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Study of the potential utilization of local Lampung Province resources in development of dental implant bioceramics

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Abstract. The increasing of dental implants needs to be supported by local materials' development as a form of independence for a nation. With its rich natural resources, Indonesia has the potential to be used as a dental implant material. Dental implant materials can be in bioceramic materials consisting of bioactive, bioresorbable, and bioinert. One of the bioactive materials of concern today is glass-ceramics from basalt rock. Meanwhile, the hydroxyapatite material sourced from limestone is the most widely used bioresorbable type. These materials, basalt, and limestone are very much found in Indonesia, including Lampung Province. However, the use of these two materials as bioceramic materials is still very little. Several methods of treating basalt as glass-ceramics and limestone as Hydroxyapatite are described in this article review. The utilization of local potential as a source of dental implant material will provide support for the independence of a nation in the welfare of its people.

Keywords: bioceramics, basal rock, glass-ceramics, dental implant

1. Introduction

The need for dental implants to replace missing teeth and improve tooth structure to support craniofacial reconstruction and orthodontic treatment is increasing. Three main types of synthetic biomaterials for dental implants are ceramics and carbon, metals and alloys, and polymer [1]. Metal and alloy materials are the primary choices because of their high strength. However, in its use, artificial bone made of metal needs careful attention. Corrosion, biofilm development, and hypersensitivity reactions are the most significant risk factor for metallic materials. However, titanium and its alloys are still widely used in osseointegration dental implants. There are still many confirmed cases of titanium hypersensitivity reactions [2].

Therefore, nowadays, medical devices made of metal have switched to ceramic or polymer materials because of the many innovations and excellent biocompatibility of these materials [3]. Bioceramics has been a lot conducted research and clinical professionalism of teeth with new and exciting substances for more than two decades. Various bioceramic formulations have been understood because of the chemical similarity to human bone. Bioceramics are often used as coating materials to improve the



biocompatibility of metal implants. Serve as a resorbable lattice to rebuild the replaced tissue. Bioceramics have good thermal and chemical stability, wear-resistance, and high strength [4].

Bioceramics are non-toxic and durable materials. It can interact with the surrounding tissue, are biodegradable, dissolve, or resorbable. Sugar and protein can bind with ceramics. For example, Blood vessels can penetrate some ceramic prosthetics and bone materials, eventually replacing them. Bioceramics is a unique biomedical material.

1.1. History of bioceramics development

The first bioceramics research was carried out, namely the "Paris" plaster ($\text{CaSO}_4, \text{H}_2\text{O}$). This plaster was first used to repair bone damage in 1892, which Dressman published. Furthermore, in 1920 the use of tricalcium phosphate was successfully used. The development of bioceramic materials began in the 1960s with Hulbert's work. It continued to be developed until the 1970s and 1980s [5]. In 1977 a study was carried out regarding the very low coefficient of friction between zirconia and alumina. History shows that 400 thousand hip joint femoral heads made of zirconia have been used from 1985 to 2001. The use of bioceramic materials in dental implants is classified as shown in Figure 1 [6].

