

**DEVELOPMENT OF POROUS CERAMIC CLAY BODIES USING
FOUR DIFFERENT TYPES OF BIORESOURCE WASTES**

by

SENGPHET KEOKANGDONG

**Thesis submitted in fulfillment of the
requirements for the degree
of Doctor of Philosophy**

December 2014

ACKNOWLEDGEMENTS

I would like to express my most sincere thanks that come deeply from my heart to those who in one way or another contributed to make this research study possible.

Firstly, I am deeply grateful to my main supervisor, Prof. Dr. Radzali Othman for his supervision and advice from the early to the final stage of this research work. He has always been patient and encouraging in times of new ideas and difficulties. He has listened to my ideas and discussed frequently with me that led to the key insights of my work. He is a true scientist and a dedicated teacher that I want to be. Above, all he made me feel a friend, which I appreciate from heart. I keep in my mind his impressive saying to me “Take a seat and talk to me as friend”.

I would like to express my sincere gratitude to my co-supervisor Prof. Dr. Ahmad Fauzi Mohd Noor for his helps in all the time of this research. I have never forgotten his supports for his patience, motivation, enthusiasm and immense knowledge. He is great teacher that I have met.

I am grateful to Prof. Dr. Hanafi Ismail as the Dean of the School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia and staffs for their kindness and support.

I also would like to deliver my thanks to my Japanese advisor co-supervisors, Prof. Dr. Tsutumo Sato, Graduate School of Engineering, Hokkaido University (Japan), for his guidance and advice on my research for during the time of my study in Japan.

I am grateful to JICA-AUN/SEED-Net program for the opportunity to undertake this work and financial support. I would like to deliver my sincere thanks

and deepest gratitude for their generosity in giving me this opportunity to pursue my PhD degree.

My special thanks and appreciation are also extended to those people who, in one way or another, helped me accomplish this research.

To Mdm. Fong, Mr. Khairi, Mr. Rashid, Mr. Sharul, Mr. Masabura, Mr. Nakayashi, Ms. Fara, Ms. Era for their kindness, help and assistance.

To all my friends: Dr. Umar, Dr. Uday, Dr. Nabil, Dr. Norzida, Ms. Kee, Mrs. Eriva, Mr. Zaw, Ms. Davanh, Ms. Vanhnaly, Mr. Phoumiphon, Mr. Thithphanith, Mr. Fisal, Mr. Fahmi and others.

Last but not least, I would like to take opportunity to express my gratitude to my family for their love, especially my parents.

Thank you very much.

Sengphet Keokangdong

5th December, 2014

TABLE OF CONTENTS

| | |
|--|-------|
| ACKNOWLEDGEMENTS | ii |
| TABLE OF CONTENTS..... | iv |
| LIST OF TABLES..... | xi |
| LIST OF FIGURES..... | xiii |
| LIST OF ABBREVIATIONS..... | xxii |
| ABSTRAK..... | xxiii |
| ABSTRACT..... | xxv |
| | |
| 1 CHAPTER 1 INTRODUCTION | 1 |
| 1.1 Introduction | 1 |
| 1.2 Problem statements..... | 3 |
| 1.3 Objectives of the study | 7 |
| 1.4 Scope of research..... | 7 |
| | |
| 2 CHAPTER 2 LITERATURE REVIEW | 8 |
| 2.1 Types of clays..... | 8 |
| 2.1.1 Kaolin (China clay) | 8 |
| 2.1.2 Ball clays | 8 |
| 2.1.3 Fireclays..... | 9 |
| 2.1.4 Bentonites | 9 |
| 2.2 Types of clay mineral groupings | 10 |
| 2.2.1 Kaolinite group | 10 |
| 2.2.2 Illite group | 10 |
| 2.2.3 Smectite group..... | 10 |
| 2.3 Structure of clay minerals..... | 10 |
| 2.3.1 Physical properties of the clay minerals | 14 |
| 2.3.2 Effect of heat on the clay minerals and phases of transformation . | 15 |
| 2.3.3 The effect of impurities | 17 |
| 2.3.4 Thermal decomposition of illite | 17 |
| 2.4 Bioresource..... | 18 |

| | | |
|--------|--|----|
| 2.4.1 | Bioresource wastes | 18 |
| 2.4.2 | Kenaf | 19 |
| 2.4.3 | Banana stem waste..... | 20 |
| 2.4.4 | Sugarcane waste (SC)..... | 20 |
| 2.4.5 | Recycling of wastes | 21 |
| 2.5 | Firing of clays..... | 22 |
| 2.5.1 | The drying and firing of clays | 24 |
| 2.5.2 | Identification of clays by X-ray diffraction..... | 25 |
| 2.5.3 | Quantitative analysis of minerals | 25 |
| 2.6 | Porous ceramics | 26 |
| 2.7 | Application of porous ceramics..... | 29 |
| 2.7.1 | Filters | 29 |
| 2.7.2 | Thermal insulators | 30 |
| 2.7.3 | Heaters and heat exchangers..... | 30 |
| 2.8 | Porous clay ceramics | 31 |
| 2.9 | Porous clay ceramic produced pore-forming agent (PFA)..... | 32 |
| 2.9.1 | Solid method of adding pore-forming agents | 33 |
| 2.9.2 | Liquid method of adding pore-forming agents..... | 33 |
| 2.9.3 | Drying and firing of porous clay ceramics | 34 |
| 2.9.4 | Development of porous clay ceramic by addition of wastes | 35 |
| 2.10 | Utilization of wastes additive on the properties of porous clay ceramics . | 38 |
| 2.10.1 | The phases transformation with adding of wastes..... | 38 |
| 2.10.2 | Weight loss | 39 |
| 2.10.3 | The shrinkages and density of porous clay ceramics | 39 |
| 2.10.4 | Density and porosity of porous clay ceramics..... | 40 |
| 2.10.5 | Water absorption of porous clay ceramics | 41 |
| 2.10.6 | Mechanical properties of porous clay ceramics | 42 |
| 2.10.7 | The microstructures of porous clay ceramics | 43 |
| 3 | CHAPTER 3 MATERIAL AND METHODOLOGY | 46 |
| 3.1 | Introduction | 46 |
| 3.2 | Starting Raw Materials | 47 |
| 3.2.1 | Clays | 47 |
| (a) | Laotian clay (LC) | 47 |

| | | | |
|-------|-----|---|----|
| | (b) | Malaysian clay (MC)..... | 48 |
| 3.2.2 | | The bioresource wastes..... | 49 |
| | (a) | Kenaf powder and kenaf fibre (KP and KF) | 49 |
| | (b) | Banana stem waste (BW) | 49 |
| | (c) | Sugarcane waste (SC)..... | 49 |
| 3.3 | | Preparation of Raw Materials | 49 |
| 3.3.1 | | Preparation of clays | 49 |
| 3.3.2 | | Preparation of bioresources | 50 |
| | (a) | Kenaf powder and kenaf fibre | 50 |
| | (b) | Banana stem waste (BW) | 51 |
| | (c) | Sugarcane waste (SC)..... | 52 |
| 3.4 | | Characterization of raw materials..... | 52 |
| 3.4.1 | | X-ray diffraction (XRD)..... | 52 |
| 3.4.2 | | Chemical analysis by using X-ray fluorescence (XRF) | 55 |
| 3.4.3 | | Loss on Ignition (LOI)..... | 55 |
| 3.4.4 | | Thermogravimetric analysis (TGA/DSC) | 56 |
| 3.4.5 | | Specific surface area | 56 |
| 3.4.6 | | Particle sizes distribution analysis | 57 |
| 3.4.7 | | Evaluation of plasticity (ASTM D 4318-00; 2005)..... | 58 |
| 3.5 | | Preparation of clay bodies | 58 |
| 3.5.1 | | Mixing process | 59 |
| 3.5.2 | | Pressing process..... | 60 |
| 3.5.3 | | Drying process | 61 |
| 3.5.4 | | Preparation of porous clay bodies | 61 |
| 3.6 | | Firing of porous ceramic bodies | 62 |
| 3.6.1 | | Firing of clays bodies | 62 |
| 3.6.2 | | Firing of porous clay bodies | 63 |
| 3.6.3 | | Shrinkages measurement (ASTM C 326-03; 2005) | 63 |
| 3.6.4 | | Density and porosity measurements (ASTM C 373 - 88; 2005) ... | 64 |
| 3.6.5 | | Water absorption measurement (ASTM C 373- 88; 2005) | 66 |
| 3.6.6 | | Diametral Tensile strength (DTS) | 67 |
| 3.6.7 | | Field Emission Scanning Electron Microscope (FESEM) | 68 |
| 3.6.8 | | X-ray Computed Tomography (CT)..... | 68 |

| | | |
|--------|---|-----|
| 4 | CHAPTER 4 RESULTS AND DISCUSSION | 69 |
| 4.1 | Introduction | 69 |
| 4.2 | Characterization of raw materials..... | 69 |
| 4.2.1 | Mineralogical analysis of clays by using XRD | 69 |
| 4.2.2 | Chemical analysis of the clays, bioresource wastes and ashes..... | 73 |
| 4.2.3 | Characterization of ashes by using XRD..... | 75 |
| 4.2.4 | Thermal analysis of LC and MC | 76 |
| 4.2.5 | Thermal analysis of bioresource wastes | 78 |
| 4.2.6 | Particle size analysis of clays | 81 |
| 4.2.7 | Evaluation of plasticity of clays | 83 |
| 4.2.8 | Microstructural observation of clays by using FESEM..... | 84 |
| 4.2.9 | Microstructural observation of bioresource powders by FESEM . | 86 |
| 4.2.10 | Microstructural observation of cross-section bioresources by using FESEM | 87 |
| 4.3 | Effect of firing on LC clay | 89 |
| 4.3.1 | Firing temperature of the LC clay | 89 |
| | (a) Colour upon firing | 89 |
| | (b) Phase identification by XRD analysis | 90 |
| | (c) Shrinkage..... | 93 |
| | (d) Bulk density, porosity and water absorption | 94 |
| | (e) Diametral tensile strength (DTS)..... | 96 |
| | (f) Microstructural observation by using FESEM..... | 97 |
| 4.3.2 | Effect of firing on MC clay | 99 |
| | (a) Colour upon firing | 99 |
| | (b) Phase identification by XRD analysis | 100 |
| | (c) Shrinkages | 101 |
| | (d) Bulk density, porosity and water absorption | 102 |
| | (e) Diametral tensile strength (DTS)..... | 104 |
| | (f) Microstructural observation by using FESEM..... | 105 |
| 4.4 | Effects of KP addition to the LC clay powder | 107 |
| 4.4.1 | Phase identification by XRD analysis | 107 |
| 4.4.2 | Shrinkage and density..... | 109 |
| 4.4.3 | Porosity and water absorption | 110 |
| 4.4.4 | Diametral tensile strength (DTS)..... | 112 |

