

**Y<sub>2</sub>O<sub>3</sub> AND CaO ZIRCONIA AS REINFORCEMENT  
FOR HYDROXYAPATITE BIOCOMPOSITE**

**ZAW LINN HTUN**

**UNIVERSITI SAINS MALAYSIA**

**2016**

**Y<sub>2</sub>O<sub>3</sub> AND CaO ZIRCONIA AS REINFORCEMENT FOR  
HYDROXYAPATITE BIOCOMPOSITE**

**by**

**ZAW LINN HTUN**

**Thesis submitted in fulfilment of the  
requirements for the degree  
of Master of Science**

**September 2016**

## DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitles “Y<sub>2</sub>O<sub>3</sub> and CaO Zirconia as Reinforcement for Hydroxyapatite Biocomposite”. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

Name of Student: Zaw Linn Htun

Signature:

Date: 29<sup>th</sup>, August, 2016

Witness by

Supervisor: Prof. Dr. Ahmad Fauzi Mohd Noor

Signature:

Date: 29<sup>th</sup>, August, 2016

## ACKNOWLEDGEMENTS

Firstly, I gratefully acknowledge financial support from Japan International Cooperation Agency (JICA), ASEAN University Network/ Southeast Asia Engineering Education Development Network (AUN/SEED-Net) for giving me the opportunity to undertake this research work.

I cherish this chance to express my deepest thankfulness to my supervisor Prof. Dr. Ahmad Fauzi Mohd Noor and co-supervisor, Dr. Nurazreena Ahmad for their support, patient, motivation, guidance and inspiration to accomplish this research project. I also would like to thank my advisor, Prof. Dr. Mitsugu TODO at Division of Renewable Energy Dynamics, Research Institute for Applied Mechanics, Kyushu University, for his valuable comment and suggestions.

I would like to convey my appreciation to Prof. Dr. Zuhailawati Bt. Hussain, Dean of SMMRE (School of Materials and Mineral Resources Engineering), for her concern and valuable helps during my study. I am also grateful to University Sains Malaysia (USM) for offering an opportunity for me to study MSc in bioceramics with adequate research facilities, great supports from administrative, academic and technical staffs. I would like to express my special thanks to all lecturers for their innovative teaching.

I like to express my gratitude to all of my friends, local students as well as international ones, studying in School of Materials and Mineral Resources Engineering, USM. I really appreciated in knowledge sharing, taking care each other

and making activities together during my study, and it will make me unforgettable in my life.

I would like to take this opportunity to convey my gratitude to all of my teachers starting from Primary School until now, especially Daw Aye Aye Myint, Assoc. Prof. Dr. Lwin Lwin Than, Assoc. Prof. Daw Lian Tial and Prof. Dr. Aye Aye Thant. Their enthusiasm and words of encouragement facilitated me to reach this height. This thesis is dedicated to them.

Finally, it is the time to describe my endless thanks to my beloved parents; U Maung Maung and Daw Aye Myint for supporting and encouraging me to try my best. Thanks for always being there for me during the good and the bad. Most of all, thanks a million for always believing in me, even when I fail to believe in myself. I am being one of the happiest people and so lucky to have you.

Thank you indeed.

Zaw Linn Htun

August 2016

## TABLE OF CONTENTS

|                                            | Page  |
|--------------------------------------------|-------|
| <b>ACKNOWLEDGEMENTS</b>                    | ii    |
| <b>TABLE OF CONTENTS</b>                   | iv    |
| <b>LIST OF TABLES</b>                      | ix    |
| <b>LIST OF FIGURES</b>                     | x     |
| <b>LIST OF SYMBOLS</b>                     | xvi   |
| <b>LIST OF ABBREVIATIONS</b>               | xv    |
| <b>ABSTRAK</b>                             | xviii |
| <b>ABSTRACT</b>                            | xx    |
| <br>                                       |       |
| <b>CHAPTER ONE : INTRODUCTION</b>          |       |
| 1.1 Background                             | 1     |
| 1.2 Problem Statement                      | 4     |
| 1.3 Research Objectives                    | 6     |
| 1.4 Research Overview                      | 6     |
| <br>                                       |       |
| <b>CHAPTER TWO : LITERATURE REVIEW</b>     |       |
| 2.1 Introduction                           | 8     |
| 2.2 Bone Tissue                            | 9     |
| 2.2.1 Mechanical Characteristic of Bone    | 9     |
| 2.2.2 Biology of Natural Human Bone        | 11    |
| 2.2.3 Destructive Testing of Bone          | 14    |
| 2.3 Biocomposites for Medical Applications | 17    |
| 2.3.1 Types of Biocomposite Materials      | 18    |