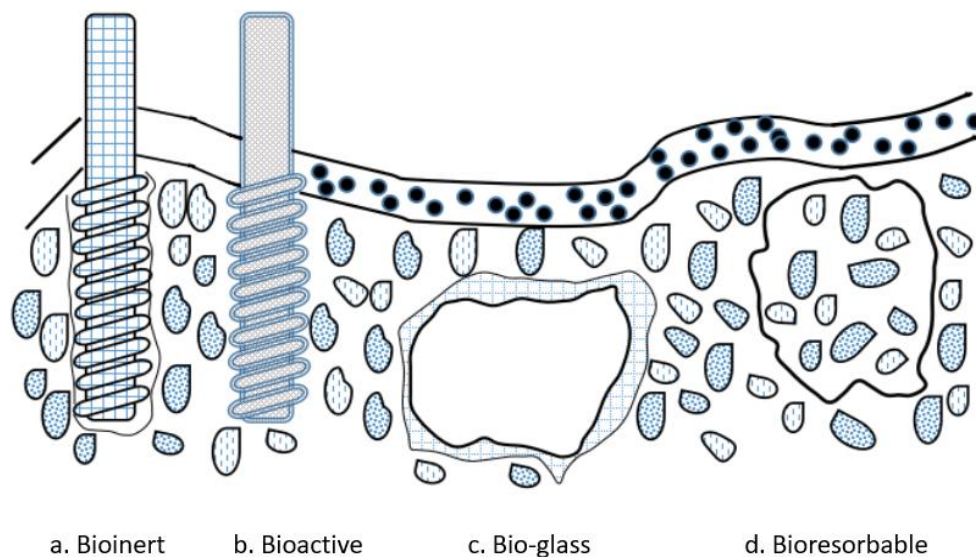


Figure 1. Classification of bioceramics according to their bioactivity [6]

There are four types of body response to the implanted matter, which allow the attachment of the material to the muscles: (a). bioinert (alumina dental implant); (b). bioactive (hydroxyapatite); (c). surface-active (bioglass); and (d). bioresorbable (tri-calcium phosphate/ $\text{Ca}_3(\text{PO}_4)_2$). The main groups of bioceramics are divided according to the tissue reaction to the implant surface. Bioactive materials include bioglass and glass ceramics. Bioresorbable materials such as calcium phosphate and hydroxyapatite (HAp). Bioinert include alumina, zirconia, and carbon.

Bioinert has a high level of stability in vivo, high mechanical properties, and when implanted in living bone tissue, the material fuses according to the osteogenetic contact pattern. Bioactive ceramic is osteoconduction and can bind chemically with living bone. In general, the mechanical strength of bioactive ceramics is lower than that of bioinert ceramics [7]. Meanwhile, bioresorbable is a ceramic material that can degrade when it is replaced by regenerating tissue [8].

Several types of bioactive and glass-ceramics have been developed. Glass-ceramics with different functions, such as superior mechanical properties and quick setting capabilities. Glass which is the most widely used research in the implant field, is mainly based on silica (SiO_2) which may contain several other critical phases. The use of silicate ceramics ($\text{SiO}_2 - \text{Na}_2\text{O} - \text{CaO}$) with a silica content of 65% or

more. Bioglass 45S5 with a composition of 45% SiO₂, 24.5% CaO, 24.5% NaO has been used since 1971 but is brittle and brittle. The addition of 6% P₂O₅ provides a high strength increase.

Produced glass-ceramics named AW glass-ceramics were reported. These glass-ceramics were containing oxy-fluor-apatite Ca₁₀(PO₄)₆ (OH, F₂) and wollastonite (CaO.SiO₂) in a MgO-CaO-SiO₂ glass matrix [9]. These glass ceramics spontaneously bind to living bones without the formation of surrounding fibrous tissue. The development of machine-capable bioactive glass with appetite and phlogopite phases has been carried out. Used clinically as a vertebra makean [6].

1.2. Basalt as Glass-Ceramics Material

In the early 1980s, glass-ceramics from basalt rock were developed. The method of forming glass-ceramics from basalt rock was patented since 1977. It is described as making glass-ceramic from basalt rock melted and enriched with CaO, MgO, and SiO₂ to reach a specific ratio. The melted basalt is then cooled and thermally forms rigid glass-ceramics crystals. Other studies studying the effects of basalt on the bodies of living things have also been reviewed. They experimented on the development of asbestos and basalts fiber on mice for six months [10]. In the case of using asbestos fiber in mice, one-third of the mice died, and at a dose of 2.7 g/kg of asbestos, all mice died. In the case of basalt fiber, all mice survived at doses up to 10 g/kg. Likewise, the experiment explained in his investigation that basalt showed a reaction that was not harmful to the human body [11].