| | | |
|-------|--|-----|
| 4.4.5 | Microstructural observation by using FESEM | 112 |
| 4.4.6 | X-ray computed tomography observation | 114 |
| 4.5 | Effect of KF addition to the LC clay powder | 115 |
| 4.5.1 | Phase identification by XRD analysis | 115 |
| 4.5.2 | Shrinkage and density..... | 118 |
| 4.5.3 | Porosity and water absorption | 119 |
| 4.5.4 | Diametral tensile strength (DTS)..... | 120 |
| 4.5.5 | Microstructural observation by using FESEM | 121 |
| 4.5.6 | X-ray computed tomography observation | 122 |
| 4.6 | Effect of BW addition to the LC clay body..... | 124 |
| 4.6.1 | Phase identification by XRD analysis | 124 |
| 4.6.2 | Shrinkage and Density..... | 126 |
| 4.6.3 | Porosity and Water absorption | 128 |
| 4.6.4 | Diametral tensile strength (DTS)..... | 129 |
| 4.6.5 | Microstructural observation by using FESEM | 130 |
| 4.6.6 | X-ray Computed tomography observation | 131 |
| 4.7 | Effects of SC addition to the LC clay powder..... | 133 |
| 4.7.1 | Phase identification by XRD analysis | 133 |
| 4.7.2 | Shrinkage and Density..... | 135 |
| 4.7.3 | Porosity and Water absorption | 136 |
| 4.7.4 | Diametral tensile strength (DTS)..... | 137 |
| 4.7.5 | Microstructural observation by using FESEM | 138 |
| 4.7.6 | X-ray computed tomography observation | 139 |
| 4.8 | Effect of KP addition to the MC clay powder..... | 141 |
| 4.8.1 | Phase identification by XRD analysis | 141 |
| 4.8.2 | Shrinkage and Density..... | 142 |
| 4.8.3 | Porosity and Water absorption | 144 |
| 4.8.4 | Diametral tensile strength (DTS)..... | 146 |
| 4.8.5 | Microstructural observation by using FESEM | 147 |
| 4.8.6 | X-ray computed tomography observation | 148 |
| 4.9 | Effect of KF addition into the MC clay powder..... | 149 |
| 4.9.1 | Phase identification by XRD analysis | 149 |
| 4.9.2 | Shrinkage and Density..... | 150 |
| 4.9.3 | Porosity and Water absorption | 152 |

| | | |
|--------|---|-----|
| 4.9.4 | Diametral tensile strength (DTS)..... | 154 |
| 4.9.5 | Microstructural observation by using FESEM | 154 |
| 4.9.6 | X-ray computed tomography observation | 156 |
| 4.10 | Effect of BW addition to the MC clay powder..... | 157 |
| 4.10.1 | Phase identification by XRD analysis | 157 |
| 4.10.2 | Shrinkage and Density..... | 158 |
| 4.10.3 | Porosity and Water absorption | 159 |
| 4.10.4 | Diametral tensile strength (DTS)..... | 160 |
| 4.10.5 | Microstructural observation by using FESEM..... | 161 |
| 4.10.6 | X-ray computed tomography observation | 162 |
| 4.11 | Effect of SC addition into the MC clay | 163 |
| 4.11.1 | Phase identification by XRD | 163 |
| 4.11.2 | Shrinkage and Density..... | 165 |
| 4.11.3 | Porosity and Water absorption | 166 |
| 4.11.4 | Diametral tensile strength (DTS)..... | 168 |
| 4.11.5 | Microstructural observation by using FESEM | 168 |
| 4.11.6 | X-ray computed tomography observation | 169 |
| 4.12 | Summary of different types bioresource additions in both clay bodies... 170 | |
| 4.12.1 | The LC clay/ bioresource wastes..... | 171 |
| (a) | Phase identification by XRD analysis | 171 |
| (b) | Shrinkage and Density..... | 172 |
| (c) | Porosity and Water absorption | 174 |
| (d) | Diametral tensile strength (DTS)..... | 176 |
| (e) | Microstructural observation by using FESEM..... | 176 |
| (f) | X-ray computed tomography observation | 177 |
| 4.12.2 | The MC clay/bioresources waste..... | 178 |
| (a) | Phase identification by XRD analysis | 178 |
| (b) | Shrinkage and Density..... | 179 |
| (c) | Porosity and Water absorption | 181 |
| (d) | Diametral tensile strength (DTS)..... | 182 |
| (e) | Microstructural observation by using FEESM..... | 183 |
| (f) | X-ray computed tomography observation | 184 |
| 4.13 | Comparison of LC and MC clay properties | 185 |

| | |
|---|-----|
| CHAPTER 5 CONCLUSION AND RECOMMENDATION | 188 |
| 5.1 Conclusions..... | 188 |
| 5.2 Suggestions for future work..... | 189 |
| REFERENCES..... | 190 |
| APPENDIX..... | 205 |
| LIST OF PUBLICATION..... | 206 |

LIST OF TABLES

| | | Page |
|------------|---|-------------|
| Table 2.1 | The properties of the clay minerals | 13 |
| Table 2.2 | Properties of porous ceramic materials | 29 |
| Table 2.3 | Several techniques found in literatures that have been used for fabrication of porous clay ceramics | 36 |
| Table 2.4 | Density and porosity of porous clay ceramics | 41 |
| Table 3.1 | The standard speed of centrifugation for the separation of clay minerals | 54 |
| Table 4.1 | Mineral content of the raw clays and with their <2 µm clay fractions | 72 |
| Table 4.2 | XRF results of raw clays, raw bioresource and bioresource ash powders | 74 |
| Table 4.3 | Endothermic and exothermic DSC peaks observed for LC and MC clays | 78 |
| Table 4.4 | Summary of TG analysis results of raw bioresource wastes | 80 |
| Table 4.5 | Summary of DSC analysis results of raw bioresource wastes | 81 |
| Table 4.6 | Atterberg plasticity of the LC and MC clays | 83 |
| Table 4.7 | Colour change of LC clay specimens upon firing | 90 |
| Table 4.8 | Quantitative identification of crystalline phases of fired LC clay at different temperatures | 92 |
| Table 4.9 | Colour change MC clay specimens upon firing. | 99 |
| Table 4.10 | Quantitative identifications of crystalline phases of MC after firing at different temperature | 101 |
| Table 4.11 | Quantitative identification of crystalline phases in the LC/KP mixtures fired at different temperatures | 108 |
| Table 4.12 | Quantitative identification of crystalline phases in LC/KF mixtures fired at different temperatures. | 117 |
| Table 4.13 | Quantitative identification of crystalline phases in the LC/BW mixtures fired at different temperatures | 125 |
| Table 4.14 | Quantitative identification of crystalline phases in the | 134 |

| | | |
|------------|--|-----|
| | LC/SC mixtures fired at different temperatures | |
| Table 4.15 | Quantitative identification of crystalline phase in the MC/KP mixture fired at different temperatures | 142 |
| Table 4.16 | Quantitative identification of the crystalline phases in MC/KF mixtures fired at different temperatures | 150 |
| Table 4.17 | Quantitative identification of crystalline phases in the MC/BW mixtures fired at different temperatures | 158 |
| Table 4.18 | Quantitative identification of crystalline phases in the MC/SC mixtures fired at different temperatures | 164 |
| Table 4.19 | Summary quantitative identified of LC/bioresource wastes at fired 1125°C | 171 |
| Table 4.20 | Comparison, quantitative identified of MC/bioresource wastes at fired 1125°C | 179 |
| Table 4.21 | Summary of the properties on both clays added with 30 wt% of bioresource wastes fired at 1125°C with a soaking time of 3 hours | 186 |
| Table 4.22 | Typical values of porosity | 187 |

LIST OF FIGURES

| | | Page |
|-------------|--|-------------|
| Figure 2.1 | Layers structures of clay minerals | 11 |
| Figure 2.2 | Structure of the main clay minerals: (a) kaolinite, (b) illite and (c) montmorillonite based on combined sheets | 14 |
| Figure 2.3 | FESEM images of illite kaolinite clay minerals | 15 |
| Figure 2.4 | XRD patterns of kaolinite fired at various temperatures | 17 |
| Figure 2.5 | Highlights of the types of waste being recycled process | 21 |
| Figure 2.6 | Diffusion processes | 23 |
| Figure 2.7 | The clay particles (a): before drying, (b): after drying and (c): after firing | 24 |
| Figure 2.8 | FESEM micrographs of various types of porous ceramic materials produced by different methods (a): polymeric sponge, (b): polymers such as PMMA, (c): Granular poppy-seed and (d): Fibers | 27 |
| Figure 2.9 | Fabrication of porous clay ceramics using pore forming agent | 33 |
| Figure 2.10 | X-ray diffraction patterns of the clay mixed with granite (10-40 wt%) when fired at 1100°C | 39 |
| Figure 2.11 | Water absorption with the incorporation of different waste materials | 42 |
| Figure 2.12 | Mechanical strength with the incorporation of different waste materials | 43 |
| Figure 2.13 | The FESEM images of the fired samples containing paper waste addition of (a): 0wt%, (b):10wt.%, (c):20 wt% and (d): 30 wt% | 44 |
| Figure 3.1 | Flow chart of sampling and preparation of clay powder samples | 47 |
| Figure 3.2 | The location of LC clay study area in Laos | 48 |
| Figure 3.3 | The location of MC clay study area in Perak state of Malaysia | 48 |
| Figure 3.4 | The dried raw clay samples (a, c): before grinding, (b, d): | 50 |

