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CHARRACTERISTICS OF HYBRID COMPOSITES MADE FROM HIDROXYAPATITE (HAp)/METAL POWDER AND CERAMIC

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ABSTRACT (Cambria 11, Bold, Centered)

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Milkfish bones/*chanos-chanos forsk* (CCF) contain of 4% calcium, 3% phosphorus, and 32% protein. CCF is heated at certain temperatures (500-700ºC) then can be turned into hydroxyapatite (HAp) as a biomaterial application. The selection of materials in accordance by HAp is aluminum (Al), magnesium (Mg) and titanium (Ti). Al is one of the non-ferrous metals with very wide applications. It has specific properties such as; being light weight, ductile and a lower melting point compared to many other common engineering materials. The combining some of metals by HAp, is a composite material term, which is currently the latest development for processing various elements of different materials. Processing of composite for multi-alloy materials, requires a complex process in resulting of products, both in terms of parameters and process variables. Self-propagating high temperature synthesis (SHS) is a relatively novel and simple method for making certain advanced composites and intermetallic compounds. The SHS method is very suitable to be used as a composite multi-alloy material processing because it has a series of processes capable of producing strong bonds between the elements combined, such as HAp, Al, Mg and Ti. The HAp material from milkfish bones was combined by several metal materials such as Al, Mg and Ti. The use of this material is expected to improve mechanical properties especially eliminating fragility in composite materials. Variation of composition on hybrid composites consist of 3 types: (hybrid composites). There are three combinations of compositions in hybrid composite manufacturing, namely: 80% HAp; 10% Al; 5% Mg; 5% Ti, 80% HAp; 10% Al; 5% Mg; 5% Cu and 80% HAp; 10% Al; 5% Mg; 5% SiC. Characterization carried out ware mechanical and microstructure to determine the properties of hybrid composites, from the values obtained can be recommended for biomaterial applications. (Cambria 10, spasi tunggal, justify)

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Keywords: Hydroxyapatite. Hybrid composites. Aluminum. Self-propagating High Temperature Synthesis and Biomaterials.

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INTRODUCTION

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Milkfish bones in scientific terms, called chanos-chanos forsk (CCF). It is one of the typical foods is in province of Banten in Indonesia. Which has been passed down for generations from the Sultanate of Sultan Ageng Tirtayasa till now [Hasanudin D, 2018]. But the remains of bones have not been used optimally. Therefore, efforts to utilize CCF are carried out by adding metal elements such as aluminum (Al), magnesium (Mg) and titanium (Ti) [Pramono A, 2018]. Fish bone can be used as cheap source of biological hydroxyapatite (HAp), to give added value to fishing by-products as well as reduced on undesirable environmental impact [Boutinguiza M, 2012]. HAp is one of the bioactive biomaterials for bones. It is a synthesis material that can be implanted into living systems as a substitute for function of living tissue or organs. At this time the need for biomaterials is very high and has had a considerable impact especially in the field of orthopedic medicine, for example for bone repair, both in repair of fractured bones and broken bones. The material used in the treatment must be bioactive, biocompatible, and non-toxic [Johansson P, 2015 – Nayak AK, 2011].

CCF contain of: 4% calcium, 3% phosphorus, and 32% protein, but this composition depends on the environment of the milkfish, such as an example: used sea water as a source of its hydrology so that it can be polluted easily. Sea waters have been polluted by industrial wastes, such as: Concentration of Pb in the milkfish, water and sediment are analyzed by quantitatively descriptive statistics and compared by quality standard (water <0.03 ppm and the. fish < 0.1 ppm). The results show that concentration of Pb in the milkfish meat 0.041 ppm still under the quality standard (< 0.1 ppm), but this at fishpond water is 2.27 ppm and milkfish pond sediment 0.17 ppm which concentration are over the quality standard (< 0.03 ppm), therefore, it is necessary to process new products so that the bones as waste can be used to the fullest [Robi'atul A, 2014 – Purnomo T, 2017]. The selection of materials in accordance with HA is aluminum (Al), magnesium (Mg) and titanium (Ti). Al is one of the non-ferrous metals with very wide applications. It has specific properties such as being light weight, ductile and a lower melting point compared to many other common engineering materials [Pramono A, 2014]. The role of Mg as a wetting material in order to bind other elements, while the role of Ti is material for compatibility with bone applications. The combining some of metals by HAp, is a composite material term, which is currently the latest development for processing various elements of different materials [Pramono A, 2008 – Pramono A, 2018]. Processing of composite for multi-alloy materials, requires a complex process in resulting of products, both in terms of parameters and process variables. Self-high-propagating temperature synthesis (SHS) is a relatively novel and simple method for making certain advanced composites and intermetallic compounds.

