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HYBRID MICRO-NANO ZRO_2 REINFORCEMENT: ENHANCING DENTAL AMALGAM PERFORMANCE

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ABSTRACT

The conventional dental amalgam has some multifarious drawbacks which lead to increasing demand for improving them to overcome the present limitations. The present study aimed to increase the dimensional stability and improve the mechanical properties by introduction of hybrid composite. The improvement is carried out by the addition of zirconia powder in both nano and micron particle size. Nano zirconia increases the structural cohesion of the amalgam due to the high surface area, which improves the bond between the particles and the matrix. While the micron sized zirconia acts as internal reinforcements that prevent the growth and propagation of microcracks, improving long-term compressive strength. The addition resulted in an improvement in compression strength in one hour by 48% and by 10 % for 24 hours. Creep resistance improved by 44% and dimensional stability improved by 96%. In overall, the hybrid modification of nano and micro ZrO_2 provides a synergistic effect, enhancing the durability and performance of dental amalgam. This modification can be a promising approach to overcoming the conventional limitations of dental amalgam, leading to more reliable and long-lasting restorative fillings.

KEYWORDS

Amalgam, ZrO_2, admix, creep, compressive strength, dimensional change.

1. INTRODUCTION

One of the most versatile fillings in dentistry is dental amalgam and made nearly seventy percent of all materials used for restorative dentistry. This is due to several unique advantages like its longevity, cost-effectiveness, and ease of manipulation. Despite these advantages, ordinary dental amalgam shows several limitations, such as lack of aesthetics, susceptibility to corrosion, and marginal breakdown over time (Ramesh Bharti et al., 2010), (Hasheminezhad et al., 2012). By backing to the golden time of the dental amalgam, significant studies focused on modifying the ordinary amalgam filling to overcome this limitation and enhance the overall performance.

Dental amalgams are prepared by mixing a powdered alloy that is predominantly silver–tin with liquid mercury. The process of mixing silver–tin alloy particles with mercury for clinical use is known as trituration. The freshly mixed amalgam is a viscous paste that can be extruded from the capsule into the cavity, where it sets. (Nicholson, J.W., 2020), (Zafar, M.S. and Khurshid, Z., 2020).

Dental amalgam is the result of the partial dissolution of alloy particles in mercury, where new mercury-rich phases emerge as the matrix holding the unreacted portion of the alloy particles together (Shen, C. et al., 2021).

Amalgam readily heats up and expands or cools and contracts with a small temperature changeCeramics, composites, acrylics, and cements are examples of nonmetals that are extremely poor conductors. It is possible to utilize poor conductors as insulators. For example, the insulation created by the acrylic denture base may prevent a patient wearing a denture from sensing the temperature of a liquid.(Eakle, W.S. and Bastin, K.G., 2019)

The quality of dental amalgams has significantly improved after a new atomization method was introduced. The durability of amalgam has been strengthened by adding copper components in large quantities, resulting in a 12-year serving time. As a result, post-processing polishing is not necessary after placement. (Rezaie, H.R. et al., 2020)

At that time, Zirconia was widely utilized in the dentistry applications. This is because of the superior mechanical properties, high fracture toughness, and outstanding biocompatibility. (Hua Lin et al., 2021). amalgams, are among the most widely used composites (Sabu Thomas · R. M. Baiju 2023). Nano-ceramics used to reinforce dental amalgam to improve hardness and other mechanical properties of amalgam fillings (Noorhana Yahya et al., 2013).

Early studies predominantly investigated the effects of adding either micro- or nano-sized oxides particles separately, each contributing distinct benefits: micro-sized particles enhance load-bearing capabilities and provide effective crack deflection, whereas nano-sized particles improve the homogeneity of the microstructure and fill voids, leading to a refined composite network (Haydar Jamal Al-Deen and Nabaa Muthana Mahdi 2017), (Rehman A et al., 2020). High-strength multiphase alloys, dental amalgams are susceptible to intergranular or localized galvanic corrosion between the various phases. Conventional silver tin amalgam and high-copper amalgam are the two alloy types make the most in used dental amalgams. The high-copper amalgams are more corrosion-resistant and have better therapeutic qualities. (Kaur G et al., 2022)

Considering its long clinical history, durability, wear resistance, self-sealing ability, and method insensitivity, amalgam has shown to be an effective restorative material for rear restorations. Amalgam exhibited better compressive strength and fracture resistance and can be used for restoring posterior teeth by adding ceramic reinforcement. (Azmy E et al., 2022). Adding nanomaterials to dental fillings is an approved procedure to increase the resistance of fillings and improve mechanical properties such as: zirconium dioxide (ZrO_2), titanium dioxide (TiO_2), and silicon dioxide (SiO_2) (Elmarsafy SM. 2024; Al-Qahtani et al., 2025;Gomes, A.C et al., 2022;Park, J.M et al., 2023). The aims of this work are to evaluate the effect of hybrid nano-micro ZrO_2 reinforcement addition on mechanical properties of dental amalgam.