| | | |
|-------------|---|----|
| | after grinding and sieving | |
| Figure 3.5 | The kenaf samples (a): kenaf trees (b): kenaf core and kanaf bast (c,e): dried fiber and bast before grinding and (d,f): after grinding | 51 |
| Figure 3.6 | The banana sample (a): banana tree, (b): stem waste of (c) dried outer skin before grinding and (b) after grinding and sieving | 51 |
| Figure 3.7 | The sugarcane sample (a): sugarcane trees, (b): sugarcane stem, (c): Dried sample of sugarcane waste before grinding and (d) after grinding and sieving | 52 |
| Figure 3.8 | Sedimentations of clay sample to produce $<2\mu\text{m}$ clay fraction | 53 |
| Figure 3.9 | Flowchart for processing of clay ceramics | 59 |
| Figure 3.10 | Schematic diagram showing for pressing | 60 |
| Figure 3.11 | Flowchart for production of porous clay ceramic | 62 |
| Figure 3.12 | The firing profile of specimens | 63 |
| Figure 3.13 | Schematic illustration of the liquid displacement method for measuring density and porosity of a porous specimen | 66 |
| Figure 3.14 | The definition of diametral tensile strength test in clay ceramic materials | 67 |
| Figure 4.1 | XRD patterns of the raw clay (a): LC clay and (b): MC clay | 70 |
| Figure 4.2 | XRD patterns of the $< 2\mu\text{m}$ clay fraction (a): LC clay (b): MC clay | 71 |
| Figure 4.3 | XRD patterns of oriented $<2\mu\text{m}$ clay fractions of (a): LC and (b): MC clays | 72 |
| Figure 4.4 | XRD patterns of bioresource ashes fired at 1100°C | 75 |
| Figure 4.5 | TG/DSC curves of the LC raw clay powder | 76 |
| Figure 4.6 | TGA/DSC curves of the MC raw clay powder | 77 |
| Figure 4.7 | TGA curves different of raw bioresource wastes | 79 |
| Figure 4.8 | DSC curves different of raw bioresource wastes | 81 |
| Figure 4.9 | Particle size distributions of the clay samples | 82 |
| Figure 4.10 | Location of LC and MC samples on the Casagrande chart | 84 |

| | | |
|-------------|---|-----|
| Figure 4.11 | FESEM images of the raw clay powders (a): LC and (b): MC | 85 |
| Figure 4.12 | EDX results of the raw clay minerals in (a): LC and (b): MC clay samples | 86 |
| Figure 4.13 | FESEM images of raw bioresource (a): KP; (b): KF; (c): BW and (d): SC powders after their grinding | 87 |
| Figure 4.14 | FESEM micrographs of the cross-sections of different types of bioresource wastes: (a), (c), (e), (g) surface structures and (b), (d), (f) and (h) longitudinal surfaces of the KP, KF BW and SC | 88 |
| Figure 4.15 | The colour of LC pellets fired at different temperatures for 3 hours | 90 |
| Figure 4.16 | XRD patterns with fired different temperatures (a): raw material of powder; (b): 1100; (c): 1150; (d): 1200 and (e): 1250°C | 92 |
| Figure 4.17 | The thickness and diameter shrinkages of the LC clay specimens fired at different temperatures | 94 |
| Figure 4.18 | Density, porosity and water absorption of LC clay specimens fired at different temperatures | 95 |
| Figure 4.19 | Strength of the LC clay specimens fired at different temperatures | 96 |
| Figure 4.20 | FESEM micrographs of the fracture surfaces of LC clay specimens fired at different temperatures of (a): 1100, (b): 1125, (c): 1150, (d): 1175, (e): 1200, (f): 1225 and (g): 1250°C | 98 |
| Figure 4.21 | The colour of MC pellets fired at different temperatures for 3 hours | 99 |
| Figure 4.22 | XRD patterns of MC specimen, raw and fired at different temperatures (a): raw, (b): 1100, (c): 1150, (d): 1200 and (e): 1250°C | 101 |
| Figure 4.23 | The thickness and diameter of shrinkages of the MC clay specimens fired at different temperatures | 102 |
| Figure 4.24 | Density, porosity and water absorption of the MC clay | 103 |

| | | |
|-------------|---|-----|
| | specimens after firing at different temperatures | |
| Figure 4.25 | Strength of the MC clay specimens fired at different temperatures | 104 |
| Figure 4.26 | FESEM images of the fracture surface of MC clay specimens fired at different temperatures of (a): 1100, (b): 1125, (c):1150, (d):1175, (e): 1200, (f): 1225 and (g):1250°C | 106 |
| Figure 4.27 | XRD patterns of LC30KP fired at different temperatures (a): 1100; (b): 1125; (c): 1150 and (d): 1175°C | 107 |
| Figure 4.28 | The diameter shrinkage of the fired LC clay-KP mixture versus KP content at different temperatures | 110 |
| Figure 4.29 | Density of the fired LC clay-KP mixture versus KP content at different temperatures | 110 |
| Figure 4.30 | Porosity of the fired LC clay-KP mixture versus KP content at different temperatures | 111 |
| Figure 4.31 | Water absorption of the fired LC clay-KP mixture versus KP content at different temperatures | 111 |
| Figure 4.32 | Strength of the fired LC clay-KP mixture versus KP content at different temperatures | 112 |
| Figure 4.33 | FESEM micrographs of fracture surface of the LCKP mixture versus KP content (10, 20 and 30 wt%) fired at: (a, b, c): 1100; (d, e, f): 1125, (g, h, i):1150, (j, k, l):1175°C. | 113 |
| Figure 4.34 | CT-images of the LCKP mixture versus KP content (10 & 30 wt.%) fired at :(a, b): 1100; (c,d): 1125, (e, f):1150, (g, h):1175°C | 115 |
| Figure 4.35 | XRD patterns of LC30KF fired at different temperatures (a):1100°C; (b): 1125°C; (c): 1150°C and 1175°C | 116 |
| Figure 4.36 | The diameter shrinkage of the fired LC clay-KF mixture versus KF content at different temperatures | 118 |
| Figure 4.37 | Density of the fired LC clay-KF mixture versus KF content at different temperatures | 119 |
| Figure 4.38 | Porosity of the fired LC clay-KF mixture versus KF | 120 |

| | | |
|-------------|---|-----|
| | content at different temperatures | |
| Figure 4.39 | Water absorption of the fired clay-KF mixture versus KF content at different temperatures | 120 |
| Figure 4.40 | Strength of the fired LC clay-KF mixture versus KF content at different temperatures | 121 |
| Figure 4.41 | FESEM micrographs of fracture surface of the LCKF mixture versus KF content (10 & 30 wt%) fired at : (10, 20 and 30 wt%) fired at: (a, b, c): 1100; (d, e, f): 1125, (g, h, i):1150; (j, k, l):1175°C | 122 |
| Figure 4.42 | CT-images of the LCKF mixture versus KF content (10 and 30wt.%) fired at (a): (a, b): 1100°C; (c, d): 1125°C; (e, f): 1150°C and (g, h): 1175°C | 124 |
| Figure 4.43 | XRD patterns of LC30BW fired at different temperatures (a): 1100; (b): 1125 and (c): 1150 and (d): 1175°C | 125 |
| Figure 4.44 | The diameter shrinkage of the fired LC clay-BW mixture versus BW content at different temperatures | 127 |
| Figure 4.45 | Density of the fired LC clay-BW mixture versus BW content at different temperatures | 128 |
| Figure 4.46 | Porosity of the fired LC clay-BW mixture versus BW content at different temperatures | 129 |
| Figure 4.47 | Water absorption of the fired LC clay-BW mixture versus BW content at different temperatures | 129 |
| Figure 4.48 | Strength of the fired LC clay-BW mixture versus BW content at different temperatures | 130 |
| Figure 4.49 | FESEM micrographs of the fracture surface of the LCBW mixture versus BW content (10, 20 and 30 wt%) fired at: (a, b, c): 1100; (d, e, f): 1125, (g, h, i):1150, (j, k, l):1175°C | 131 |
| Figure 4.50 | CT- images of the LCBW mixture versus BW content (10 and 30 wt.%) fired at (a): (a, b): 1100°C; (c, d): 1125°C; (e, f): 1150°C and (g, h): 1175°C | 132 |
| Figure 4.51 | XRD patterns LC30SC fired at different temperatures (a): 1100; (b): 1125; (c): 1150 and (d): 1175°C | 133 |

| | | |
|-------------|--|-----|
| Figure 4.52 | The diameter shrinkage of the fired LC clay-SC mixture versus SC content at different temperatures | 135 |
| Figure 4.53 | Density of the fired LC clay-SC mixture versus SC content at different temperatures | 136 |
| Figure 4.54 | Porosity of the fired LC clay-SC mixture versus SC content at different temperatures | 137 |
| Figure 4.55 | Water absorption of the fired LC clay-SC mixture versus SC content at different temperatures | 137 |
| Figure 4.56 | Strength of the fired LC clay-SC mixture versus SC content at different temperatures | 138 |
| Figure 4.57 | FESEM micrographs of the fracture surface of the LCSC mixture versus SC content (10, 20 and 30 wt%) fired at: (a, b, c): 1100; (d, e, f): 1125, (g, h, i):1150, (j, k, l):1175°C | 139 |
| Figure 4.58 | CT-images of the LCSC mixture versus SC content (10 and 30wt.%) fired at (a): (a, b): 1100°C; (c, d): 1125°C; (e, f): 1150°C and (g, h): 1175°C | 140 |
| Figure 4.59 | XRD patterns MC30KP after firing at different temperatures (a): 1100; (b): 1125 and (c): 1150°C | 142 |
| Figure 4.60 | The diameter shrinkage of the fired MC clay-KP mixture versus KP content at different temperatures | 143 |
| Figure 4.61 | Density of the fired MC clay-KP mixture versus KP content at different temperatures | 144 |
| Figure 4.62 | Porosity of the fired MC clay-KP mixture versus KP content at different temperatures | 145 |
| Figure 4.63 | Water absorption of the fired MC clay-KP mixture versus KP content at different temperatures | 145 |
| Figure 4.64 | Strength of the fired MC clay-KP mixture versus KP content at different temperatures | 146 |
| Figure 4.65 | FESEM micrographs of fracture surface of the MCKP mixture versus KP content (10, 20 and 30 wt%) fired at: (a, b, c): 1100; (d, e, f): 1125 and (g, h, i):1150°C | 147 |
| Figure 4.66 | CT-images of different temperature of the MCKP mixture | 148 |