|         |                                                             |    |
|---------|-------------------------------------------------------------|----|
| 2.4     | Ceramics and Bioceramics Implants                           | 19 |
| 2.4.1   | Three Generations of Bioceramics                            | 21 |
| 2.4.1.1 | Bioinert Ceramics                                           | 22 |
| 2.4.1.2 | Bioresorbable Ceramics                                      | 22 |
| 2.4.1.3 | Bioactive Ceramics                                          | 23 |
| 2.5     | Calcium Phosphate-based Ceramics                            | 24 |
| 2.5.1   | Hydroxyapatite                                              | 26 |
| 2.5.1.1 | Hydroxyapatite for Implantation                             | 27 |
| 2.5.1.2 | Manufacturing of HAp Biocomposite and Mechanical Properties | 28 |
| 2.5.1.3 | Mechanisms of Apatite Formation on Hydroxyapatite           | 32 |
| 2.5.2   | $\beta$ -Tricalcium Phosphate ( $\beta$ -TCP)               | 33 |
| 2.5.3   | Biphasic Calcium Phosphate (BCP)                            | 34 |
| 2.6     | Ceramic Biocomposites                                       | 37 |
| 2.7     | Zirconia                                                    | 38 |
| 2.7.1   | Stabilization of Zirconia                                   | 41 |
| 2.7.2   | Yttria Stabilized Zirconia ( $Y_2O_3$ - $ZrO_2$ )           | 43 |
| 2.7.3   | Transformation Toughening                                   | 44 |
| 2.7.4   | Mechanical Properties of Zirconia                           | 45 |
| 2.8     | $CaF_2$ Addition on $ZrO_2$ /HAp Biocomposites              | 46 |
| 2.9     | Biological Performance Evaluation                           | 47 |

### **CHAPTER THREE : MATERIALS AND METHODOLOGY**

|     |               |    |
|-----|---------------|----|
| 3.1 | Introduction  | 51 |
| 3.2 | Raw Materials | 51 |

|         |                                                                                                       |    |
|---------|-------------------------------------------------------------------------------------------------------|----|
| 3.3     | Y <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub> /HAp Biocomposite                                     | 52 |
| 3.3.1   | Effect of Y <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub> and CaF <sub>2</sub> Addition to HAp Matrix | 52 |
| 3.3.1.1 | Batching and Powders Mixing                                                                           | 55 |
| 3.3.1.2 | Drying and Sieving                                                                                    | 55 |
| 3.3.1.3 | Dry Pressing                                                                                          | 55 |
| 3.3.1.4 | Sintering                                                                                             | 56 |
| 3.4     | CaO-ZrO <sub>2</sub> /HAp Biocomposite                                                                | 57 |
| 3.5     | Evaluation of Bioactivity <i>In Vitro</i>                                                             | 59 |
| 3.5.1   | Preparation of Simulated Body Fluid                                                                   | 59 |
| 3.5.2   | Samples Immersion in SBF Solution                                                                     | 60 |
| 3.6     | Characterization                                                                                      | 62 |
| 3.6.1   | X-ray Diffraction (XRD)                                                                               | 62 |
| 3.6.2   | Field Emission Scanning Electron Microscope (FESEM)                                                   | 64 |
| 3.6.3   | Particle Size Analysis                                                                                | 65 |
| 3.6.4   | Density and Porosity Measurement                                                                      | 66 |
| 3.6.5   | Linear Shrinkage Measurement                                                                          | 68 |
| 3.6.6   | Hardness Test                                                                                         | 69 |
| 3.6.7   | Fracture Toughness Measurement                                                                        | 70 |
| 3.6.8   | Flexural Strength Test                                                                                | 71 |

