Phase characterization and electrical properties of fluorhydroxyapatite: influence of molarity variation and microwave irradiation

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Abstract. Hydroxyapatite is one of the calcium phosphates that is most often used to repair tissue hard as teeth and bones due to its excellent osteoconductive properties and bioactivity, but hydroxyapatite has low chemical stability at high temperatures, high dissolution values in the biological environment and low resistance to damage in acidic environments. The addition of fluorine to hydroxyapatite can make hydroxyapatite have superior mechanical properties because of its higher thermal stability. It also can increase calcium phosphate mineralization and crystallization in the process of forming teeth and bones. This research was carried out by synthesis of fluorhydroxyapatite using microwave irradiation-assisted precipitation method, by varying the molarity ratio and the microwave irradiation used. The XRD results show that samples at high microwave irradiation (100P) both in molarity variations of [P]/[F] 4 and 6, fluorhydroxyapatite has the least impurity intensity and the highest fluorhydroxyapatite intensity among the others. FTIR analysis also shows that all samples have the same group and fluorhydroxyapatite has been formed which is shown in the OH...F functional group at wave number 3539-3544 cm⁻¹. Microwave irradiation and molarity ratio [P]/[F] showed no relationship with conductivity value of fluorhydroxyapatite.

1. Introduction
Recent decades, several recent studies have shown an increase in dental caries globally. This increase occurs in children and adults, both in primary and permanent teeth [1]. WHO estimates that DMFT (Decayed, Missing and Filled Teeth) globally occurs in 12-year-old children in 209 countries included in their database. Of the total 3.681.724.312 teeth, around 244.571.686 teeth had caries. This is based on data available in 2015 from the WHO Oral Health Database, Country / Area Profile Program (CAPP) [2].

Dental caries is a scientific term for tooth decay or cavities. This is caused by certain types of bacteria that produce acids that destroy tooth enamel and dentin [3]. Initially, the remnants of food in the teeth decay which then makes the teeth become porous, hollow, and even broken. The process of tooth decay occurs due to microorganism activity in carbohydrates, which makes carbohydrates gradually become acidic due to the decay process. The acidic environment (pH below 5.5) [4] is what makes demineralization in hard tooth tissue [5]. This happens because the concentration of hydrogen ions increases (which indicates an increase in acidity) and calcium ions decrease. This demineralization...
process will then form small pores on the enamel surface which for a long time allow it to become a hole so as to allow the bacterial invasion to the inside of the teeth [6].

Hydroxyapatite \([\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]\) is one of the most commonly used calcium phosphates to repair hard tissues [7] such as teeth and bones due to osteoconductive properties [8] and bioactivity [9] which is very good. Hydroxyapatite is a special mineral component found in tissues, specifically dental and bone tissue [7]. In addition, synthetic hydroxyapatite has the ability to bind directly with teeth and bones because of its chemical composition which is the same as teeth and bones [10].

Behind the advantages of hydroxyapatite, it turns out there are some deficiencies found in its use as a biomaterial. Hydroxyapatite has low chemical stability at high temperatures as indicated by the formation of other phases such as tricalcium phosphate which often pollutes the results [10]. In addition, hydroxyapatite also has a high dissolution value in the biological environment and low resistance to damage in the acidic environment [7].

Fluorine has a role in the formation of tooth enamel. The presence of fluoride ions makes teeth more resistant to demineralization by acids from bacteria, and influences bacterial metabolism, and influences the formation of polysaccharides in carbohydrates in cells that are used as reserves to produce acids [11]. When fluoride (F\(^-\)) substitutes the hydroxyl group (OH\(^-\)), the solubility of bone mineral minerals decreases because some fluoride substitutes hydroxyapatite (commonly called fluorhydroxyapatite) which is less soluble than hydroxyapatite [10]. Substitution of fluoride into hydroxyapatite material will increase stability and prevent second caries by inhibiting bacterial metabolism [12]. Fluorine also has superior mechanical properties when sintered at high temperatures because of its higher thermal stability than hydroxyapatite. The presence of fluorine also increases calcium phosphate mineralization and crystallization in the process of the tooth and bone formation [13] and influences cell addition, proliferation, differentiation and morphology of osteoblast cells [14].