| | | |
|-------------|---|-----|
| | versus KP content (10 & 30 wt.%) fired at : (a, b): 1100; (c, d): 1125 and (e, f):1150°C | |
| Figure 4.67 | XRD patterns of MC30KF fired at (a): 1100°C, (b): 1125 and (c):1150°C | 149 |
| Figure 4.68 | Shrinkage of the fired MC clay-KF mixture versus KF content at different temperatures | 151 |
| Figure 4.69 | The density of the fired MC clay-KF mixture versus KF content at different temperatures | 152 |
| Figure 4.70 | Porosity of the fired MC clay-KF mixture versus KF content at different temperatures | 153 |
| Figure 4.71 | Water absorption of the fired MC clay-KF mixture versus KF content at different temperatures | 154 |
| Figure 4.72 | Strength of the fired MC clay-KF mixture versus KF content at different temperatures | 154 |
| Figure 4.73 | FESEM micrographs of fracture surface of the MCKF mixture versus KF content (10, 20 and 30 wt%) fired at: (a, b, c): 1100; (d, e, f): 1125 and (g, h, i):1150°C | 155 |
| Figure 4.74 | CT-images of the MCKF mixture versus KF content (10 & 30 wt%) fired at: (a, b): 1100; (c, d): 1125 and (e, f):1150°C | 156 |
| Figure4.75 | XRD patterns of MC30BW fired samples (a): 1100°C, (b): at 1125 and (c): 1150°C | 157 |
| Figure 4.76 | Shrinkage of the fired MC clay-BW mixture versus BW content at different temperatures | 159 |
| Figure 4.77 | Density of the fired MC clay-BW mixture versus BW content at different temperatures | 159 |
| Figure 4.78 | Porosity of the fired MC clay-BW mixture versus BW content at different temperatures | 160 |
| Figure 4.79 | Water absorption of the fired MC clay-BW mixture versus BW content at different temperatures | 160 |
| Figure 4.80 | Strength of the fired MC clay-BW mixture versus BW content at different temperatures | 161 |
| Figure 4.81 | FESEM micrographs of fracture surface of the MCBW | 162 |

| | | |
|-------------|--|-----|
| | mixture versus BW content (10, 20 and 30 wt%) fired at: (a, b, c): 1100; (d, e, f): 1125 and (g, h, i):1150°C | |
| Figure 4.82 | CT-images of the MCBW mixture versus BW content (10 & 30 wt%) fired at: (a, b): 1100; (c, d): 1125 and (e, f):1150°C | 163 |
| Figure 4.83 | XRD patterns of MC30SC fired samples (a): 1100°C, (b): 1125 and (c):1150°C | 164 |
| Figure 4.84 | Shrinkage of the fired MC clay-SC mixture versus SC content at different temperatures | 165 |
| Figure 4.85 | Density of the fired MC clay-SC mixture versus SC content at different temperatures | 166 |
| Figure 4.86 | Porosity of the fired MC clay-SC mixture versus SC content at different temperatures | 167 |
| Figure 4.87 | Water absorption of the fired MC clay-SC mixture versus SC content at different temperatures | 167 |
| Figure 4.88 | Strength of the fired MC clay-SC mixture versus SC content at different temperatures | 168 |
| Figure 4.89 | FESEM micrographs of fracture surface of the MCSC mixture versus SC content (10, 20 and 30 wt%) fired at : (a, b, c): 1100; (d, e, f): 1125 and (g, h, i):1150°C | 169 |
| Figure 4.90 | CT-images of the MCSC mixture versus SC content (10 & 30 wt%) fired at : (a, b): 1100; (c, d): 1125 and (e, f):1150°C | 170 |
| Figure 4.91 | XRD patterns of LC clay/bioresource waste specimens with (30 wt%) of wastes (a): LC30KP, (b):LC30KF, (c): LC30BW and (d): LC30SC were fired at 1125°C | 171 |
| Figure 4.92 | Shrinkages the LC clay with different bioresource waste fired at 1125°C | 173 |
| Figure 4.93 | Densities the LC clay with different bioresource waste fired at 1125°C | 174 |
| Figure 4.94 | Porosities the LC clay of adding different bioresource waste fired at 1125°C | 175 |
| Figure 4.95 | Water absorption the LC clay of adding different | 175 |

| | | |
|--------------|--|-----|
| | bioresource waste fired at 1125°C | |
| Figure 4.96 | Strength of the LC clay with different bioresource waste fired at 1125°C | 176 |
| Figure 4.97 | FESEM micrographs of fracture surface of the LC clay with adding 30wt% of different wastes content fired at 1125°C | 177 |
| Figure 4.98 | CT-images of LC clay addition 30 wt% of different bioresource wastes fired at 1125°C | 178 |
| Figure 4.99 | XRD patterns of MC30SC fired samples (a): MC30KP, MC30KF, MC30BW and MC30SC fired at 1125°C | 179 |
| Figure 4.100 | Shrinkage the MC clay of with different bioresource waste fired at 1125°C | 180 |
| Figure 4.101 | Density the MC clay of adding different bioresource waste fired at 1125°C | 181 |
| Figure 4.102 | Porosity the MC clay of adding different bioresource waste fired at 1125°C | 182 |
| Figure 4.103 | Water absorption the MC clay of with different bioresource waste fired at 1125°C | 182 |
| Figure 4.104 | Strength the MC clay of with different bioresource waste content fired at 1125°C | 183 |
| Figure 4.105 | FESEM micrographs of fracture surface of porous clay ceramic with adding of different waste contents and fired at 1125°C | 184 |
| Figure 4.106 | CT-images of MC clay addition 30 wt% of different bioresource wastes fired at 1125°C | 185 |

LIST OF ABBREVIATIONS

| Abbreviation | Full names |
|---------------------|-----------------------------------|
| BW : | Banana stem waste |
| CT : | Computed Tomography |
| D : | Density |
| DSC : | Differential Scanning Calorimetry |
| DTS : | Diametral Tensile Strength |
| FD : | Firing shrinkage in Diametral |
| FL : | Firing shrinkage in Length |
| KF : | Kenaf fibre |
| KP : | Kenaf powder |
| LC : | Laotian clay |
| LL : | Liquid Limit |
| LOI : | Loss In ignition |
| MC : | Malaysian clay |
| P : | Porosity |
| PI : | Plastic Index |
| PL : | Plastic limit |
| rpm : | rounds per minute |
| SC : | Sugarcane cane waste |
| SEM : | Scanning Electron Microscopy |
| TGA : | Thermal gratuity Analysis |
| WA : | Water Absorption |
| XRD : | X-ray Diffraction |
| XRF : | X-ray Fluorescence |

PEMBANGUNAN JASAD SERAMIK TANAH LIAT BERLIANG MENGUNAKAN EMPAT JENIS SUMBER BIO TERBUANG

ABSTRAK

Objektif utama kajian ini ialah untuk mengesahkan kemungkinan untuk menghasilkan bahan seramik tanah liat berliang. Bahan mentah yang digunakan adalah terdiri daripada tanah liat berkaolinit dari Laos (LC) dan tanah liat berilit dari Malaysia (MC) yang dicampur dengan sumber bio terbuang (serbuk kenaf, gentian kenaf, sisa batang pisang dan hampas tebu) sebagai agen pembentuk liang (PFA). Pencirian serbuk mentah tanah liat LC dan MC serta sisa sumber bio dijalankan terlebih dahulu menggunakan XRF, XRD dan TGA/DSC. Beberapa jenis dan amaun sisa sumber bio yang berbeza telah dicampur ke dalam jasad anum tanah liat. Amaun sisa yang digunakan adalah 10, 20 dan 30 % berat. Campuran serbuk tergranul telah dimampat dengan penekan hidraulik menggunakan acuan keluli tahan karat berdiameter 23 mm pada tekanan 50MPa. Pemerhatian menunjukkan penggunaan sisa sumber bio tidak mendatangkan sebarang masalah kepada pembentukan sampel. Selepas dikeringkan, jasad anum seramik dibakar pada suhu berbeza (1100, 1125, 1150 dan 1175°C) selama 3 jam pada kadar 5°C/min. Kesan penambahan sisa ke atas sifat-sifat seramik berliang dinilai melalui ujian pengecutan, ketumpatan pukal, keliangan, serapan air, kekuatan mampatan, mikroskop imbasan electron (FESEM) dan tomografi komputer. Analisis XRD mengesahkan komposisi mineral bahan mentah tanah liat adalah kuarza dan kaolinit sebagai fasa utama dalam tanah liat LC, manakala tanah liat MC mengandungi fasa kuarza dan illit. Selepas pembakaran, hanya fasa hablur kuarza dan mulit yang dikesan. Kesemua sisa sumber bio berjaya menghasilkan jasad berliang seramik bagi kedua-dua tanah liat (LC dan MC) pada

darjah yang berbeza. Kajian ini juga berjaya mengesahkan bahawa kesan relatif setiap sumber bio ke atas kedua-dua tanahliat adalah sama. Sebagai contoh, sisa hampas tebu memberikan keliangan yang tertinggi pada semua suhu bakar dan peratus kandungan yang diuji. Ini diikuti oleh gentian kenaf, serbuk kenaf dan sisa batang pisang. Sejar ini, sifat lain seperti ketumpatan akan menjadi yang terendah mengikut urutan sisa yang telah dinyatakan. Selain itu juga, kajian mikrostruktur menggunakan kaedah tomografi komputer memberi maklumat tambahan yang berguna terhadap bentuk liang disamping imej 3 dimensi yang dihasilkan dengan FESEM. Sebagai kesimpulan, hasil kerja ini telah berjaya membuktikan bahawa sisa sumber bio boleh menyumbang terhadap pembangunan teknologi hijau yang berkaitan dengan penghasilan jasad seramik berliang.

DEVELOPMENT OF POROUS CERAMIC CLAY BODIES USING FOUR DIFFERENT TYPES OF BIORESOURCE WASTES

ABSTRACT

The main objective of this study is to ascertain the possibility of fabricating porous clay ceramic materials. The raw materials consist of a kaolinitic Laotian clay and an illitic Malaysian clay, mixed with bioresource wastes (kenaf powder, kenaf fiber, banana stem and sugarcane wastes) as the pore-forming agents (PFA). The raw powders, i.e. Laotian clay (LC), Malaysian clay (MC) and bioresource wastes were initially characterized using XRF, XRD and TGA/DSC. The clay ceramic green bodies were fabricated with different types and amounts of bioresource wastes in the clay bodies (10, 20 and 30 wt%). The granulated powder mixtures were pressed hydraulically using a round stainless steel mould 23 mm diameter, under a pressure of 50MPa. It was observed that different types of bioresource waste additions did not create any shaping problems. After drying, the ceramic green bodies were fired at different temperatures (1100, 1125, 1150 and 1175°C) for 3 hours at a heating rate of 5°C/min. The effects of adding these wastes on the properties of the porous clay ceramics were assessed by shrinkage, density, porosity, water absorption, compressive strength, scanning electron microscopy (FESEM) and computed tomography (CT) tests. XRD analyses confirmed that the mineralogical composition of the raw clays consisted of quartz and kaolinite as the major minerals in the LC clay, whilst illite and quartz were in the MC clay. Upon firing, the crystalline phases detected were only quartz and mullite. All the four bioresource wastes were successful in producing porous ceramic bodies in both clays but with varying degrees of porosity. This work had succeeded in establishing that the relative effects of the

different bioresourc e wastes were the same. For example, the sugarcane waste gave the highest porosity at all temperatures and percentages tested. This was followed by kenaf fibre, kenaf powder and banana stem wastes. Correspondingly, property such as density will be the lowest for the sequence of wastes mentioned. It was also established that the microstructural study using computed tomography provided useful additional information on the shape of the pores apart from the 3- dimensional image by FESEM. In conclusion, this work has successfully proven that bioresource wastes can contribute towards promoting green technology with regards to porous ceramic body production.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Over the last few years, there have been increasing interests in porous ceramic materials which are particularly important for ceramics and other industrial applications (Perez-villarejo et al., 2012; Sutcu and Akkurt, 2009). For industrial applications, porous ceramics with open-pores are required for gas and liquid filtration (Li et al., 2008a), membrane support and purification (Dong et al., 2006), whilst porous ceramics with closed-pore are suitable for thermal insulation and structural components because of their good thermal shock resistance and low specific gravity, respectively (Barea et al., 2005; García et al., 2010).

