

Hardness Improvement of Dental Amalgam Using Zinc Oxide and Aluminum Oxide Nanoparticles

Noorhana Yahya, Poppy Puspitasari
and Noor Rasyada Ahmad Latiff

Abstract Strength tests of a dental amalgam material were conducted. Zinc oxide and aluminium oxide nanoparticles were used as fillers to enhance the hardness and other mechanical properties of dental amalgam material. The zinc oxide nanoparticles were synthesized by using a sol–gel technique, the samples of which were characterized by X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscope (FESEM) and Raman spectroscopy and then mixed with the material and compacted into cylindrical-shaped pellets for green density, compressibility and Vickers hardness evaluation. Increment of 183 % in hardness was observed with average Vickers hardness of 0.95 GPa by using 250 °C zinc oxide as nanofiller. On the other hand, the Al_2O_3 nanoparticles filled composite observed 1.12 GPa of average Vickers hardness with 229 % of increment as compared to without the fillers. All in all, that the application of Al_2O_3 nanoparticles as filler result in improved hardness. This work offers the dentistry industry a potential contender in the market place.

Keywords ZnO · Al_2O_3 · Dental amalgam · Hardness

N. Yahya (✉)

Fundamental and Applied Science Department, Universiti Teknologi PETRONAS Bandar Seri Iskandar, 31750 Bandar Seri Iskandar, Malaysia
e-mail: noorhana_yahya@petronas.com.my

P. Puspitasari · N. R. A. Latiff

Electrical and Electronic Engineering Department, Universiti Teknologi PETRONAS Bandar Seri Iskandar, 31750 Bandar Seri Iskandar, Malaysia
e-mail: povopivi@gmail.com

N. R. A. Latiff

e-mail: syasya.latiff@gmail.com

P. Puspitasari

Mechanical Engineering Department, Universitas Negeri Malang, Semarang Street, Malang 65145, Indonesia

1 Introduction

Dental amalgam has been used in mouth as a permanent dental restorative material since long time ago. Appearing almost indestructible, it always seems to pull through, no matter how it is mistreated. Amalgam, a mixture of mercury with at least one other metal, is chosen due to its low cost, easy application, high strength and durability [1]. Recently, many problems have been faced in dentistry for the usage of amalgam containing excess mercury that simply becomes the cause of illnesses and brings pollution to the environment. A new type of dental amalgam currently being used constitutes less mercury when amalgamated in the correct ratio. In aesthetics view, metallic color is not well-blended with the natural tooth color [2, 3]. This is where the incorporation of zinc oxide nanopowders into the mixture of the new dental amalgam becomes important. Zinc oxide is naturally white and its incorporation into this new dental amalgam might fade the metallic color of the conventional amalgam out. However, the addition of zinc oxide was primarily intended to improve the hardness of that material. Microparticles and fibers can also be used to reinforce dental resin-based composites. By adding a small amount of short or networked fiber to the composite, a modest increase in strength was proven [4].

Zinc oxide (ZnO) is a unique material that has prompted an enormous number of researches. Various morphologies and sizes of ZnO materials have led to a wide range of promising applications, such as additive in the production of paints, ceramics, catalysts, electronics, optoelectronics and many more. These unique nanostructures clearly demonstrate that ZnO probably has the richest family of nanostructures of all materials, both in structures and in properties. Various ZnO nanostructures with different morphology such as nanorods, nanotubes, nanospheres and many more have been found [5]. Meanwhile, properties of ZnO nanomaterial powders are dependent on their micro structural and morphological characteristics, which may vary according to the selected method of synthesis.

Due to a wide range of applications in engineering and biomedical areas, aluminum oxide has become one of the most versatile ceramic oxides employing unique properties such as high elastic modulus, thermal and chemical stability, high strength and toughness -thus enabling it to tremendously perform under tension or bending conditions. A lot of efforts using various methods have been put on synthesizing one-dimensional Al_2O_3 nanostructure with different morphologies including nanowires, nanoribbons, nanorods, nanofibres and nanotubes [6]. The temperature at above 1200 °C, however, has been used in synthesizing alumina nanostructures. It triggers the need to synthesize this material at low temperature by using simple techniques. In this regard, this work premise deals with only zinc oxide nanoparticles as filler.

Nanopowders are produced by a wide number of synthesis methods such as self-combustion, sol-gel, hydrothermal, precipitation and oxidation. In combustion synthesis, the high temperature means that only coarse nano-size particles greater

Table 1 Standards of dental alloy compositions^a

	EN 21559 ^b	ISO 1559 ^c	ANSI/ADA ^d
Silver (Ag)	40 % (min.)	40 % (min.)	— ^f
Tin (Sn)	32 % (max.)	32 % (max.)	— ^f
Copper (Cu)	30 % (max.)	30 % (max.)	— ^g
Zinc (Zn)	2 % (max.)	2 % (max.)	— ^{g,i}
Mercury (Hg)	3 % (max.)	3 % (max.)	— ^g
Indium (In)	— ^e	5 % (max.)	— ^h
Palladium (Pd)	— ^e	1 % (max.)	— ^h
Platinum (Pt)	— ^e	1 % (max.)	— ^h

^a min. = minimum concentration (% , by wt.); max. = maximum concentration (% , by wt.). The composition or purity of the dental mercury used in amalgamating the dental alloy to form the silverfilling is given in EN 21560 (1991) and ISO 1560 (1985), which are identical; greater than or equal to 99.99% elemental mercury (Hg).

^b European standards or European Norms: EN 21559 (1991).

^c International Organization of Standards: ISO 1559 (1995).

^d ANSI: American National Standard Institute; ADA: American Dental Association

^e No standards currently available for these metals.

^f According to ANSI/ADA Specification No. 1 (1979), Reaffirmed (1993), “The chemical-composition shall consist essentially of silver and tin”.

^g Further to ANSI/ADA Specification No. 1 (1979), Reaffirmed (1993), “Copper, Zinc , gold and/or mercury may be present in amounts less than the silver and tin content”.

^h Further to ANSI/ADA Specification No. 1 (1979), Reaffirmed (1993), “Other elements may be included provided the manufacturer submits the composition of the alloy and results of adequate clinical and biological investigations to the Council on Dental Materials and Devices, American Dental Association, to show that the alloy is safe to use in the mouth as directed in the manufacturer’s instructions”.

ⁱ Further to ANSI/ADA Specification No. 1 (1979), Reaffirmed (1993), “Alloys containing zinc in excess of 0.01% shall be described as zinc-containing. Those alloys containing zinc equal to or less than 0.01% shall be designated as nonzinc”.

than 100 nm can be produced [7]. The sol–gel process being at low temperature conversely offers the greatest scope for the smallest nanosize material. The final product may be ensured to possess high homogeneity and fine grain size [8]. The actual reaction takes a few hours and other steps such as calcination are split into separate operations of a few hours on each. Realizing the quality of the nano-powders produced by the sol–gel method, the study is done on synthesizing ZnO nanoparticles by sol–gel method and investigates the addition of ZnO as nanofiller to improve mechanical strength of the dental amalgam. This study will relate to the standard for dental alloy composition as mention in Table 1.