Local basalt material from Mount Kopaonik as a glass-ceramic material was done. The phenomenon of glass crystallization formation was studied using X-ray (X-RD) phase analysis, optical microscopy, and several other techniques. In this study, heat treatment experiments were carried out and their influence in controlling the microstructure and properties of the product. The heat treatment used is by melting the basalt rock in a ladle over a temperature range of 1,250 - 1,300 °C. Crystallization by reheating at 950, 1,000, and 1,050 °C for 3 to 8 hours. The results of the phase formation observations obtained Diopside CaMg (SiO₃)₂ and Hypersthene ((Mg, Fe.) SiO₃) as crystalline phases. The size of the crystals formed ranged from 8 to 480 μm. Microhardness from 6.5 to 7.5, compressive strength between 2,000 - 6,300 kg/cm² and wear resistance between 0.1 to 0.2 g/cm² [12].

Due to its tough nature and good biocompatibility, glass ceramics from basalt rock are being developed. In its use, it is often made in powder form and used as a coating or as a reinforcing filler in bioceramic composites. Glass-ceramic made from basalt rock with heat treatment in various temperatures of 800, 900, and 1,000 °C for 60, 120, 180, and 240 minutes [13]. Glass-ceramics is used as a coating material for AISI 1040 using the plasma spray technique. The use of the plasma spray method aims to form crystalline oxide-based ceramics suitable for glass formation. The formation of amorphous glass structures is required to make glass-ceramic before crystallization heat treatment. From the DSC test, it is known that the glass transition temperature (T_g) is in an endothermic condition of around 804 °C and two exothermic peaks at 841 °C and 880 °C indicate crystal formation. The appearance of two crystallization peaks on the DSC curve implies that are two different crystal phases were formed during the heat treatment. From the XRD test, it was found that the heat treatment was 800, 900, and 1,000 °C for 2 hours to form a crystalline phase of augite [(CaFeMg) -SiO₃], aluminian-diopside [Ca(Mg,Al) (Si,Al)₂O₆], and diopside [Ca(Mg_{0.15}Fe_{0.85}) (SiO₃)₂]. This diopside-augite phase provides superior wear resistance and chemical resistance. The presence of Fe oxidation explained the glass-ceramics made of basalt rocks do not require a nucleant agent. Fe oxidized to Fe₃O₄, which acts as a nucleating agent and a site for crystal growth. The X-Ray Defragment analysis showed that the higher the crystallization temperature caused, the higher the diopside-augite peak. The heat treatment temperature leads to the formation of a large number of crystal phases in the glass.

The use of glass-ceramic basalt as a reinforcing filler in HAp composites against the possible dangers of use in the human body has been carried out in several studies on the safety and resistance of the body to implanted artificial materials. Even the use of basalt in the medical world has been widely used as a traded material. Service-disabled veteran-owned small business (SDVOSB) produces advanced materials. One of which is basalt. States that basalt products do not cause toxic reactions to water or air are not flammable and explosive. When in contact with chemicals, basalt does not produce chemical

reactions that can damage health and the environment [14]. The physical and chemical stability of powdered basalt (BS) to the biological environment is complete. In this research, composites from HAp powder add 5 and 10% wt of basalt to HAp are safe. The powder is then stirred and pressed, and then the sintering process is carried out. The selected sintering temperatures are 700, 900, and 1,200 °C.

The biological liquid environment was 0.9% NaCl solution at pH 6.7; Ringer's solution (NaCl; and KCl; and CaCl₂); Ringer – Locke's solution (NaCl; NaHCO₃CaCl₂; KCl; and glucose). By increasing the BS content by up to 10% and the anneal temperature to 900 °C, the X-phase lines which are part of the BS become clearer. The interaction of the HAp composite system with 5 and 10% BS was almost the same. It has been shown that the HAp + 10% BS at sinter temperature 900 °C composite system is a promising material for reconstructive surgery, given its strength properties. The hardness of 0.86 GPa Hv; modulus of elasticity 23.7 GPa, close to natural bone properties. From these studies, that BS is safe for the living environment of organisms [15]. The research about physical and mechanical tests of basalt powder reinforced HAp composites showed that the addition of 5% and 10% basalt powder as a filler increased the physical and mechanical properties of HAp products. At low temperatures, the β-TCP phase is formed. The β-TCP phase builder is considered to be more biocompatible than the α-TCP phase. The possibility of adjusting the HAP - β-TCP ratio is very promising for producing materials with bio-resorbing properties. The highest compressive strength that the HAp-BS composite can accept was obtained from the addition of 5% basalt to HAp, while 10% basalt strength decreased [16]. The manufacture and development of glass-ceramic materials from raw materials can improve mechanical and physical properties. Besides, this method is a significant segment of the story of the modern world [15,16].