## CHAPTER FOUR : RESULTS AND DISCUSSION

|       |                                |    |
|-------|--------------------------------|----|
| 4.1   | Introduction                   | 73 |
| 4.2   | Raw Materials Characterization | 73 |
| 4.2.1 | Particle Size Distribution     | 74 |
| 4.2.2 | Morphological Analysis         | 75 |



|         |                                                                                              |     |
|---------|----------------------------------------------------------------------------------------------|-----|
| 4.2.3   | Elemental Analysis                                                                           | 77  |
| 4.3     | Y <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub> /HAp Biocomposite                            | 78  |
| 4.3.1   | Comparison for Pure Mixing and Milling-mixing Biocomposites                                  | 78  |
| 4.3.1.1 | XRD Analysis and Particle Size Distribution                                                  | 79  |
| 4.3.1.2 | Physical Properties of Pure Mixing and Milling-mixing Composites                             | 82  |
| 4.3.2   | Effect of Y <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub> Addition and Sintering Temperature | 86  |
| 4.3.2.1 | XRD Analysis                                                                                 | 86  |
| 4.3.2.2 | Physical Properties of Y <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub> /HAp Biocomposites    | 92  |
| 4.3.2.3 | Microstructural Observation                                                                  | 97  |
| 4.3.2.4 | Mechanical Properties of Y <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub> /HAp Biocomposites  | 100 |
| 4.3.2.5 | Evaluation of Bioactivity in SBF                                                             | 103 |
| 4.4     | CaO-ZrO <sub>2</sub> /HAp Biocomposite                                                       | 105 |
| 4.4.1   | Characterization of Commercial CaO-ZrO <sub>2</sub> Powder                                   | 105 |
| 4.4.2   | Effect of CaO-ZrO <sub>2</sub> Addition and CaF <sub>2</sub> on HAp                          | 107 |
| 4.4.2.1 | XRD Analysis                                                                                 | 108 |
| 4.4.2.2 | Physical Properties of CaO-ZrO <sub>2</sub> /HAp Biocomposites                               | 112 |
| 4.4.2.3 | Microstructural Examination                                                                  | 117 |
| 4.4.2.4 | Evaluation of Mechanical Properties                                                          | 121 |
| 4.4.3   | Evaluation of Bioactivity in SBF                                                             | 124 |

## CHAPTER FIVE : CONCLUSION AND FURTHER WORK

|     |                                    |     |
|-----|------------------------------------|-----|
| 5.1 | Conclusion                         | 127 |
| 5.2 | Recommendation for Future Research | 129 |

## **REFERENCES**

131

## **APPENDICES**

## **LIST OF PUBLICATIONS**

## LIST OF TABLES

|           |                                                                                                                                  | Page |
|-----------|----------------------------------------------------------------------------------------------------------------------------------|------|
| Table 2.1 | Hard tissue components of the human adult. Weight % except for Ca/P molar ratio                                                  | 14   |
| Table 2.2 | Important calcium phosphate compounds with their Ca/P ratios and $PK_s^a$ values                                                 | 26   |
| Table 2.3 | Appropriated grain size of $\beta$ -TCP bone grafts for different clinical scenarios                                             | 34   |
| Table 2.4 | Characteristic of $ZrO_2$ based ceramics                                                                                         | 46   |
| Table 3.1 | Summary of raw materials used for $ZrO_2$ /HAp biocomposite                                                                      | 52   |
| Table 3.2 | Summary of composition for $Y_2O_3$ - $ZrO_2$ /HAp with various $CaF_2$ content. (wt% HAp = 95%, wt% $Y_2O_3$ - $ZrO_2$ = 5%)    | 53   |
| Table 3.3 | Summary of variable parameters in $Y_2O_3$ - $ZrO_2$ /HAp biocomposite                                                           | 54   |
| Table 3.4 | Summary of composition for $CaO$ - $ZrO_2$ /HAp with different amount of $CaO$ - $ZrO_2$ and $CaF_2$ content                     | 57   |
| Table 3.5 | Summary of variable parameters in $CaO$ - $ZrO_2$ /HAp biocomposite                                                              | 58   |
| Table 3.6 | Ion concentration of simulated body fluid and human blood plasma                                                                 | 59   |
| Table 3.7 | Reagents for preparation of SBF (pH 7.25)                                                                                        | 60   |
| Table 4.1 | Relative percentage of HAp and $\beta$ -TCP phases present in the $Y_2O_3$ - $ZrO_2$ /HAp samples calculated from Equation (4.5) | 91   |
| Table 4.2 | Relative percentage of HAp and $\beta$ -TCP phases present in the $CaO$ - $ZrO_2$ /HAp samples                                   | 112  |