2 Methodology

2.1 Synthesis of Zinc Oxide

The zinc oxide sol was obtained by dissolving zinc nitrate, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ salt into 100 ml of 65 % concentrated nitric acid, HNO_3 . After being stirred for 2 days, the homogeneous sols then heated up until gelatine is formed. The samples were dried in an oven at 110 °C for 3 days and then crushed for at least 4 h to obtain nanosize particles. Done with the crushing process, the zinc oxide powder was separated into two parts and annealed at temperature 250 and 350 °C, respectively to investigate the effect of temperature variation on morphology and crystallite size.

2.2 Morphological Characterization and Elemental Analysis

The surface morphology of all samples was characterized by Field Emission Scanning Electron Microscope (FESEM), followed by elemental analysis using Energy Dispersive X-Ray Spectroscopy (EDX).

2.3 Mechanical Strength Test

All samples act as nanofiller to improve the strength of the new amalgam powder, known as Silverfil powder which consists of 60 % reactive silver (Ag) + 40 % silver-mercury (Ag_3Hg_2). The amalgam composites were prepared by mixing up the Silverfil powder and ZnO nanopowder at once in manual handling at different ratio and weight percentage of zinc oxide nanopowder. The ratios of the composite materials are presented in Table 2 in which three different ratios were chosen to investigate the change in material hardness.

Table 2 Ratios of weight percentage of the composite materials

Sample		Weight percentage (%)	
		Silverfil	Zinc oxide/aluminium oxide
ZnO annealed at 250 °C	1	100	0
	2	90	10
	3	80	20
ZnO annealed at 350 °C	4	100	0
	5	90	10
	6	80	20

For mechanical strength test, hardness of the sample was tested using a Microhardness Tester according to ASTM E 384. Microindentation hardness tests are applicable to materials which are too thin or too small for macro indentation hardness tests. In this research, the Vickers diamond-shaped indenter was chosen for its tendency to produce a geometrically similar indentation at all test forces. Except for tests at very low forces e.g. 1 gf that produces indentations with diagonals smaller than about 25 μm , the hardness number will be essentially the same as produced with test forces of 0.1 kgf, provided that the material being tested is homogeneous. For isotropic materials, the two diagonals of a Vickers indentation are equal in size [10].

Preparation of samples needs to be conducted prior to the hardness test. Powder composites were compacted into pellets by pouring them into a mould and pressed by 1000 kg load and dwelled for 0.5 min in the Carver 25 Ton Auto Pellet Press Machine.

Following to compression, physical quantities e.g. mass, thickness and diameter of the cylindrical pellets were measured to determine the green density, ρ_g . It was specified by this formula:

$$\begin{aligned}\rho_g &= \text{Green density, g/cm}^3 \\ &= ((4/\pi) \times 1000 \times M)/(d^2 \times t) \\ &= 1273(M/d^2 \times t)\end{aligned}$$

where,

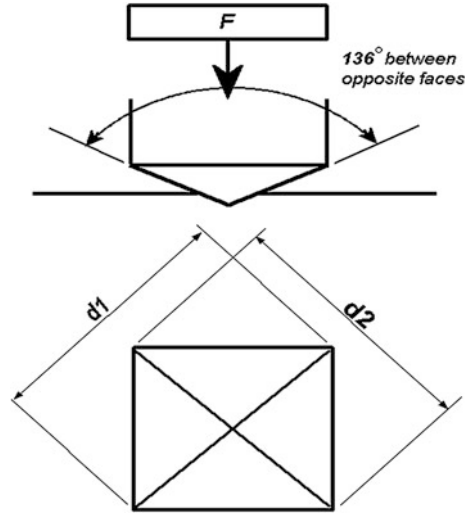
$$\begin{aligned}M &= \text{mass of pellet in gram,} \\ d &= \text{diameter of pellet in millimeter (mm),} \\ t &= \text{thickness of pellet in millimeter (mm).}\end{aligned}$$

The pellets were prepared for hardness testing. In this case, the microindentation hardness test was conducted since the samples were too thin. It allows specific phases or constituents and regions or gradients which are too small for macroindentation testing to be evaluated.

The Vickers indenter usually produces a geometrically similar indentation at all test forces (Fig. 1). For isotropic materials, the two diagonals of a Vickers indentation meanwhile are equal in size. Vickers hardness number, HV, is an expression of hardness obtained by dividing the force applied to a Vickers indenter by the surface area of the permanent impression made by the indenter. In practice, test loads are in grams-force and indentation diagonals are in micrometers. The Vickers hardness, $\text{gf}/\mu\text{m}^2$ is calculated as follows:

$$HV = 1854.4 \times P/d^2$$

Fig. 1 Vickers microhardness geometry [11]



where,

P = force, gf, and

d = mean diagonal length of the indentation, μm .

In SI units (GPa), Vickers hardness is determined as follows:

$$HV = 0.0018544 \times P_1 / d_1^2$$

where,

P_1 = force, N, and

d_1 = length of the long diagonal of the indentation, mm.

Indentations were done on three different points of each pellet and the average hardness obtained was considered to be the hardness number on the Vickers scale.

2.4 Chemical Composition of Silverfil Dental Amalgam

Silverfil dental amalgam is a revolutionary restorative dental material used for filling tooth cavities. Unlike conventional dental amalgams, the highly reactive powder of Silverfil Argentum completely absorbs all of the mercury used for amalgamation leaving no traces of any excess mercury behind in the fillings. Users as a result need not to worry about their safety due to handling and consuming this product.

This material consists of 60 % Reactive Silver (Ag) and 40 % Silver-Mercury (Ag_3Hg_2), which constitutes 74 % of total silver content and 26 % of total mercury one in the composition. Aim of this research is to improve the hardness of the material without altering the original composition, which is achievable by adding a little portion of nanoparticles which acts as fillers.

3 Results and Discussions

3.1 X-Ray Diffraction

Annealing temperatures of 250 and 350 °C were chosen based on results obtained in the previous work. The lowest possible annealing temperature is desired; therefore strong focus was given to the lower temperature region. From our previous work, the samples were characterized by X-Ray Diffraction (XRD).

XRD patterns of as-synthesized zinc oxide samples via sol-gel method at different annealing temperature are shown in Fig. 2 with all peaks that appear coinciding with the standard card of zinc oxide provided in Table 3. The samples prepared show the [101] major peak at 2θ of 9.33° , 36.27° and 36.29° which was annealed at 100, 200, 300 and 400 °C, respectively. From Fig. 2 it is observed that at lower annealing temperature around 200–400 °C peaks obtained nearly matched to the spectrum emitted by the standard card of zinc oxide.