1.3. Hydroxiapatite (HAp)

This time, significant progress has been made in the use of dental implants to replace missing teeth and damage. Calcium phosphate-associated hydroxyapatite (HAp) is the primary inorganic material in human teeth. The natural components of teeth have a comparable chemical composition and HAp properties. HAp has the potential to be used for many dental applications due to its high biocompatibility.

Hydroxyapatite (HAp) with the chemical formula Ca₁₀(PO₄)₆(OH)₂ is a mineral that occurs naturally in the inorganic components of human bones and teeth [17]. The constituent elements of HAp are mainly calcium and phosphorus, with the stoichiometric ratio of calcium to phosphorus is 1.667. In the synthesis of HAp, a sufficiently high source of calcium is required. Several materials can be used to make HAp, such as beef bone [18], eggshell [19], shells [20], limestone [21], and others. Of the several main ingredients, limestone is the largest source of calcium. Limestone is an inorganic mineral with calcium as the main constituent. The calcium carbonate (CaCO₃) content in limestone is around 95%. Calcium is obtained by purifying calcium carbonate. Therefore, limestone has many direct applications in various applications such as clinical, medical, biomaterial development and is suitable as a material in the manufacture of HAp. The structure of HAp consists of calcium, phosphorus, and hydroxyl ions Ca₁₀(PO₄)₆(OH)₂. It's often used as a substitute for bone mineral and dental tissue because of the chemical content that it has in common so that HAp can bind chemically with human bones and teeth [22]. About 65% of the mineral fraction in human bones consists of hydroxyapatite. HAp has been widely used to repair, fill, augment, and reconstruct damaged bone and tooth tissue as well as soft tissue [23].

Pure HAP cannot be used as an implant in load-bearing applications because of its highly brittle nature. Metal implants must also be coated to obtain biocompatibility properties with the local tissue environment. Therefore, coating metal surfaces with biocompatible materials such as HAp in dentistry is very promising. Many studies are carried out about the HAP coating of substantially load-bearing implants. A screw implant used in the maxillary anterior and posterior mandibula with a depth of more than 10 mm is recommended with HAp resurfacing. HAp coating is also recommended for the less dense cortical layer and spongiosis. HAp-coated cylindrical implants are recommended in the posterior maxilla or where the cortical layer is skinny with low density [24]. HAP coating on metal surfaces offers advantages in mechanical properties; it does not affect the load-bearing capacity due to the low density

and the biocompatible texture. CP titanium and HAP-coated titanium have observed that the HAP-coated system develops five to eight times [25].

1.4. Hydroxyapatite (HAp) Based Limestone

Hydroxyapatite can be synthesized in various ways, including the wet method and dry method. There are three types of wet methods, namely the method of precipitation, hydrothermal, and hydrolysis. The damp method is commonly used for HAp synthesis because it is economical and straightforward. Also, the HAp crystals formed are easily regulated in composition and physical properties.

Another advantage, the byproduct of its synthesis is water, so the possibility of contamination during processing is very low [26]. Experiments on the manufacture of HAp from limestone in Lampung Province have been started in the last few years. The experiment with making HAp from the limestone of Mount Branti using a mechanochemical method done by smoothing limestone in a ball mill machine with various grinding time and sintering process at 600 °C for 2 hours for all samples.

The following procedure is mixing 5 grams of limestone powder after sintering with 5.34 grams of Na_2HPO_4 , plus 10 ml of ethanol and stirring on a ball mill machine. In the last process, the sample is dried using an oven at 80 °C for 17 hours. Furthermore, the samples were tested for XRD, FTIR, and whiteness. The test results show that the highest degree of the white color is obtained from Mount Branti limestone, namely 85.7%, and the hardness obtained is 13.60 HV [27].