## LIST OF FIGURES

|             |                                                                                                                                                       | Page |
|-------------|-------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| Figure 2.1  | Multi-scale and multi-material characteristics of bone                                                                                                | 10   |
| Figure 2.2  | (a) Mechanical behaviour of a structure (b) Micro-scale (c) Whole bone                                                                                | 11   |
| Figure 2.3  | Typical load-displacement curve of a structure                                                                                                        | 15   |
| Figure 2.4  | Whole bone tested in three-point loading configuration. Force is applied through the upper plate. The span is the distance between the lower supports | 17   |
| Figure 2.5  | Classification of biocomposites based on their reinforcement form                                                                                     | 18   |
| Figure 2.6  | Schematic representation of mechanism of apatite formation on the sintered hydroxyapatite in SBF                                                      | 32   |
| Figure 2.7  | Variation of zeta potential and Ca/P ratio on the surface of sintered hydroxyapatite as a function of soaking time in SBF                             | 33   |
| Figure 2.8  | Three crystallographic phases of zirconia                                                                                                             | 40   |
| Figure 2.9  | Phase diagram of $Y_2O_3$ - $ZrO_2$                                                                                                                   | 42   |
| Figure 2.10 | Partial phase diagram of $CaO$ - $ZrO_2$                                                                                                              | 42   |
| Figure 2.11 | Transformation toughening of partially stabilized tetragonal zirconia                                                                                 | 44   |
| Figure 2.12 | SEM micrographs of the surfaces of the natural HA/zircon coatings soaked in SBF for 7 days                                                            | 49   |
| Figure 2.13 | SEM micrographs of the glass-ceramic surfaces after immersion in SBF for 14 days                                                                      | 49   |
| Figure 3.1  | Flow chart of $Y_2O_3$ - $ZrO_2$ /HAp biocomposite sample preparation                                                                                 | 54   |

|            |                                                                                                                                                                                                 |    |
|------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 3.2 | Green bodies of ZrO <sub>2</sub> /HAp biocomposite                                                                                                                                              | 56 |
| Figure 3.3 | Flow chart of CaO-ZrO <sub>2</sub> /HAp biocomposite sample preparation                                                                                                                         | 58 |
| Figure 3.4 | Arrangement of sample being soaked in SBF                                                                                                                                                       | 62 |
| Figure 3.5 | Schematic illustration of density measurement by Archimedes method                                                                                                                              | 67 |
| Figure 3.6 | Schematic illustration of ZrO <sub>2</sub> /HAp biocomposite sample                                                                                                                             | 68 |
| Figure 3.7 | Schematic diagram of indentation mark in Vickers microhardness measurement                                                                                                                      | 69 |
| Figure 3.8 | Schematic diagram of radial crack by indentation                                                                                                                                                | 70 |
| Figure 3.9 | Illustration of a three-point bending test                                                                                                                                                      | 72 |
| Figure 4.1 | Particle size distribution curve for HAp powder                                                                                                                                                 | 74 |
| Figure 4.2 | Particle size distribution curve for Y <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub> powder                                                                                                     | 75 |
| Figure 4.3 | SEM images of HAp powder at (a) 1000X and (b) 3000X magnifications                                                                                                                              | 76 |
| Figure 4.4 | SEM images of Y <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub> powder at (a) 10,000X and (b) 20,000X magnifications                                                                              | 77 |
| Figure 4.5 | SEM image and EDX spectrum of HAp powder                                                                                                                                                        | 77 |
| Figure 4.6 | XRD patterns of pure mixing and milling-mixing Y <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub> /HAp composites with 1 wt% of CaF <sub>2</sub> addition sintered at (a) 1050°C and (b) 1250°C    | 81 |
| Figure 4.7 | Particle size distribution curves for (a) pure mixing sample and (b) milling-mixing sample                                                                                                      | 82 |
| Figure 4.8 | Bulk densities of pure mixing and milling-mixing Y <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub> /HAp composites with 1 wt% of CaF <sub>2</sub> addition as a function of sintering temperature | 83 |