The research that will be carried out in the synthesis of fluorhydroxyapatite based on chicken eggshells using precipitation method assisted by microwave irradiation. The use of microwaves in the synthesis process is expected to help increase the degree of crystallinity, reduce energy consumption and produce nano-sized particles, because in several previous studies such as those conducted by Hassan et al. (2015) the use of microwaves has succeeded in increasing the degree of crystallinity, reducing energy consumption and producing nano-sized particles [15].

2. Experimental

2.1. Materials and tools

The materials used in this study was CaO powder from chicken eggshells, distilled water, \(\text{H}_3\text{PO}_4\), and \(\text{NH}_4\text{F}\). The tools used in the study include sample containers, measuring cups, Erlenmeyer, goblets, crucible, dropper pipettes, magnetic stirrers, plastic wrap, Vulcan furnaces, Nabertherm furnaces, digital balance sheets, funnels, mortar, spatula, infusion tools, glass cups measuring, drip flask, Perkin Elmer Spectrum One FT-IR Spectrometer, and x-ray diffraction (XRD) Shimadzu XRD-7000, x-ray diffraction (XRD) Rigaku MiniFlex and HiTESTER 3522 -50 LCR Meters.

2.2. Methods

2.2.1. Synthesize of fluorhydroxyapatite with precipitation method. Synthesize fluorhydroxyapatite with varying the molarity ratio and the microwave irradiation were synthesized through precipitation method. The molarity ratio \([P]/[F]\) were 6 and 4 in order to have corresponding compositions of \(\text{Ca}_{10}(\text{PO}_4)_6\text{F}_{\text{P}}\text{OH}_{1-x}\), \(\text{Ca}_{8}(\text{PO}_4)_6\text{F}_{1.5}\text{OH}_{0.5}\) (by replacing the OH group with F ions in molar ratios of 0.5 and 0.75 [15]. The varying microwave irradiation are 30P, 50P and 100P (30P or 30 percent means the microwave oven is producing microwaves 30 percent of the time and 70% other times, microwaves are turned off, neither does the 50P and 100P microwave irradiation).

0.5 M of CaO powder was dissolved into 100 ml distilled water, 0.3 M \(\text{H}_3\text{PO}_4\) was dissolved into 100 ml of distilled water and also \(\text{NH}_4\text{F}\) was dissolved into 100 ml of distilled water following a variation
of [P]/[F] molarity that is 6 and 4. A total of 50 ml of 0.3M H₃PO₄ was mixed into 50 ml of NH₄F solution to obtain a mixed solution of H₃PO₄ and NH₄F as much as 100 ml then drops into a CaO suspension accompanied by a stirring process during precipitation process at a speed of 300 rpm. Then the suspension is put into the microwave oven to be given microwave irradiation. At this stage, the samples were treated in the form of variations of microwave irradiation used, i.e 30P, 50P and 100P for 45 minutes. After the sample is irradiated with microwaves, the sample is dried using a furnace at 100 °C for 45 minutes then sintered at 600 °C for 2 hours.

2.2.2. X-ray diffraction analysis. The fluorhydroxyapatite powder were characterized with X-ray diffraction (XRD) Shimadzu XRD-7000, and Rigaku MiniFlex) to determine the phase. Data obtained from XRD analysis then matched with Joint Committee on Powder Diffraction Standard (JCPDS) with numbers 15-0876 (fluorapatite) and number 09-0432 (hydroxyapatite).

2.2.3. Fourier transform infrared spectroscopy (FTIR). The fluorhydroxyapatite powder was analysis using Perkin Elmer Spectrum One FT-IR Spectrometer, It was prepared by means of 1 mg of the sample mixed with 300 mg KBr and then formed into transparent pellets. These pellets are then analyzed using FTIR with a wavenumber range of 350 to 4000 cm⁻¹

2.2.4. LCR-meter characterization. Electrical conductance of samples was measured by using an HiTESTER 3522-50 LCR Meter. The measurement is carried out using a frequency interval of 50 Hz to 50 kHz. The sample to be tested is placed between two electrodes and connected to the LCR meter for scanning.

3. Results and discussions

3.1. Phase characterization

This research was carried out by the method of precipitation assisted by microwave irradiation by mixing 0.5M CaO suspension and 0.3M H₃PO₄ solution to obtain a Ca/P molarity ratio of 1.67. Henceforth varying the molarity ratio [P]/[F] and the irradiation of the microwaves used. The resulting sample will be adjusted to the fluorhydroxyapatite database, namely with the Joint Committee on Powder Diffraction Standards (JCPDS) literature number 15-0876 belonging to fluorapatitite and number 09-0432 of hydroxyapatite since the literature data for fluorhydroxyapatite is not yet available. Figure 1 and figure 2 are the results of the XRD characterization of fluorhydroxyapatite samples with each treatment.