2. MATERIALS AND METHODS

The samples were made in compliance with ADA standard No. 1. (Richared M. et al. 2003) by mixing the powdered alloy and mercury at 1/0.9 admix Amalgams the reduced amount of mercury increased the strength of the amalgam (Holland RI et al., 1985) the mercury of purity 99.99% and the powder composited of Ag 40%, Sn 31.3%, Cu 28.7% purchased from SDI made in Australia, these capsules conform to ISO 24234 all together with the ceramic addition that fall in to two particle size micro sized zirconium oxide of purity 99.99% purchased from Macklin made in China and nano zirconium oxide purchased US Research Nanomaterials of particle size ranged from (10 to 20) nm by mechanical amalgamator for thirty seconds. The addition of the ceramics reinforcement were (0, 1, 2, and 3) wight percent. The specimens have the following measurements: four millimeters in diameter and eight millimeters in height. A standard two millimeters diameter condensing point was used to manually pack the mixture into a mold made of Teflon shown in Fig. 1 with the appropriate dimensions, setting on a horizontal surface. Compressive load of 14 MN/m2 was then applied for two minutes, after that the die opened and the specimen was ejected. The specimens aged at 37±1 ºC in an incubator tell the test time. Fig 2 shows the amalgam specimen.

Fig. 1 shows the used Teflon mold .

Fig. 2 shows the amalgam specimen.

For the observation of microstructure polyester resin that cures at room temperature is used to cold mount the amalgam specimen. With the use of progressively finer grades of emery paper (220 to 3000) and diamond past, the samples were grinded and polished. Before being etched, the specimens were properly cleaned with distilled water, dried in an air blast. The polished amalgam alloy specimens etched using a etchant consisting of 30 % nitric acid. After that the samples examined by optical microscopy by 400x magnification.

Phases of the used dental amalgam before the addition and for the 3% addition were inspected by X-ray diffractometer (AL-2700b, H.S. Japan) Scherer's formula using copper radiation with a wavelength of 0.15406 nm and an angle range of 2θ between 30^{o} and 80^{o}).

A universal testing machine of type WDW 200, manufactured in China, shown in Fig. 3 was used to perform compressive strength tests. A steady loading speed of 0.5 mm/min was used for the testing. One hour after completion of trituration, the first measurement was taken, and twenty-four hours later, the second measurement. Until the tests were completed, these specimens were maintained at a consistent temperature of 37±1°C. Compressive strength (σ) it’s calculated by as follows in Eq.1 (Wang, Linda et al., 2003), (Nuran Dinçkal et al., 2020),:

$$\sigma = \frac{F}{A} \qquad (1)$$

Where: -

σ: compressive strength in Mpa

F: Maximum force in N

A: cross sectional area in mm

Fig. 3 shows the universal testing machine type WDW 200.

Three specimens of each addition were kept in an incubator at 37± 1°C for seven days to before measuring the creep. Prior to conducting the test, emery paper was used to flatten the specimen's two sides. Prior to the load application it is necessary to measure the specimen length of the specimen. The specimens subjected to a axial stress of 38 MN/m^{2}were applied for four hours at constant temperature of 37± 1 °C. The specimen length was then measured after four hours of load application, and it's calculated by Eq.2 (Richared M. et al. 2003) as follows: -

The change in length between 1and 4 hours of the spacemen under the applied load divided by the original length is creep percentage.

$$\text{Creep Percent } \% = \frac{L_{\circ} - L}{L_{\circ}} \times 100 \qquad (2)$$

where:

L_o = original length,

L = final length.