Clays are one of the most important raw materials for producing porous ceramic materials and have been widely used today, because clay materials are of low cost. Nowadays, several techniques for producing porous clay ceramics include addition of organic compounds as pore-forming agents (PFA). Porous clay-based ceramics are also useful where there is a need for high abrasion resistance (Kiyoshi et al., 2010; Kizinievič et al., 2013). These qualities are dependent on the chemical composition of the clays, the fabrication methods and firing temperatures (Malaiškienė et al., 2011; Rafael et al., 2005). The purpose of firing is to improve the durability of the clay products and that is achieved through vitrification. Vitrification is the bonding process of clay particles that can only be achieved under the influence of heat as similarly reported by Liu et al., (2011).

In general, porous clay ceramics are based on natural clays, such as kaolin, where there is a high volume fraction of a glassy phase due to the vitrification of impurities in the clays. The porosity in a material also affects changes in mechanical properties. A highly open porosity is desirable to increase of the specific surface area (Plappally et al., 2011), but an increase in the porosity also decreases the mechanical strength (Demir et al., 2005; Demir, 2006; 2008). High open porosity may be required concurrently in order to use porous materials under severe operating conditions (Alves et al., 2012).

Therefore, the preparation of porous ceramics with controlled of microstructure has been a subject of constant interest during the last decades. Common processing techniques include dipping (sponge method) and so-gel techniques (Gregorova and Pabst, 2007). The foams produced by dipping (sponge method) produce large pores and high porosity whilst the so-gel technique produces pores in the nanometer size range and extremely high porosity (Gregorova and Pabst, 2007). There are also other methods such as biomimetic processing (using pyrolyzed wood templates), ceramic hollow spheres process and sacrificial (pyrolyzable) pore forming agents (PFA), i.e. natural biopolymers which burn out during firing (Korat et al., 2013; Shujing et al., 2008; Wen et al., 2008). A number of PFAs have been proposed and used in porous ceramic technology such as polyvinyl chloride, polystyrene, polyethylene (Hwu et al., 2002; Jui-Ming Yeha and Sheng-Chieh Hsua, 2009), rice husk (Atta et al., 2012; Görhan and Şimşek, 2013), paper waste and tea waste (Demir, 2006).

1.2 Problem statements

Clays are one of the most abundant natural materials on earth. In general terms, clays have good properties such as high strength, low thermal expansion, high thermal shock resistance and, most importantly, they are readily available at low cost when compared to other ceramic materials like Al_2O_3 , ZrO_2 , SiO_2 , TiO_2 and SiC . Clays have been widely used as a raw material with many industrial applications such as ceramics, paper, paint, petroleum industry and catalysis (Kizinievič et al., 2013). Their applications are tightly dependent on their structures, as well as their chemical composition and physical properties (Meseguer et al., 2010; Njoya et al., 2012; Pardo et al., 2011a). Knowledge of these properties is very important for understanding the technology of ceramic fabrication and the optimization of the firing schedules (Alcântara et al., 2008; Gaidzinski et al., 2011).

In this study, porous clay ceramics were fabricated using two clays deposits and in this regards two types of clay were used i.e. one from Lao, PDR and one from Malaysia. The Lao PDR clay (LC clay) has so far been used for brick making only. Furthermore, there are not many available literature on Laotian clays. So this work aims to diversify the use of the Laotian clay and also to increase the literature on clay from Laos. The Malaysian clay (MC) has been used for cosmetic and flux in welding rods. So this work aims to diversify its use.

The volume of wastes from daily human activities and industrial production continue to increase rapidly in tandem with a growing world population (Mucahit et al., 2012). Most nations are considering controls on industrial products in order to reduce the rate of solid waste generation. Local and regional governments worldwide

have mandated wastes to be separated for recycling. Many countries in the world, especially the developing countries, see industrialisation as a necessity to build self-reliance and uplifting the nation's economy (Rambaldi et al., 2007; Raut et al., 2011). In most cases, the wastes are thrown away in dumps or dispose by open firing. Here, environmental pollution is a major problem associated with rapid industrialisation, urbanisation and rise in living standards of the people (Pardo et al., 2011). The different types of wastes can be sourced from 2 groups, viz those that can be classified as industrial wastes (granite dust, marble dust, glass rejects and petroleum waste) (Monteiro et al., 2004; Eliche-Quesada et al., 2011), and those that can be classified as wastes of bioresource origin (sawdust, starch, tea waste, rice husk, palm husk, and paper waste) (Sutcu and Akkurt, 2010; Atta et al., 2013).

Accumulation of unmanaged industrial or agricultural solid waste especially in developing countries has resulted in an increased environmental concern (Şan et al., 2009). At present, various governments have imposed that all household units have to manage their wastes in terms of reuse and recycling. Recycling of the wastes as a sustainable material appears to be a viable solution, not only to pollution problems but also as an economical option to reuse the waste materials (Cusido and Cremades, 2012). Recycling of waste materials is rapidly increasing and becoming very important today. The utilizations of wastes are intended to reduce the negative effects of their disposal towards the improvement in the quality of life (Eliche-Quesada et al., 2011).

The natural bioresource wastes are one of the important materials that have been widely used for the construction industry, apart from being soil organic and

environmental friendly (George et al., 2002; Chen et al., 2012). They also have other potentialities such as to conserve non-renewable resources, save energy, improve human health, environmental friendly, and most importantly, readily available and of low cost when compared to other materials (Demir, 2008; Raut et al., 2011).

Recently, there has been an increasing interest in the applications of porous ceramic materials in many industrial areas (Shujing et al., 2008). Clay as the ceramic raw material is one of the most important candidate materials to form porous ceramic with good performances. The creation of porous ceramic material is attractive because its properties are more stable in severe environments and can be engineered to satisfy specific requirements (Bai, 2010; Alonso-Santurde et al., 2012).

Porous clay ceramic materials can be developed by several techniques, via the adding of chemicals, polymers, industrial wastes and bioresource wastes as the pore-forming agents (PFA). PFA has been widely used in the development of porous clay ceramics (Korat et al., 2013).

Different types of pure raw ceramic materials (Al_2O_3 , ZrO_2 , SiC and TiO_2), polymers (PMMA, polystyrene foam and PVA), and composite materials were also used to prepare the porous ceramic materials. However, these materials are of high cost and need high firing temperatures (Hwu et al., 2002). Other materials that influence the development of porous clay ceramics have witnessed the incorporation of industrial wastes (granite dust, marble dust, waste glass and petroleum waste) into ceramic bodies. Nowadays, the range of materials used is increasingly worldwide.

As an example, Vieira et al. (2004) have evaluated the effect of granite dust incorporation into a ceramic clay body.

Lastly, it can be seen that the development of porous clay ceramics has been carried out by using bioresource wastes (rice husk, sawdust and tea waste and coffee waste) as PFAs. Several types of different bioresource wastes have also been used as the raw material to develop porous clay ceramics. Şan et al. (2009) reported the successful investigation of the effect of rice husk additives on the porosity of fired clay. Demir (2006; 2008) also investigated the organic nature of the tea waste in clay ceramic bodies. Many authors conducted and demonstrated that by using bioresource waste materials of high potentialities that can save energy, cost of production and enhance porous clay ceramic quality (Chen et al., 2011; Fangli et al., 2009; Fethi et al., 2006).

This study compares the properties of porous ceramics by adding different bioresource wastes e.g. kenaf powder, kenaf fibre, banana stem waste and sugarcane waste as pore-forming agents (PFAs). Previous studies in many research works have shown the successful incorporation of chemicals, polymers, industrial wastes and some bioresource wastes. Unfortunately, no researcher has studied the use of kenaf powder, kenaf fibre, banana stem waste and sugarcane waste in terms of incorporations to develop porous clay ceramics. The types of pores produced (open or closed) will be part of this study. Different type of the green raw materials (clays and bioresource wastes) can be used to ensure a more comfortable way of life, energy saving and environmental friendliness. It is believed that this approach of using clays and bioresource wastes is a step for promoting green technology.

1.3 Objectives of the study

Therefore, the objectives of this research are:

- ❖ To study two raw clay materials i.e. Laotian clay (LC) and Malaysian clay (MC), in order to increase knowledge and literature on the vitrification behaviours of the two clays upon firing.
- ❖ To study the use of kenaf powder, kenaf fibre, banana stem waste and sugarcane waste as pore-forming agents (PFA), in terms of incorporations to develop porous clay ceramics and the consequent properties.

1.4 Scope of research

In general, the research work is divided into two parts that are described in detail as follows. The first part is the preparation of the Laotian clay (LC) to obtain results after firing at different temperatures. Then selected temperatures were chosen for firing of clay body mixed with bioresource wastes (kenaf powder, kenaf fiber, banana stem waste and sugarcane waste) respectively at different amounts. Similarly, the second part is the preparation of the Malaysian clay (MC) which was fired on its own before being followed with bioresource wastes additions into the clay body. The products produced were then characterized for all properties such as XRD, density, porosity, water absorption, strength, and morphology using a Field Emission Scanning Electron Microscope (FESEM) as well as computed topography (CT).

CHAPTER 2

LITERATURE REVIEW

2.1 Types of clays

Clay is the oldest ceramic raw material. Clay has been defined as a geological deposit, less than 2 micron in size, that forms a coherent sticky mass when mixed with water and hardens when fired. It consists primarily of hydrated aluminium silicates and widely used in the manufacture of many traditional clay-based ceramics such as the bricks, tile, pottery and cements (Gualtieri et al., 2010; Jordán et al., 1999; Jordán et al., 2009). The mineralogical and chemical compositions of clays determine the ceramic behavior such as plasticity, shrinkage upon drying and firing fineness of grain and colour after firing (Jordán et al., 2009). There are four main types of clays.

