Zinc Oxide Fabrication for Dental Amalgam Strength

by

Muhammad Uwais Qarni bin Mohd Salleh

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Universiti Teknologi PETRONAS

Bandar Seri Iskandar

31750 Tronoh

Perak Darul Ridzuan.

CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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Approved by:

_____

PROF. DR. NOORHANA YAHYA

Project Supervisor

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

September 2011

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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MUHAMMAD UWAIS QARNI BIN MOHD SALLEH

ABSTRACT

Dental amalgam has been used widely as dental restorative material although one of the major components in it is mercury which is well known for its toxicity. Silverfil amalgam produced by Dunia Perwira Manufacturer Sdn. Bhd.which is said to contain no excess mercury. Zinc oxide nanopowders are synthesized via sol-gel method and are sintered using conventional method and microwave sintering. Zinc oxide sintered at 300 °C obtained high crystillanity with smallest size nanoparticles, 44.95 nm. Both zinc oxide nanopowders sintered using microwave for 25 and 30 minutes have obtained single phase with particle size of 55.26 nm and 56.85 nm. Nanoflakes structure was obtained for these three nanopowders. Mixtures of Silverfil amalgam with different weight percentage of zinc oxide nanopowders ranging from 10% - 50% are compressed and green density of the compacts are measured. Green density of the compact increases with the increasing weight percentage of the zinc oxide nanopowders in the amalgam. Highest green density of 47.467 g/cm^3 is obtained with the addition of 40% zinc oxide nanopowders sintered at 300 °C into the Siverfil amalgam. This is because zinc oxide nanopowders filled in the empty spaces between amalgam particles and thus increase the hardness of the compact. Compact's hardness is measured using microindentation hardness test. As the content of zinc oxide nanopowders in the amalgam increases, the hardness of the amalgam also increases. The addition of 40% of zinc oxide nanopowders sintered at 300°C into the amalgam increase the hardness of the amalgam from 32.3 HV to 104.7 HV. The increasing of the amalgam hardness is due to the high hardness properties exhibit by smaller size materials which in this case is the zinc oxide nanopowders. Zinc oxide sintered at 300°C give the highest improvement on the amalgam strength which green density of 47.467 g/cm^3 and hardness value of 104.7 HV are obtained with the addition of 40% zinc oxide nanopowders into the amalgam. This is because zinc oxide nanopowders sintered at 300°C has the smallest nanoparticles size, 44.95 nm and also high purity content with 2.18% of atomic deviation percentage.

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NOMENCLATURE

ZnO – Zinc oxide

FESEM - Field Emission Scanning Electron Machine

XRD – X-Ray Diffraction

EDX – Energy Dispersive X- Ray

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Dental amalgam has been used for the treatment of dental cavities for the past 150 years and it is still being used nowadays as the dental restorative material for dental fillings. The dental amalgam is widely used because it has excellent mechanical properties such as strength and durability. Other than that, it is also available at low cost and easy to apply to the tooth.

Dental amalgam or silver filling is usually consists of equal ratio of metal alloy and mercury. However, the weight composition between these two materials might differ depends on the manufacturer or supplier. The alloy is primarily composed of silver (40%), tin (32%) and copper (30%). Some of the alloy contains small amounts of zinc and other materials such as palladium, platinum and others.

Mercury is used in dental amalgam since it is one of the very few metallic elements that are in liquid phase at room temperature. The advantages of mercury are that it can undergo an alloying reaction with other elements in a short space of time and it is strong enough to resist the forces of occlusion for a long time.

1.2 Problem Statement

There have been lots of issues regarding the use of dental amalgam in dentistry since it contains mercury. Mercury is well known for its toxicological characteristics and its effects not just to the human being but also towards the environment. Dental amalgam usually contains excess mercury in it which can cause illness to its user.

Exposure to mercury can cause harm to the human such as disruption of the nervous system, DNA and chromosomal damage, damage to brain functions and so on. However, mercury is still being used as one of the dental amalgam components although it can cause lots of bad effects to the human. The inhalation of mercury vapor itself is already hazardous to the human, but for the case of dental amalgam, the mercury is put inside a human mouth for a certain period of time. Thus, the effects will be greater since the mercury will be entering human body system directly from the mouth. The main issue is regarding the usage of dental amalgam with high mercury content inside of human mouth although it is well known that mercury can cause give significant effect to the human health.

However, Dunia Perwira Manufacturer Sdn. Bhd. had successfully produced a new dental amalgam, Silverfil. Silverfil is manufactured from reactive silver powder (60%) and silver-mercury powder (40%) with the absence of any other materials [1]. It has been proved scientifically that Silverfil does not have any excess mercury in it [1].

The addition of zinc oxide nanopowders into Silverfil dental amalgam is purposely to increase the hardness of the amalgam. Other than that, zinc oxide also comes naturally in white color. So, the addition of zinc oxide into the mixture of Silverfil amalgam might able to reduce the metallic color of the conventional amalgam thus make the new amalgam look more aesthetics.

A further study is conducted to determine whether nanoparticles can be used to increase the strength of dental amalgam and thus reducing the mercury content in it.

1.3 Objectives

The main objectives of this research are:

- To develop zinc oxide via sol gel method with two different sintering method; conventional method and microwave sintering.
- To examine the morphology characteristics and elemental analysis of zinc oxide nanopowders prepared.

- To investigate nanofillers effects to the mechanical strength of Silverfil amalgam.
- To compare between zinc oxide nanopowders that gives the highest strength improvement to the Silverfil amalgam.

1.4 Scope of Study

The study is divided into four major parts as follows:

1.4.1 Literature Review

In the literature review stage, the existing procedure to synthesize zinc oxide via sol gel are referred and reviewed. The experimental procedure, morphological characterization and elemental analysis of zinc oxide nanostructures by previous researchers are the most important input that needs to be studied in this stage.

1.4.2 Experimental Preparation

Chemicals and equipments to be used for this project will be identified. The appropriate chemicals and equipment need to be use to ensure that accurate result can be obtained. All the parameters involved in the sol gel method are highlighted.

1.4.3 Experimental Activities

A series of experiments are conducted to obtain zinc oxide with the right morphology and composition. Some parameters such as heating temperature and sintering time need to be adjust accordingly in order to have the desired results.

1.4.4 Analysis of Results

Results obtained from the experiment activities will be analyzed and interpreted by using the appropriate test method. The result is important in order to achieve all the objective of the project.

1.5 Project Relevancy

This project can contribute something to the human community since lots of people tend to use dental amalgam. By increasing the strength of the amalgam, the life span of the amalgam can be increased thus they can use the dental amalgam for more years. Other than that, by reducing the mercury content in dental amalgam, the dental amalgam will become safer to be used by people.

1.6 Project Feasibility

This project can be finished in the timeframe given to complete final year project 1 and 2. In terms of financial feasibility, the amount of MYR 500.00 is enough to buy all the chemicals that will be used throughout the completion of this project.

CHAPTER 2

LITERATURE REVIEW

2.1. Nanotechnology

The development and improvement of materials are essential for the advancement of human society. Nanotechnology is one of the advancement in materials science that is rapidly growing nowadays. This fast growing technology happens due to the increased knowledge and understanding in the chemistry and physics of materials, advances in processing methods, and also the availability of advanced equipment for characterization. Nanotechnology refersto a field of applied science and technology which the main focus is regarding the control of matter on molecular level in a scale, smaller than 1 μm, normally between 1 to 100 nm, and the fabrication of device within that scale. Nanotechnology products are rapidly being commercialized in the world market. These include nanoscale materials, powders, solutions and suspensions of nanoscale materials as well as composite materials and devices having a nanostructure.

2.2 Nanotechnology in Medical Science

Nanotechnology has been applied widely in medical fields such as oncology, cardiovascular medicine and also in treatment of chronic diseases. The urge for nanotechnology in medical field is due to the need for development of new medicine and the nanoscale size of the biological component in living cells [2].

Nanotechnology has been used in diagnostics, pharmacology and therapeutics. Nanotechnology is being applied is to biomarker-based proteomics and genomics technologies. Nanoparticles can be used for qualitative or quantitative *in vivo* or *ex vivo* by concentrating, amplifying, and protecting a biomarker from degradation, in order to provide more sensitive analysis [2]. Nanotechnology also is used for molecular

diagnosis since imaging diagnosis involving gross description of anatomic structures and imaging of cellular signaling. Molecular imaging use nanoparticles to gain a more precise diagnosis with high quality images. Different nanoparticles have been used for molecular imaging with magnetic resonance images (MRI), ultrasound, fluorescence, nuclear, and computed tomography [2]. Figure 1 shows how nanoparticles carry chemotherapy drugs into cancer cells.

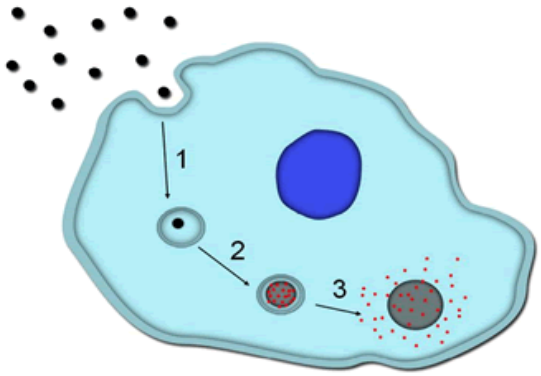

Figure 1: Nanoparticles carry chemotherapy drugs (shown as black dots) into cancer cells

It is not surprising that nanoparticles are used for drug delivery systems in human body since there are problems with the current drug delivery system available. Many drugs have a poor solubility, low bioavailability, and they can be cleared quickly from the body through the reticuloendothelial system [2]. The efficiency of different drugs is limited by dose dependent side effects. The use nanotechnology is significantly to target the drug molecules to the right area in human body so that drug effect on other parts of human system can be minimized and therapeutic effect can be maximized. This action can be achieved due to the small size of nanoparticles which make them easy to penetrate across different barriers through small capillaries into individual cells.

2.3 Nanomaterials

Nanomaterials are defined as materials that have at least one dimension 100 nanometres or less [3]. Nanomaterials can be nanoscale in one dimension (eg. surface films), two dimensions (eg. strands or fibres), or three dimensions (eg. particles) [3]. Nanomaterials are designed at the nanometer level to take advantage of their small size and properties

which cannot be seen in their original bulk material. Nanomaterials have been used in producing wide range of products including cosmetics, sunscreens, electronics, paints and varnishes. One nanometer is 10-3 micrometer or 10-9 meter. The size of nanomaterial is greatly reduced from its original materials.

Based on theory, the smaller the size of a material, the larger the surface area it has. As example, imagine that we have a cube with the length of 20 m. The surface area formula is given by:

Surface area = height x width x number of sides x number of cubes (1)

Based on the formula, the surface area of the cube is 2400 m^2. The cube is then divided into 1,000 small cubes with the length of 2 m; the total surface area of the cubes will be 24000 m^2. The total volume for the cube is taken as 8000 m^3. The total volume of the cubes is the same as the original cube. The formula for surface area to volume ratio is:

Surface area to volume ratio = Surface area/ total volume (2)

By using the given formula, the ratio value for the 1000 cubes is 3 compare to the original cube which is only 0.3. This proves that materials with smaller size have high surface area. Due to the high surface area over volume ratio, nanomaterials do have greater chemical reactivity and better strength. Figure 2 shows the effect of particles size to the surface area of the material. Materials in micrometer scale mostly exhibit the same properties as the bulk materials but it is different for the case of nanoscale materials. Materials in the nanometer scale may exhibit different physical properties from its bulk materials [4]. It shows that the properties of nanomaterials are different depending on their particles size. This is due to the increasing of atoms behavior at the particle surface compared to the inside as the particle becomes smaller.