For dimensional change the first record was taken after 5min after the end of trituration, the length of specimen was measured by digital micrometer with 0.1µm accuracy. Twenty-four hours following the completion of trituration, the specimens' length was measured. During the test the specimens were stored at a temperature of 37± 1°C. The A.D.A. specification No.1 and ISO 24234 (ISO 24234, 2015) states that the dimensional change shall fall between -0.15 to +20 µm/cm to be accepted. Dimensional change percent is calculated by dividing the change in length between five minutes and 24 h after the end of trituration to the original length by Eq.3 (Richared M. et al., 2003) as follows:

$$\text{Dimensional change Percent } \% = \frac{L_{\circ} - L}{L_{\circ}} \times 100 \qquad (3)$$

where:

L_o = length after five minutes

L = length after 24h.

secondary caries at the interface of the amalgam restoration and the tooth, linked the development of carious lesions to microleakage (Mazumdar, P. and Chowdhury, D., 2021).

3. RESULTS AND DISCUSSION

The amalgam microstructure shown in Fig. 4 illustrates the microstructure of the 30% nitric acid etching. The unreacted particles have a darkish appearance and are enveloped by a continuous $\gamma 1$ matrix and η phase.

The $\gamma 1$phase presents as a lighter-colored matrix. The voids appear as dark, out-of-focus regions under a microscope. As a result, the set amalgam mass's final microstructure is mostly made up of unreacted particles encircled by a matrix of reaction products. The matrix holds the unreacted particles together.

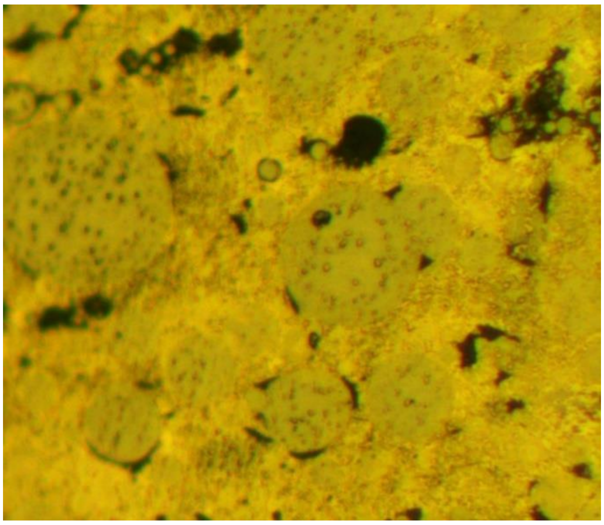

Fig. 4 shows the amalgam microstructure.

The tested specimens for phases evaluation shown in Fig. 5 present the x-ray diffraction patterns obtained from this amalgam. By comparing the alloys to standard XRD cards, the phases were identified. The phase determination shows the amalgam filling composed of two main phases are $\gamma(Ag_3Sn)$ and ε (Cu_3Sn), and one other phase η (Cu_6Sn_5).

Relative intensity of the three-phase presented in the alloy lead to the conclusion that the predominate phase was γ phase which represented the matrix of the amalgam microstructure, the ε phase has the latter intensity peaks this is lead to conclusion that the ε phase represented network in the matrix. The η phase intensity peak was relatively small with respect to the other phase's peaks, which gives an indicator to its small amount.

It can be seen that the sample with 3% addition (red curve) shows changes in the intensity of the peaks compared to the sample without addition (blue curve). The addition of the nano zirconia to the amalgam effects the width of the peaks which is effect of adding nanomaterials which involve components that lack long-range crystallographic order