Based on the Raman spectroscopy results, shown in Fig. 3 below, the intensity of the Raman shift of the zinc oxide sample decreased when the annealing temperature increased to 200 °C. It shows that the Raman shift are 1055.3 cm^{-1} (for samples annealed at 100 and 200 °C), 439.696 cm^{-1} (for the sample annealed at 300 °C) and 438.177 cm^{-1} (for the sample annealed at 400 °C).

From XRD and Raman spectra, it is observed that the crystallite size of the samples began to decrease at annealing temperature region around 200–400 °C and increased beyond that particular region (Table 4). Raman shift also began to decrease at this region and got close to the standard zinc oxide peak. Therefore, the annealing temperatures at 250 and 350 °C were chosen based on these results. The Raman shift for ZnO is in the range of $200\text{--}1500\text{ cm}^{-1}$. In this case, as previously mentioned, the Raman shift for ZnO as prepared samples is 380, 407, 437, and 583 cm^{-1} , while the Raman bands above 800 cm^{-1} have been assigned as second order Raman bands [12]. It is furthermore concluded that Raman bands for ZnO bulk obtained were at 379, 410, and 439 cm^{-1} [13]. ZnO annealed at 100 and 200 °C shows the shifted peak at 1055.300 cm^{-1} , which probably means that after the annealing process, there was still much oxygen vacancy since the Raman shift has consistency with the oxygen deficiency in the sample.

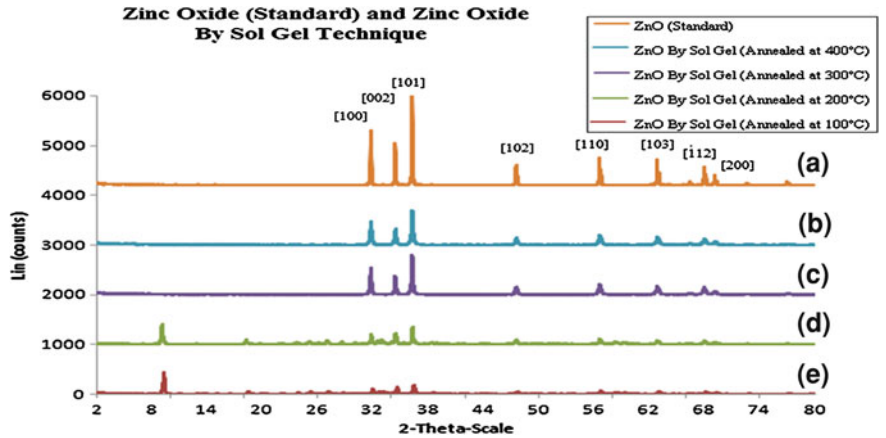


Fig. 2 XRD patterns of as-synthesized zinc oxide samples with a major peak [101] **a** zinc oxide standard; and samples prepared via sol gel technique that were annealed at, **b** 400 °C; **c** 300 °C; **d** 200 °C; and **e** 100 °C

Table 3 Standard card of zinc oxide

Sample (°C)	Standard card
ZnO SG(100)	SS-NNNN 72-0627
ZnO SG(200)	SS-NNNN 89-0511
ZnO SG(300)	SS-NNNN 65-3411
ZnO SG(400)	SS-NNNN 79-2205

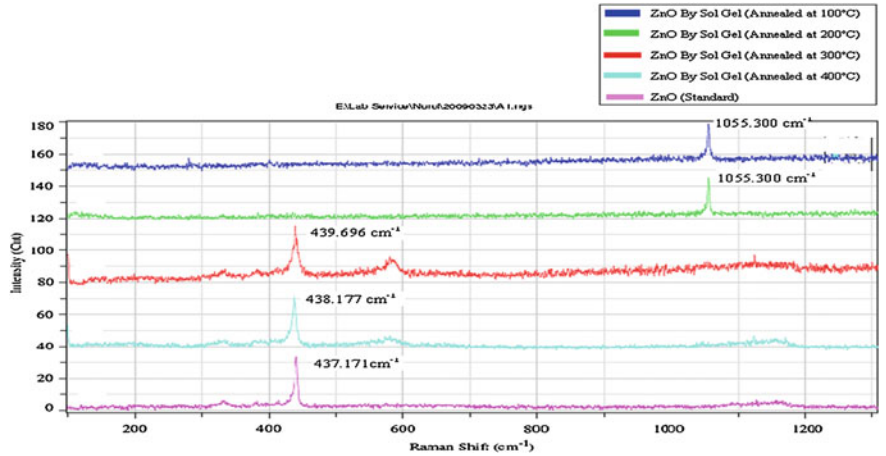


Fig. 3 Raman spectroscopy results for samples subjected to different annealing temperature; **a** 100 °C; **b** 200 °C; **c** 300 °C; **d** 400 °C; and **e** standard zinc oxide Raman shift

Table 4 XRD and Raman spectroscopy results

Samples	X-Ray diffraction				Raman spectroscopy			
	Intensity (counts)	FWHM	d-spacing (Å)	Crystallite size (nm)	a	b	c	Intensity (counts)
ZnO SG(100 °C)	9.332	0.222	9.469	38.490	19.48	6.238	5.517	42.140
ZnO SG(200 °C)	36.287	0.163	2.473	50.700	3.249	3.249	5.205	36.569
ZnO SG(300 °C)	36.269	0.201	2.474	33.290	3.249	3.249	5.269	55.048
ZnO SG(400 °C)	36.285	0.216	2.4737	38.290	3.250	3.250	5.207	43.830

3.2 Surface Morphologies from FESEM Analysis

The morphology of the resulting ZnO samples was directly examined by FESEM without carbon or gold coating due to the semi-conducting nature of ZnO [14]. Figure 4 depicts images magnified at 10,000, 25,000 and 50,000, showing formation of nanorods due to annealing temperature 250 °C for 2 days stirring period. The lengths of the nearly uniform nanorods are about 800–900 nm.

From Fig. 5, it can be observed that annealing at different temperatures can produce different nanostructure in comparison to Fig. 4. Nanoflake structure was formed when the ZnO powder was annealed at 350 °C with a dimension of approximately 1.200–2.000 μm . These results, shows that producing uniform zinc oxide nanostructures is challenging and a small change of synthesis parameters can generate nanostructures with totally different morphologies.