2.1.1 Kaolin (China clay)

Kaolin is a primary clay formed over many millions of years by the decomposition of granite rocks (Horrocks, 2005). Normally, it is deposited near the parent rock without much transportation. Hence, kaolin is almost pure and has bigger particle size. Kaolin is normally white in colour and is used in ceramic bodies for its whiteness, e.g. paper filler, paper coating, paints, etc.

2.1.2 Ball clays

Ball clay is a secondary clay deposit formed after the decomposition products of granitic rocks are transported by rain, snow, etc. As such, the particles size is finer and it contains more impurities compared to kaolin. Ball clay is valued for its high

plasticity, dry strength, green strength, bonding nature, etc. The high plasticity facilitates shaping and finishing of ceramic bodies, and the high strength allows undried clay article to keep their shape and withstand all types handling (Aras, 2004; Bruce and Meunier, 2008).

2.1.3 Fireclays

Fireclay, like the china clays and ball clays was formed by the kaolinisation of feldspars. It is also a secondary clay and normally deposited together with fallen trees that turned into coal under pressure over long periods of time. Hence, fireclay is normally formed together with coal deposits. (Horrocks, 2005; Lee and Yeh, 2008). Fireclay find restricted use in some sanitary ware bodies, but find their main usage in refractory products (Jordán et al., 1999; Jordán et al., 2009).

2.1.4 Bentonites

This is a general term for clays containing smectites (or montmorillonites) as the main clay mineral. The clay minerals are not kaolinite compared to the previous three clay types. The clay mineral has a structure that can absorb water between the layers of the structure. This interlayer absorption results in swelling of the clay and hence this type of clay is termed an expanding clay (Gualtieri et al., 2010; Lingling et al., 2005), often used in cosmetics and drilling muds. Although they are extremely plastic and show very high dry strength, bentonites are never used in high proportion in whiteware bodies since they induce very high drying shrinkage and adversely affect deflocculation characteristics (Meseguer et al., 2010).

2.2 Types of clay mineral groupings

Clay minerals are layer silicates that are formed usually as products of chemical weathering of other silicate minerals on the Earth's surface (Cultrone et al., 2005; Garrido-Ramírez et al., 2010). There are three main groups of clay minerals.

2.2.1 Kaolinite group

This includes kaolinite, dickite, nacrite, and halloysite, which are formed by the decomposition of orthoclase feldspar (e.g. granite).

2.2.2 Illite group

This includes hydrous micas, phengite, brammalite, celadonite, and glauconite (a green clay sand) formed by the decomposition of some micas and feldspars predominantly in marine clays and shales.

2.2.3 Smectite group

This includes of the montmorillonite, bentonite, nontronite, hectorite, saponite and sauconite, formed by the alteration of mafic igneous rocks rich in Ca and Mg, and form weak linkage by cations (e.g. Na⁺, Ca²⁺).

2.3 Structure of clay minerals

The different types of clay minerals result in unique chemical and behavioral properties due to the structure and arrangements of the aluminium silicate building blocks (Kwame et al., 2012). The two basic building blocks of all clay minerals are the silica tetrahedron and the aluminum octahedron (Garrido-Ramírez et al., 2010). When scientists talk about the 1:1 or 2:1 clays, it is based on the number and

arrangement of the tetrahedral (silica) and octahedral (alumina-magnesia) sheets contained in the crystal units.

The layer structure of clays minerals can be classified into two different groups.

- (a) the 1:1 clay minerals consisted of one tetrahedral sheet and one octahedral sheet, and examples would be kaolinite and serpentine,
- (b) the 2:1 clay mineral consisted of an octahedral sheet sandwiched between two tetrahedral sheets as in illite, smectite, attapulgite and chlorite.

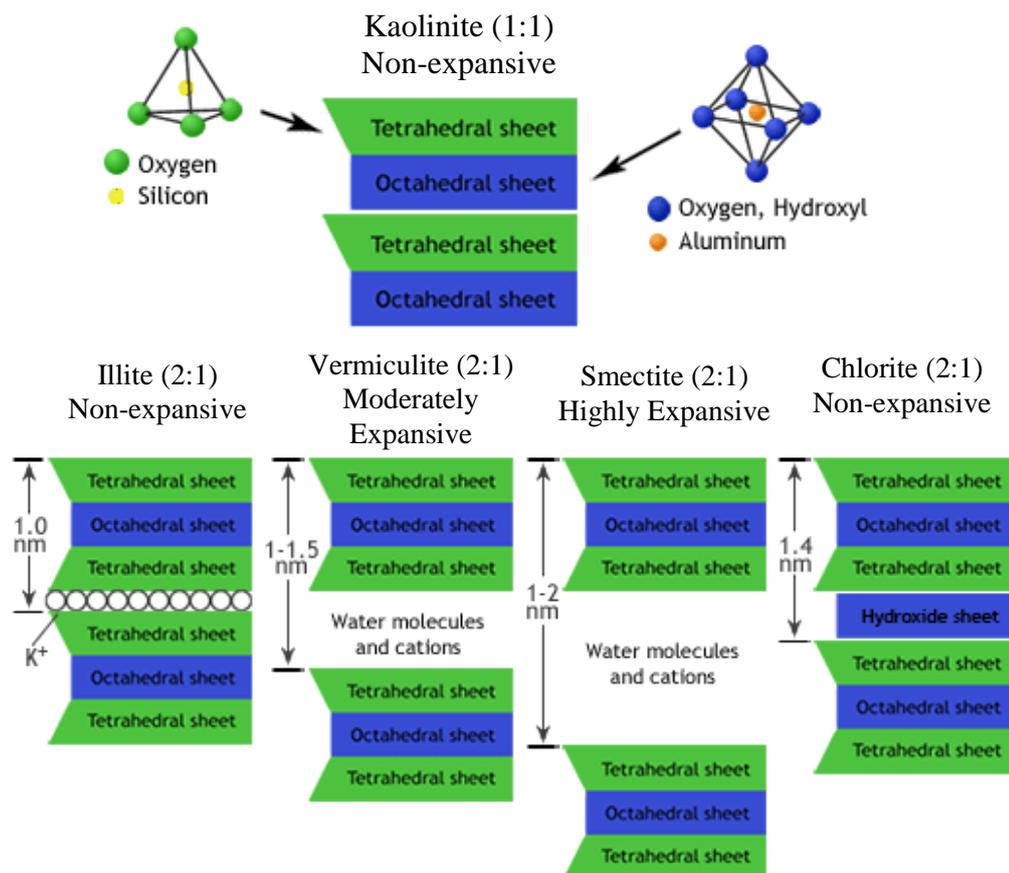


Figure 2.1: Layers structures of clay minerals (Brindley and Brown, 1980)

Kaolinite is a two layer 1:1 silicate, ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), and is the principal example of its group. It is structurally formed by one layer of tetrahedral silica (SiO_2) and one layer of octahedral gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) and bearing no cations or H_2O molecules between the structural layers (George et al., 2002). It is well-known that kaolinitic clays is one the most widely used clay as raw material in the manufacture of ceramics (pottery, tile and whitewear), cements (Guggenheim, 1995).

The 2:1 types of clay minerals are divided into two parts, i.e. expanding layer and non-expanding layer as shown follows.

Expanding layer: The 2:1 group (mostly, montmorillonite) is structurally formed by three layer of clay minerals e.g. Tetrahedron - Octahedron - Tetrahedron (TOT) layers as presented in Figure 2.1. Table 2.1 shows the properties of clay minerals (Bruce and Meunier, 2008).

Non-Expanding layer: The fine-grained micas or illite is a phyllosilicate or layered clay. Its structure is constituted by the repetition of Tetrahedron – Octahedron – Tetrahedron (TOT) layer as presented in Figure 2.1. The interlayer space is about 10 \AA and is mainly occupied by poorly hydrated potassium cations responsible for the absence of swelling (Buchwald et al., 2009). Structurally illite is quite similar to muscovite with slightly more silicon, magnesium, iron, and water, and slightly less tetrahedral aluminum and interlayer potassium (Meseguer et al., 2011). Summary of the clay properties is also shown in Table 2.1.

Table 2.1: The properties of the clay minerals

| Formula | Properties |
|---|---|
| <p style="text-align: center;">Kaolinite: $(Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O)$</p> | <p>Fixed layer type</p> <ul style="list-style-type: none"> - No shrink-swell - No interlayer activity - Low cation adsorption - Larger particle size (0.1 - 5 μm) |
| <p style="text-align: center;">Illite: $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(HO)]$</p> | <p>Very limited expansion</p> <ul style="list-style-type: none"> - Medium cation adsorption - Limited internal surface - Properties between kaolinite and vermiculite - Very fine-grained |
| <p style="text-align: center;">Montmorillonite: $(Na,Ca)_{0,3}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot n(HO)$</p> | <p>Freely expanding</p> <ul style="list-style-type: none"> - Water in interlayer - Large shrink-swell - Large internal surface - Poorly crystallized - Small size - Large cation adsorption |

By comparison, to the illite and kaolinite, the swelling behavior of montmorillonite is beneficial in many applications such as nanocomposites (Guggenheim, 1995), but causes problems in ceramic processing by affecting ceramic suspensions and in fired products (Kwame et al., 2012). Structures and formulas of kaolinite, illite and montmorillonite are presented in Figure 2.2

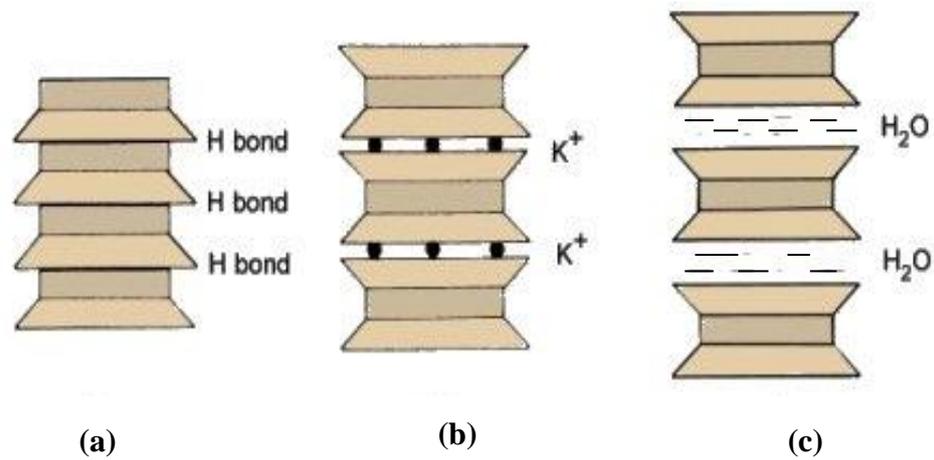


Figure 2.2: Structure of the main clay minerals: (a) kaolinite, (b) illite and (c) montmorillonite based on combined sheets (Bruce and Meunier, 2008)

2.3.1 Physical properties of the clay minerals

The properties of clay minerals include plasticity, shrinkage upon firing and air-drying, fineness of grain, colour after firing, hardness, cohesion, and capacity of the surface (Dionisio et al., 2009). On the basis of such qualities, clays are variously divided into classes or groups. Kaolinite exists only as very small, hexagonally shaped platy crystals, varying from less than 0.1 μm to 2 μm in diameter, although occasionally larger crystals of up to 20 μm in diameter are formed (Cultron et al., 2005). The kaolinite particles are flaky in shape. Some large kaolin flakes are stacked together to form agglomerates.