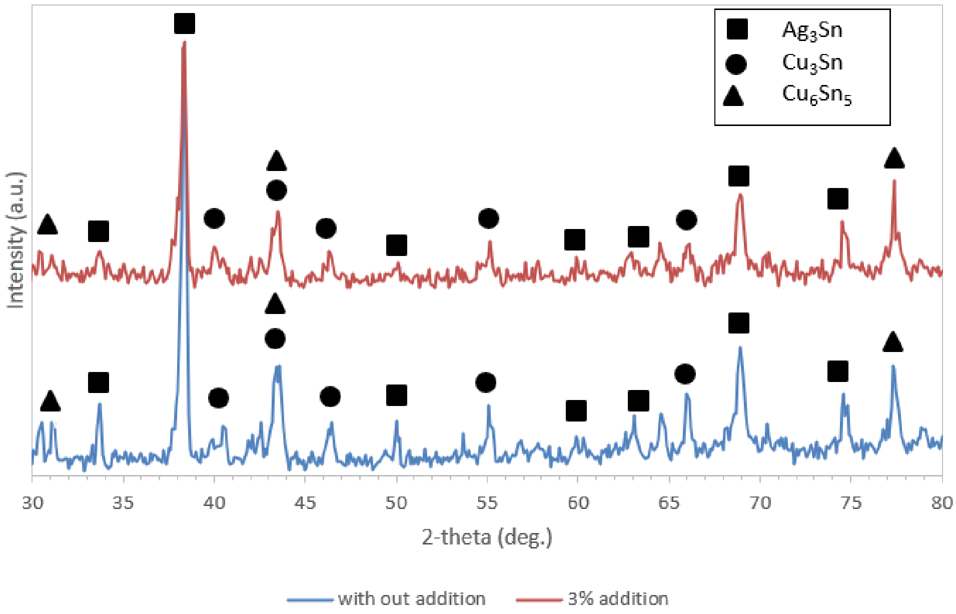

Fig.5 present the complete x-ray diffraction patterns obtained from the amalgam alloys.

Mean value of compression strength was reported by result of four specimens of each amalgam alloy in two aging times (1 & 24 hours) from the end of the trituration are presented in Fig. 6. It’s noted that there is a considerable increase in compression strength at 24 h aging time compared to 1 h. This is all because there could be some unreacted mercury present and the setting reaction is incomplete. The amalgam will be weakened by mercury. As a result, the amalgam reaches its maximum strength after a 24 h, at which point the mercury is totally reacted and its final phases are formed.

The nano and micro addition of ZrO_2 increases the compression strength of the dental amalgam. Nano zirconia increases the structural cohesion of the amalgam due to the high surface area, which improves the bond between the particles and the matrix. While the micron sized zirconia acts as internal reinforcements that prevent the growth and propagation of microcracks, improving long-term compressive strength.

Fig. 7 displays the findings derived from the average creep value of three specimens of each addition. The allowed creep value in a dental amalgam should be less than 1%, according ADA standard No. 1 . All of the existing amalgams had creep values below the 1% ADA limit. The amalgam's creep resistance and compressive strength showed similar trends when hybrid zirconia was added.

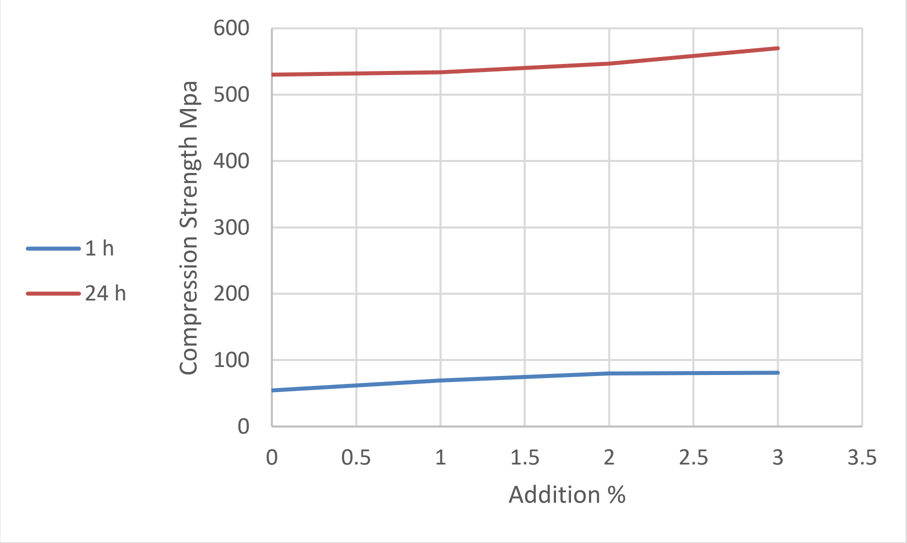

Fig. 6 shows the effect of the addition on compression strength and aging time.

