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Properties of Calcium Hydroxyapatite Formed Using Waste Oyster Shell and Ammonium Dihydrogen Phosphate

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Abstract: Muar is also well-known for its oyster farming, and the principal component of oyster shell is calcium carbonate. Besides, calcium hydroxyapatite is a biomaterial that may be extracted from waste. In this research the properties of calcium hydroxyapatite formed using waste oyster shell and ammonium dihydrogen phosphate was recorded. The aims of this research were to prepare calcium hydroxyapatite from a stoichiometry mixture of waste oyster shell and ammonium dihydrogen phosphate and to characterizes microstructural properties of selected calcium hydroxyapatite samples using scanning electron microscopy. The waste oyster shell was dried for 24 hours before being heated at 700°C and sintered at 1000°C for 2 hours. To guarantee high homogeneity and fine powder samples, the heat-treated waste oyster shell was ground and sieved < 50 µm. OriginLab was used to calculate the mass loss of calcium hydroxyapatite. The impact of sintered at 1000°C was analyzed using Fourier Transform Infrared (FTIR), X-ray diffraction (XRD), AccuPyc II 1340 gas displacement pycnometer and COXEM EM-30 Scanning Electron Microscopy (SEM). Calcium hydroxyapatite is predicted to be extracted from waste oyster shells, and it is expected that it's properties will be analyzed when mixed with ammonia dihydrogen Phosphate.

Keywords: Hydroxyapatite, Oyster shell.

1. Introduction

At this present time, human tend to use and produce a product that is more conventionally, easy to get, profitable, and more efficient in our daily life. Reuse is one of the best ways to prevent waste, pollution that come from a human being or nature. Recycling is one of the best methods to produce more product with more efficient and less cost. For example, the produce of hydroxyapatite from the waste oyster shell. Oyster shell, which is primarily calcium carbonate with a few impurities, has become one of the recyclable wastes used to make Hydroxyapatite (HA) powder due to its easy availability and inexpensive cost (1).

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Based on the stated statement, the aim for this research to investigate the properties of calcium hydroxyapatite formed using waste oyster shell and ammonium dihydrogen phosphate. In this study the solid state technique turned the waste oyster shell to calcium hydroxyapatite with different composition of oyster shell powder and ammonium dihydrogen phosphate.

1.1 Hydroxyapatite

Hydroxyapatite (HA) is one of the bio-ceramics that responds to the vast quantity of regenerative unite material in the market. The hard apatite structure is tightly bound to HA. Its natural network is restricted; thus, it coexists with other mineral minor components in typical bone (2). There are many ways to produce hydroxyapatite. Due to its superb bioactivity, high biocompatibility, and magnificent osteoconduction qualities, HA has been generally utilized in biomedical applications attributable. Recently, attention has been drawn to the use of HAP as a sorbent material for natural sources. Because of its low water dissolvability and high dependability in oxidizing and diminishing circumstances, HAP has been extensively explored for the adsorption of significant metals, resulting in its excellent adsorption properties (3).

Hydroxyapatite (HA) is a calcium phosphate that has the same form and composition as human hard tissues. It has a hexagonal structure and a stoichiometric Ca/P proportion of 1.67, which is identical to bone apatite. When compared to other calcium phosphates, hydroxyapatite has a substantial strength. Under physiological parameters such as temperature, pH, and fluid production, hydroxyapatite is the most stable calcium phosphate compound.

1.2 Oyster shell

The scientific term for oysters is Ostreidae. Muar is an oyster provider, and the type of oyster found there is Crassostrea gigas. The commercial oyster (Crassostrea gigas) is 14-60-16 cm long and its principal component is pure calcium carbonate. It has been discovered that oyster shell is entirely composed of $CaCO^3$(about 96 percent) and other minor minerals. Calcium carbonate's mineral structure is calcite (4), and it also includes protein polysaccharides and minerals including calcium, magnesium, sodium, copper, iron, nickel, strontium, and some microelements.

The oyster shell accounts for almost 90% of the total weight and contains 52.55 percent calcium oxide, making it a valuable raw material in the calcium carbide, lime, fertilizer, cement, and other industries (5). In contrast to the physical qualities, because of the chemical nature of oyster waste, it is one of the few marine resources capable of producing hydroxyapatite at a cheap cost. Biological apatite is of special importance because to HA substitutions at the OH, Ca^{2+} and PO_4^3 sites, as well as the inclusion of numerous trace elements, which can improve the biomaterial's overall biological performance.