|             |                                                                                                                                                                                     |     |
|-------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 4.9  | Apparent porosities of pure mixing and milling-mixing $Y_2O_3$ - $ZrO_2$ /HAp composites with 1 wt% of $CaF_2$ addition as a function of sintering temperature                      | 84  |
| Figure 4.10 | SEM images of pure mixing samples at (a) 1200°C and (b) 1250°C                                                                                                                      | 85  |
| Figure 4.11 | SEM images of milling-mixing samples sintered at (a) 1200°C and (b) 1250°C                                                                                                          | 85  |
| Figure 4.12 | XRD patterns of $Y_2O_3$ - $ZrO_2$ /HAp biocomposites with various $CaF_2$ amount sintered at (a) 1050°C (b) 1150°C and (c) 1250°C                                                  | 88  |
| Figure 4.13 | Firing shrinkages of $Y_2O_3$ - $ZrO_2$ /HAp biocomposites with various $CaF_2$ addition as a function of sintering temperature at (a) length (b) width and (c) thickness direction | 93  |
| Figure 4.14 | Picture of fully densify 5YZH-9CF sample compared with 5YZH-5CF and 5YZH-7CF samples sintered at 1150 °C                                                                            | 94  |
| Figure 4.15 | Bulk densities of $Y_2O_3$ - $ZrO_2$ /HAp biocomposites with various $CaF_2$ addition as a function of sintering temperature                                                        | 95  |
| Figure 4.16 | Apparent porosities of $Y_2O_3$ - $ZrO_2$ /HAp biocomposites with various $CaF_2$ addition as a function of sintering temperature                                                   | 97  |
| Figure 4.17 | SEM images of (a) 5YZH-1CF, (b) 5YZH-3CF, (c) 5YZH-5CF and (d) 5YZH-7CF composites sintered at 1250°C for 5 hours                                                                   | 98  |
| Figure 4.18 | SEM image of 5YZH-9CF composite sintered at 1150°C for 5 hours                                                                                                                      | 99  |
| Figure 4.19 | SEM images for fracture surfaces of 5YZH-3CF composite sintered at (a) 1100°C (b) 1150°C, (c) 1200°C and (d) 1250°C for 5 hours                                                     | 99  |
| Figure 4.20 | SEM images for fracture surfaces of 5YZH-5CF composite sintered at (a) 1100°C (b) 1150°C, (c) 1200°C and (d) 1250°C for 5 hours                                                     | 100 |

|             |                                                                                                                                                                                                      |     |
|-------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 4.21 | Flexural strength (MOR) of $\text{Y}_2\text{O}_3\text{-ZrO}_2/\text{HAp}$ biocomposites with various $\text{CaF}_2$ addition as a function of sintering temperature                                  | 101 |
| Figure 4.22 | Microhardness of $\text{Y}_2\text{O}_3\text{-ZrO}_2/\text{HAp}$ biocomposites with various $\text{CaF}_2$ addition as a function of sintering temperature                                            | 102 |
| Figure 4.23 | Fracture toughness of $\text{Y}_2\text{O}_3\text{-ZrO}_2/\text{HAp}$ biocomposites with various $\text{CaF}_2$ addition as a function of sintering temperature                                       | 103 |
| Figure 4.24 | SEM images of the surfaces of 5YZH-3CF sample sintered at 1250 °C at (a) 5000X and (b) 20,000X magnification after soaking in SBF for 7 days                                                         | 104 |
| Figure 4.25 | SEM images of the surfaces of 5YZH-5CF sample sintered at 1250 °C at (a) 5000X and (b) 20,000X magnification after soaking in SBF for 7 days                                                         | 105 |
| Figure 4.26 | XRD pattern for $\text{CaO-ZrO}_2$ raw powder                                                                                                                                                        | 106 |
| Figure 4.27 | Particle size distribution curve of $\text{CaO-ZrO}_2$ raw powder                                                                                                                                    | 107 |
| Figure 4.28 | SEM images for $\text{CaO-ZrO}_2$ raw powder                                                                                                                                                         | 107 |
| Figure 4.29 | XRD patterns of (a) 5CZH-3CF, (b) 5CZH-5CF, (c) 10CZH-3CF and (d) 10CZH-5CF composites sintered at temperatures between 1150 °C to 1350 °C                                                           | 109 |
| Figure 4.30 | XRD patterns of various $\text{CaO-ZrO}_2/\text{HAp}$ composites sintered at 1350°C                                                                                                                  | 111 |
| Figure 4.31 | Firing shrinkages of $\text{CaO-ZrO}_2/\text{HAp}$ biocomposites with 3 and 5 wt% $\text{CaF}_2$ addition as a function of sintering temperature at (a) length (b) width and (c) thickness direction | 114 |
| Figure 4.32 | (a) Bulk densities and (b) apparent porosities of $\text{CaO-ZrO}_2/\text{HAp}$ biocomposites with 3 and 5 wt% $\text{CaF}_2$ addition as a function of sintering temperature                        | 116 |
| Figure 4.33 | (a) SEM images of 5CZH-5CF composite after sintering at (i) 1250°C, (ii) 1300°C and (iii) 1350°C, and (b) 10CZH-5CF composite after sintering at (iv) 1250°C, (v) 1300°C and (vi) 1350°C for 5 hours | 119 |