Since clay minerals are so small, they are best observed under an electron microscope. The montmorillonite consist of thin, platy crystals, so small that their shape is difficult to discern, even with the electron microscope. An estimate of the illite sizes is in range from 0.1 to 2 μm in diameter. The illites are very fine-grain particles, as small as 0.05 μm (Figure 2.3a), as compared to kaolinite (Figure 2.3b) and montmorillonite (Kwame et al., 2012).

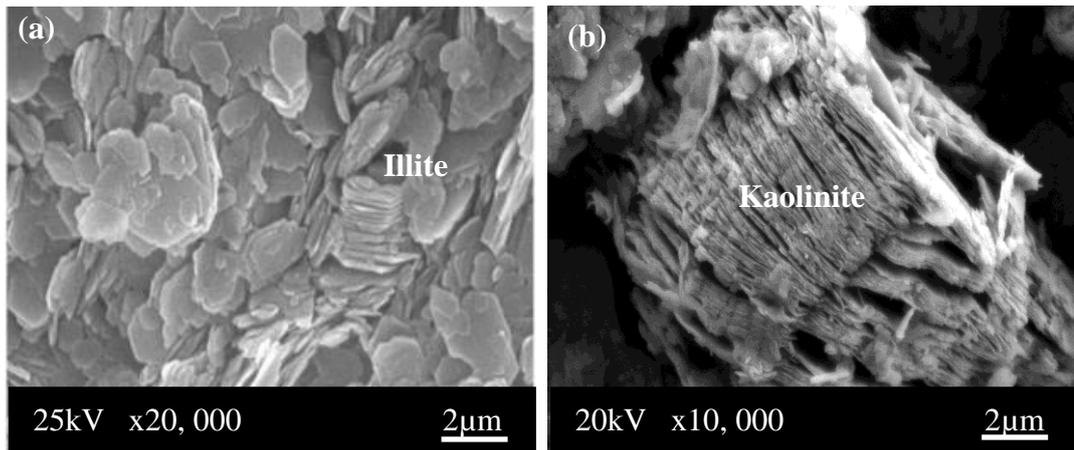
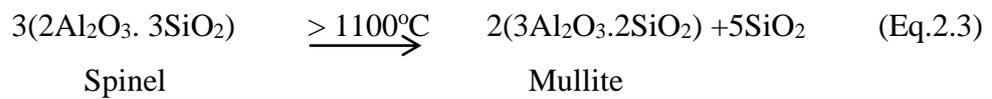
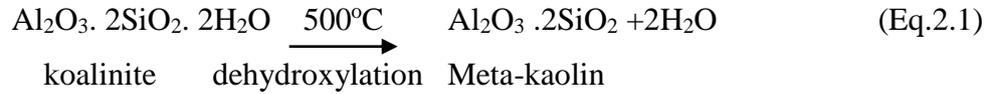


Figure 2.3: FESEM images of (a): illite and (b): kaolinite clay minerals (Aras, 2004)

2.3.2 Effect of heat on the clay minerals and phases of transformation

Many researchers studied the structural modifications of clay minerals especially kaolinite during dehydration (Bakr, 2011). Most hydrated minerals lose water when they are heated. This effect of heat on clay minerals as a pure kaolinite has attracted a great deal of attention, including natural phase composition, microstructure, physical, chemical, mechanical properties and colour changes which determine predominantly their ceramic properties (Chen et al., 2004). These changes vary significantly according to the type of clay (Safeer et al., 2008). Clays may be classified on the basis of their chemical composition, softening point, melting behavior, mineralogical composition, and plasticity. Since clays are produced from natural deposits formed during various long geological processes, they are complex mixtures of different minerals. Clays usually contain clay minerals, such as kaolinitic and or illitic, and accessory minerals such as quartz, feldspars, smectites, micas, etc. These minerals influence remarkably the firing behavior, which makes it extremely difficult to formulate a rigid classification of clays (Bakr, 2011). It has been known that, after the removal of adsorbed water at just over 100°C, kaolinite decomposes above about 500°C. This process is called dehydroxylation and the product is

metakaolin. Further heating cause phase transformations as presented by the following Equations:



The phase transformation of kaolinite can be monitored by differential thermal analysis. The dehydroxylation reaction is an endothermic peak occurring at 600°C for well crystallised kaolinite and about 580°C for disordered kaolinite. About 700°C, the clay mineral breaks down, giving up water of constitution to form metakoalin and an amorphous form of silica (Trindade et al., 2009; Vieira et al., 2008). On being heated to a higher temperature, the metakaolin undergoes further reactions to form crystalline compounds and the end products are free silica and mullite as shown in Figure 2.4. X-ray work strongly suggests that mullite is not formed until much higher temperature are attained i.e. 1200 - 1600°C as reported by Chen et al., (2000a) and presented in Figure 2.4.

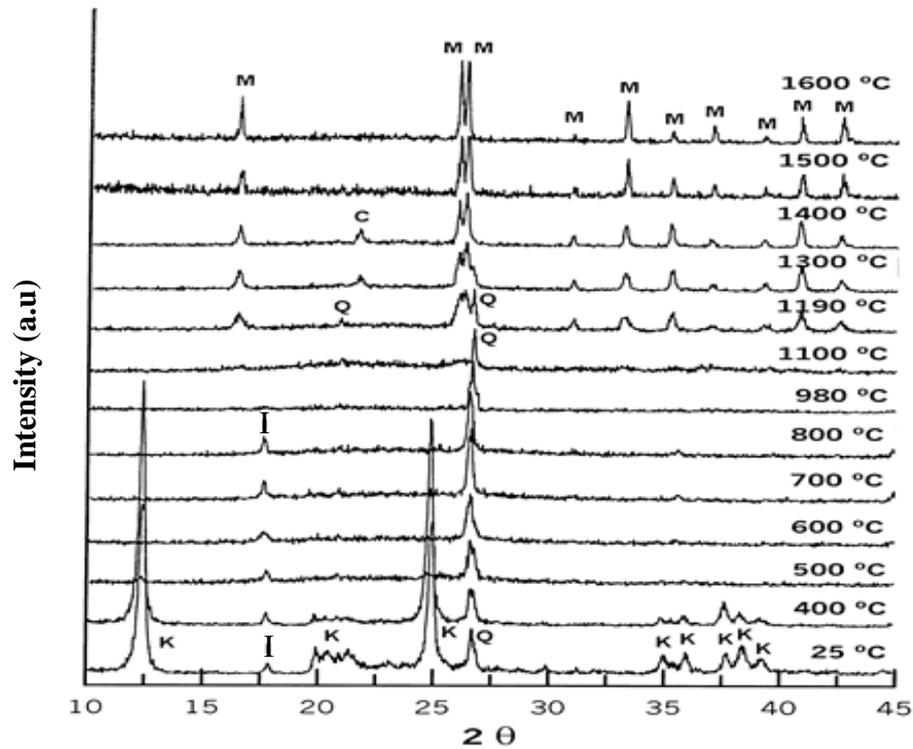


Figure 2.4: XRD patterns of kaolinite fired at various temperatures (Chen et al., 2000a)

K: Kaolinite; Q: Quartz; I: Illite and M: Mullite

2.3.3 The effect of impurities

Naturally occurring clays in general contains minerals other than kaolinite, the most common being quartz and mica, although a large number of minor constituents, notably pyrite (FeS_2), oxides of iron, calcite (CaCO_3) dolomite (CaMgCO_3), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and anatase (TiO_2). One of the most important effects of impurities is that due to fluxing ions namely, Na, K, Ca and Mg, derived from micas and other compounds (Bruce and Meunier, 2008; Dionisio et al., 2009).

2.3.4 Thermal decomposition of illite

Data on the decomposition of muscovite (the equivalent to illite) are somewhat conflicting. Some researchers have reported a gradual loss of water at

temperatures up to about 850°C, while others maintain that there is a period of relatively rapid dehydration between 450 and 850°C. Similar results have been reported for phlogopite and biotite (Aras, 2004). Illites have decomposition characteristics remarkably similar to those of kaolinite. Thus, there is a small loss of water below 100°C and major evolution of water between 350 and 600°C. However, it is reported that the structure of illite is not completely destroyed until a temperature of 850°C is attained (Buchwald et al., 2009).

2.4 Bioresource

A bioresource is any resource that is biological or natural in origin. The main chemical composition consists of organic matter e.g. cellulose, hemicellulose, lignin, etc. Nowadays, bioresource is attractive and more important in order to promote the utilization of natural resources. It is necessary to understand of their properties and performances (Liu et al., 2009; Zhang et al., 2013).

2.4.1 Bioresource wastes

Bioresource wastes included all types waste that are no longer of any use and are intended to be thrown away. There are many types of wastes e.g. rice husk, coffee husk, sugarcane waste and many others (Atta et al., 2012). Thus, all daily activities can give rise to a large diversity of wastes from different sources. Bioresource wastes are attractive and important to extent the application of resources (Deepa et al., 2011; Zhang et al., 2013). Bioresource wastes are one of the very important materials that have been widely used in many fields today such as construction industry, fertilizer, etc. These potentialities such as conservation of renewable resources, source of energy(biomass), environmental friendly (no toxic

chemical), and most importantly, they are readily available and of low cost when compared other materials (Ounas et al., 2011).