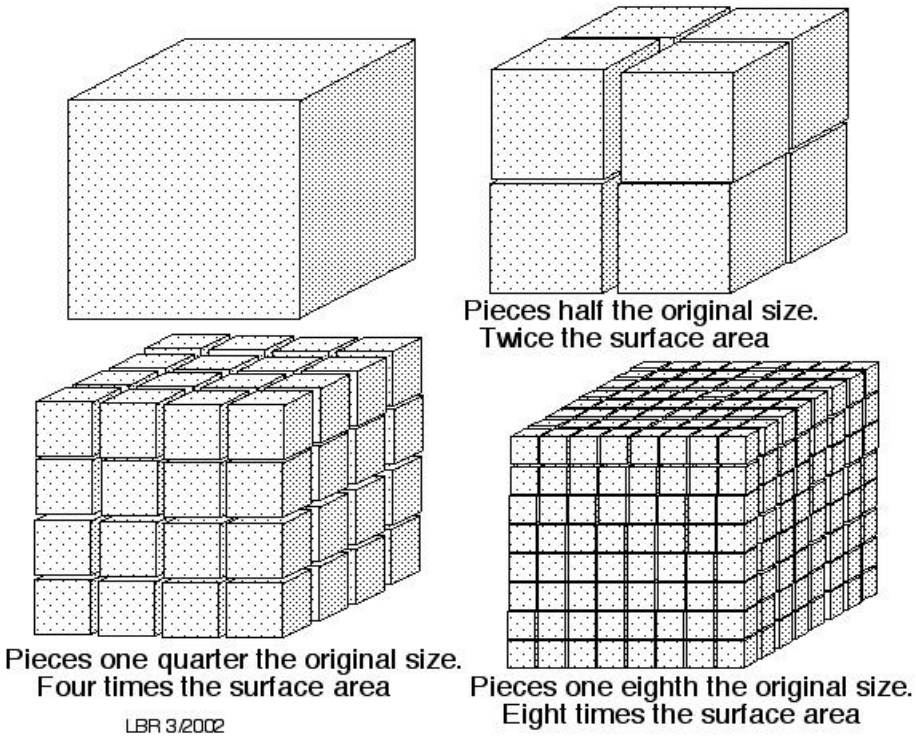

Figure 2: Effect of particle size to the surface area

2.4 Dental Amalgam Standard

Dental amalgam has been used for the treatment of dental cavities for the past 150 years and it is still being used nowadays as the dental restorative material for dental fillings. The dental amalgam is widely used because it has excellent mechanical properties such as strength and durability.

An amalgam is an alloy of mercury combined with one or more metals. Dental amalgams are often called as silver amalgam since silver is the main constituent that reacts with mercury. The kinetics of reactions between mercury and silver are not appropriate for clinical use, so that the silver is provided as an alloy with other element [5]. This alloy is known as dental amalgam alloy or alloys for dental amalgam based on ISO standard. There are several types of dental amalgam alloy, which all containing tin, most having some copper and, to a lesser extent, zinc.

The amalgam alloys are mixed with mercury before clinical placement at a 1 to 1 weight-ratio [5]. Most of dental amalgams usually compose of 50% mercury and 50%

amalgam alloys. High purity elemental mercury is used for dental amalgam since there are European and International standard for dental mercury. The European and International standard for dental mercury, i.e., EN 21560 (1991) and ISO 1560 (1985), respectively, are identical and require dental mercury purity to be greater than or equal to 99.99% elemental mercury (Hg) [6].

There has been a compositional flexibility regarding the amalgam standards which have been adopted by professional organizations such as American National Standard Institute (ANSI) and American Dental Association (ADA). This flexibility is due to the fact that standard specifications regarding amalgams need to address the materials properties of the alloy of filling, namely its compressive strength, dimensional stability, and creep [6]. Table 1 shows the standards for dental alloy compositions and figure 3 is the footnote for table 1.

Table 1: Standard for Dental Alloy Compositions

	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 silver filling is given in EN 21560 (1991) and ISO 1560 (1985), which are identical: greater than or equal to 99.99%
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 consists 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 amount 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 the results of adequate clinical and biological investigations to the Council on Dental Materials and Devices, American Dental Association, to show that the allo is safe to use in the mouth as directed in the manufacturer's
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."

Figure 3: Table 1 Footnote

2.5 Mercury

Mercury is a metallic element that occurs naturally and in the form of ore. Mercury and its compounds have been used widely in the industries which lead to the large amount of mercury release into the atmosphere. In addition, mercury compound are also used in a variety of medical and cosmetic products such as dental amalgam and so on.

There are several different forms of mercury. First, is the elemental mercury which is liquid mercury in a volatile form and is referred as Hg^0. Secondly, mercury is stable in two other oxidation states (Hg^{1+} and Hg^{2+}) and is able to form inorganic compounds, of either monovalent or diavalent form, including mercuric chloride ($HgCl_2$), mercurous chloride (Hg_2Cl_2), mercuric sulphide (HgS), and mercuric selenide (HgSe) [5]. Lastly, mercury also can form a variety of organic compounds, including methylmercury. The three forms of mercury are somehow connected to each other based on the global cycle of mercury.

Elemental mercury may be converted to soluble inorganic forms, which may be methylated in water, especially by microorganisms, which enter the food –chain and accumulate in the tissues of large predatory fish [5]. The ratio of methylmercury in these fish to the mercury concentration in the water can be as high as 10^5 [5]. Different forms of mercury have different toxicological profile. Generally, the form with highest toxicity is the organic mercury compounds, followed by elemental mercury and inorganic mercury compound.

Inhalation of elemental mercury can cause neurological and behavioural disorders including tremors, emotional lability, insomnia, memory loss and others. In addition, exposure to elemental mercury also has effects to the kidney and thyroid. Methylmercury is a neurotoxicant compound, which has particular adverse effects on the developing brain and cardiovascular system. Acrodynia disease is a disease that happens to children that inhale mercury vapor. The children will have symptoms such as pink rash at their hands and feet and they will have anorexia problem. The most concern regarding methylmercury is that it may harm the development of baby's brain if exposed to the pregnant women since this compound can passes both the placental barrier and the blood-brain barrier. Figure 4 and 5 shows the bad effect of mercury to human.

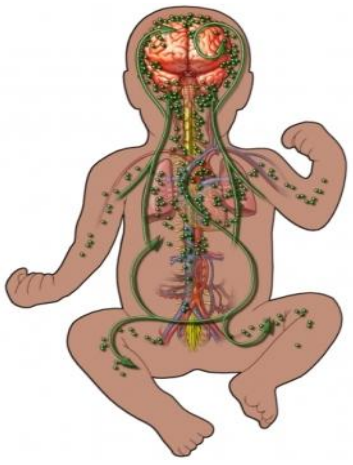

Figure 4: Effect of Mercury to Baby's Brain

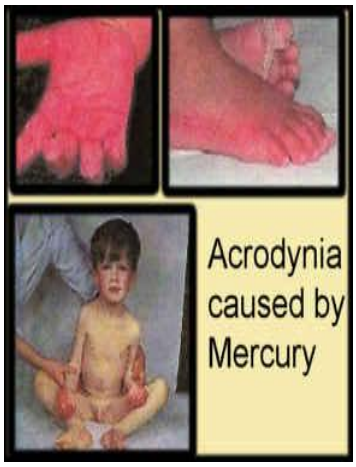

Figure 5: Acrodynia Disease

2.6 Zinc Oxide

Zinc oxide nanopowders have been extensively studied in the past several years due to their promising physical and chemical properties. Various morphologies and sizes of zinc oxide have led to a wide range of technologically important applications such as catalysts, electronic, solar cell, chemical sensors, antibacterial activity and others.

A lot of zinc oxide nanostructures such as nanorods, nanowires, nanotubes, nanorings, nanoflakes and others have been synthesized by using different synthesis methods. These unique nanostructures unambiguously demonstrate that zinc oxide probably has the richest family of nanostructures among all materials, both in structure and in properties [7]. Different structure and morphological characteristics of zinc oxide nanomaterials represent different properties. Their structure and morphological characteristics depends on the synthesis method. Zinc oxide nanoparticles synthesis methods are summarized in the table 2 below:

Table 2: Zinc Oxide Synthesis Methods

Method	Starting Materials	Annealing Temperature (°C)	Results	References
Gel combustion	Zinc nirate with 3 different fuels of glycine, urea and citric acid	400 - 600	Zinc nitrate with citric acid at 0.5 fuel to material ratio, neutral pH and calcined temperature of 500 °C produced better nanoparticles with the size of 30 nm.	[8]
Simple and novel route	Zn(CH3COO)2. 2H2O,H2C2O4. 2H2O, surfactant nonyl phenyl ether NaCl flux	910	Zinc oxide nanorods with diameter of 10-60 nm	[9]
Hydrothermal	Zinc nitrate, NaOH, deionized water, (C2H5OH), ethylenediamine (C2H4(NH2)2, EDA	180	Zinc oxide nanorods with diameter below 50 nm	[10]
Direct precipitation	Zinc nitrate (Zn(NO3)2) and Ammonium carbonate ((NH4)2CO3)	550	Nanoparticles size with average size of 32.5 nm	[11]

2.7 Sol-gel Method

Nowadays, a lot of synthesis methods to develop zinc oxide nanomaterials have been studied and recognized by the world such as chemical solution, hydrothermal, self combustion, sol gel and many more. Zinc oxide nanoparticles can be prepared on a large scale at low cost by using simple solution-based synthesis method such as vapor decomposition, precipitation and thermal decomposition.

However, agglomeration and secondary growth often occur in these zinc oxide nanoparticles when the wet particles are dried separately from the reaction solution. This is because large numbers of hydroxyl groups exist on the wet particle surface [12]. The agglomeration of zinc oxide nanoparticles during their formation from a homogenous aqueous solution can be avoided by applying organic dispersant as the coating to the zinc oxide surface. Unfortunately, the usage of organic dispersant will lead to high productivity cost of zinc oxide nanoparticles. Grind processing is the physical technique that has been used to directly break bulk materials to form fine particles but for this method is not suitable to be used in preparing nanoparticles [12].

Due to the fast development of nanomaterial applications, the best synthesis method is supposed to be the one that is simple and can be prepared on a large scale at low cost. Sol-gel method can be considered the best method to synthesis zinc oxide nanopowders for the time being since it is simple and can be used to produce large scale of nanopowders at low cost. The advantages of sol-gel method are low processing temperatures, short annealing times, high purity of materials produced, and good control of the particles size and shape even at atomic dimensions [12]. Other than that, high quality less-agglomerated zinc oxide nanoparticles can be produced via sol-gel method with low production cost. Table 3 below summarized previous researches done in synthesizing zinc oxide nanopowders by using sol-gel method.

Table 3: Previous researches on zinc oxide nanopowders via sol-gel method

Starting Materials	Annealing Temperature (°C)	Result	References
Zinc acetate dihydrate (Zn(CH3COO)2·2H2O, ethylene glycol, 2-propyl alcohol and glycerol	700	Quasi-spherical zinc oxide nanoparticles with diameter around 20 nm	[12]
Zinc acetate dihydrate $(CH_3COO)_2Zn.2H_2O$, methanol, sodium hydroxide	400	Maximum size nanocrystallite (14 nm) of ZnO powder was obtained for pH value of 9	[13]
Zinc acetate dihydrate $(C_4H_6O_4Zn{\cdot}2(H_2O)$, ethylene glycol ((C2H602), n-propyl alcohol (CH3CHx-CH2-OH), and glycerol (C3HsO3),	450	ZnO has been crystallised in a hexagonal wurtzite form. Nanoparticles size has not been mentioned in the journal	[14]

2.8 Microwave Sintering Method

Microwave sintering method has been researched for about two decades. Although there is still a few of applications in the industry but the advantages of microwave sintering is quite promising. Microwave heating in which the materials couple with microwaves, absorb the electromagnetic energy volumentrically, and transform into heat [15]. This is different with conventional method where heat is transferred between objects through convection, conduction and radiation.