|             |                                                                                                                                                                                                                                         |     |
|-------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 4.34 | (a) SEM images for cross-section of 5CZH-5CF composite after sintering at (i) 1250°C, (ii) 1300°C and (iii) 1350°C, and (b) cross-section of 10CZH-5CF composite after sintering at (iv) 1250°C, (v) 1300°C and (vi) 1350°C for 5 hours | 120 |
| Figure 4.35 | Flexural strength (MOR) of CaO-ZrO <sub>2</sub> /HAp biocomposites with 3 and 5 wt% CaF <sub>2</sub> addition as a function of sintering temperature                                                                                    | 122 |
| Figure 4.36 | Microhardness of CaO-ZrO <sub>2</sub> /HAp biocomposites with 3 and 5 wt% CaF <sub>2</sub> addition as a function of sintering temperature                                                                                              | 123 |
| Figure 4.37 | Fracture toughness of CaO-ZrO <sub>2</sub> /HAp biocomposites with 3 and 5 wt% CaF <sub>2</sub> addition as a function of sintering temperature                                                                                         | 124 |
| Figure 4.38 | SEM images of the surfaces of 5CZH-5CF sample at (a) 5000X and (b) 20,000X magnification after soaking in SBF for 7 days                                                                                                                | 125 |
| Figure 4.39 | SEM images of the surfaces of 10CZH-5CF sample at (a) 5000X and (b) 20,000X magnification after soaking in SBF for 7 days                                                                                                               | 126 |



## LIST OF SYMBOLS

|           |                           |
|-----------|---------------------------|
| %         | Percentage                |
| <         | Less than                 |
| >         | Greater than              |
| ≈         | Approximately             |
| °         | Degree                    |
| °C        | Degree Celsius            |
| °C/min    | Degree Celsius per minute |
| cm        | Centimetre                |
| h         | Hour                      |
| L         | Litre                     |
| m         | Metre                     |
| min       | Minute                    |
| mL        | Millilitre                |
| mm        | Millimetre                |
| rpm       | Revolution per minute     |
| wt %      | Weight percent            |
| nm        | Nanometre                 |
| g         | Gram                      |
| $\lambda$ | Wavelength                |
| $\theta$  | Theta (Angle)             |

## LIST OF ABBREVIATIONS

|                                |                                                 |
|--------------------------------|-------------------------------------------------|
| Al <sub>2</sub> O <sub>3</sub> | Alumina                                         |
| BCP                            | Biphasic Calcium Phosphate                      |
| c-ZrO <sub>2</sub>             | Cubic Zirconia                                  |
| Ca                             | Calcium                                         |
| CaF <sub>2</sub>               | Calcium Fluoride                                |
| CaO                            | Calcia                                          |
| CaO-ZrO <sub>2</sub>           | Calcia Stabilized Zirconia                      |
| CaP                            | Calcium Phosphate                               |
| CDA                            | Calcium Deficient Apatite                       |
| CeO <sub>2</sub>               | Ceria                                           |
| EDX                            | Energy Dispersive X-ray                         |
| FAp                            | Fluorapatite                                    |
| FESEM                          | Field Emission Scanning Electron Microscope     |
| FSZ                            | Fully Stabilized Zirconia                       |
| HAp                            | Hydroxyapatite                                  |
| ICDD                           | International Centre for Diffraction Data       |
| JCPDS                          | Joint Committee on Powder Diffraction Standards |
| MgO                            | Magnesia                                        |
| MOR                            | Modulus of Rupture                              |
| MPa                            | Megapascal                                      |
| m-ZrO <sub>2</sub>             | Monoclinic Zirconia                             |
| PSZ                            | Partially Stabilized Zirconia                   |
| SBF                            | Simulated Body Fluid                            |

|                                                 |                                                 |
|-------------------------------------------------|-------------------------------------------------|
| SEM                                             | Scanning Electron Microscope                    |
| SiC                                             | Silicon Carbide                                 |
| TEM                                             | Transmission Electron Microscopy                |
| TTCP                                            | Tetra Calcium Phosphate                         |
| t-ZrO <sub>2</sub>                              | Tetragonal Zirconia                             |
| XRD                                             | X-ray Diffraction                               |
| XRF                                             | X-ray Fluorescence                              |
| Y <sub>2</sub> O <sub>3</sub>                   | Yttria                                          |
| Y <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub> | Yttria Stabilized Zirconia                      |
| ZrO <sub>2</sub>                                | Zirconia                                        |
| ZrO <sub>2</sub> /HAp                           | Zirconia Reinforced Hydroxyapatite Biocomposite |
| α-TCP                                           | Alpha Tricalcium Phosphate                      |
| β-TCP                                           | Beta Tricalcium Phosphate                       |

