Characterization of duck egg shells and bioceramic materials in making denture applications

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Abstract. Duck egg shells contain higher calcium which potent to be use as materials of denture-bio-ceramic. Denture bioceramics were made from feldspar, quartz, kaolin, and duck egg shells. In this work, characterization and synthesis hydroxyapatite from duck egg shells as bioceramics for the manufacturing of artificial tooth was carry out. X-Ray Diffraction (XRD) was used to analyze the characteristics of hydroxyapatite. Synthesis hydroxyapatite from duck egg shells were produced calcium (Ca) is 99.63%, and CaO is 99.41%. Furthermore, calcination methods were used by XRD. The XRD results at the calcination temperature of 900°C were feldspar CaO content of 96.87%, SiO$_2$ of 1.85%, quartz CaO of 1.58%, SiO$_2$ of 95.47%, and Kaolin CaO of 68.08%. Among of three various samples used, sample of B with compositions of Ca and Si are 62.89, and 26.89, XRD results of eggshell powder produced the largest CaO compound at a burning temperature of 900°C for 1 hour with a hexagonal-shaped compound with a Ca / P ratio of 1.61. respectively has good result. In addition, bioceramics obtained is in accordance to standard manufacturing of denture. Therefore, synthesis hydroxyapatite from Duck egg shells contains very high calcium which is component that potential to be used for Dentures based bioceramic.

1. Introduction
The development of ceramics is a new breakthrough, especially in terms of bioceramics development. Bioceramics are a well-known implant material and are widely used for repair, replacement, bone and teeth. [1]. In dentistry and medicine, ceramics are one of the important materials used for the reconstruction and replacement of decaying or damaged dental and medical materials [2]. One of the materials that has the potential as a bioceramic material that is very easy to obtain is egg shells[3]. Egg shells have very high calcium which can be used in the development of medical science technology, especially in dentistry[4]. Eggshells consist of a network of protein fibers, linked to crystals of calcium carbonate (CaCO$_3$), magnesium carbonate (MgCO$_3$) and calcium phosphate (Ca$_3$(PO$_4$)$_2$), as well as organic matter and water.

CaCO$_3$, the main constituent of eggshells (96%), is an amorphous crystal that occurs naturally in the form of calcite (hexagonal crystals)[5]. In general, eggshells are considered to have no economic value, whereas in fact eggshells are rich in minerals and amino acids that can form and be used in the basis of several industries, especially the health industry in the field of dentistry. [6] Synthetic HA finds application in various medical and dental applications as a promising material for healing damaged bones and teeth[7]. Hydroxyapatite (HA) has been widely used as an implant material due to its close similarity in composition to natural bone. Many studies have shown that HA ceramics show no toxicity, no inflammatory response, no pyrogenetic response, no fibrous tissue formation between implant and bone, and the ability to bond directly to the host bone[8]. HA powders derived from natural materials
such as bovine bone, fish bone, oyster shell or coral inherit some properties of the raw materials such as pore structure and carbonate content[9] Calcium oxide (CaO) is produced by pyrolysis of calcium carbonate at 900 °C in 1 hour[2] Dentures made of porcelain based ceramic consist of feldspar, quartz and kaolin.

This denture has several advantages, namely the higher the mechanical properties, the color can be adjusted to the natural teeth, and has good biocompatibility.[10] A ceramic material made by mixing kaolin, quartz, and feldspar in the right proportions and fired at high temperatures [11]. Several previous studies have developed bioceramic dentures from various materials obtained from nature such as feldspar, quartz, kaolin and added egg shell powder from chicken egg shells,[2] blood clam shells[12], cow bone[13]. In this study, we conducted a preliminary study by testing the characterization of natural basic materials that are used as a basis for making artificial teeth applications with the addition of duck egg shell powder to improve the mechanical properties of artificial teeth applications.

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Duck egg shells are used in this study as raw material because they are easy to find around and are abundant. The content of duck egg shells was CaO 99.41% and the sintering process up to 900°C obtained pure hydroxiapatite (HAp) from duck egg shells 41.20%

2. Methodology
2.1 Materials and tools
The material used in this research is natural material in the form of natural sand Feldspar taken from Bira Bulukumba beach, Kaolin, Quartz, duck egg shell which has been sieved by 200 mesh, LabTech Furnace, XRF, XRD Thermo Scientific and FTIR.