2. Materials and Methods

2.1 Sample preparation

Muar oyster shell (OS) was meticulously cleansed and rinsed with flowing distilled water. The discarded oyster shells were then dried in an oven (MEMMERT) at 110°C for 24 hours. Following the completion of the dry process, discarded oyster shells were calcined in a furnace (PROTERM) at 700°C for around 5 hours at a rate of 5°C /min. During the calcination process, calcium carbonate will be produced. Following the calcination procedure, the heat-treated discarded oyster shells were crushed and ground using an agate mortar and pestle, and the sample was ground and sieved about 50µ using a test sieve. The calcium carbonate powder was then combined with Ammonium Dihydrogen Phosphate and ground until it became a homogenous powder using an agate and mortar. The calcium carbonate powder and Ammonium Dihydrogen phosphate were combined in the ratio stated in the table below.

Table 1: The Composition of OS and $NH_4H_2PO_4$ sintered at 1000℃

Batch Composition (wt%)		Designation
Oyster shell	Ammonium Dihydrogen Phosphate	
50	50	50OS50A
60	40	60OS40A
70	30	70OS30A
80	20	80OS20A
90	10	90OS10A
100	0	100OS

The next process is pressing powdered sample was weighed for 2g for one sample. The Hydraulic pressure machine was used for this process. The sample was put into the mould and being pressed using pressing machine. The force of pressing was 3 tonnes for about 1 minute. The last process for preparation is sintering. Before the sintering process, mass of the sample was weighed and recorded. After that all the sample was sintered at 1000°C for 2 hours using a Chamber furnace.

2.3 Sample Characterization

OriginLab software was used to tabulate the mass loss data of waste oyster shell and a mixture of waste oyster shell and Ammonia Dihydrogen Phosphate. Fourier Transform Infrared (FTIR) was also utilized to assess the organic component and chemical bond in the sample. X-ray Diffraction (XRD) was utilized to analyze crystalline materials and determine unit cell size. For sample collection and preparation using XRD, the powder of crushed discarded oyster shells will be ground till fine powder, and all equipment has been cleaned using acetone to reduce sample loss during grinding and to minimize structural damage to the phases in the sample that can be caused by grinding. The density of the sample is then determined using an AccuPye ll 1340 displacement pycnometer. This characterization method provides information about the powder density of the produced sample. Finally, in order to fulfil the goal and finish this work, COXEM EM-30AX Scanning Electron Microscopy (SEM-EDX) was used for the morphological surface characterization.

3. Results and Discussion

3.1 Mass loss

The mass loss results for this study are illustrated in Figure 1 and Table 2. The mass before and after the sintering process is used to determine the mass loss of the prepared sample. Noticed that mass before the sintering process is heavier than mass after the sintering process for this study. Based on table 2 below, the lowest mass loss is 36.3337 when the composition is of oyster shell is 50 %, meanwhile the highest mass loss is 40.9808, when the composition was not mixed with Ammonium Dihydrogen Phosphate and was used totally 100% of oyster shell. Figure 1 shown that, the mass loss of the sample for this research is increasing when the composition oyster shell is increasing. This reaction happens because during the sintering process calcium dioxide was release as a gas.

Table 2: Mass Loss result on the different composition of OS and $NH_4H_2PO_4$.

OS (wt%)	$NH_4H_2PO_4$ (wt%)	Mass Loss (wt%)
50	50	36.3337
60	40	36.9892
70	30	39.0459
80	20	39.4315
90	10	40.1887
100	0	40.9808

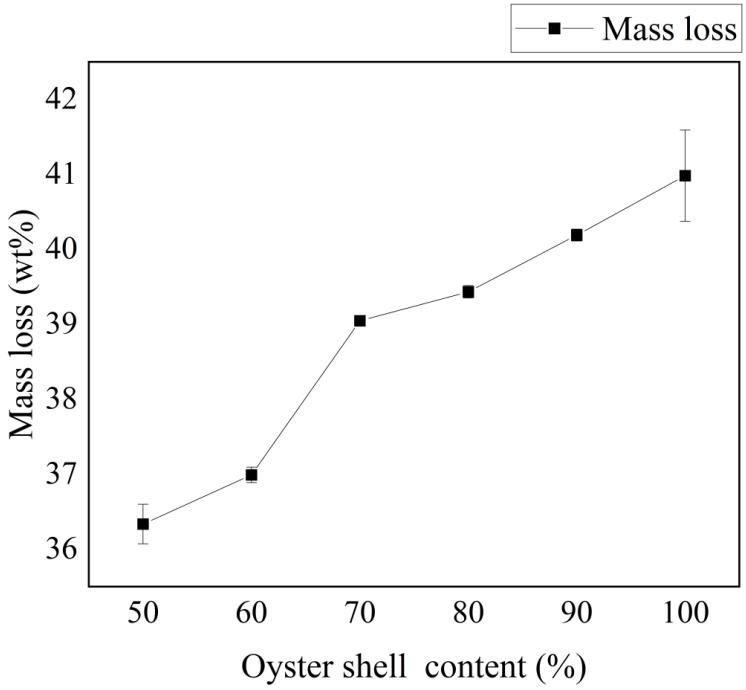

Figure 1: Graph of mass loss against Oyster shell content at sintering temperature of 1000℃.