# **ZIRKONIA $Y_2O_3$ DAN CaO SEBAGAI PENGUAT DALAM BIOKOMPOSIT HIDROKSIAPATIT**

## **ABSTRAK**

Biokomposit hidroksiapatit diperkuat zirkonia ( $ZrO_2/HAp$ ) telah difabrik untuk menambahbaik kekuatan dan keliatan patah bioseramik HAp tunggal.  $Y_2O_3-ZrO_2$  dan CaO- $ZrO_2$  komersial dipilih sebagai bahan penguat untuk matrik HAp. Sampel  $ZrO_2/HAp$  telah dihasilkan dengan cara konvensional pemrosesan seramik, iaitu melibatkan pencampuran serbuk, pemadatar dan persinteran. Pemrosesan sampel dimulakan dengan pencampuran atau pengisaran-pencampuran untuk membandingkan kehasilan kedua-dua sistem ini. Hasil sifat fizikal dan mekanikal adalah lebih baik dengan penggunaan cara pengisaran-pencampuran. HAp yang diperkuatkan sebanyak 5 bt%  $Y_2O_3-ZrO_2$  komersial yang seterusnya ditambah dengan berlainan amaun  $CaF_2$  amaun (1, 3, 5, 7 and 9 bt%) sebagai pembantu sinter dalam biokomposit  $ZrO_2/HAp$ . Sampel dipadat dengan mampatan ekapaksi sebanyak 90 MPa. Sampel kemudian disinter pada suhu  $1050^{\circ}C$  sehingga  $1250^{\circ}C$  dalam udara selama 5 jam. Semakin tinggi amaun  $CaF_2$  digunakan, semakin besar kemungkinan fasa HAp dikekalkan. Kekuatan lentur dan keliatan patah optima dicapai ialah 61.10 MPa dan  $1.15 MPa.m^{1/2}$  selepas penambahan 3 bt%  $CaF_2$  (komposit 5YZH-3CF). Dengan ini, 3 dan 5 bt%  $CaF_2$  dipilih sebagai amaun optima. Dalam bahagian kedua, penambahan 5 dan 10 bt% CaO- $ZrO_2$  dalam HAp dibanding dengan  $Y_2O_3-ZrO_2$  dari segi kesan kekuatan dan keliatan. Amaun  $CaF_2$  yang terpilih sebelum ini juga ditambah ke biokomposit CaO- $ZrO_2/HAp$ . Sifat mekanikal biokomposit CaO- $ZrO_2/HAp$  adalah lebih baik daripada optima HAp tunggal, iaitu kekuatan lentur dan ketahanan lentur ialah 54.77 MPa dan  $1.33 MPa.m^{1/2}$  dengan ketumpatan  $3.14 gcm^{-3}$ . Bahagian terakhir

adalah pengujian bioaktiviti biokomposit HAp diperkuat  $Y_2O_3$  dan  $CaO-ZrO_2$ . Pembentukan lapisan apatit dijumpai di atas permukaan sampel terpilih menandakan bioserasi dan potensi keupayaan pembentukan tulang.