In conventional heating, the surface of material is heated first followed by the heat moving inward which means that there is a temperature gradient from the material's surface to its inside. However, it is different with microwave sintering since heat is generated first within the material before entire volume is heated. This heating mechanism is advantageous due to the following facts: enhanced diffusion processes, reduced energy consumption, very rapid heating rates and considerably reduced

processing times, decreased sintering temperatures, improved physical and mechanical properties, simplicity, unique properties, and lower environmental hazards [15]. The process of sintering material by using conventional method in a sintering furnace requires a large number of expensive heating elements, fuel and refractory materials to maintain high temperature for a long time. In addition, this technique also consumes lots of electrical power, fuel and longer time is needed for the sintering process.

Microwave sintering is different from conventional sintering method because it facilitates the transfer of energy directly into the materials, providing volumetric heating. Microwave sintering method reduce the energy consumption, particularly when compared with high temperature processes where heat losses increase drastically with rising process temperatures, and it is possible to reduce the time required to complete a process [15]. Microwave use low power consumption since it is the sample that heats up and acts as the source of heat. Consequently, the effective thermal mass reduction lowers the required power input [15]. Microwave can interact directly with materials which make it able to avoid heating other parts which are not involved in the process such air or the oven's walls. The product produced by using microwave sintering usually have better mechanical properties compared to material sintered by conventional method because the heating is more uniform and volumetric.

CHAPTER 3

METHODOLOGY

3.1 Methodology and Project Activities

In order to achieve all the objectives for this project, the research methodology is divided into several parts. The parts are:

3.1.1 Preparation of zinc oxide gel by using sol-gel method

Zinc oxide gel is prepared by using sol-gel method. First, zinc nitrate hexahydrate salt is mixed with nictric acid with the ratio of 1:5. Then, the mixture is stirred by using magnetic stirrer. The minimum duration for the stirring is 24 hours. After the stirring part is done, the solution is heated with temperature of 80°C until gelatin is formed. Figure 6 and 7 show the stirring and heating process of zinc nitrate hexahydrate and nitric acid solution.

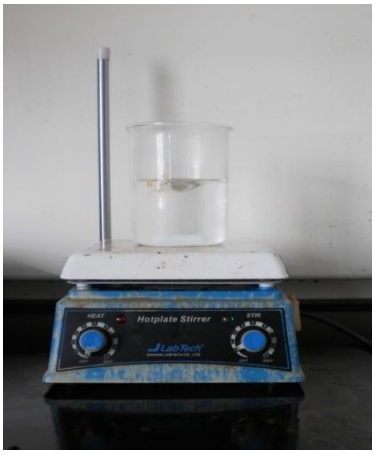

Figure 6: Stirring Process

Figure 7: Heating Process

3.1.2 Analyze the properties of zinc oxide nanopowders

The properties of the nanopowders is analyze by using equipments such as X-ray powder diffraction (XRD) which is used to check the formation and identify the compounds present in the obtained powder [12], Field Emission Scanning Electron Microscope (FESEM) and Energy Dispersive X-ray (EDX) for the morphology analysis of the powders and its composition. Figure 8 shows the FESEM machine.

Figure 8: FESEM Machine

3.1.3 Compressibility test

The strength for zinc oxide nanopowders will be tested. In order to determine the effect of nanofillers addition into the amalgam, the samples are compressed into round compact. The samples are compressed by putting them into a die and pressed by 1000 kg load, dwelled for 0.5 minutes in the Carver 25 Ton Auto Pellet Press Machine, ejected sample from the die and measured the green density. This test method covers determination of compressibility of metal powders as measured by the extent to which they can be densified in a specified die under controlled condition [16]. The amalgam samples are prepared by mixing both the Silverfil amalgam and zinc oxide nanopowders together with

different weight percentage of zinc oxide nanopowders. The composition of the amalgam samples are shown in table 4 below.

Table 4: Composition of the amalgam samples

No.	Weight Percentage of Silverfil (%)	Weight Percentage of ZnO (%)	Weight of Silverfil Amalgam (g)	Weight of ZnO (g)	Total Weight of Amalgam Samples (g)
1	100	0.0	2.0	0.0	2.0
2	90	10	1.8	0.2	2.0
3	80	20	1.6	0.4	2.0
4	70	30	1.4	0.6	2.0
5	60	40	1.2	0.8	2.0
6	50	50	1.0	1.0	2.0

3.1.4 Microindentation hardness test

Hardness of amalgam samples is measured by using microindentation hardness test. This test is conducted by using Vickers Indenter. The indenter is indent at three different spots on the compact and the hardness of the compact is measured. Average reading of the hardness is calculated and is taken as the hardness value for the compact.

3.1.5 Strength comparison between zinc oxide nanopowders sintered using conventional method and microwave sintering.

After the mechanical strength test is conducted to both of the nanopowders, the test result is compared to see which nanopowders give the highest strength improvement to the dental amalgam.

3.2 Experimental Procedure to Synthesis Zinc Oxide Nanopowders

3.2.1 Calculation for Zinc Oxide Nanopowders Amount

Before zinc oxide nanopowders can be produced, the amount of starting materials which are zinc nitrate hexahydrate, $Zn(NO_3)_2.6H_2O$ and 65% nitric acid need to be calculated first in order to get the amount of nanopowders

desired. The calculation is based on the molecular weight for zinc nitrate hexahydrate. The calculation is showed below:

Molecular weight of Zinc Nitrate Hexahydrate, $Zn(NO_3)_2.6H_2O$,

MW $Zn(NO_3)_2.6H_2O$ = 297.48 g

Molecular weight of Zinc Nitrate, $Zn(NO_3)_2$,

MW $Zn(NO_3)_2$ = 189.39 g

In order to prepare 10 g of zinc oxide nanopowders, the estimated amount of zinc nitrate hexahydrate required as starting material is calculated by using the formula given:

$$\text{Amount of Zinc Nitrate Hexahydrate} = \frac{\text{MW Zinc Nitrate Hexahydrate}}{\text{MW Zinc Nitrate}} \times \text{Amount of Zinc Oxide to be produced} \quad (3)$$

$$\text{Amount of Zinc Nitrate Hexahydrate} = \frac{297.48\text{g}}{189.39\text{g}} \times 10\text{g}$$

$$= 15.70 \text{ g}$$

Amount of 65% nitric acid, HNO_3 that needs to be used to prepare 10g of zinc oxide nanopowders is five times the amount of zinc nitrate hexahydrate.

$$\text{Amount of 65\% Nitric Acid} = 15.70 \times 5 \text{ ml}$$

$$= 78.5 \text{ mL}$$

By using the formula above, the estimated amount of zinc nitrate hexahydrate and 65% nitric acid to be used to produce 10 g of zinc oxide nanopowders are 15.70 g and 78.5 mL respectively.

3.2.2 Experimental Procedures for Zinc Oxide Nanopowders Synthesis using Sol-gel Method

The following steps are taken in order to produce 10 g zinc oxide nanopowders:

1. Dissolve 15.70 g of zinc nitrate hexahydrate, $Zn(NO_3)_2.6H_2O$ in 78.5 mL 65% nitric acid, HNO_3.

2. Stir the solution for seven days. The minimum stirring period is 24 hours. Longer stirring period will be better since smallest nanoparticles size will be obtained. Stirring process is shown in figure 9.

Figure 9: Stirring Process

3. Heat the homogenous solution with temperature of 80 °C until gelatine is formed. The solution is kept stirring during the heating process. Both stirring and heating procedure is shown in figure 10.

Figure 10: Stirring and Heating Process

4. Dry the sample in an oven at 110 °C for 3 days. If the sample is not totally dry after 3 days, put it back in the oven until it is dry.

5. Crush the sample for two hours or more to obtain small size particles. Sample of zinc oxide nanopowders is shown in figure 11.

6. Sinter the nanopowders using microwave at high power. Heating time is the manipulative variable. The sintering time will be 15 minutes, 20 minutes, 25 minutes and 30 minutes. Figure 12 shows microwave that will be used for sintering part.

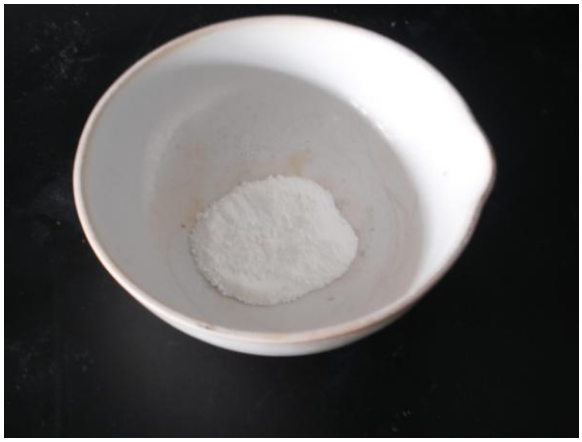

Figure 11: Zinc Oxide Nanopowdes

Figure 12: Sintering using Microwave

3.3 Tools

Since this is an experimental oriented project, the materials and equipments needed are basically for lab purpose. The materials and equipments required for this project are:

3.3.1 X- Ray Diffaction (XRD)

X-ray diffraction (XRD) is a technique that reveals detailed information about the chemical composition and crystallographic structure of materials. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. The interaction of the incident rays with the sample produces constructive interference and a diffracted ray when the conditions satisfy Bragg's Law. This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample.

These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d- d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns.

3.3.2 Field Emission Scanning Electron Microscope (FESEM)

A field-emission cathode in the electron gun of a scanning electron microscope provides narrower probing beams at low as well as high electron energy, resulting in both improved spatial resolution and minimized sample charging and damage. Some of the applications of FESEM are to analyze the cross section of semiconductor device, determine coating thickness and structure uniformity and measure small contamination feature geometry and elemental composition of material. The advantages of FESEM are:

- Can produce clear; less electro statically distort images with spatial resolution down to 1.5 nm.
- Smaller-area contamination spots can be examined at electron accelerating voltages compatible with Energy Dispersive X-ray Spectroscopy.
- Reduced penetration of low kinetic energy electrons probes closer to the immediate material surface.

- High quality, low voltage images are obtained with negligible electrical charging of samples.

Figure 13: ZEISS Supra 55VP Field Emission Scanning Electron Microscope

3.3.3 Energy Dispersive X-ray spectroscopy (EDX)

Energy Dispersive X-Ray Spectroscopy (EDS or EDX) is a chemical microanalysis technique used in conjunction with scanning electron microscopy. The EDX technique detects x-rays emitted from the sample during bombardment by an electron beam to characterize the elemental composition of the analyzed volume. When the sample is bombarded by the electron beam, electrons are ejected from the atoms comprising the sample's surface. The resulting electron vacancies are filled by electrons from a higher state, and an x-ray is emitted to

balance the energy difference between the two electrons' states. The x-ray energy is characteristic of the element from which it was emitted.