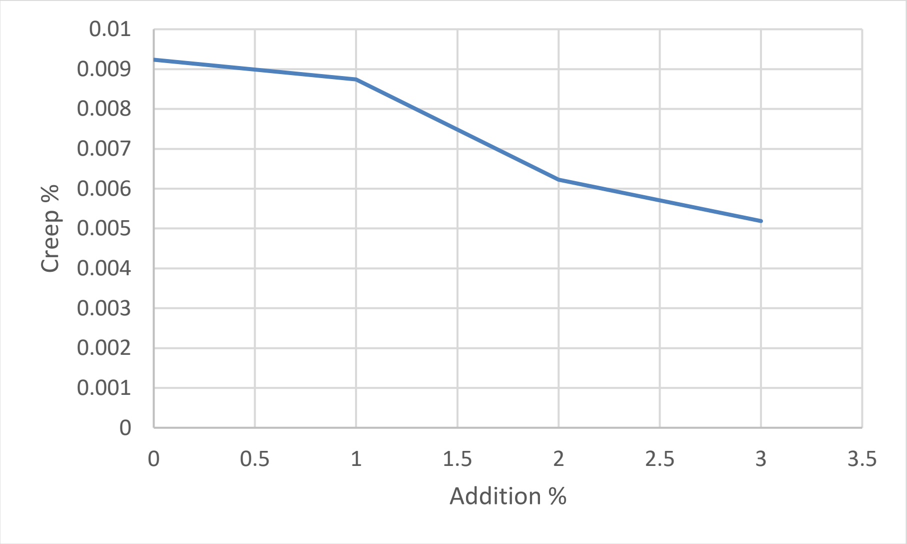

Fig.7 . Effect of hybrid ZrO2 (Micro and nano) Addition on The Creep%

As shown in Fig. 4, the percent of creep of the amalgam droped with increasing additional percent. The hybrid reinforcement (combination of both micro and nano ZrO_2) has been shown to reduce creep deformation in dental amalgam. The fine particles can obstruct dislocation motion and hinder plastic deformation, leading to better resistance against creep over time. The interaction between micro and nano-sized particles might produce a synergistic effect, improving creep resistance more effectively than either particle size alone.

Additionally, it is seen that the volume of the examined specimens decreases with every amalgam test. The closure of the porosity created during trituration and the condensation processes are the causes of this decrease.

Five samples of each amalgam were used to determine the mean value of the dimensional change, which is displayed in Fig. 8. According to ADA standard No.1, allowed dimensional change ranges from -0.15 to +20 µm/cm. According to the results displayed in the Fig.5, all amalgams were found to be within the ADA-established acceptable limit, and the amalgam's dimensional change stabilized when the amount of nano and micro ZrO2 was increased.

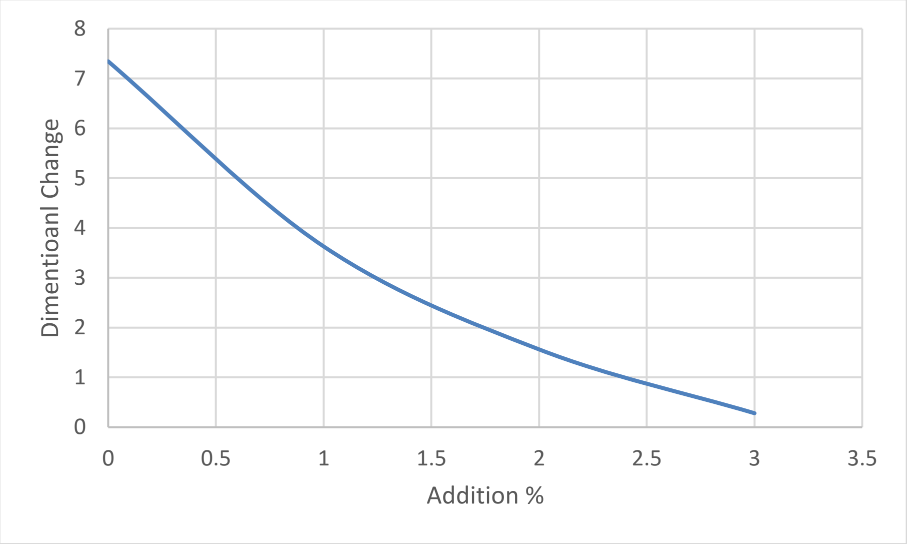

Fig. 8 presents the effect of addition on dimensional change.

4. CONCLUSIONS

The addition of hybrid ZrO_2 led to a 48% increase in compressive strength after one hour and 10% after 24 hours. Creep resistance improved by 44%, while dimensional stability reached up to 96% improvement, all within the acceptable ADA range. The results confirm the potential of hybrid ceramic reinforcement in improving the performance of dental amalgam

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