The effect of temperature and sintering time of limestone from Bandar Lampung on HAp characterization has also been studied. The highest temperature and the longest sintering time make the hardness of HAp increased. Xrd diffraction shows the same pattern as commercial HAp. However, the Ca / P ratio is still greater than 1.67 [28]. As an implant material, HAp has weak mechanical properties. Due to its low mechanical properties but bioresorbable properties, HAp is often used as a coating. For example, porous tantalum coating using HAp through the plasma spray method [29].

To obtain superior mechanical properties, HAp is usually combined with other materials to form a composite. The addition of 20% of silica increase the hardness of HAp 2 times compared to without the addition of silica [30]. HAp and polymer are combined to obtain a scaffolding product. The pectin extracted from the leaves of green grass jelly (*Premna oblongifolia* Merr) and hydroxyapatite (HA) as a scaffolding. The 3% Hap mixture with pectin was prepared.

The resulting scaffold had pore sizes ranging from 8.25 to 115 μm while the resistant to loads of 0.03 to 0.15 MPa. The porosity of the scaffold made is 15.33 to 40.97%, while the density is 0.69 to 1.02 g/cm^3 [31]. The use of HAp made from branti limestone in HAp - PLA composites also have been done. The production of HAp begins with an extraction process which is then continued with the hydroxyapatite synthesis stage at a temperature of 1,000 °C. The method of makes composites with the addition of PLA during the heating process. The results show the Ca / P ratio is 1.63, still below 1.67, which indicates that this process is still less than perfect [32].

2. The Potential Limestone and Basalt from Lampung Province

Limestone as the primary material for making HAp is often finding in Lampung Province. This limestone is mainly located on limestone hills which are mined by the community and industry. In the West Lampung area (Lemong District), there are hypothetical limestone resources of 20 million tonnes [33].

Tanggamus Regency is scattered in the Batu Mountain Block area with 45 million tonnes of limestone reserves. In Hilian Baji Block inferred 151 million tons, Cempaka Block 18 million tons [34], Pesawaran District, Tegineneng, and Teluk Pandan [35]. South Lampung district in the Gunung Branti area [32], Natar and others. Bandar Lampung district in the Bukit Sukamenanti area [36].

Complete data on basalt reserves in Indonesia are not yet available, only in several areas that have been researched. There are at least 12,036 million tons of basalt rock spread across Sumatra Island (1,310 million tons), Java (546 million tons), Kalimantan Island (4,138 million tons), Sulawesi (6,042 million tons) [37].

On the island of Sumatra, basalt which is a volcanic product, is often found in the Sipongi area (Mandailing Natal, North Sumatra), Silungkang (Sawahlunto, West Sumatra) [38]. According to the geological agency of the Ministry of Energy and Mineral Resources, basalt can be found in East Lampung, in the areas of district Sukadana, Mataram Baru, Bumi Agung, Marga Tiga, Jabung, and Labuhan Maringgai. Basalt resources in Lampung Province are estimated at more than 18 million tons. In the Sukadana district, basalt in the form of a lava flow, solid dark gray-black, the top contains many gas holes, locally has xenolith in the form of gas perforated basalt (vesicular), undergoes weathering, peels onions [39].

It is necessary to develop research from basalt and limestone as a material for glass-ceramics and Hydroxyapatite. The potential local utilization as a source of dental implant material will provide support for the independence of a nation in the welfare of its community.

3. Conclusions

Lampung Province has potential natural resources that can be used as dental implant materials. The bioceramic materials most commonly used as dental implant materials are glass-ceramics and hydroxyapatite (HAp). glass-ceramic material. Basalt stone is a material that can be used as a glass-ceramics material. The basalt rock in Lampung Province is found in the Sukadana area and several other places. The potential of natural resources originating from basalt rock needs attention because its current use is only used as building stone. In contrast, the rock has tremendous benefits in the field of dental implants. Limestone has been mined by many companies and local communities in Lampung. Several companies use this limestone as an ingredient in cement and agricultural lime. The use of limestone as a HAp material is still very limited in research. And until now, the investigation has not reached maximum results.

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