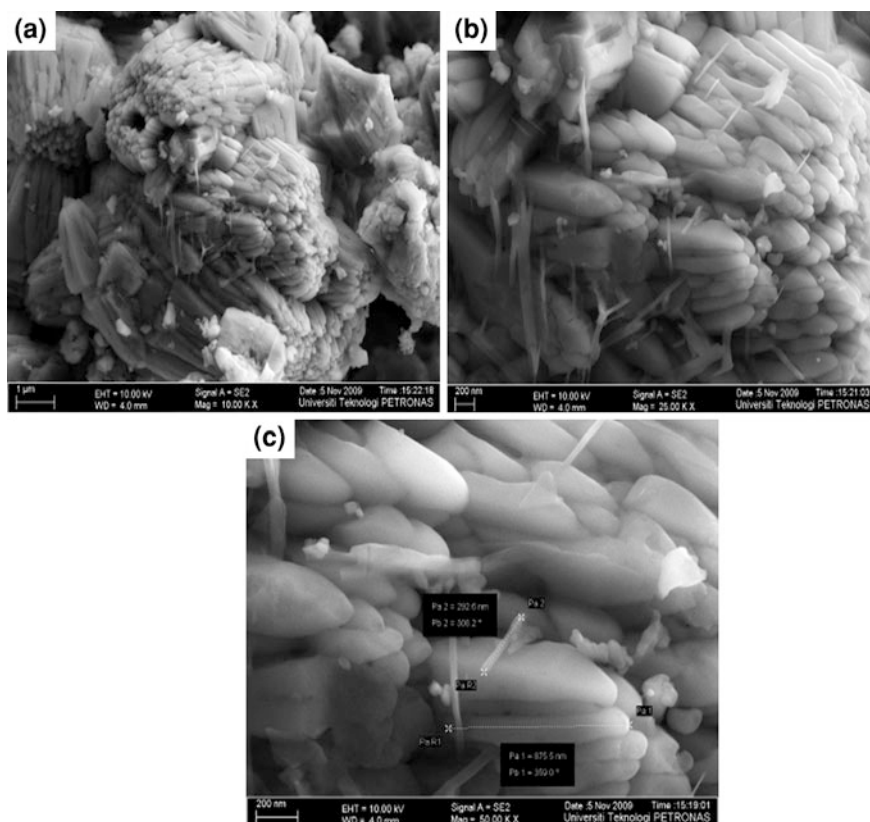


Fig. 4 FESEM images of the ZnO nanostructures, synthesized by sol–gel method, annealed at temperature 250 °C, with magnification at **a** 10,000, **b** 25,000, and **c** 50,000

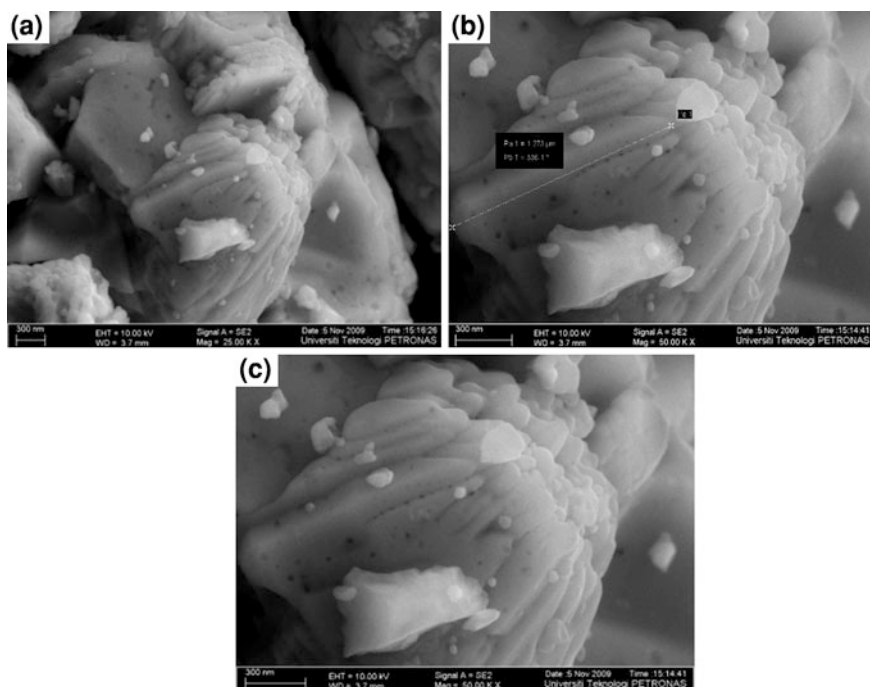


Fig. 5 FESEM images of the ZnO nanostructures, synthesized by sol-gel method, annealed at temperature 350 °C, with magnification at **a** 25,000 $\times$, **b** and **c** 50,000 $\times$

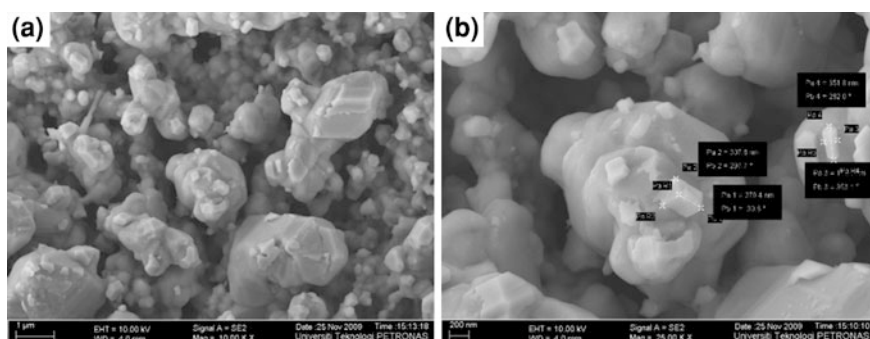


Fig. 6 FESEM images of silverfil powder under **a** 10,000 $\times$, **b** 25,000 $\times$ magnification

FESEM and EDX analyze were also done to the Silverfil, reactive silver and silver mercury powder. Figure 6 shows the images of pure Silverfil powder at 10,000 and 25,000 times magnification.

Figure 7 on the other hand shows images of pure silver mercury powder at 500, 10,000 and 25,000 times magnification. Figure 8 shows images of reactive silver at 10,000 and 25,000 times magnification.

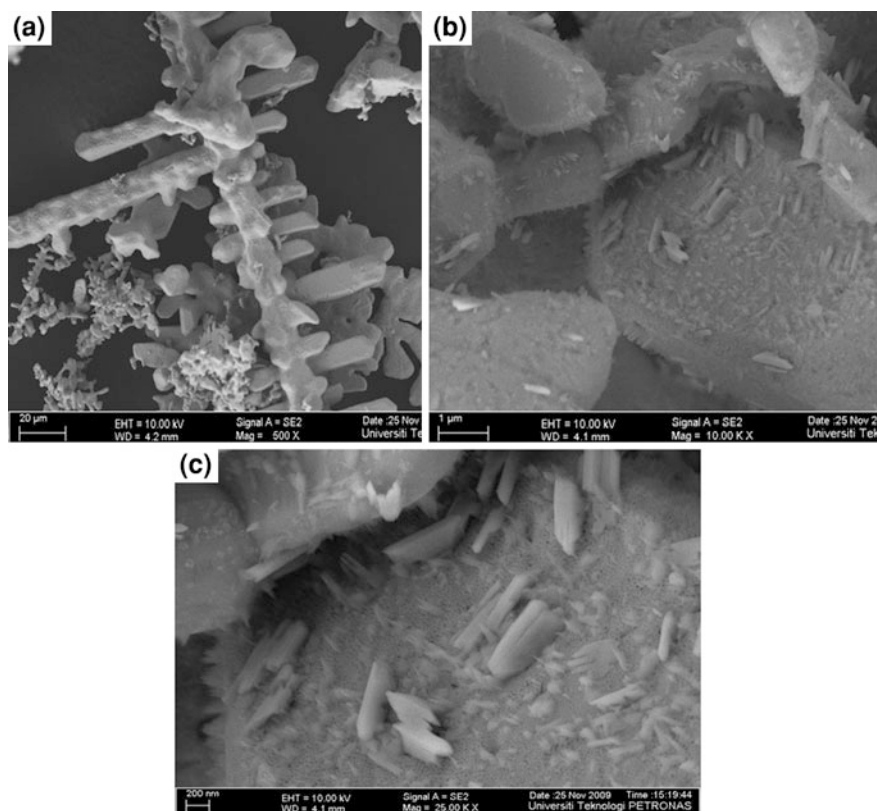


Fig. 7 FESEM images of pure silver mercury powder at **a** 500 $\times$, **b** 10,000 $\times$ and, **c** 25,000 $\times$ magnification