3.3.4 Carver 25 Ton Auto Pellet Press Machine

This equipment is used to compress powder into uniaxial loading in a standardized die of rectangular or of round cross section. This machine has 5 inch diameter platen and integral safety shield cabinet enclosing electrically powered hydraulic system. Rigid slab side construction maintains precise alignment and includes provision for a vacuum line connection to the pellet die. Microprocessor control system with digital display of force permits programmed operation and selectable bleed-off pressure. Figure 14 shows the picture of Carver 25 Ton Auto Pellet Press Machine and the die used for compacting powder is as shown in figure 15.

Figure 14: Carver 25 Ton Auto Pellet Press Machine

Figure 15: Die for compacting powder

3.3.5 Vickers Indentation

Microindentation test is a hardness test using a calibrated machine to force a diamond indenter of specific geometry into the surface of the material being evaluated, in which the test forces range from 1 to 1000 gf, and the indentation diagonal, or diagonals are measured with a light microscope after load removal; for any microindentation hardness test, it is assumed that the indentation does not undergo elastic recovery after force removal [17]. Microindentation tests allow specific phases or constituents and regions or gradients too small for macroindentation testing to be evaluated [17]. Vickers indentation equipment is represented in figure 16.

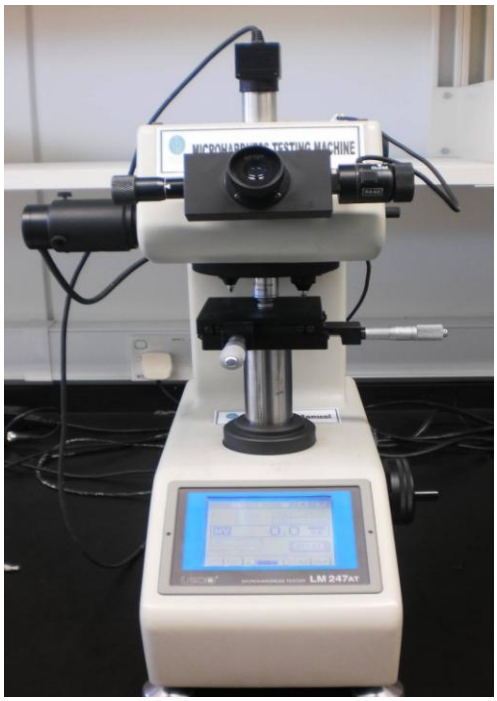

Figure 16: Vickers Indentation equipment

3.3.6 Other Tools/ Materials

Other tools that are used in completing this project are as listed below:

- Zinc nitrate hexahydrate
- Nitric acid with 65% concentration
- Distilled water
- Magnetic stirrer
- Oven
- Microwave

3.4 Gantt Chart

No.	Details / Week	1	2	3	4	5	6		7	8	9	10	11	12	13	14
1	Selection of Project Topic	■	■													
2	Preliminary Research Work		■	■	■											
3	Seminar 1						■									
4	Submission of Progress Report						■									
5	Project Work						■		■	■	■	■	■	■		
6	Seminar 2										■	■	■	■		
7	Submission of Interim Report Final Draft														■	
8	Oral Presentation															■

Mid-semester break

Figure 17: Gantt chart for FYP 1

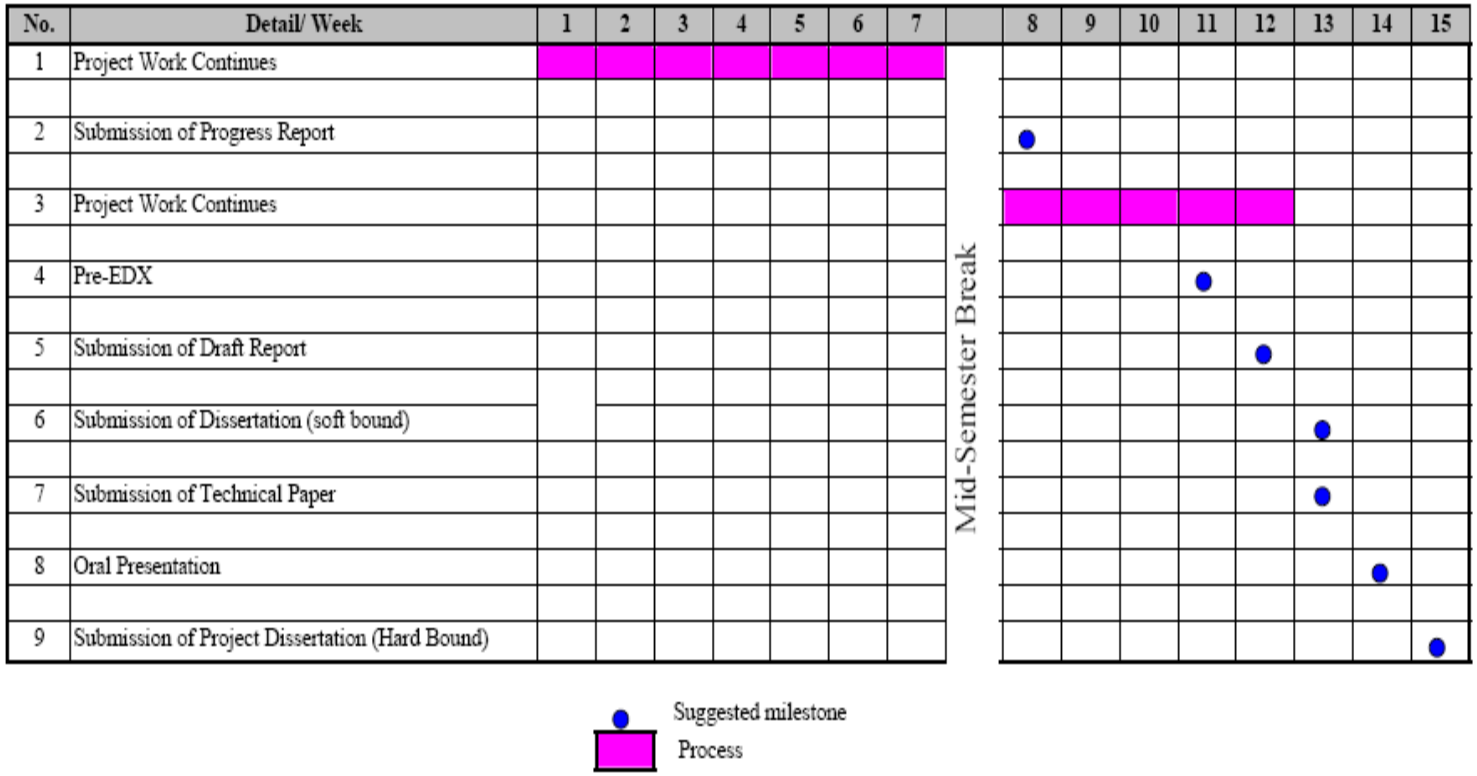

Figure 18: Gantt chart for FYP 2

CHAPTER 4

RESULTS AND DISCUSSION

Zinc oxide (ZnO) nanopowders produced is sintered by using sintering furnace and microwave. For zinc oxide nanopowders sintered using conventional method, the sintering temperature is set at three different values which are 200 °C, 250 °C and 300 °C. For zinc oxide nanopowders sintered using microwave, the sample is sintered using low power for 3 minutes, 6 minutes, 9 minutes, 12 minutes, and 15 minutes with interval time of 3 minutes. The nanopowders are also sintered for 1 hour, 2 hours, 3 hours, and 4 hours with the interval time of 5 minutes. Lastly, the zinc oxide nanopowders is sintering by using high power at four different sintering times which are 15 minutes, 20 minutes, 25 minutes and 30 minutes. The sintered zinc nanopowders are sent for X-Ray Diffraction (XRD) and Field Emission Scanning Electron Microscope (FESEM), in sync with the elemental analysis by Energy Dispersive X-Ray Spectroscopy (EDX). All these tests are crucial in order to determine the characteristics and morphology structure of the nanopowders.

4.1 X- Ray Diffraction (XRD)

4.1.1 Zinc Oxide Nanopowders sintered using Conventional Method

Zinc oxide nanopowders sintered using conventional method is sent to XRD analysis to determine its characteristics and crystallite size. XRD patterns of the zinc oxide nanopowders sintered at 200 °C, 250 °C and 300 °C are shown in the figure 19. From figure 19, it shows that the all peaks of the nanopowders matched with the peaks of standard zinc oxide. Based on the XRD diffraction pattern, both zinc oxide nanopowders sintered at 250 °C and 300 °C at shows hexagonal wurtzite structure. The diffraction peaks of zinc oxide nanopowders

sintered at 300 °C show stronger peak intensities, indicating that the nanoparticles have high crystallinity. Crystallite size of the samples is calculated by using Scherrer equation. Scherrer equation is shown below:

$$D = \frac{K\lambda}{(\beta \cos \theta)} \qquad \textbf{(4)}$$

Where,

D = crystallite size

K = Scherrer constant

λ = wavelength of X-ray used

β = the integral breadth of a reflection (in radians 2θ) located at 2θ

= (FWHM X 2π) / 360°

Θ = Scattering angle

The lattice parameter and crystallite size of the nanopowders are summarized in the table 5 below:

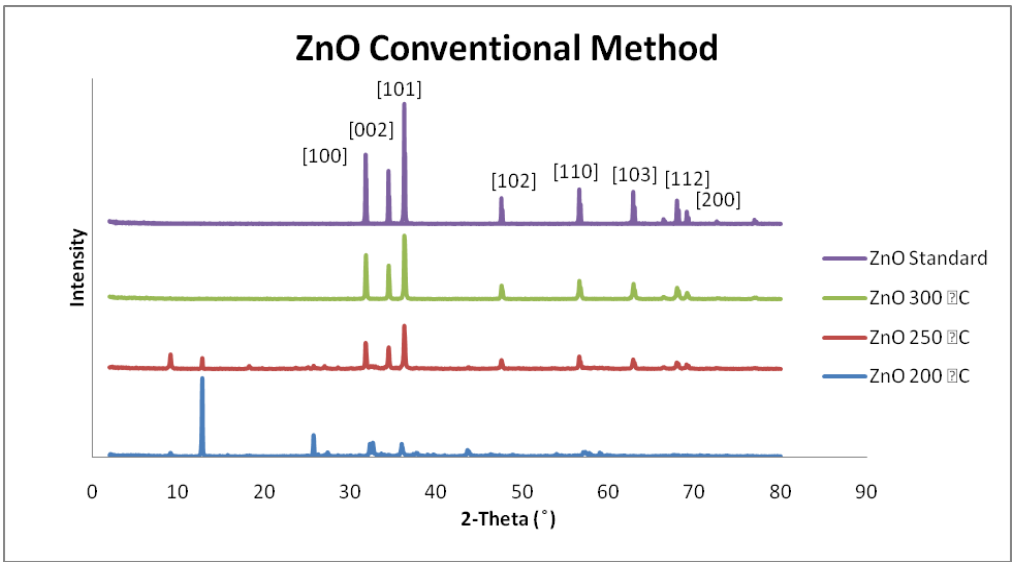

Figure 19: XRD Pattern of Zinc Oxide Sintered using Conventional Method

Table 5: XRD Result for Zinc Oxide sintered using Conventional Method

Samples	XRD Diffraction						
	Intensity (Counts)	FWHM	d-spacing (Å)	Crystallite Size (nm)	a	b	c
ZnO sintered at 200°C	1234.8	0.117	2.473	67.57	3.249	3.249	5.205
ZnO sintered at 250°C	683.91	0.181	2.474	45.67	3.249	3.249	5.269
ZnO sintered at 300°C	1007.9	0.184	2.474	44.95	3.250	3.250	5.207

The result shows that zinc oxide nanopowders sintered at 300 °C have the smallest crystallite size and also the highest intensity compared to the other two samples. The crystallite size of 44.95 nm obtained by the zinc oxide nanopowders sintered at 300 °C is good since the size of nanomaterials should be in the range of 10 nm to 100 nm. Smaller size nanoparticles will be better since it will have larger contact area.