3.2 Fourier Transform Infrared (FTIR).

Figure 2 demonstrated the infrared spectra of absorption and emission of the prepared sample was obtained using FTIR. According to prior studies, the production of HA was signified by a wide phosphate band centered between 100 cm^{-1} and 1100 cm^{-1} (9), with the band 960 cm^{-1} to 965 cm^{-1} and 546 cm^{-1} to 601 cm^{-1} , corresponding to the ion PO_4^3 (10) (11). Figure 2 shows that when sintered at 1000°C, the production of ions PO_4^3 in the range of 1314 $cm^{-1}$to 1566 cm^{-1}, and the stretching and liberation modes of OH at 3599 cm^{-1} and 739 cm^{-1}, respectively, are related with HA.

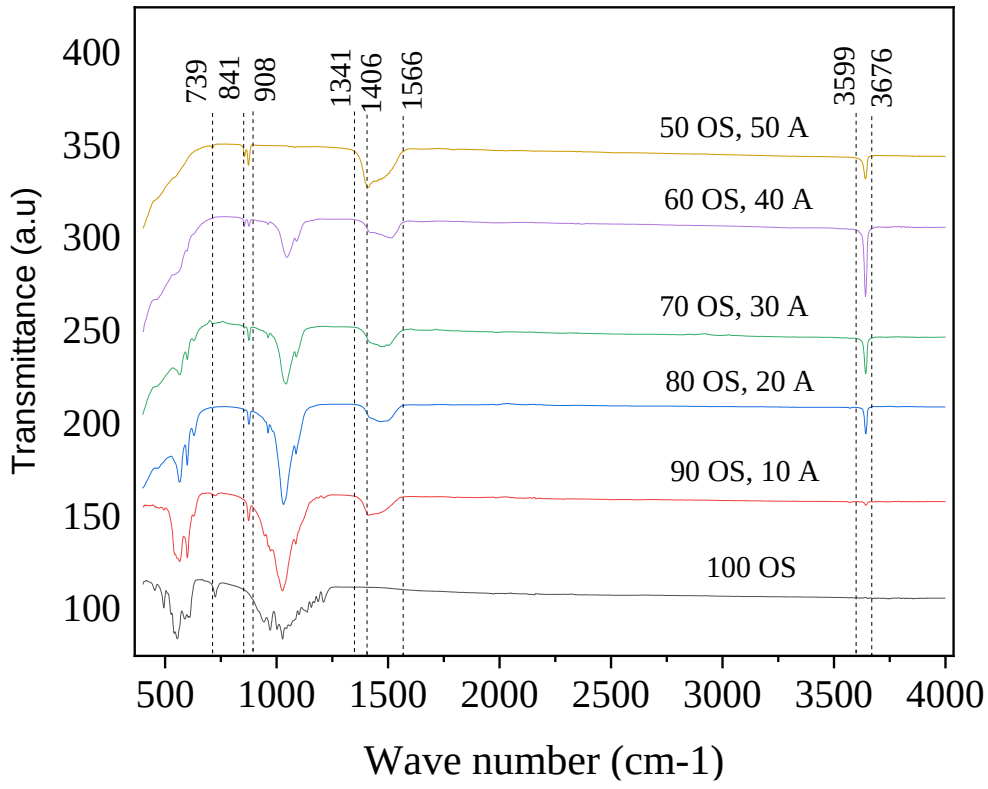

Figure 2: FTIR spectra of Oyster Shell mixed with Ammonium dihydrogen phosphate in different composition sintered at 1000℃.

3.3 XRD

XRD can determine the phase of crystalline material as well as the size of unit cells. According to prior research, an oyster shell contains roughly 96 percent $CaCO_3$, and the rest is made up of various minerals (6). The Hydroxyapatite XRD pattern is given in Figure 3. As indicated in the image, the Hydroxyapatite is more defined, which may be attributed to the increase in size. Because of the amorphous nature of Hydroxyapatite, the peaks blended. According to another study (7), the XRD pattern revealed the existence of 100 percent Hydroxyapatite, with the highest peak at 31.90° and an intensity of 615 counts.