2.4.2 Kenaf

Kenaf (*Hibiscus cannabinus* L), is a member of the Malvaceae family and is grown in tropical and subtropical regions. It is an important source of fibres for use in polymer composites and other industrial applications (Macías-García et al., 2012). Many countries in the world have planted kenaf trees especially in Malaysia, India, Bangladesh, Thailand, and to a small extent in Southeast Europe and some parts of Africa, as well as in Brazil where it is cultivated throughout the year (Akil et al., 2011; Amel et al., 2013). In the early-1970s, it was first introduced in Malaysia, and then in the late 1990s it was recognized to be of potential to manufacture particleboard and fibreboard (Abdul Khalil et al., 2010). Kenaf stem comprises of two distinct parts, i.e. the core and the bast (the core is the woody inner part, and the bast is the fibrous outer bark), with a makeup of about 35% and 65%, respectively (Elsaid et al., 2011; Herbert et al., 1999). The core is light and also highly porous compared to the bast. The kenaf core (KP) and kenaf bast or fibre (KF) have different chemical compositions. The bast is higher in cellulose whilst the core is higher in hemicellulose and lignin. Both parts are also very different in morphologies. Nowadays, there are many applications that have been made using kenaf core (KP) and kenaf bast (KF) including pulp, paper products, bio-composites, automotive door trimmings and interior shelving. In Malaysia, realizing the diverse possibilities of commercially exploitable derived products from kenaf, the National Kenaf Research and Development Program has been formed in an effort to develop kenaf as a possible new industrial crop for Malaysia. The government has

allocated RM 12 million for research and further development of the kenaf-based industry under the 9th Malaysia Plan (2006 – 2010) in recognition of kenaf as a commercially viable crop (Edeerozey et al., 2007; Jonoobi et al., 2011; Ninomiya et al., 2012).

2.4.3 Banana stem waste

Banana is one of the most important fruit crops and widely cultivated in tropical and subtropical countries. After the fruit has been harvested, the rest of the plant would be cut and thrown away. Generally, banana by-products include the stem (pseudostem), leaves, inflorescence, fruit stalk (floral stalk), rhizome, and peels (Zhang et al., 2013). The banana stem waste can be used for several processes, such as pulping in the paper industry and for making natural fibers, animal feeds, and biofuels (Satyanarayana et al., 2007; Sgriccia et al., 2008; Ververis et al., 2007).

2.4.4 Sugarcane waste (SC)

Sugarcane crop is planted in more than 110 countries in the world. The largest producers in the world include Brazil, India, China, and Thailand (Faria and Holanda 2012). Jackson et al. (2011) have reported that during 2008/2009 harvest, more than 629 million tons of Brazilian sugarcane were crushed, which generated around 229 million tons of solid waste. In 2012/2013, it has increased very rapidly by generating about 597 million tons of solid wastes (Faria and Holanda 2012). This waste material is mainly reused in the industry as fuel in boilers for energy co-generation of around 4 million tons per year, from the Brazilian sugarcane waste generated (Guimarães et al., 2009). Meanwhile, the rest of the waste has been

mainly used as soil fertilizer and others. The ceramics sector can incorporate large amounts of sugarcane waste materials without additional process modifications (Sutcu and Akkurt, 2009).

2.4.5 Recycling of wastes

Recently, the development of technology has led to the treatment of larger quantities of wastes, improvements in properties and a reduction in harmfulness of the wastes generated (Eliche-Quesada et al., 2011; 2012; Martínez-García et al., 2012; Perez-Villarejo et al., 2012). Recycling is a suitable method for subsequent reuse of these wastes, either in its original form or in pre-treated forms. It includes recycling of organic wastes and include energy recovery. Recycling benefits the environment by reducing the use of virgin materials. Many different materials can be recycled (Faria et al., 2012; Martínez-García et al., 2012). It can also be seen that numerous waste materials from industries have been used such as from mining, industrial activities and construction processes. Figure 2.5 shows that the largest fraction of recycled wastes is paper (35%), followed by organic materials (25%) as reported by Chen et al., (2012).

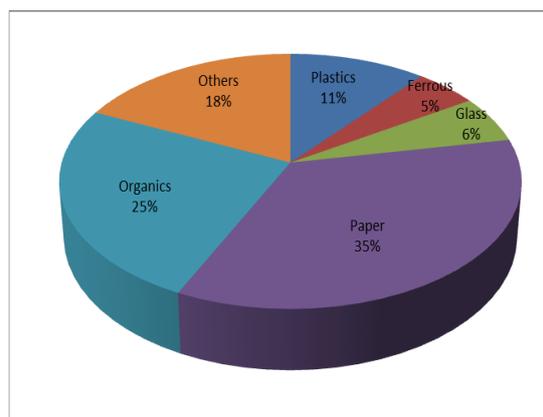


Figure 2.5: Highlights of type waste after reducing and recycling process (Martínez-García et al., 2012)

2.5 Firing of clays

Firing forms a key stage in the fabrication route of ceramics where a compacted powder or specimen is heated to a certain temperature and converted to a dense body by removal of pores between the starting particles (Chen et al., 2000a; Fangli et al., 2009). It involves heating of powder compacts at elevated temperatures, where diffusional mass transport is appreciable which results in a dense polycrystalline solid (Johari et al., 2010; Lecomte-Nanna et al., 2011). A ceramicist, physicist, chemist and metallurgist have to work together to produce a material with particular properties, identify the required microstructure, and then design the processing conditions that will produce the required microstructure (Ptáček et al., 2012). The objectives of firing studies are therefore normally carried out to identify and understand how the processing variables such as temperature, particle size, soaking duration, applied forming pressure, composition and firing atmosphere influence the microstructure that is produced (Yürüyen and Toplan, 2009). Thermodynamically, firing is an irreversible process in which during this process the constituent atoms redistribute themselves in such a way so as to reduce the energy in the system (Gualtieri et al., 2010; Lee and Yeh, 2008). It involves association of the powder compact by diffusion on an atomic scale, occasioning in a decrease of the surface area and grain boundary formation, neck growth between particles and densification of the system (Alonso-Santurde et al., 2011; Dionisio et al., 2009; Dubois et al., 1995; Johari et al., 2010; Jordán et al., 1999). The effect of firing temperature variations on the physical properties and microstructure of the finished product have always been a subject of great importance in ceramic literature since several decades ago (Chen et al., 2000b; Fangli et al., 2009; Lecomte- Nana et al., 2011; Monteiro et al., 2004). Through the different diffusion mechanisms, matter

moves from the particles into the void spaces (Figure 2.6) between the particles causing densification and resulting in shrinkage of the part and thus microstructural developments will occur (Ptáček et al., 2012; Romero et al., 2008). Several variables influence the rate of densification. Some of them are initial density, type of material, particle size, firing atmosphere, temperature, time and heating rate (Johari et al., 2010; Jordan et al., 2008). Figure 2.6 shows the diffusion process in the sintering phenomena which is of two types, viz. 1) Solid-state sintering, where all densification is achieved through changes in particle shape. 2) liquid-phase firing, where some liquid is present at the firing temperatures to aid compaction (Chen et al., 2000a; Buchwald et al., 2009).

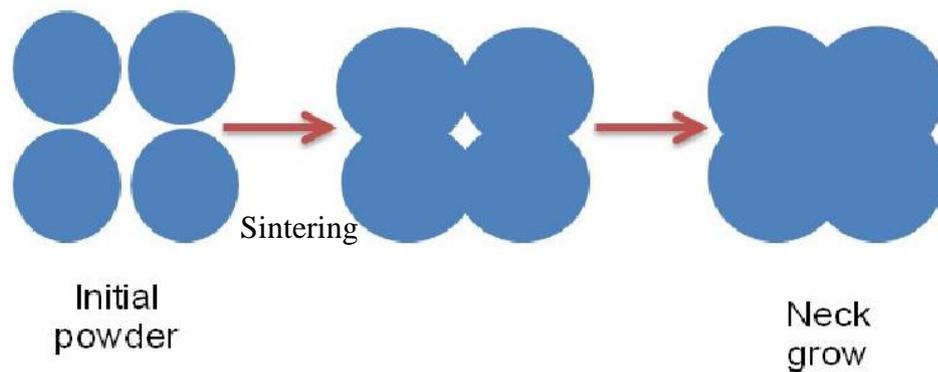


Figure 2.6: Diffusion processes (Chen et al., 2000a)

All clays upon being heated to a high temperature will form a viscous liquid, which consists principally of silica, together various impurities such as Na_2O , K_2O , CaO and MgO . These oxides lower the melting point of silica, enabling liquid to form at a comparatively low temperature of 1200°C , and for this reason are called fluxing oxides (Guggenheim, 1995).

2.5.1 The drying and firing of clays

The influence of drying conditions can be evaluated by adopting a standard drying method at 110°C for 24 hours. The drying of clays is of considerable technological importance. When a plastic clay body is dried, shrinkage occurred. If drying is rapid and uneven, the shrinkage may give rise to cracks in the products. When completely dry, clays have considerable strength (Monfort et al., 2008; Rodrigues et al., 2012; Lee and Yeh, 2008).

Figure 2.7(a) shows that as drying proceeds, water evaporates from the outer surface and the particles of clay is drawn progressively closer together by surface tension forces. Eventually, the particles will come into mutual contact (Figure 2.7(b)), forming loosely packed assembly. When this stage has been reached no further contraction is possible during drying and no further shrinkage occurs. The residual water is contained in the voids between particles (Yürüyen and Toplan, 2009), and the water content at this stage is known as the critical moisture content. Further drying now results in the loss of water from the pores of the body, then water is being drawn to the surface by capillary action. Thus, the original packing is maintained and air replaces the water in the pores resulting finally in a dry porous body (McConville and Lee, 2005; Sahnoune et al., 2008).

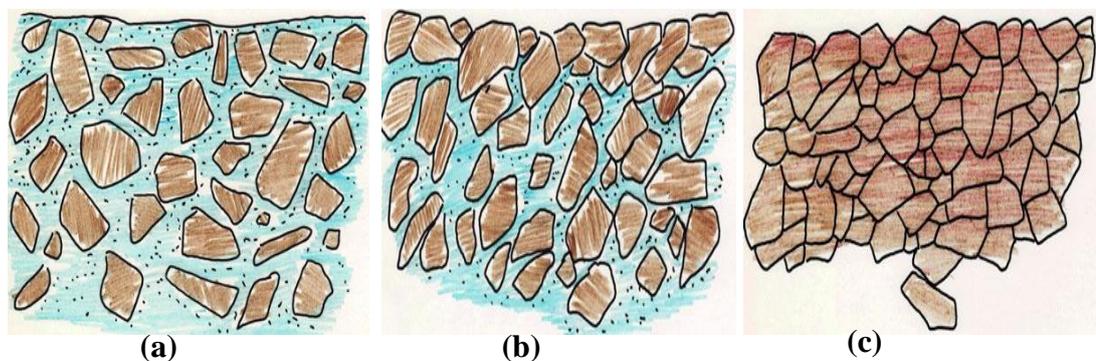


Figure 2.7: The clay particles (a): before drying, (b): after drying and (c): after firing (Lee and Yeh, 2008)