2.2. Preparation of Bioceramic Samples
a. Duck egg shell powder has been crushed then sieved using 200 mesh sieve then to characterization XRF, XRD and FTIR
b. Feldspar, kaolin, quartz sieved using 200 mesh sieve then to characterization XRF and XRD
c. Duck egg shell powder has been crushed then sieved using 200 mesh sieve, and mixed with feldspar, kaolin, and quartz. There are 4 variation composition to characterization by XRF and XRD

| Sample | Total Mass of Material 6 gr |
|--------|---------------------------|
|        | Feldspar   | Quartz    | Kaolin    | Duck Egg Shell |
| A      | 1,5004     | 1,5002    | 1,5004    | 1,5007         |
| B      | 2,4009     | 1,2034    | 1,2015    | 1,2027         |
| C      | 2,0099     | 2,0093    | 1,0019    | 1,0016         |

2.3. Sample Characterization
Characterization of duck egg shell powder and denture application materials by X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD) and the Fourier Transform Infrared (FTIR) which was conducted in Science Laboratory Faculty MIPA Hasanuddin University and Heat Treatment State Polytechnic Ujung Pandang.
3. Results and Discussion

3.1 Characterization of X-Ray Fluorescence (XRF)

The X-Ray Fluorescence spectrometer is used to analyze the chemical composition of duck egg shell powder and the basic materials for the application of dentures, both in the form oxide and chemical composition, see table 2.

| Sample   | Oxide (%)         |
|----------|-------------------|
| SiO2     | 47.90             |
| Al2O3    | 12.31             |
| Fe2O3    | 0.611             |
| CaO      | 38.02             |
| K2O      | 0.52              |
| SrO      | 0.345             |
| TiO2     | 0.233             |

The results of XRF Denture Application Materials which can be seen in table 3 as follows:

| Sample   | Oxide (%)         |
|----------|-------------------|
| SiO2     | 39.86             |
| Al2O3    | 10.61             |
| Fe2O3    | 0.525             |
| CaO      | 47.78             |
| K2O      | 0.44              |
| SrO      | 0.601             |
| TiO2     | 0.129             |

The result of XRF Oxide Composition of Denture Application Samples

| Sample   | Oxide (%)         |
|----------|-------------------|
| SiO2     | 40.77             |
| Al2O3    | 18.34             |
| Fe2O3    | 0.413             |
| CaO      | 35.52             |
| K2O      | 0.40              |
| SrO      | 0.457             |
| TiO2     | 0.113             |

The results of the chemical composition test for denture application samples are in table 5 as follows:

| Sample   | Chemical Composition |
|----------|----------------------|
| Ca       | 54.16                |
| Si       | 34.31                |
| Al       | 8.55                 |
| Fe       | 1.05                 |
| K        | 0.77                 |
| Sr       | 0.716                |
| Ti       | 0.341                |

3.2 Characterization of X-Ray Diffraction (XRD)

The X-Ray Diffraction spectrometer used in materials science to determine the crystallographic structure of duck egg shell powder and the basic materials for the application of dentures the result see figure as follows:

The result XRD Duck Egg Shell Powder in figure 1.
Figure 1. The Result XRD Duck Egg Shell Powder

Based on the XRD duck egg shell powder test, the content contained in it is as table 2 follows:

| Content          | (%) |
|------------------|-----|
| Hydroxyapatite (H) | 40.9 |
| Porlender (P)     | 38.5 |
| Calcium (Ca)      | 9.6  |
| Lime (CaO)        | 2.7  |
| Not detected      | 8.09 |

Table 6. Results of XRD Duck Egg Shell Powder

The results of the XRD test for duck egg shell powder at a temperature of T = 800°C and 900°C for 2 hour in figure 2 are as follows:

3.3. Characterization of Fourier Transform Infrared (FTIR)

The result of characterization of FTIR test by duck egg shell, powder can be seen in the figure 3 as follow:
Figure 3. The Result of FTIR by Duck Egg Shell Powder