4.1.2 Zinc Oxide Nanopowders sintered using Microwave

For the first trial, zinc oxide nanopowders are sintered for 12 and 15 minutes with interval time of three minutes. XRD patterns of the zinc oxide nanopowders sintered using microwave for 12 and 15 minutes are shown in the figure 20 below. Based on the result, it shows that the peaks of all the nanopowders sintered for 12 and 15 minutes do not match the peak of standard zinc oxide.

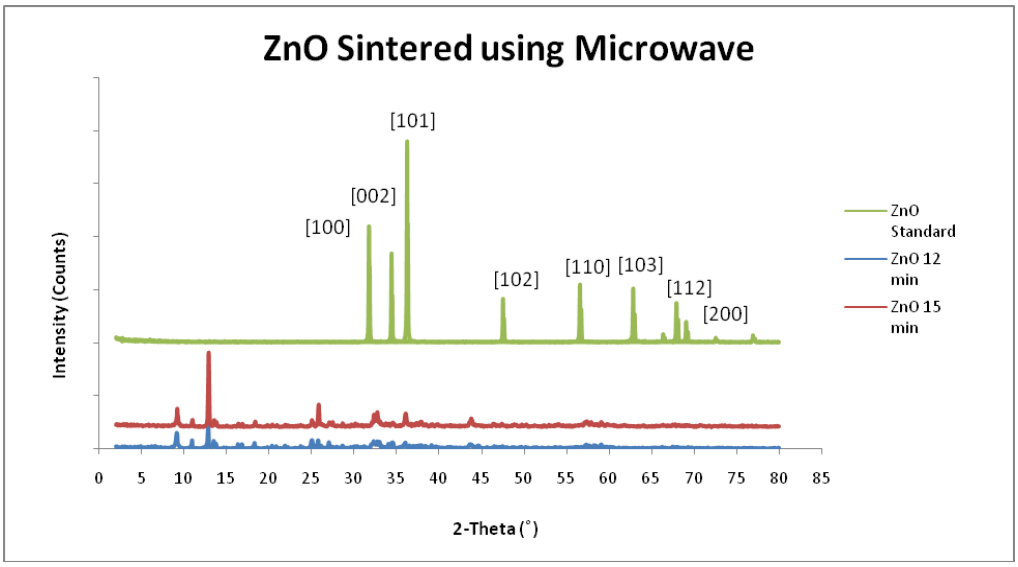

Figure 20: XRD Pattern of Zinc Oxide Sintered using Microwave for 12 and 15 minutes

All of the nanopowders are still in hydroxide form and do not gain single phase yet. These happen due to insufficient sintering time. So, the sintering times for the zinc oxide nanopowders need to be increased in order for the nanopowders to gain single phase structure.

Cystallite size and the intensity of the samples are listed in the table below. Both zinc oxide nanopowders sintered for 12 and 15 minutes obtained monoclinic structure. The XRD data are summarized in table 6 below:

Table 6: XRD Result for Zinc Oxide Nanopowders Sintered using Microwave for 12 and 15 minutes

Samples	X-Ray Diffraction						
	Intensity (Counts)	FWHM	d-spacing (Å)	Crystallite Size	a	b	c
ZnO sintered for 12 minutes	216	0.132	6.88625	61.69 nm	7.038	9.658	11.182
ZnO sintered for 15 minutes	703	0.139	6.85413	58.59 nm	7.038	9.658	11.182

For the second trial, zinc oxide nanopowders are sintered for one hour to four hours with the interval time of 5 minutes. XRD patterns of zinc oxide nanopowders sintered using microwave for one hour, two hours, three hours and four hours are shown in the figure 21 below. Based on the result, it shows that the peaks of all samples sintered using microwave in this trial do not have peaks that match the peaks of standard zinc oxide sample.

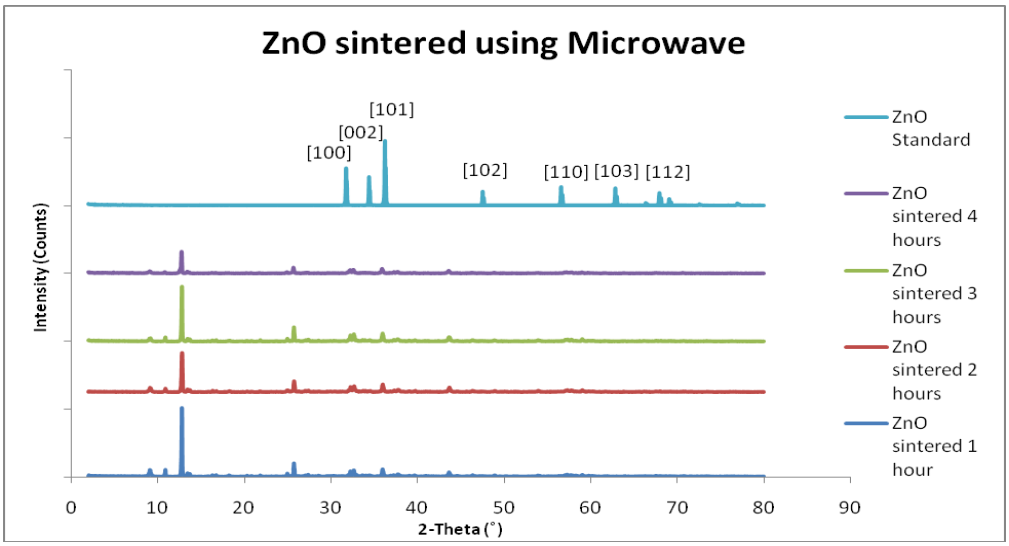

Figure 21: XRD Pattern of Zinc Oxide Sintered using Microwave for One to Four Hours

The nanopowders do not obtain single phase due to the insufficient sintering time. Sintering time should be increased in order for the nanopowders to obtain single phase structure with high crystallinity.

Cystallite size and the intensity of the samples are listed in the table below. Both zinc oxide nanopowders sintered for 12 and 15 minutes obtained monoclinic structure. The XRD data are summarized in table 7:

Table 7: XRD Result for Zinc Oxide Nanopowders Sintered using Microwave for One to Four Hours

Samples	X-Ray Diffraction						
	Intensity (Counts)	FWHM	d-spacing (Å)	Crystallite Size	a	b	c
ZnO sintered for 1 hour	2052	0.078	12.810	10.45 micrometer	7.046	9.635	11.221
ZnO sintered for 2 hours	1156	0.111	12.823	73.5 nm	7.038	9.658	11.182
ZnO sintered for 3 hours	1604	0.081	12.807	10.01 micrometer	7.038	9.658	11.182
ZnO sintered for 4 hours	636	0.094	12.768	86.52 nm	7.038	9.658	11.182

Lastly, zinc oxide nanopowders are directly sintered for 15, 20, 25 and 30 minutes in microwave. XRD patterns of the nanopowders are shown in the figure 22 below. Zinc oxide nanopowders sintered for 25 and 30 minutes shows diffraction peaks that matched the diffraction peaks of standard zinc oxide. Based on the result, the sample sintered for 25 and 30 minutes obtained single phase while the other two are still in zinc nitrate hydroxide form. Based on figure 22, it shows that both zinc oxide nanopowders sintered for 25 and 30 minutes show peaks at plane [100], [002], and [101].

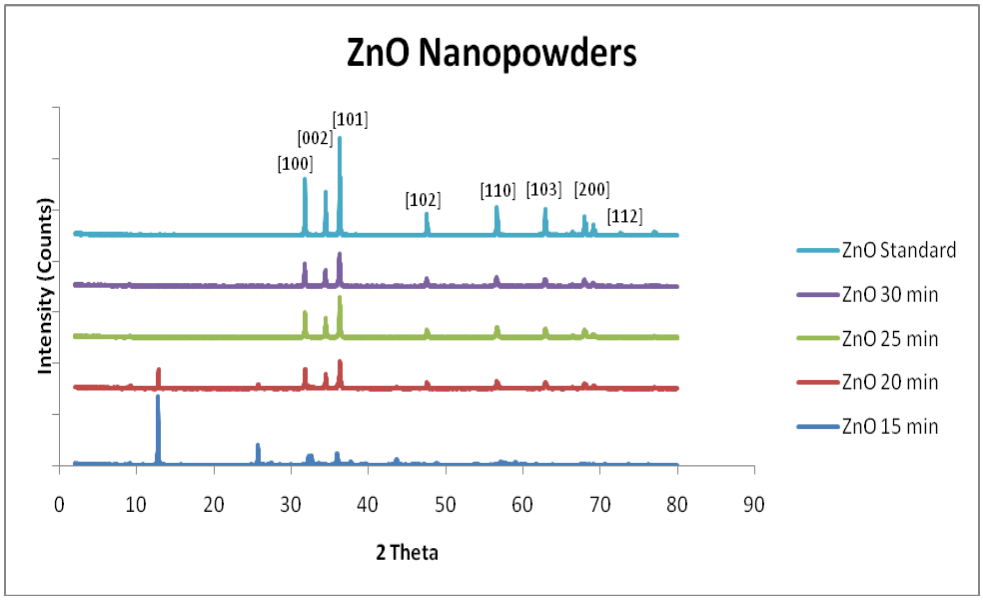

Figure 22: XRD Pattern of Zinc Oxide Sintered Continuously using Microwave

Cystallite size and the intensity of the samples are listed in the table below. Both zinc oxide nanopowders sintered for 25 and 30 minutes obtained hexagonal wurtzite structure. The XRD data are summarized in table 8 below:

Table 8: XRD Result for Zinc Oxide Nanopowders Sintered Continuously using Microwave

Samples	X-Ray Diffraction						
	Intensity (Counts)	FWHM	d-spacing (Å)	Crystallite Size	a	b	c
ZnO sintered 15 min	1329	0.103	6.93219	78.92 nm	7.046	9.635	11.221
ZnO sintered 20 min	377	0.073	6.91109	11.16 micrometer	7.038	9.658	11.182
ZnO sintered 25 min	765	0.194	2.47492	55.26 nm	3.249	3.249	5.2052
ZnO sintered 30 min	628	0.191	2.47709	56.85 nm	3.253	3.253	5.213

Zinc oxide sintered for 25 minutes has the smallest crystallite size among the samples which is 55.26 nm. It also has the highest intensity which is 765 counts compared to the zinc oxide sintered for 30 min which its intensity is 628 counts.