Figure 3 illustrate the XRD pattern for Calcium Hydroxyapatite that undergoes sintering process for different composition at 1000°C for 2 hours. With the information that provided by the figure, the result shown the presence 100% of Calcium Hydroxyapatite is at the peak of 31.793. It was also the highest peak of this figure where the composition of oyster was 80 %.

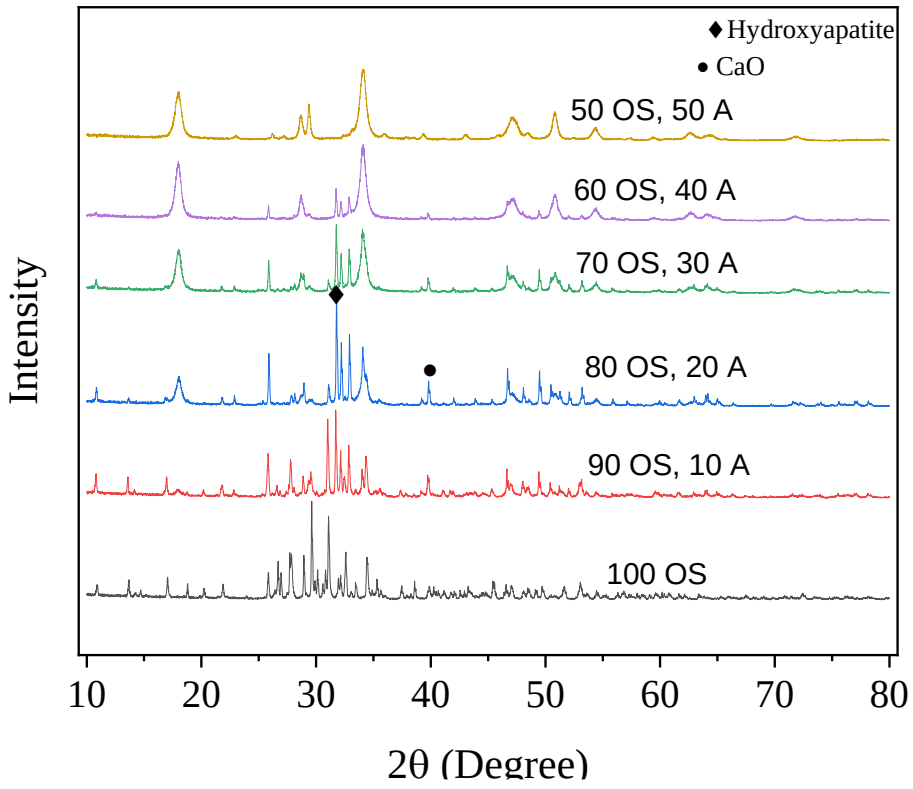

Figure 3: XRD pattern for different composition of OS and $NH_4H_2PO_4$.

3.4 DENSITY

Table 3 and Figure 4 shown the result for powder density and the oyster content. Based on Table 3, the highest powder density is when the composition of oyster shell content was 50 % of the sample. Figure 4 shows that the powder density value decreasing when the oyster content is increasing. This is due to the fact that when the oyster concentration increases, so should the calcium carbonate content.

Table 3: Powder density for different Oyster Shell content.

OS (wt%)	Powder density (g/cm3)
50	3.0484
60	2.9581
70	2.7557
80	2.5469
90	2.3525
100	2.2940