3.3 Elemental Analysis

Table 5 gives exhibits the chemical composition of both ZnO samples annealed at 250 and 350 $^{\circ}\text{C}$. In conclusion that the ZnO produced were of high purity with the presence of no element other than Zn and O.

The ratio of Zn-O atoms should be 50–50 from the chemical formula, yet from the elemental analysis, a little deviation in the atomic percentage can be observed. The standard atomic weight of oxygen atom is $15.9994 \text{ g}\cdot\text{mol}^{-1}$, whereas $65.38 \text{ g}\cdot\text{mol}^{-1}$ is for zinc. Compared with the EDX results, there is a huge deviation in weight percentage for both elements as shown in Table 5.

For Silverfil powder sample, a little deviation can be observed from this analysis. As given in the datasheet, the total silver content should be 74 %, whereas 26 % of mercury constitutes the rest percentage. However, from the elemental analysis, deviation in the weight percentage of both elements were

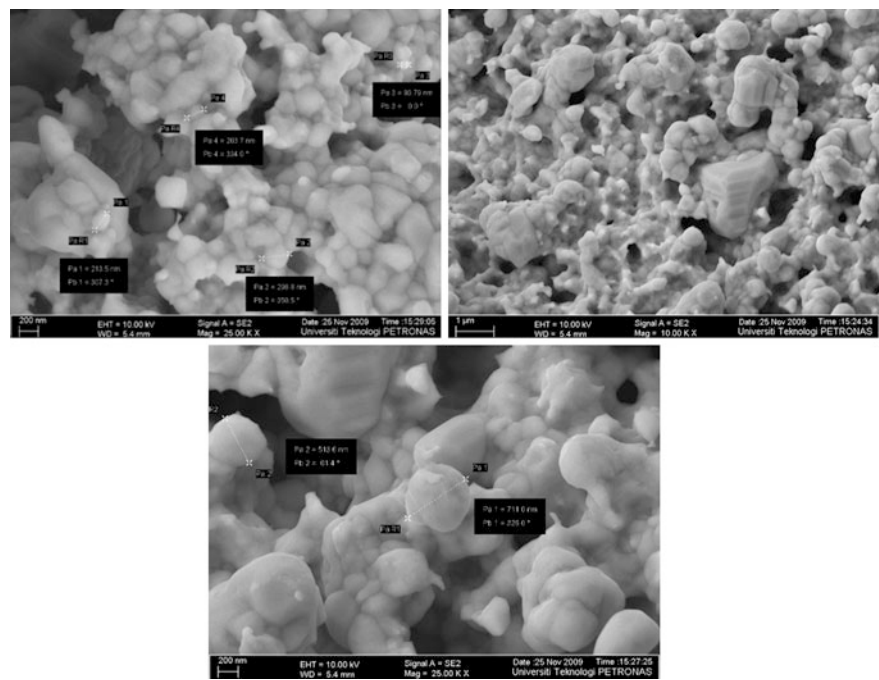


Fig. 8 FESEM images of reactive silver at different magnification. Clockwise direction; 10,000×, and 25,000× magnification

Table 5 Chemical composition obtained from elemental analysis via energy dispersive X-Ray spectroscopy (EDX)

Sample	Element	Atomic (%)	Deviation (%)	Weight (%)	Deviation (%)
ZnO 250 C	O	58.12	16.24	25.35	58.54
	Zn	41.88	−16.24	74.65	14.18
ZnO 350 C	O	47.28	−5.44	18.12	13.25
	Zn	52.52	5.04	81.88	25.24
Pure silverfil	Ag	86.02		76.79	3.77
	Hg	13.98		23.21	−10.73
Pure silver mercury (Ag ₃ Hg ₂)	Ag	50.27	−16.22	35.22	−21.35
	Hg	49.73	24.33	64.78	17.04
Pure reactive silver (Ag)	Ag	100.00	0.00	100.00	0.00

detected which is about an increment of 3.77 % for silver and a reduction of 10.73 % for mercury from the theoretical value.

EDX analysis for silver mercury shows a huge deviation in atomic percentage for both silver and mercury elements. For silver, a reduction of 16.22 % of the expected value and a 24.33 % increment was observed in mercury and reactive silver exhibited 100 % purity of argentums element with the absence of any other impurities.

Table 6 Measurement of the green density obtained from powder compaction using (a) ZnO 250 °C, (b) ZnO 350 °C

Sample	Percentage of ZnO Nanofillers (%)	Load (kg)	Mass of sample (g)	Diameter (mm)	Thickness (mm)			Green density (g/cm ³)			
					1	2	3	1	2	3	Mean
(a)											
1	0	1000	1.9054	13.000	2.600	2.600	2.500	5.52	5.52	5.74	5.59
2	10	1000	1.8925	13.000	2.600	2.500	2.500	5.48	5.70	5.70	5.63
3	20	1000	1.9762	13.000	3.050	3.050	3.000	4.88	4.88	4.96	4.91
(b)											
4	0	1000	1.8765	13.000	2.550	2.700	2.650	5.54	5.24	5.33	5.37
5	10	1000	1.8175	13.000	2.450	2.500	2.450	5.59	5.48	5.59	5.55
6	20	1000	1.9406	13.000	3.000	2.900	3.000	4.87	5.04	4.87	4.93

3.4 Mechanical Strength Test

3.4.1 Compression Test

From the compression tests, the compressibility and the green density of the compacted powder were determined. Compressibility of powders is an ability to reduce the volume of powders under an applied pressure. Powder particles hardness possesses great influence on compressibility of the powders. Compressibility is expressed by the mean of three green density measurements as tabulated in Table 6 [15]. From Fig. 9, it can be observed that the green density is decreasing with the addition of ZnO nanofillers both annealing temperature. Lower green density indicates that the powder material has low compressibility, thus exhibiting higher particle hardness [16]. From the results in Table 6, it is observed that the addition of zinc oxide nanofillers into Silverfil powder has improved its compressibility and hardness.