The absorption band in the area of wave number 3428 cm\(^{-1}\) indicates the presence of an OH group, this is supported by the absorption of the C-O group at wave number 1068 cm\(^{-1}\). The absorption band in the region of wave number 2976 cm\(^{-1}\) which is the vibration of the Csp\(^3\)-H bond and absorption and in the region of wave number 1425 cm\(^{-1}\) confirms the presence of the methyl group of the C=O group. Meanwhile, the sharp absorption in the wave number 1797 cm\(^{-1}\) indicates the presence of the C=O (carbonyl) group. For absorption at wave number 876 cm\(^{-1}\), the presence of a C-O group and a wave number of 711 cm\(^{-1}\) in the presence of a Ca-O group indicates a stretching vibration of Csp\(^3\)-H on the alkane chain. The numbers on the 900-700 cm\(^{-1}\) wave are also still in the CO category but the typical peak at that time is CaCO\(_3\). The CaO group is a typical peak of asymmetrical vibrations PO\(_3\). The presence of such clusters indicates the egg shell contains phosphate groups. The phosphate group is the group that has the sharpest peak wave number because the main HAp group is a phosphate group [14].

4. Discussion

The Fluorescence X-Ray Spectrometer is used to analyze the chemical composition of bioceramic samples, both in the form of oxides and chemical compositions. The XRF test results of the four natural ingredients as the basis for dentures, namely Kaolin, Quartz, Feldspar and eggshells obtained the results of oxide levels, namely Kaolin SiO\(_2\) of 68.08, which is very good, higher than the standard of 62%, Al\(_2\)O\(_3\) of 26.93% exceeding the standard of 18.79%, Fe2O3 of 2.01%, K2O of 1.36% and TiO2 is 0.64%, although it does not contain CaO, the SiO2 and Al2O3 content increase the strength of porcelain. SiO2 quartz is 95.47 which is very high from the standard of 62%, Fe2O3 is 1.58%, CaO is 1.85%, K2O is 0.758%, SrO is 0.026% and TiO2 is 0.25% even though the CaO content is low but it is covered with SiO2 content. SiO2 feldspar is 1.85%, lower than the standard but CaO is 95.87% which is very high, more than the standard of 58.87%.

The strength of the ceramic is added by the high calcium content which increases the strength of the ceramic. Fe2O3 is 0.392% and TiO2 is 0.073% while CaO duck eggshell is 99.[15]. Of the three samples of denture application materials, sample B is the best for a mixture of denture applications where the Ca chemical composition is 62.89, the Si chemical composition is 26.98, the Al chemical composition is 7.34, the Fe chemical composition is 0.821, the K chemical composition is 0.57, the chemical composition Sr is 1.13 and the Ti chemical composition is 0.173. XRD results of eggshell powder produced the largest CaO compound at a combustion temperature of 900°C for 1 hour with a hexagonal-shaped compound with a Ca/P ratio of 1.61 although it had not yet reached the standard of 1.67[16].
5. Conclusion

Based on the results of research on the characteristics of natural materials as the basis for the manufacture of dentures, it can be concluded that after doing the XRD, XRF and FTIR tests, the composition of natural ingredients in the laboratory can be stated that the four bioceramic materials, namely feldspar, quartz, kaolin and duck egg shells can be used as basic materials in the manufacture of dentures where the chemical composition meets the standards as the basic material for the manufacture of dentures which Synthesis hydroxyapatite from duck egg shells were produced CaO is 99.41% and calcium (Ca) is 99.63%. The XRD results at the calcination temperature of 900°C were feldspar CaO content of 96.87%, SiO$_2$ of 1.85%, quartz CaO of 1.58%, SiO$_2$ of 95.47%, and Kaolin CaO of 68.08%.

Among of three various samples used, sample of B with compositions of Ca and Si are 62.89, and 26.89, XRD results of eggshell powder produced the largest CaO compound at a burning temperature of 900°C for 1 hour with a hexagonal-shaped compound with a Ca / P ratio of 1.61.

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