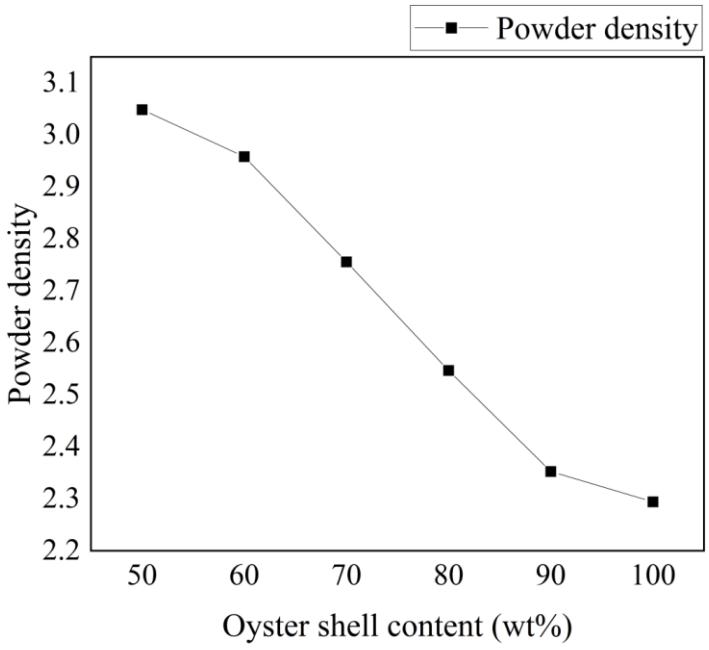

Figure 4: Powder density versus Oysters Shell content

3.5 SEM-EDX

Figure 5 depicts the SEM -EDX picture for a 50 wt percent OS/50 wt percent mixture. According to earlier study, the picture shape of the Calcium Hydroxyapatite was clearly achieved when the calcining temperature was equivalent to or more than 600°C (8). Figure 5 shows the shape of sintered platelets derived from powder calcining at 1000°C. It appears to be an extremely tiny HA particle. Furthermore, this may be demonstrated by examining the SEM-EDX data of spectrum 12, spectrum 13, spectrum 14, and spectrum 15 in Tables 4. The elements in the sample are shown in the table below. The overall results suggest that oxygen (O), calcium (Ca), and phosphorus (P) are the most abundant elements in the sample.

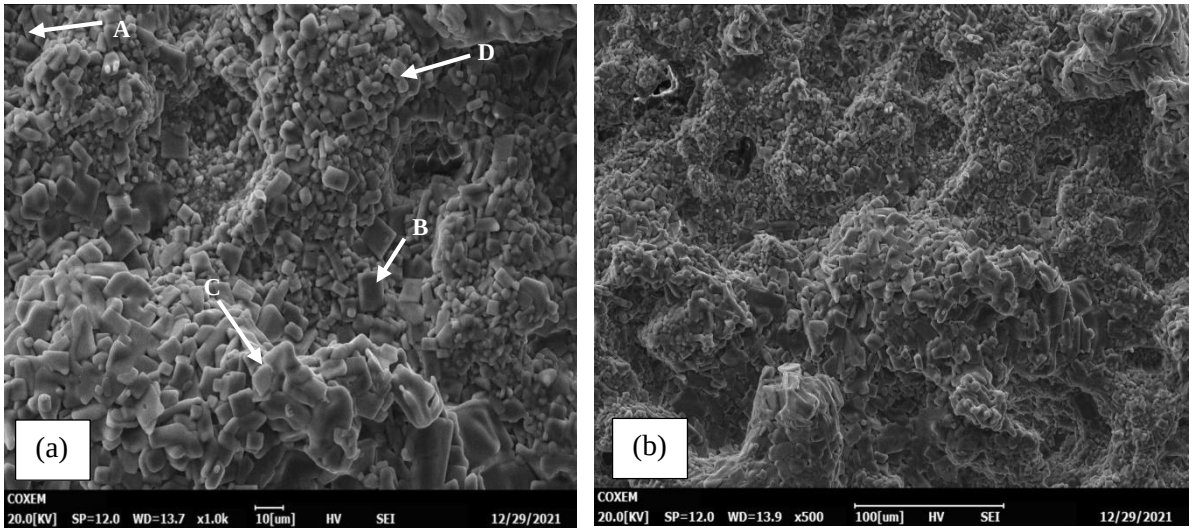

Figure 5: (a) SE image (b) BSE image of 50OS50A

Table 4: Elements in area

Element	Area a	Area b	Area c	Area d
	Atomic Percent (at %)			
O	73.67	77.95	72.63	73.82
P	12.93	11.44	13.74	11.66
Ca	12.99	10.35	13.32	14.26
Au	0.27	0.25	0.31	0.26
Al	0.14	0	0	0
Ir	0	0	0	0
Total	100	99.99	100	100

4. Conclusion

In this research, Calcium Hydroxyapatite was formed successfully using Waste Oyster Shell and Ammonium Dihydrogen Phosphate. The result indicated that when the OS content increasing, it would also affect the result of mass loss of calcium hydroxyapatite. Besides, we can see the formation and asymmetrical stretching and bending modes of OH and PO_4^{3-} ion based on FTIR spectra. The result of XRD shown the presence 100% of Calcium Hydroxyapatite is at the peak of 31.793. The data for powder density also recorded and we can see that powder density of HA are decreasing due to the increasing of OS. Lastly, we can see the clear image of HA with the composition of 50 wt% OS mixed with 50 wt% when sintered at 1000°C for 2 hours using SEM-EDX.

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