Fig. 9 Green density of compacts at different ratio of ZnO addition

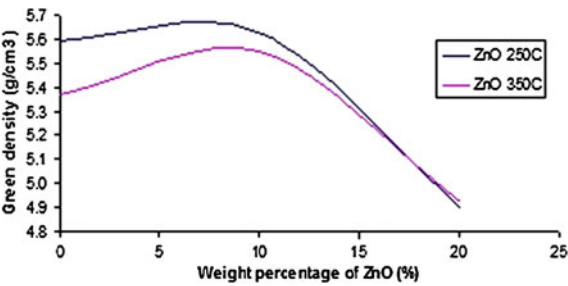


Table 7 Change in hardness of the composite with the addition of ZnO 250 °C

Sample	Percentage of ZnO nanofillers (%)	Load (kg)	Force (gf)	Dwell time (s)	D1 (μm)	D2 (μm)	Hardness (HV)	Mean hardness (HV)
4	0	1,000	100	10	70.99	65.60	39.8	43.20
					62.19	62.19	41.1	
					60.19	63.31	48.7	
5	10	1,000	100	10	86.88	86.88	25.8	23.57
					100.27	79.67	22.9	
					87.55	87.55	22.0	
6	20	1,000	100	10	98.23	98.23	16.6	15.83
					118.38	111.27	14.1	
					113.71	96.54	16.8	

Table 8 Hardness of the composite with the addition of ZnO 350 °C

Sample	Percentage of ZnO nanofillers (%)	Load (kg)	Force (gf)	Dwell time (s)	D1 (μm)	D2 (μm)	Hardness (HV)	Mean hardness (HV)
1	0	1,000	100	10	81.29	81.21	27.7	27.40
					93.45	93.45	21.6	
					74.86	74.86	32.9	
2	10	1,000	100	10	71.93	46.77	52.6	52.03
					55.08	63.01	53.2	
					59.77	61.63	50.3	
3	20	1,000	100	10	58.10	58.10	55.4	68.53
					50.90	50.90	70.1	
					38.45	38.45	80.1	

3.5 Micro Vickers Hardness Test

Hardness is defined as the resistance of a solid material against the penetration of another harder material into its surface. A higher number on the Vickers scale indicates that a material employs higher particles hardness. Therefore, from the MicroVickers indentation, force and dwelling time were fixed and the diagonal reading was recorded together with Vickers hardness. With the addition of zinc oxide ZnO 250 and 350 °C, we can observe a huge difference in the hardness value.

Tables 7 and 8 depict the change in hardness of the composite with the addition of ZnO nanofillers in different ratios. Two different annealing temperatures of ZnO seem to bring a significant effect on the material hardness. From Fig. 10, it can be observed that hardness of the composites increases with the increasing amount of ZnO annealed at temperature 250 °C added into it. Nevertheless, the inversion occurs when ZnO is annealed at temperature 350 °C. This might be due to higher annealing temperature used in the production of ZnO nanopowder which creates a

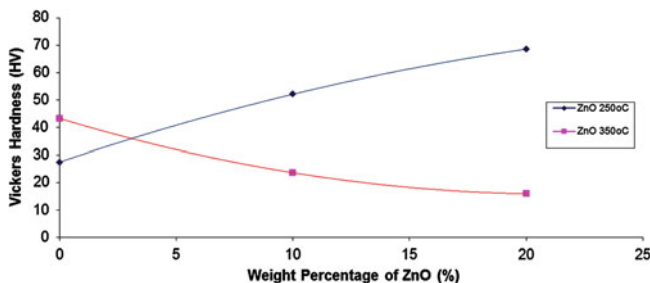


Fig. 10 Change in hardness measured at different ratio of zinc oxide of two different annealing temperatures

coarser grain size. Mechanical properties of a material vary with the decrease in particle size. It is well known that the strength of metal and ceramic materials improves by decreasing grain size to nanosize or making a composite at the nano-scale. Therefore, the hardness of compacted silver mercury with the addition of ZnO nanofillers will increase when finer grain size of ZnO nanopowder is added. The largest Vickers hardness number observed is $68.53 \text{ gf}/\mu\text{m}^2$, corresponding to the 20 % of 250 °C ZnO nanofillers that was added. The hardness of the composite however, decreases when 350 °C ZnO nanofillers were added, which Vickers hardness number obtained from the indentation is $15.83 \text{ gf}/\mu\text{m}^2$, much lower from the hardness of pure silver mercury of $43.20 \text{ gf}/\mu\text{m}^2$.

From the results above, it shows that powder composites added with 250 °C ZnO nanofillers exhibit a better hardness compared to the ones with 350 °C. Hence, extension was made to this research to investigate the effect of adding 250 °C ZnO at higher filler loading for Silverfil dental amalgam and its components.

3.6 Investigate the Change in Compressibility and Hardness of the Silverfil and its Components with the Addition of 250 °C ZnO

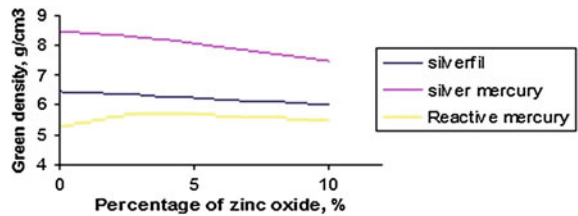
Table 9 shows that 250 °C zinc oxide powders was added into Silverfil, silver mercury and reactive silver at different ratios. It is found that as the filler loading increases, the green densities decreases—implying that compressibility of the materials is decreasing, which in turn shows that their hardness increases.

Hardness tests were also conducted on all samples at the same filler loading ratio. From Fig. 11, it is clear shows that the presence of ZnO as nanofiller is able to enhance the hardness of powder materials. For instance, by considering the Silverfil region in Table 10 and Fig. 12, there is an increment of 27.58 % in hardness when 10 % of ZnO was added into it.

Table 9 Variation of filler loading ratio for different material

Sample	Percentage of ZnO Nanofillers (%)	Green density (g/cm ³)			
		1	2	3	Mean
Silverfil powder	0	6.345	6.483	6.483	6.437
	3.5	6.319	6.319	6.319	6.319
	10	6.021	6.021	6.021	6.021
Silver mercury	0	8.551	8.551	8.314	8.472
	3.5	8.279	8.279	8.055	8.205
	10	7.496	7.496	7.496	7.496
Reactive silver	0	5.229	5.323	5.323	5.292
	3.5	5.711	5.711	5.711	5.711
	10	5.458	5.458	5.458	5.458

Fig. 11 Green density of different material with 0, 3.5 and 10 % of zinc oxide addition



3.7 Determining the Compressibility, Green Density and Hardness of the Silverfil Powder Material at Higher Filler Loading

Compressibility of the Silverfil powder was determined by applying different compaction pressure on the pellets. Then, a compressibility curve in Fig. 13 can be plotted based on the data in Table 11. It is observed that the green density of Silverfil powder increases as the compaction pressure increases.