## **Y<sub>2</sub>O<sub>3</sub> AND CaO ZIRCONIA AS REINFORCEMENT FOR HYDROXYAPATITE BIOCOMPOSITE**

### **ABSTRACT**

Zirconia reinforced hydroxyapatite (ZrO<sub>2</sub>/HAp) biocomposites were fabricated to improve the strength and fracture toughness of monolithic HAp. Commercial Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> and CaO-ZrO<sub>2</sub> were selected as the reinforcement for the HAp matrix. The ZrO<sub>2</sub>/HAp samples were produced by conventional ceramic processing route. The samples were initially produced by pure mixing as well as milling-mixing system. Better physical and mechanical properties were observed from milling-mixing. 5 wt% of commercial Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> was used to reinforce HAp and various amount of CaF<sub>2</sub> (1, 3, 5, 7 and 9 wt%) were added to the ZrO<sub>2</sub>/HAp biocomposite as sintering aid. Samples were compacted with a uniaxial pressure of 90 MPa. The samples were then sintered from 1050°C to 1250°C for 5 hours. The optimum flexural strength of 61.10 MPa and fracture toughness of 1.15 MPa.m<sup>1/2</sup> was achieved by 3 wt% of CaF<sub>2</sub> addition. From this study, 3 and 5 wt% of CaF<sub>2</sub> were selected as optimum addition. Subsequently, 5 and 10 wt% of CaO-ZrO<sub>2</sub> were incorporated to HAp to improve the strength and toughness of the HAp as compared with Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> addition. The selected amounts of CaF<sub>2</sub> were also added to CaO-ZrO<sub>2</sub>/HAp biocomposites. The mechanical properties of CaO-ZrO<sub>2</sub>/HAp biocomposite were found to be better than the optimum properties of monolithic HAp. The biocomposite achieved better flexural strength of 54.77 MPa with higher density 3.14 gcm<sup>-3</sup> and fracture toughness of 1.33 MPa.m<sup>1/2</sup>. The bioactivity test on both Y<sub>2</sub>O<sub>3</sub> and CaO-ZrO<sub>2</sub> reinforced HAp biocomposites revealed the formation of apatite layer on the surfaces, indicating the biocompatibility and potential bone forming ability.

## CHAPTER ONE

### INTRODUCTION

#### 1.1 Background

Biomaterials are generally based on the groups of materials such as metals, polymers, and ceramics (Park & Lakes 2007; Hermansson 2014). Biomaterials based ceramics, also known as bioceramics, are found within all the classical ceramic families such as traditional ceramics, special ceramics, glasses, glass-ceramics, coatings, and chemically bonded ceramics (Hermansson 2014). Bioceramics can be classified into bioinert, bioactive and resorbable bioceramics (Hench 1991). Depending on the applications, type of bioceramics can be selected. For instance, hard tissue and bone replacements are synthesized mainly from bioactive ceramics such as dense non-porous bioglass, ceravital and hydroxyapatite (HAp) (Best et al. 2008).

HAp, however, is the most largely used material than the others primarily because of its compositional and biological similarity to human bone, biocompatibility, bioactivity and osteoconduction characteristic (Jun et al. 2003; Sadjadi et al. 2010). It possesses exceptional biocompatibility and unique bioactivity, and it will form an artificial bone-like structure with the surrounding bone tissue when implanted (Hench & Wilson 1993). The reason for using hydroxyapatite as a bone substitute material is because the major constituent of bone is HAp and natural bone is approximately 70% hydroxyapatite by weight and 50% hydroxyapatite by volume (Shors & Holmes 1993; Vasconcelos 2012). HAp is frequently used for reconstruction and replacement of damaged bone or tooth zones in plastic and dental surgeries as well

as in coatings on dental and orthopaedic implants (Muster 1992; An et al. 2012; Oyefusi et al. 2014). Metals coated with hydroxyapatite have also been introduced as artificial bones. The hydroxyapatite coating will assist the surrounding tissue to bond firmly with the implant while the metal provides the strength for the artificial bone (Oonishi 1991; Mohseni et al. 2014; Pylypchuk et al. 2015).

Hydroxyapatite is reported as a low soluble basic calcium phosphate with Ca/P ratio of 1.67 (Daniel Arcos 2014). It has consistent bioactive properties and therefore is well suited as a calcium phosphate coating for total joint arthroplasty and total knee arthroplasty. As a result of its biocompatible, nontoxic, and capable of bonding directly to bone, HAp possesses true osteointegration (Epinette 1999). However, although HAp offers high biocompatibility, relatively low density, high compressive strength and high hardness, application of HAp as a load bearing implant is limited because of its brittleness, relatively low mechanical properties and a high dissolution rate in body fluid. Hence, the necessity of reinforcement to HAp without hampering its biocompatibility plays a crucial role (Balani et al. 2009).

Based on this understanding, the development of biocomposite materials is attractive as the advantage properties of two or more types of materials can be combined to suit better physical and mechanical properties of the matrix (Raucci et al. 2016). The introduction of bioinert ceramics with better properties as reinforcement into HAp ceramic is one effective way in producing a biocomposite with acceptable strength in order to sustain the cyclic loading. Bioinert ceramics are chosen to enhance the properties of bioactive HAp because it can maintain their physical and mechanical properties while being implant in human body. Alumina ( $\text{Al}_2\text{O}_3$ ), zirconia ( $\text{ZrO}_2$ ) and