4.2 Surface Morphologies from FESEM Analysis

The morphologies of the zinc oxide samples are being analyzed by using FESEM. The images of zinc oxide nanopowders sintered using conventional method are shown below:

a) Zinc oxide sintered at 200°C

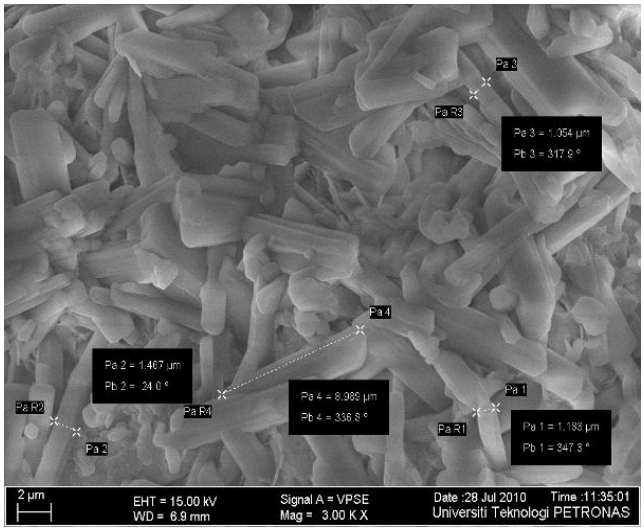

Figure 23: Image of zinc oxide sintered at 200°C magnified at 3k

Figure 23 shows the structure of zinc oxide nanopowders sintered at 200 °C. The nanostructure looks like it will become into blocks of rectangular. However, due to the insufficient sintering temperature, the nanostructures do not have any proper structure.

b) Zinc oxide sintered at 250 °C

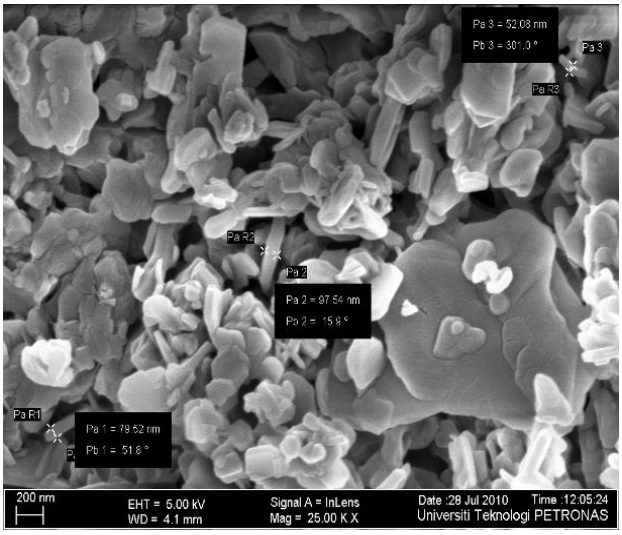

Figure 24: Image of zinc oxide sintered at 250°C magnified at 25k

From figure 24, it can be seem that the structure of the zinc oxide nanopowders sintered at 250°C is nanoflakes.

c) Zinc oxide sintered at 300 °C

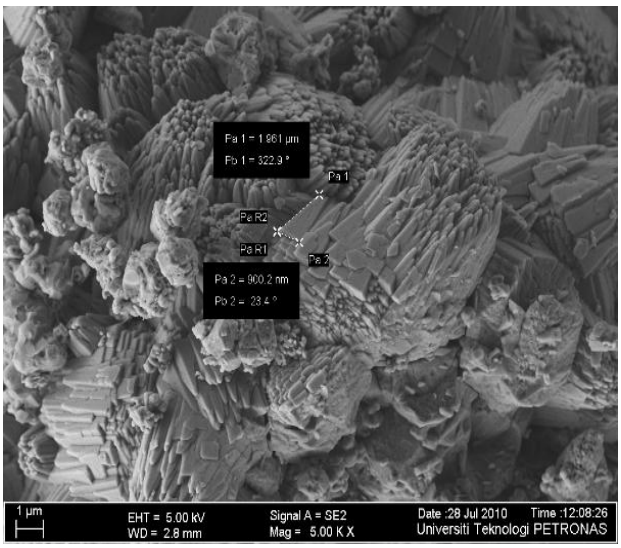

Figure 25: Image of zinc oxide sintered at 300°C magnified at 5k

Structure of zinc oxide sintered at 300 °C is shown through figure 25. A compacted combination of nanoflakes is obtained when zinc oxide nanopowders

is sintered at temperature of 300 °C. The structures of the nanopowders begin to form properly into shapes with the increasing of temperature from 200 °C to 300 °C.

The samples of zinc oxide sintered using microwave are also sent to FESEM for morphology analysis. FESEM images for zinc oxide nanopowders sintered for 12 and 15 minutes with interval time of three minutes are as shown below:

a) Zinc oxide sintered for 12 minutes

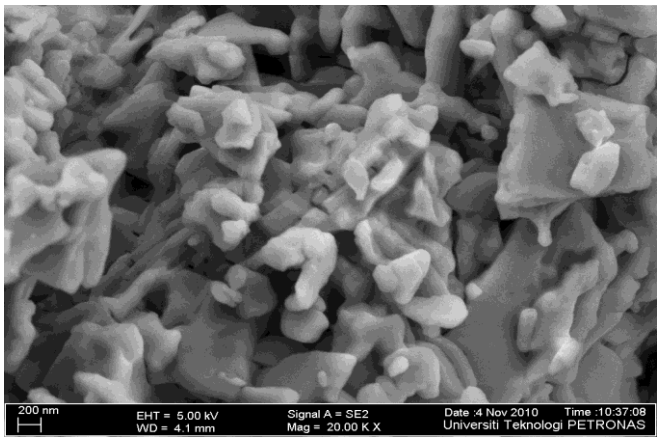

Figure 26: Image of zinc oxide sintered for 12 minutes magnified at 20k

b) Zinc oxide sintered for 15 minutes

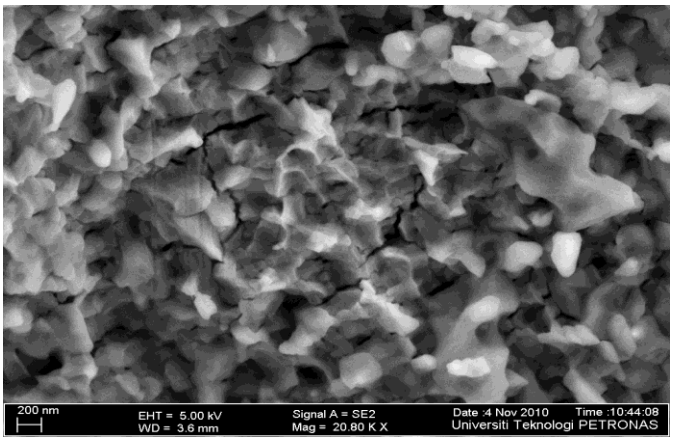

Figure 27: Image of zinc oxide sintered for 12 minutes magnified at 20k

Figure 26 and 27 shows the structure of nanopowders sintered using microwave for 12 and 15 minutes with three minutes of interval time. From the images, no proper structure was found since neither of the samples have achieve single phase. This is due to the lacking of sintering time during sintering process.

Nanopowders sintered using microwave for one until four hours with five minutes of interval time were also being sent for morphology characteristics. The images of the nanopowders are shown below:

a) Zinc oxide sintered for 1 hour

Figure 28: Image of zinc oxide sintered for 1 hour magnified at 50k

b) Zinc oxide sintered for 2 hours

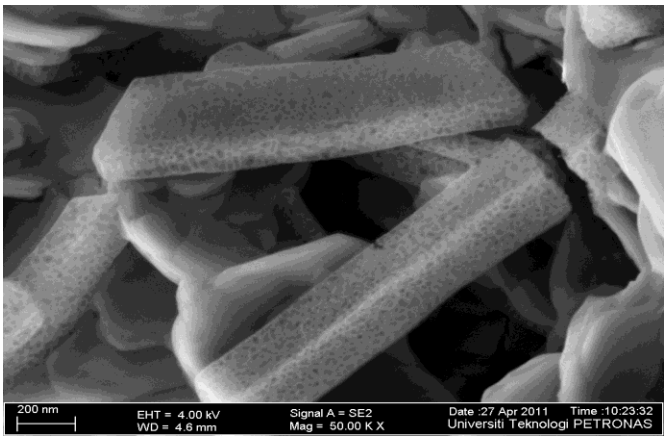

Figure 29: Image of zinc oxide sintered for 2 hours magnified at 50k

c) Zinc oxide sintered for 3 hours

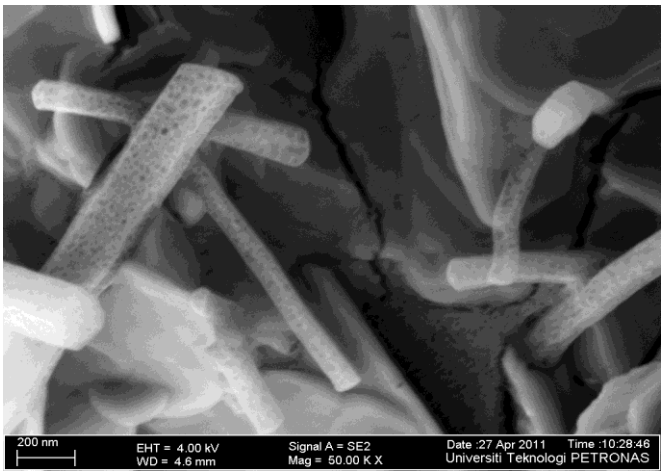

Figure 30: Image of zinc oxide sintered for 3 hours magnified at 50k

d) Zinc oxide sintered for 4 hours

Figure 31: Image of zinc oxide sintered for 4 hours magnified at 50k

From figure 28, 29, 30 and 31, it can be seen that the structure of the nanopowders are nearly formation of nanorods. From XRD results, all of these nanopowders are still in hydroxide phase which mean that they do not obtain single phase yet due to the inadequate of sintering time.

The FESEM images of zinc oxide sintered for 15, 20, 25 and 30 minutes are as shown below:

a) Zinc oxide sintered continuously for 15 minutes

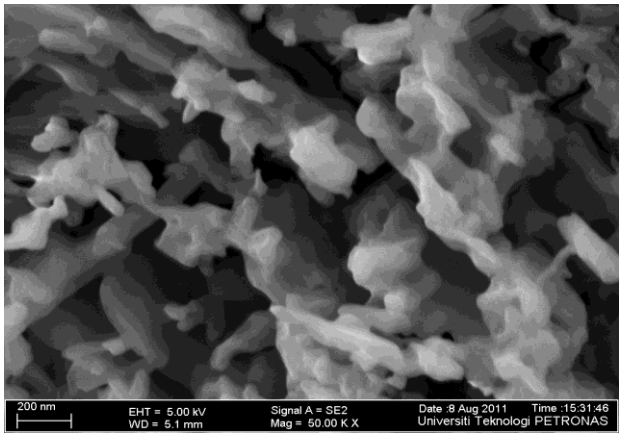

Figure 32: Image zinc oxide sintered continuously for 15 minutes magnified at 50k

There is no proper structure is shown in figure 32. This is due to the lack of sintering time of the sample. In addition, from XRD result, this sample is still in hydroxide form.

a) Zinc oxide sintered continuously for 20 minutes

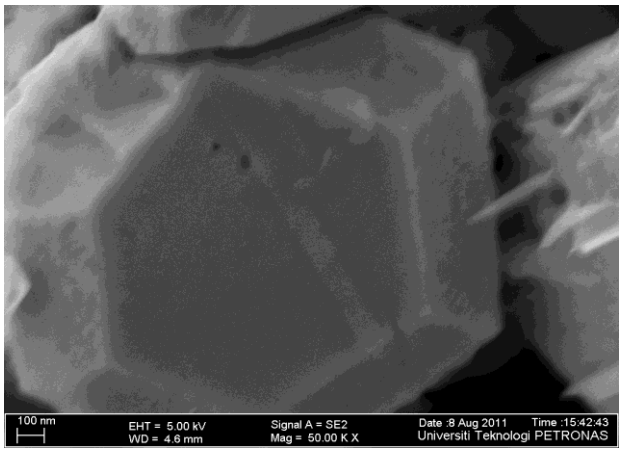

Figure 33: Image of zinc oxide sintered continuously for 20 minutes magnified at 50k