10 % ZnO indicates that 10 % of the total mass of the pellet is of zinc oxide. As different loads were applied to form the pellets, their masses and thicknesses were measured to determine their green density. Other two samples were suggested to the same procedures and their green densities were determined respectively.

From Fig. 13, it can be concluded that compressibility of Silverfil increases as the compacting pressure increases. However, when the composition of ZnO fillings increases from 0 to 10 %, the overall compressibility also decreases. The decreasing compressibility indicates that the hardness of the powder material (Silverfil) increases with the addition of ZnO as nanofillers. Compressibility of the powder material is highly dependent on the particle size distribution. It decreases with the decrease in average particle diameter. Smaller particles have more contact surfaces than bigger ones. Thus, this degrades particle mobility in the first re-ordering and particles packing decreases [17].

The composition of ZnO was further increased to study its behavior beyond the previous filler loading. From 10 % of the pellet’s total mass, it was increased to 20,

Table 10 Hardness variation at different percentage of ZnO

Sample	% of ZnO	Hardness, HV (in GPa)	Mean hardness, HV (in GPa units)	Percentage of increment (%)
Silverfil	0	0.351	0.335	N/A
		0.274		
		0.379		
	3.5	0.385	0.394	17.80
		0.372		
		0.426		
	10	0.410	0.427	27.58
		0.468		
		0.404		
Silver mercury	0	0.258	0.215	N/A
		0.234		
		0.155		
	3.5	0.353	0.384	78.06
		0.371		
		0.427		
	10	0.450	0.438	103.34
		0.429		
		0.436		
Reactive silver	0	0.361	0.338	N/A
		0.266		
		0.386		
	3.5	0.269	0.352	4.30
		0.410		
		0.379		
	10	0.655	0.525	55.24
		0.436		
		0.482		

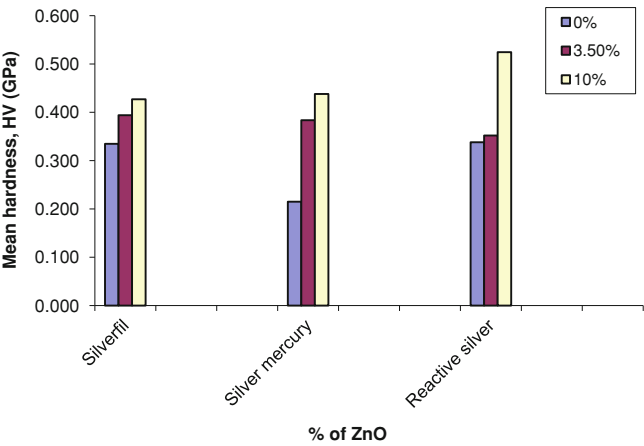


Fig. 12 Increment of hardness of the powder material when ZnO is filled at different ratio

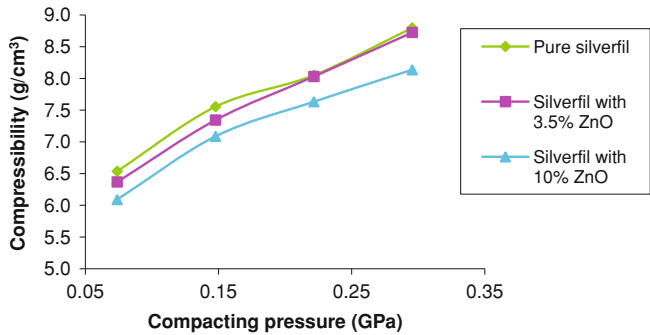


Fig. 13 Compressibility curve of silverfil powder

Table 11 Compressibility and green density of silverfil powder at different ZnO loading

Composition of ZnO (%)	Force (kgf)	Thickness (mm)		Mass (g)	Green density (g/cm ³)		Mean (g/cm ³)
		1	2				
0	1,000	2.20	2.20	1.909	6.537	6.537	6.54
	2,000	1.85	1.85	1.855	7.555	7.555	7.55
	3,000	1.75	1.70	1.843	7.934	8.167	8.05
	4,000	1.55	1.50	1.780	8.652	8.940	8.80
3.5	1,000	2.25	2.25	1.902	6.367	6.367	6.37
	2,000	1.85	1.85	1.803	7.343	7.343	7.34
	3,000	1.65	1.70	1.785	8.149	7.910	8.03
	4,000	1.50	1.55	1.766	8.867	8.581	8.72
10	1,000	2.75	2.75	2.224	6.091	6.091	6.09
	2,000	2.10	2.70	2.223	7.972	6.201	7.09
	3,000	2.15	2.20	2.204	7.721	7.545	7.63
	4,000	2.05	2.00	2.187	8.036	8.237	8.14

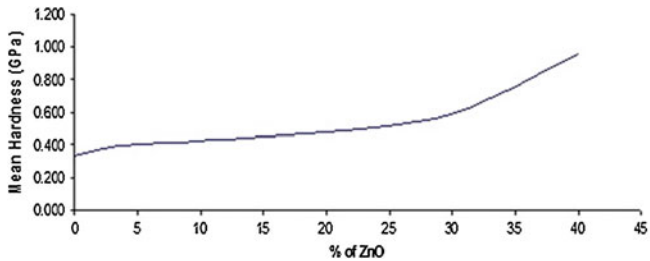


Fig. 14 Mean Hardness versus % of ZnO loading

30 and 40 %, thus hardness of the material was determined as shown in Fig. 14 and Table 12.

Table 12 Hardness and green density value at higher composition of ZnO

% of ZnO	Mass (g)	Thickness (mm)			Green density (g/cm ³)				Hardness(GPa)		% of increment
		1	2	3	1	2	3	Mean	HV	Mean Hardness	
0	1.9092	2.20	2.20	2.20	6.537	6.537	6.537	6.54	0.351 0.274 0.379	0.34	N/A
10	1.9828	2.55	2.50	2.50	5.86	5.97	5.97	5.94	0.3604 0.4008 0.4395	0.40	17.71
20	1.9963	2.70	2.70	2.70	5.57	5.57	5.57	5.57	0.4682 0.4570 0.5158	0.48	41.27
30	1.9970	2.95	2.95	2.95	5.10	5.10	5.10	5.10	0.6001 0.5805 0.5913	0.59	73.71
40	1.9867	3.10	3.15	3.10	4.83	4.75	4.83	4.80	0.9989 0.9442 0.9193	0.95	180.63

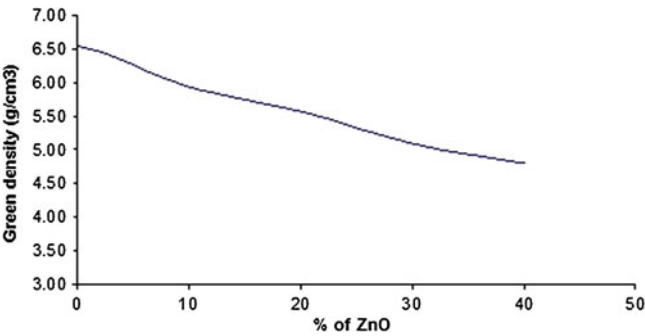


Fig. 15 Green density versus % ZnO loading

From Fig. 14, it is confirmed that the hardness of the Silverfil powder was improved by higher ZnO loading. As expected, the reverse occurred to the green density of this material. The green density decreases as the percentage of ZnO keeps on increasing as shown in Fig. 15. It is clear that the increment in the hardness of the material can be facilitated by the presence of ZnO as nanofillers. In metallic systems the Hall–Petch relationship describes the grain size dependence as a result of the interaction of dislocations and grain boundaries. Several theoretical approaches lead to a grain size dependence of the hardness or mechanical strength. Hardness increases as the inverse of the square root of the grain size. From the XRD results, we can estimate that the crystallite size of ZnO is approximately around 33–51 nm [18].

