method for measuring the strength of the material that may affect its clinical performance [13,14]. At the current study, the compressive strength of the tested materials was determined by using the method recommended by the ISO 9917-1. A sectional Teflon mold, 4x6 (4mm in diameter and 6mm in thickness), was used to prepare the specimens from each material. In previous studies, it has been proven that many elements that may affect the measurement of the compressive strength such as the size and shape of the samples, the preparation method and time for hydration, the mixing technique, the powder-to-liquid ratio, the pressure exerted while compacting the samples in the mold, in addition to the room temperature [15].

In the current study, materials were tested on day 10 and also on day 30 to evaluate and compare the compressive strength. The short term was selected to insure complete setting of the cement and to stimulate the primary strength of the cement since it is crucial for the cement material to withstand occlusal forces in the patient mouth. While the longer period was chosen to measure acquired initially strength and its long-term stability as it is important clinically for the cement material to sustain its strength in order to be able to survive within the oral environmental rigors[16]. All subgroups on day 10 compared to those on day 30 showed significant statistical difference at $p<0.05$. Where, the nano zinc oxide added to the synthesized calcium silicate cement subgroup on day 30 increased from that on day 10, the angelus white mineral trioxide aggregate subgroups experienced the same. This was in accordance with Guerreiro-Tanomaru et al. who attributed the increase in strength to the ending of the hydration phase which might enhance the hardness of the cement material [13]. This is partially in agreement with what was found by Kim et al and Shiowaza et al, who confirmed that cement maturation continued after the first day because crosswise bonds were set in the cement matrix; but they are contradicting in the part where they stated that the acid-based reaction after one week was stable [17] [18].

As for the synthesized calcium silicate cement subgroup on day 30 decreased from that on day 10, the same was observed for the theracal subgroups.

In this study, the results of different groups on day 10 showed that the highest mean compressive strength value was recorded for theracal subgroup (55.35 ± 9.82), while the lowest value was recorded for nano zinc oxide added to the synthesized calcium silicate cement subgroup (4.90 ± 1.61). The second highest mean compressive strength value was recorded for synthesized calcium silicate cement subgroup (33.29 ± 2.43), followed by the results of angelus white mineral trioxide aggregate subgroup (14.48 ± 2.40). As for the results of different groups on day 30, they showed that the highest mean compressive strength value was recorded for nano zinc oxide added to the synthesized calcium silicate cement subgroup (52.66 ± 19.30), while the lowest value was recorded for synthesized calcium silicate cement subgroup (21.70 ± 2.55). The second highest mean compressive strength value was recorded for angelus white mineral trioxide aggregate subgroup (50.11 ± 3.48), followed by the results of theracal subgroup (39.84 ± 8.55). This is in agreement with Nivethitha et al. who found that the nanoparticles of zinc oxide filled the cement pores and thus increased the compressive strength, in other words, the voids into the cement were filled by the cement nanoparticle, and thus the microstructure of the calcium silicate cement developed denser [9]. The synthesized calcium silicate cement subgroup mixing with calcium chloride lead to the acceleration of the setting reaction of the cement within 10 days that affect the compressive of this calcium silicate cement. This is beside the presence of tricalcium silicate phase within the cement which was responsible for acquiring the material strength through the formation of calcium silicate hydrate gel after mixing [19]. As per Torabienjad –the father of MTA-, the compressive strength of MTA increases with time and this was in accordance with the current study, which is also in agreement with Ghaseni et al. and Tanomaru-Filho et al. and this may be due to white MTA consists of bismuth oxide and a radiopacifying particles which did not contribute into the hydration reaction of MTA, and therefore its presence may lead to the creation of flaws within the cement matrix which in turn reflect on the compressive strength of the cement leading its measurement reduction [20] [21]. As for the TheraCal results in this paper, it might be attributed to the radiopaque material combined in the cement could be ytterbium fluoride, barium sulfate or bismuth oxidem [22]. This was contradicting with that of Zaparde et al. who found that theraCal had the highest mean compressive strength at all durations [23].

On day 10, there was statistical significant difference found between nano zinc oxide added to the synthesized calcium silicate cement subgroup and the other three subgroups. There was statistical significant difference found between theraCal subgroup and the subgroups: synthesized calcium silicate cement and angelus white mineral trioxide aggregate at $p<0.05$. There was statistical significant difference found between synthesized calcium silicate cement and angelus white mineral trioxide aggregate subgroups at $p<0.05$.

On day 30, there was significant statistical difference found between the synthesized calcium silicate cement subgroup and the subgroups: nano zinc oxide added to the synthesized calcium silicate cement and theracal at $p<0.05$. There was significant statistical difference between angelus white mineral trioxide aggregate subgroup and that of angelus white mineral trioxide aggregate at $p<0.05$.

Clinically, the radiopacity property of the dental materials is an essential factor for their distinctive visibility from their surrounding structures in the radiograph. Radiopacity is assessed by aluminum step wedge, according to ANSI/ADA specification #57 and the ISO 68766/2001. The minimum acceptable radiopacity level for an ideal cement material is 3 mm Aluminum steps of the aluminum step-wedge [24] [25]. In the present study, nano zinc oxide added to the synthesized calcium silicate cement group mean radiopacity value was 5.06 ± 0.54, which is considered an adequate radiopacity result as it is higher than 3 mm of aluminum steps as stated by ANSI/ADA specification #57. This is in accordance with Guerreiro-Tanomaru et al. who found an increase in the radiopacity values when added zinc oxide nanoparticles to Portland cements [12]. Also in accordance to Versiani et al. whose results showed an increase in radiopacity characteristics of Grossman sealer with added 25-50% of zinc oxide nanoparticles [26]. The radiopacity characteristics that were found in the group of calcium silicate cement containing nano zinc oxide particles could be attributed to the zinc that has an element number 30 which is higher than that of phosphorus and calcium (with atomic number 15 and 20 respectively) which are composed in the tooth structure [27].

In this study, the highest radiopacity was recorded for both Angelus White Mineral Trioxide Aggregate group (9.38 ± 0.63) and TheraCal group (9.43 ± 0.60). For the MTA, it has bismuth oxide in its constituent which is considered as radiopacifying material giving a good radiopacity and this was in agreement with Tanomaru-Filho et al [21]. Additionally, the theracal has radiopacifying agent incorporated in the cement and could be ytterbium fluoride, barium sulfate or bismuth oxide as stated by Xuereb et al. and the high atomic number of such materials led to their good radiopacity. In the contrast, the synthesized calcium silicate cement material that did not show any radiopacifying material did not have any ingredients containing radiopacifying material [22].

CONCLUSION

Under the limitations of this study, it was concluded that:

- The incorporation of zinc oxide nanoparticles in calcium silicate based enhances the physiomechanical properties of the cement expressed in terms of compressive strength and radiopacity in comparison to commercially available materials such as MTA and theracal.
- Compressive strength among different calcium silicate cement materials at different time periods needs further investigations clinically in the oral environmental conditions as this study was carried out in vitro and did not take into considerations different rigors that carry challenges inside oral environment.

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