The SHS method is very suitable to be used as a composite multi-alloy material processing, because it has a series of processes capable of producing strong bonds between the elements combined, such as HAp, Al, Mg and Ti. The method of SHS has received considerable attention as an alternative to the conventional furnace technology. The process is based on a system that involves an exothermic combustion. High purity of the product obtained, the possibility to obtain a metastable phase, and the possibility of simultaneous synthesis and densification. Higher purity of the product is a consequence of the high temperatures associated with combustion and the volatile impurities removed as the wave propagates through the sample. Based on the heat released from the reaction of metal powder (fuel) with oxygen (oxidizer) in the presence of other metal oxides hence, after the initial ignition by an external heat source, the reaction is able to regenerate itself while the resulting high temperature sufficient for the synthesis of the desired ceramic product [Pramono A, 2016 - Agrafiotis C.C, 2004].

MATERIALS AND EXPERIMENTAL METHODS

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The first step was washed of CCF used water and soap to remove the fat and dirt that stick to the bones of milkfish. Next step is the heating process (calcination) to get HAp. The heating was applied at a temperature of ±600^{0}C [El-Din, H, 2002]. The HAp material from CCF was then combined with several metal materials such as Al, Mg and Ti. The used of this material was expected to improve mechanical properties especially eliminating fragility in composite materials. Variation of composition on hybrid composites consist of 3 types: (Hybrid Composites).

Table 1. Variation of composition on hybrid composites

Element	Percentage	Weight (grams)	Particle Size (mesh)
Hydroxiapatite (HA)*	80	500	200
Aluminum**	10	300	280
Copper (Cu)***	5	100	200
Titanium (Ti)**	5	200	320
Magnesium (Mg)***	5	250	180
Silicon Carbide (SiC)*	5	100	200
Alumina (Al_2O_3)*	5	100	200

Noted: *Matrix
**Reinforcement
***Coupling Agent

The tools and materials used on the research were; ring mill, mill shaker, screener, muffle furnace, tube furnace, compacting mold, the SHS dies, press machine, optical microscope and vickers hardness test. While the sintering temperature of the sample was 750^{0}C. Used of composition on materials, were presented in table 1. HAp powder, metal and ceramics were mixed until they reached a uniform powder size. After achieving uniformity, heating at 600^{0}C temperatures was done by muffle furnace and compression pressing reached ±500 MPa. The process and results of hybrid composites sample were seen in figure

1. After the preparation process is complete, the next step is setting the compressive machine tool for processing milkfish bones containing HAp, which was mixed with several metal powders. In this case Al acts as a matrix, Mg as wetting and Ti is a material to increase the value of conductivity so that metal elements easily react with other elements. The processing of HAp materials by mixing some of these metals aims to apply in the field of biomaterials, in biomedical applications of bone implants. The HAp alloys with mixture of several metal elements are used as the longest stem or hard bone component. In addition, it is also applied to the pen joint when a fracture and fracture occurs. Forms of stem bone implants on the hip joint, as well as pen on bone joints. The biomaterial applications were presented in Fig 2.

The SHS was process for milkfish bone of HAp at a temperature of 600-750°C and resulted to hybrid composite. HAp is ceramic material as matrix and SiC/Al_2O_3 as well. Al and Ti as a reinforced and for improve wetting on hybrid composites, Mg and Cu materials were used to obtain strong bonds forming. SHS with temperatures below 1000°C cannot be achieved by sintering technique without pressure, because the contact angle between matrix and reinforced was not obtained in a short time, so that densification hampered caused by chemical reactions occur faster than the reaction of capillarity between matrix and reinforced. The pressing more than ultimate strength, which is react form result the powder of rearrangement

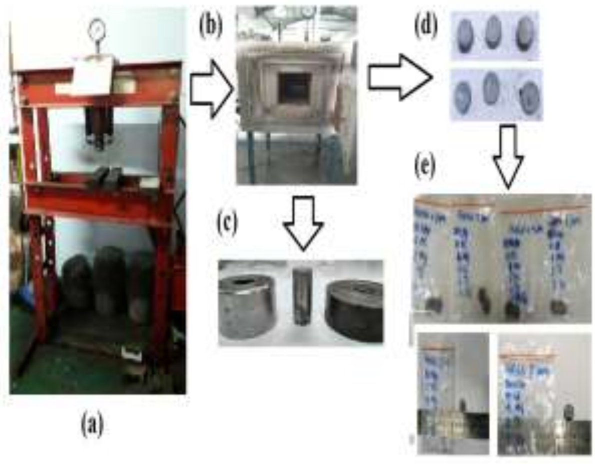

Fig 1. The process of hybrid composite: a). Krisbow Machine for pressing b). Muffle Furnace for heating c). Mold for powder materials d). Green materials e). Sample of hybrid composites.