Figure 33 shows the structure of zinc oxide nanopowders sintered for 20 minutes. The structure obtained is nanohexagon. Although this sample has a proper structure, however it does not gain single phase yet due to insufficient sintering time.

b) Zinc oxide sintered continuously for 25 minutes

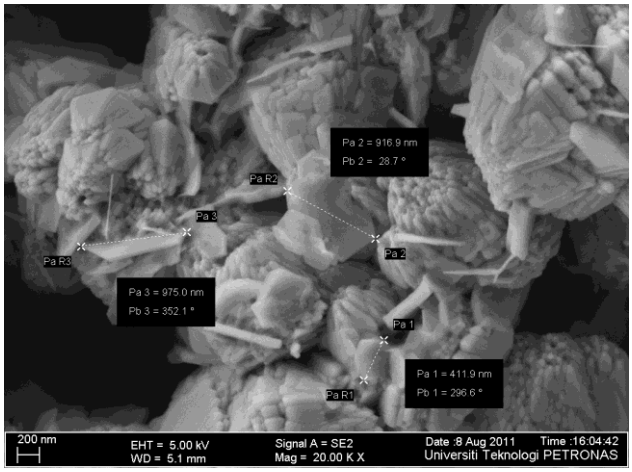

Figure 34: Image of zinc oxide sintered continuously for 25 minutes magnified at 10k

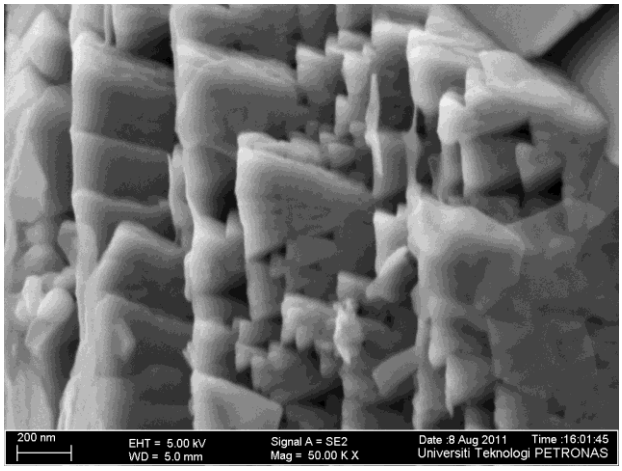

Figure 35: Image of zinc oxide sintered continuously for 25 minutes magnified at 50k

Based on figure 34 and 35, it can be seem that the structure obtained by zinc oxide sintered continuously for 25 minutes is a compacted combination of nanoflakes.

c) Zinc oxide continuously sintered for 30 minutes

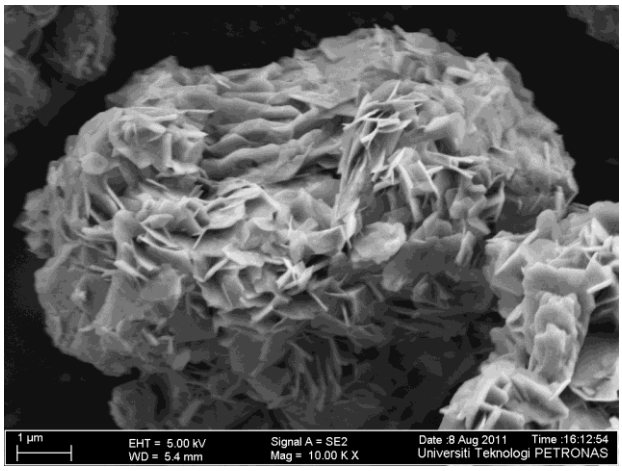

Figure 36: Image of zinc oxide sintered continuously for 30 minutes magnified at 10k

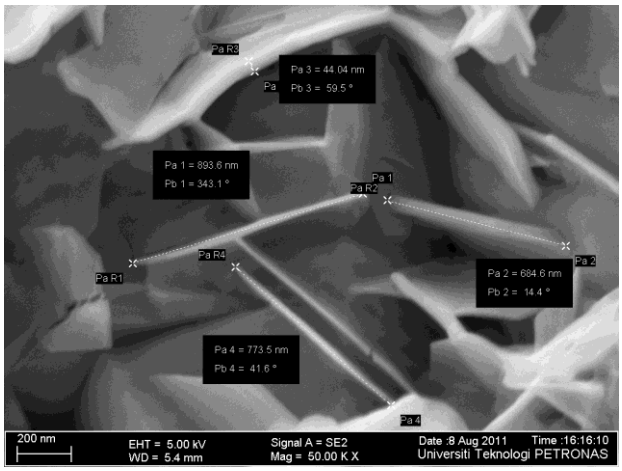

Figure 37: Image of zinc oxide sintered continuously for 30 minutes magnified at 50k

Nanoflakes structure is obtained by sintering zinc oxide nanopowders continuously for 30 minutes as shown in figure 36 and 37.

Based on all the images shown before, it seems that different sintering time and temperature will lead to different structures of the nanopowders. This is because zinc oxide ZnO is a versatile functional material that has a diverse group of growth morphologies such as nanocombs, nanorings, nanohelixes, nanosprings, nanobelts,

nanowires and nanocages [7]. All of these unique nanostructures demonstrate that zinc oxide has a rich family of nanostructures both in structure and properties.

4.3 Energy Dispersive X-Ray Spectroscopy (EDX)

a) Zinc oxide nanopowders sintered using conventional method

Elemental analysis of the zinc oxide nanopowders is done by using EDX. The elemental results of the nanopowders sintered using conventional method are listed in the table 9 below:

Table 9: Elemental Analysis of Zinc Oxide Sintered using Conventional Method via EDX

Sample	Element	Weight (%)	Atomic (%)	Deviation (%)
ZnO sintered at 200°C	Zn	48.21	18.56	62.88
	O	51.79	81.44	62.88
ZnO sintered at 250°C	Zn	71.47	38.01	23.98
	O	28.53	61.99	23.98
ZnO sintered at 300°C	Zn	79.64	48.91	2.18
	O	20.36	51.09	2.18

Atomic percentage for zinc and oxide element is supposed to be in the ratio of 50:50 based on the chemical formula. Based on the elemental analysis for the samples, it shows that there is huge deviation in the atomic percentage of the zinc and oxide element for zinc oxide sintered at 200°C. Zinc oxide nanopowders sintered at 300°C has the highest purity among the others since it has the lowest percentage of atomic deviation.

b) Zinc oxide nanopowders sintered using microwave

Zinc oxide nanopowders sintered using microwave are also being sent for EDX to obtain the elemental analysis of the samples. The elemental compositions of zinc oxide nanopowders sintered using microwave are as shown in table 10 below:

Table 10: Elemental Analysis of Zinc Oxide Sintered using Microwave via EDX

Sample	Element	Weight (%)	Atomic (%)	Deviation (%)
ZnO sintered for 12 minutes with three minutes of interval time	Zn	43.31	14.57	70.86
	O	37.52	51.57	3.14
	C	17.95	32.86	-
	Al	1.22	1.00	-
ZnO sintered for 15 minutes with three minutes of interval time	Zn	49.45	18.19	63.62
	O	37.02	55.62	11.24
	C	12.73	25.47	-
	Al	0.80	0.72	-
ZnO sintered for 1 hour with 5 minutes interval	Zn	55.03	23.05	53.90
	O	44.97	76.95	53.90
ZnO sintered for 2 hours with 5 minutes interval	Zn	68.18	34.40	31.20
	O	31.82	65.60	31.20
ZnO sintered for 3 hour with 5 minutes interval	Zn	60.75	27.47	45.06
	O	39.25	72.53	45.06
ZnO sintered for 4 hour with 5 minutes interval	Zn	56.31	23.98	52.04
	O	43.69	76.02	52.04
ZnO sintered for 15 minutes	Zn	50.27	19.84	60.32
	O	49.73	80.16	60.32
ZnO sintered for 20 minutes	Zn	62.49	28.96	42.08
	O	37.51	71.04	42.08
ZnO sintered for 25 minutes	Zn	67.46	33.66	32.68
	O	32.54	66.34	32.68
ZnO sintered for 30 minutes	Zn	71.01	37.48	25.04
	O	28.99	62.52	25.04

Atomic percentage for zinc and oxide element is supposed to be in the ratio of 50:50 based on the chemical formula. Based on the elemental analysis for the samples, it shows that there is huge deviation in the atomic percentage of the zinc and oxide element for some samples. Both zinc oxide nanopowders sintered using microwave for 25 minutes and 30 minutes show moderate deviation, 32.68% and 25.04%.

Based on the XRD, FESEM and EDX results, zinc oxide nanopowders sintered at 300 °C is chose as the best sample for conventional method that will be used in the next part

of the experiment. For microwave sintering, zinc oxide nanopowders sintered for 25 and 30 minutes are choose since both of them give good results in XRD, FESEM and EDX.

4.4 Compressibility Test

The amalgam samples consist of different weight of Silverfil amalgam and zinc oxide nanopowders are compressed by using Carver 25 Ton Auto Pellet Press Machine. The mass, thickness and diameter of the round compacts are measured to determine the green density, ρ_g of the compacts. The formula for green density is as stated below:

$$\rho_g = ((4/\pi)\times 1000 \times M)(d^2 \times t)$$

$$= 1273\ (M/\ d^2 \times t) \qquad \textbf{(5)}$$

where,

ρ_g = green density (g/cm^3)

M = mass of pellet, g

d = diameter of pellet, mm

t = thickness of pellet, mm.

Table 11: Green Density Measurement of Compact with Different Percentage of Zinc Oxide Addition

No.	ZnO Addition (%)	Type of Sintering	Load (kg)	Sample Mass (g)	Diameter (mm)	Thickness (mm)	Green Density (g/cm3)
1	0		1000	1.880	13	2.30	32.567
2	10	Conventional	1000	1.877	13	2.60	36.754
3	20		1000	1.848	13	2.90	40.364
4	30		1000	1.855	13	3.20	44.718
5	40		1000	1.853	13	3.40	47.467
6	50		1000	1.843	13	3.25	45.108
7	10	Microwave for 25 min	1000	1.818	13	2.55	34.920
8	20		1000	1.861	13	2.70	37.857
9	30		1000	1.889	13	3.05	43.394
10	40		1000	1.914	13	3.25	46.859
11	50		1000	1.850	13	3.20	44.595
12	10	Microwave for 30 min	1000	1.878	13	2.30	32.531
13	20		1000	1.891	13	2.60	37.025
14	30		1000	1.869	13	3.00	42.235
15	40		1000	1.912	13	3.20	46.085
16	50		1000	1.882	13	3.10	43.942

Based on the result in table 11, a graph of green density versus weight percentage of zinc oxide addition is plotted. The graph is shown below:

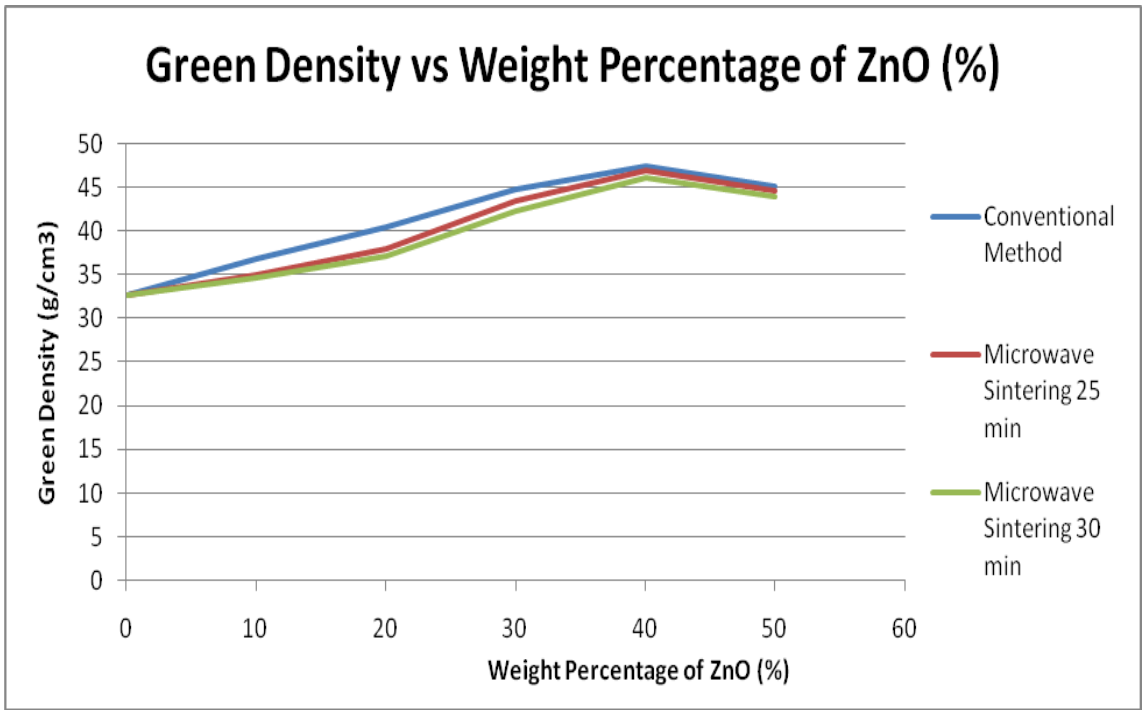

Figure 38: Green density of amalgam compacts at different percentage of ZnO addition

Figure 38 shows the relationship between green density and the weight percentage of zinc oxide. Based on the graph, it shows that the green density is increasing with the increasing of zinc oxide content in the amalgam samples. This is because powder particle hardness has huge influence on the compressibility of powders. Zinc oxide nanopowders comes in nanosize thus its can fill the empty space between Silverfil's particles and thus increase the strength of the amalgam. There are a lot of pores in powder body before compaction, so fine particles are easily filled into pores among coarser particles under impact force [19]. Therefore, the green density is improved mainly in the form of sliding, filling pores and rearranging of powder particles when the impact is apply to the powder.

From the graph, the green density of compacts with zinc oxide sintered at 300°C is higher than the other samples. This is because zinc oxide nanopowders sintered at 300°C has the smallest crystallite size, which leads to high hardness value of the material. As powder particle hardness increasing, green density is also increasing [18]. This explains why compact with zinc oxide nanopowders sintered at 300°C content has high green

density value than the other two compacts. The maximum amout of zinc oxide nanopowders that can be put inside the Silverfil amalgam is at about 40% of the total weight of the amalgam since any larger amount than that will lead to decrease in green density of the amalgam. The decrease in green density of the amalgam at 50% of amount zinc oxide might due to the fact that there is no more empty space that can be filled by the nanopowders. When there is excess zinc oxide content in the amalgam, the composition of zinc oxide will be more than the composition of reactive silver and silver-mercury and thus lead to the decrease of compact hardness. This happens because is zinc oxide is regard as soft material [20].

4.5 Microindentation Hardness Test

Hardness of round compacts consists of Silverfil amalgam and zinc oxide nanopowders are measured using Vickers Indentation. Force of 100 gf is used since the samples come in powder form. The dwell time for each indentation is set at 15 seconds. The indentation is done at three different spots on the compact and the hardness value of each spot is taken. The average value for those three readings is calculated and then the value is taken as the hardness value of the compact. The measured hardness values of the compact are listed in the table 12 below:

Table 12: Hardness Measurement of Compact with Different Percentage of Zinc Oxide Addition

No.	Percentage of ZnO (%)	Type of Sintering	Force (gf)	Dwell Time (s)	Hardness (HV)			
					1st	2nd	3rd	Average
1	0		100	15	26.40	34.80	35.70	32.30
2	10	Conventional	100	15	64.90	58.20	67.70	63.60
3	20	Conventional	100	15	76.80	84.00	68.20	76.33
4	30	Conventional	100	15	90.00	74.40	88.10	84.17
5	40	Conventional	100	15	106.50	110.60	95.10	104.07
6	50	Conventional	100	15	87.40	75.80	93.90	85.70
7	10	Microwave for 25 min	100	15	49.50	54.30	61.10	54.97
8	20	Microwave for 25 min	100	15	61.10	58.30	65.60	61.67
9	30	Microwave for 25 min	100	15	82.70	88.40	72.90	81.33
10	40	Microwave for 25 min	100	15	98.20	103.00	105.10	102.10
11	50	Microwave for 25 min	100	15	81.30	74.70	87.90	81.30
12	10	Microwave for 30 min	100	15	48.80	54.00	58.10	53.63
13	20	Microwave for 30 min	100	15	68.20	61.40	51.20	60.27
14	30	Microwave for 30 min	100	15	80.00	72.70	88.50	80.40
15	40	Microwave for 30 min	100	15	104.10	96.30	99.80	100.07
16	50	Microwave for 30 min	100	15	79.60	84.10	74.20	79.30

Based on the hardness result in table 12, a graph of hardness versus percentage of zinc oxide addition is plotted. The plotted graph is as shown in figure 39 below:

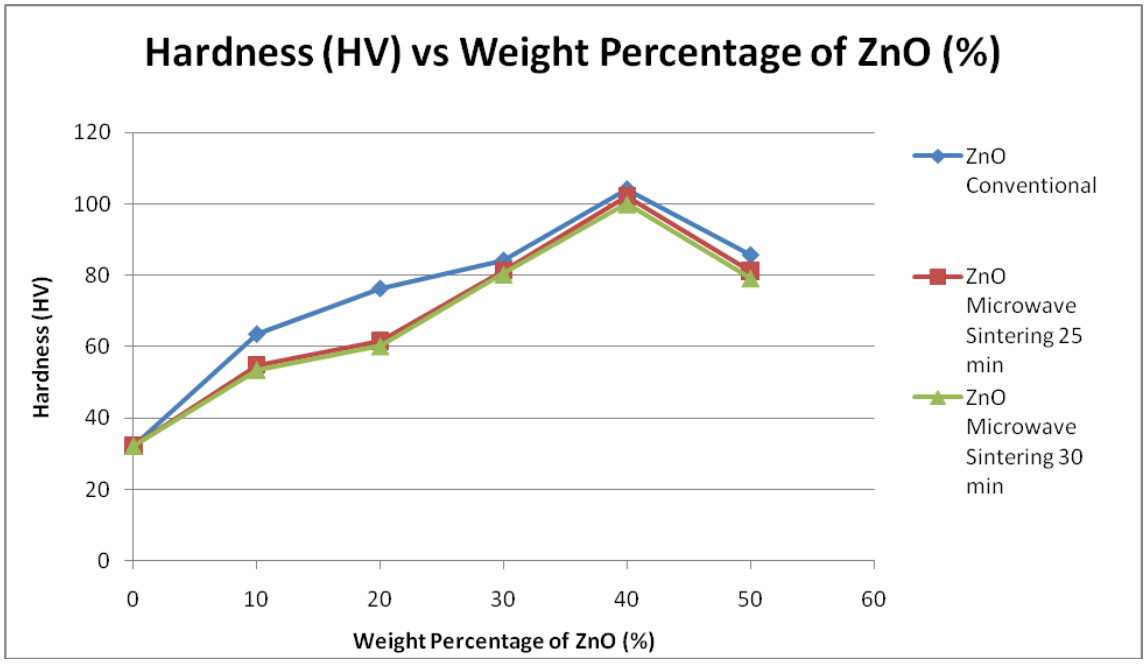

Figure 39: Hardness of amalgam compacts at different percentage of ZnO addition

Based on the graph, it shows that the hardness of the amalgam increase with increasing percentage of zinc oxide addition into the amalgam. The value of the hardness begin to drop when the weight percentage of zinc oxide inside the amalgam reach 50%. From the figure, compacts with the addition of zinc oxide nanopowders sintered at 300°C give higher hardness value than the other two compacts. This is because the hardness of the compact is affected by the particle size of the zinc oxide nanopowders added into the compact. Researches have been done proving that as particle size decrease, hardness of material increase [21, 22]. Since zinc oxide sintered at 300°C has the smallest particle size which is 44.95 nm, the incorporation of these nanopowders into Silverfil's amalgam will make the compact yield greater hardness compared to the other two samples. Other than that, smaller particle size material will have larger surface contact area for the material to react with other materials.

Based on the result of both mechanical strength test done, zinc oxide sintered using conventional method at 300 °C give the highest increment to the strength of dental amalgam than the zinc oxide nanopowders sintered using microwave. This is because zinc oxide sintered at 300 °C has the smallest naoparticles size and also high purity compared to the other two nanopowders.

However, zinc oxide sintered using microwave is practically more suitable to be applied in the industrial. It has a lot more potential and advantages than the zinc oxide nanopowders sintered using conventional method. This is because it is easier to sinter nanopowders using microwave than the conventional method. The sintering time also has been greatly reduced which from eight hours by using conventional method to about 25-30 minutes by using microwave sintering. Thus, more nanopowders can be produced by using microwave sintering than conventional method. Other than that, sintering nanopowders using microwave require low energy consumption than conventional method and thus will lead to energy saving which most industrial are looking forward to in order to save operation cost. In addition, based on XRD and FESEM results show earlier, it can be seem that the nanopowders sintered using microwave have small crystallite size, 55.26 nm and better nanoflakes structure. So, microwave sintering is a better sintering technique that can be used in the industrial compared to conventional sintering method.

CHAPTER 5

CONCLUSION

This project uses zinc oxide nanopowders to increase the strength of Silverfil's amalgam. Zinc oxide nanopowders were synthesized via sol gel method. The nanopowders were sintered by using two different sintering techniques which are conventional method and microwave sintering. For zinc oxide nanopowders sintered using conventional method, the sample was sintered for 8 hours while for microwave sintering, the sintering time is only about 25-30 minutes.

The nanopowders were sent to XRD and FESEM for morphological and characteristic analysis. Based on XRD result, zinc oxide nanopowders sintered at 300°C has the smallest particles size which is 44.95 nm and also high crystallinity. For zinc oxide nanopowders sintered using microwave, the nanopowders sintered for 25 and 30 minutes have good particles size which are 55.26 nm and 56.85 nm. From FESEM analysis, all the nanopowders produced good nanoflakes structure. Zinc oxide nanopowders sintered at 300°C has the highest purity than the other two nanopowders with atomic deviation of only 2.18%.

Based on the strength test result, both green density and hardness of the amalgam compact are increasing with the increasing of zinc oxide nanopowders content in it. Since nanopowders come in nanosize, they can fill in the empty space between the amalgams particles and thus increase the hardness of the compacts. This is because material with small particles size has higher strength and thus leads to higher green density of the material.

From the strength test result, zinc oxide sintered using conventional method at 300 °C give the highest improvement on the strength of Silverfil amalgam compared to the other two nanopowders sintered using microwave. This is due to the smallest nanoparticles size of the nanopowders and high purity content. So, zinc oxide sintered at 300°C is chose as the best nanofillers that can be used to increase the strength of Silverfil's amalgam. The additions of nanopowders into the amalgam increase the amalgam's strength and thus minimize the mercury content in it.

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