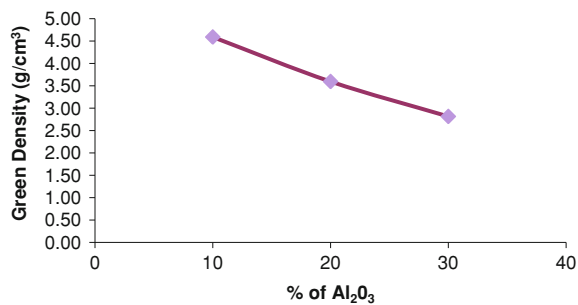


Fig. 16 Green density of the new composite with variation in the percentage of Al₂O₃

Table 13 Green density of the composites at different ratio of nanofillers loading

% of Al2O3	Mass (g)	Thickness (mm)			Green density (g/cm ³)			
		1	2	3	1	2	3	Mean
10	1.9702	3.25	3.20	3.25	4.57	4.64	4.57	4.59
20	1.9094	4.00	4.00	4.00	3.60	3.60	3.60	3.60
30	1.9682	5.25	5.30	5.25	2.82	2.80	2.82	2.82

3.8 Investigating the Change in Compressibility and Hardness of the Powder Material with the Addition of 800 °C Aluminum Oxide

In this section, the same procedure was repeated by using aluminum oxide Al₂O₃ as nanofillers. Response of the new composites to its green density, compressibility and hardness was studied to determine the best candidate for dental amalgam nanofiller material.

Figure 16 and Table 13 show the green density of dental amalgam as a function of percentage of Al₂O₃ loading. It is observed that the green density of the material decreases as more Al₂O₃ is loaded into it. This is due to the fact that material with high hardness employs lower green density. Green density also indicates compressibility of the material. It can be concluded that this new composite has lower compressibility as a higher amount of Al₂O₃ added into it. Lower compressibility means that the material might possess high strength and hardness.

The hardness of the new composite was measured and proven to be increased as the amount of Al₂O₃ increases, as shown in Fig. 17.

The hardness of the new composites added with Al₂O₃ and ZnO in Tables 14 and 15 respectively were then compared as shown in Fig. 18 below—showing that the composite filled with 10 % Al₂O₃ exhibits higher increase in hardness of about 82.35 % of the pure material, instead of 17.71 % increment by adding 10 % ZnO. Table 16 shows the hardness comparison of the composite at different filler type and percentage of loading.

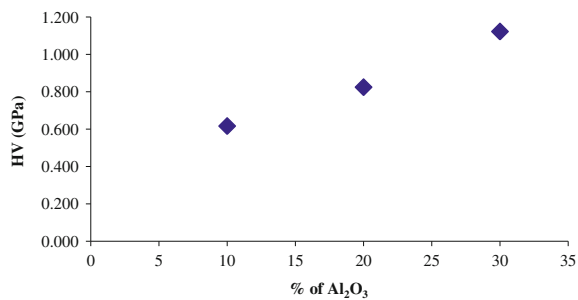


Fig. 17 Hardness of composite at different percentage of Al₂O₃

Table 14 Hardness of dental amalgam filled with Al₂O₃ at different percentage

% of Al ₂ O ₃	HV (gf/μm ²)	HV (GPa)	Mean HV (GPa)
10	67.4	0.660	0.62
	60.1	0.587	
	61.5	0.603	
20	80.9	0.793	0.82
	80.1	0.815	
	88.5	0.865	
30	117.7	1.202	1.12
	110.0	1.029	
	118.8	1.135	

Table 15 Hardness of dental amalgam filled with ZnO at different percentage

% of ZnO	Mass (g)	Thickness (mm)			Green density (g/cm3)				Hardness (GPa)		% of increment
		1	2	3	1	2	3	Mean	HV	Mean hardness	
0	1.9092	2.20	2.20	2.20	6.537	6.537	6.537	6.54	0.351 0.274 0.379	0.34	N/A
10	1.9828	2.55	2.50	2.50	5.86	5.97	5.97	5.94	0.3604 0.4008 0.4395	0.40	17.71
20	1.9963	2.70	2.70	2.70	5.57	5.57	5.57	5.57	0.4682 0.4570 0.5158	0.48	41.27
30	1.9970	2.95	2.95	2.95	5.10	5.10	5.10	5.10	0.6001 0.5805 0.5913	0.59	73.71
40	1.9867	3.10	3.15	3.10	4.83	4.75	4.83	4.80	0.9989 0.9442 0.9193	0.95	180.63

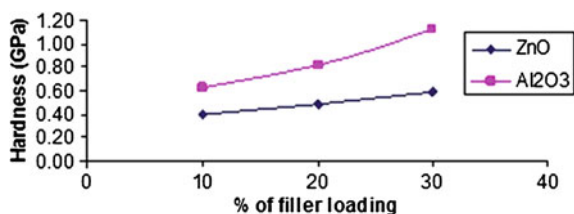


Fig. 18 Comparison of hardness of the composites at different filler type and loading percentage

Table 16 Hardness comparison of composite with different fillers

Filler	% of filler loading	Hardness (GPa)	% of increment
ZnO	10	0.40	17.71
	20	0.48	41.27
	30	0.59	73.71
Al ₂ O ₃	10	0.62	82.35
	20	0.82	141.18
	30	1.12	229.41

4 Conclusion

The hardness of Silverfil increased as the percentage of ZnO loading increased. With 0 % ZnO loading, the mean hardness recorded was 0.34 GPa, and increased to 0.40 GPa for 10 % ZnO loading. Higher reading was observed when more ZnO was incorporated into the Silverfil powder with 0.48 and 0.59 GPa for 20 and 30 % ZnO loading respectively. The highest composition of ZnO gives the hardest pellet, which is 0.95 GPa in the Vickers scale. It was found that hardness of the dental amalgam material exhibits a higher increment with the addition of Al₂O₃. An amount of 82.35 % increment was recorded for composite filled with 10 % Al₂O₃, 141.18 % for composite filled with 20 % Al₂O₃ and 229.41 % for composite filled with 30 % Al₂O₃.

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