Fig 2. Implant Hip Joint Unit and materials Alloy of Bone Connection Pen [Keaveny TM, 2004]

RESULT AND DISCUSSION

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Research used HAp study, elements found in milkfish waste was: $Ca_5(PO_4)_3(OH)_2$, as evidenced by X-ray diffraction (XRD), presented in Fig 3. Based on the data that have been tested to arrange with Al, Ti and Cu metals as a matrix, it is a solution to make strong bonds on HAp. To improve the bond, Mg acts as a wetting agent. Wetting is needed so that porosity is able to be covered by Mg and strengthen the bond between elements. XRD data processing by high-score software of CCF produces different elements, depend on preparation process. At 1-hour heating, the black color from the peak, showed the milkfish produced a small HAp. Heating time (1-hour calcination) makes heat insufficient for the monolithic structure, when 3-hours, the HAp turned into carbonate. 5-hour calcination time is enough to convert from milkfish of monolithic structure. The formation of monolithic HAp is a structure that reacts more easily with metals [El-Din, H, 2002].

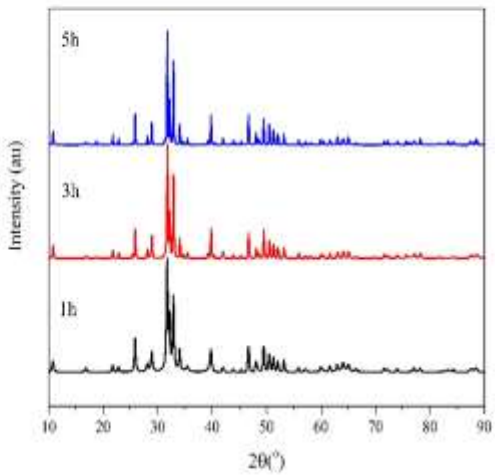

Fig 3. Result of XRD analysis: black color 1-hour heating, red color 3-hour heating, blue color 5-hour

The material research used HAp powder form as a matrix, Al 99.9% as a reinforced, and magnesium 99.9% as a wetting agent and added powder SiC, Ti, Cu in addition to the hybrid composite formed by the SHS method at temperature 700^{o}C. The SHS process is carried out using a muffle furnace. Making samples for the SHS process is by mixing using a shaker mill for 10 minutes to make all the ingredients fully mixed. Then compacting was carried out using a pressing machine for 1 minute to form a contact angle between the matrix and strengthen the material so that it would be easy to bind when heated.

Mechanical Properties of Composites Hybrid

The variations of composition with each sample shown in table 2. The highest hardness value was obtained in the composition of: 80% HAp 10% Al 5% Mg 5% SiC at 2-hours heating of time was equal to 42.83 HV. Meanwhile, the lowest hardness was: 80% HAp 10% Al 5% Mg 5% Cu which was equal: 13.09 HV. Al can avoid oxidation, the occurrence of interface bonds in composites Silicon carbide (SiC) is one type of ceramic that is used as an amplifier in a composite. SiC has a high hardness that increases the mechanical properties of the composite. Interface ties between Al/HAp and SiC occur in the solid liquid phase, where at temperatures of 700^{o}C aluminum has a liquid effect while HAp and silicon carbide are solid.

Table 2. Hardnes of composites hibrid

No	Result of Test		
	Hardness Value Test	Heating time (hour)	Average Hardness (HV)
1	HAp : 80%, Al : 10%, Mg: 5%, Ti: 5%	2	36.88
		3	34.44
		4	24.24

2	HAp : 80%, Al : 10%, Mg: 5%, Cu: 5%	2	28.34
		3	18.11
		4	13.09
3	HAp : 80%, Al : 10%, Mg: 5%, SiC: 5%	2	42.83
		3	37.58
		4	26.81

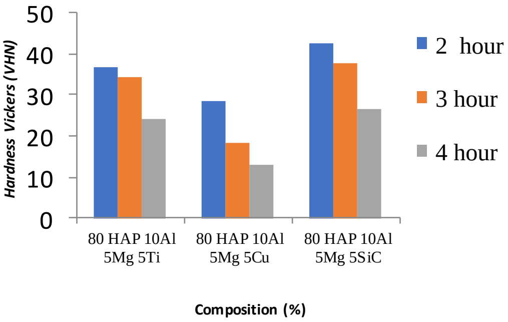

Fig 4. Effect Diagram of Composition on Hardness

Figure 4 shows the longer the hold time the value of hardness decreases. It should be the longer the processing time, the hardness value increases because the longer the process time, the more aluminum is inflated into the composite [Pramono A, 2018]. But this does not occur in the SHS process, because the process utilizes a special tube, so that heat will quickly propagate and be concentrated before reaching the sample, so that heat will be wasted. Aluminum will decompose due to the centralized heating process temperature of 700^{o}C, because aluminum has a melting point of 653-657^{o}C. In addition, in this test the furnace used is a type of muffle furnace, allowing O_2 gas to be trapped in the sample and cause porosity.

Microstructure Analysis

Hybrid composites of microstructure elements were united with HAp, as shown in figure 5. SiC acts as a matrix to increase the hardness. Hybrid composites based on HAp are among metal elements. Heating 2-hours the distribution of SiC between Al which acts as an reinforcement. During 3-hour heating, SiC surrounded of metal elements and is stacked by magnesium which acts as a wetting agent. 4-hour heating produces complete distribution, HAp, Al, and other elements, compared to other heating, 4-hour heating produces fine grains.

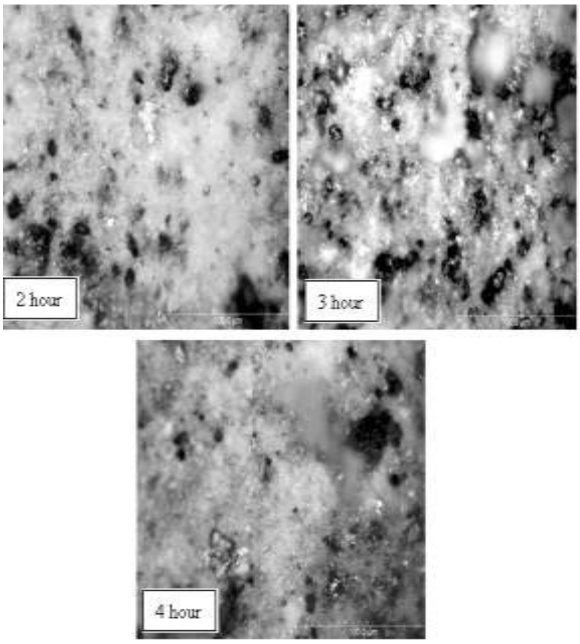

Fig 5. Optical Microscopy of Hybrid Composite, magnification 100 µm

Based on the results of mechanical properties had got it, the result of properties can be applied for biomaterial, especially cortical bone. Cortical bone has a porosity value of ≤ 30% [Pramono A, 2020] and has a hardness value of 0.396 GPa or equivalent to 40.38 HV. From this study, the sample that can be used for the application is a hybrid composite with a composition: 80% HAp 10% Al 5% Mg 5% SiC with a process time of 2 hours and has a hardness of 42.83 HV. Based on other studies, the high value of violence is influenced by the use of the right composition. As in [Slósarczyk A, 2020] The experiment used composition which maximum is influenced by the uniform distributed of pressure and the use of the wetting agent, composition must have an equal percentage. With an equilibrium percentage, the bond strength between the elements can wet all the resulting bond layers. Intensive efforts have been made to find new biomaterial solutions that are superior in the field of inorganic-organic hybrid materials. Biomicrocret containing of HAp granules prepared with various metallic and non-metallic materials, the latest development is the processing of chitosan (CTS) which is spread in a metal/non-metal matrix as α where the effect of CTS content and grain size on the physicochemical properties of the final bone implant material able to be applied as a biomaterial bearing application without load [Czechowska J, 2014].

CONCLUSSION

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The heating of milkfish bone with a temperature of 600^{0}C with a time of 1-3 hours still leaves carbon which is blocks the bond if combined with metal elements. Heating time more than 5 hours can produce HAp with perfect processing.

The use of composition: HAp: 80%, Al: 10%, Mg: 5%, SiC: 5% can produce the highest hardness compared to the use of other compositions, this is influenced by the role of SiC as the second matrix capable of increasing the hardness of hybrid composites materials.

Heating on 3-hours resulted on SiC surrounded by metal and stacked by magnesium which acts as a wetting agent. 4-hour heating produces complete distribution, HAp, Al, and other elements, compared to other heating, 4-hour heating produces fine grains.

Hybrid composites from HAp materials with metal elements such as Al, Ti, Cu and Mg can be applied to biomaterial components, especially cortical bone. The value of cortical bone hardness is 40.38 HV. From this study, the sample that can be recommended for hybrid composite applications is a material with a composition: 80% HAp 10% Al 5% Mg 5% SiC, 2 hours processing time and has a hardness of 42.83 HV.

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