The X-ray diffraction pattern in fluorhydroxyapatite samples with molarity variations [P]/[F] 4 with different microwave irradiation is shown in figure 1. From the three graphs with each microwave variation, all of them indicate the presence of the fluorhydroxyapatite phase, only the difference is the number of impurities accompanying it and the high intensity of fluorhydroxyapatite obtained. The highest intensity of fluorhydroxyapatite was found in samples with the highest variation of microwave irradiation, which is 100P, and the intensity of fluorhydroxyapatite decreased with decreasing irradiation of the microwaves used. The Ca(OH)₂ phase appeared in all three samples with different intensities. Samples with 30P microwave irradiation had the highest Ca(OH)₂ intensity between the other two samples. The intensity of Ca(OH)₂ also seems to decrease with increasing microwave irradiation used. This shows that the higher the microwave irradiation used, the more the fluorine ion will react to, replacing the hydroxyl group. In addition, the CaO phase also appeared in all samples as well as the Ca(OH)₂ phase, which was supported through the FTIR results which showed the presence of CaO functional groups in all three samples. But the results obtained, only seen in samples with 100P of microwave irradiation.
Figure 1. The X-ray diffraction pattern of fluorhydroxyapatite powder with variations in molarity of [P]/[F] 4 with variations in microwave irradiation 30P, 50P and 100P.

Figure 2. The X-ray diffraction pattern of fluorhydroxyapatite powder with variations in molarity of [P]/[F] 6 with variations in microwave irradiation 30P, 50P and 100P.

Figure 2 shows the pattern of X-ray diffraction of samples with variations in molarity of [P]/[F] 6 with variations in microwave irradiation. Fluorhydroxyapatite phase appeared in all samples with different intensities, and the highest intensity was owned by samples with a variation of 100P microwave irradiation. The Ca(OH)\(_2\) phase also appeared in all samples, but the intensity was lowest at 100P microwave irradiation. It can be seen that the greater the microwave irradiation used, the intensity of Ca(OH)\(_2\) that appears will also be smaller.

X-ray diffraction pattern from the two pictures above with the variation of molarity and microwave irradiation used, it can be seen that the intensity of fluorhydroxyapatite obtained is higher in molarity variations in [P]/[F] 4 than [P]/[F] 6. Results what is seen is the Ca(OH)\(_2\) phase which is found to be not
so significant in [P]/[F] 6 decreases when adding microwave irradiation, unlike in [P]/[F] 4 which shows a significant difference in the Ca(OH)₂ phase appears on the sample. This is appropriate because the concentration of fluorine in molarity variations of [P]/[F] 4 is greater than [P]/[F] 6 so that the existing fluorine will also replace more hydroxyl groups as the microwave irradiation is used, as evidenced by reduced intensity of Ca(OH)₂.

3.2. Functional groups
Observations using FTIR testing were carried out to determine the functional groups contained in the sample and to know the fingerprint of the sample that cannot be seen through XRD testing. Figures 3 and 4 show the FTIR spectra of samples with molarities variations [P]/[F] 4 and 6 with variations in the microwave irradiation of 30P, 50P and 100P. The same functional groups are shared by all samples namely phosphate (PO₄³⁻), hydroxyl (OH⁻ and OH...F), carbonate (CO₃²⁻) and CaO. The wavenumbers of each functional group are in table 1.

![FTIR spectra](image)

**Figure 3.** FTIR spectra for fluorhydroxyapatite with a molarity variations of [P]/[F] 4 and with variation of microwave irradiation 30P, 50P and 100P.
Figure 4. FTIR spectra for fluorhydroxyapatite with a molarity variations of [P]/[F] 4 and with variation of microwave irradiation 30P, 50P and 100P.

Table 1. The fluorhydroxyapatite FTIR assignments and wavenumber of each variations

| Assignment | Literature | \([\text{P}]/[\text{F}] \ 4\) | \([\text{P}]/[\text{F}] \ 6\) |
|------------|------------|----------------|----------------|
| \(\text{OH}\) | 744\(^1\) | 747 | 744 | 744 | 746 | 746 |
| \(v_3 \text{PO}_4^{3-}\) | 1048\(^1\) | 1042 | 1045 | 1052 | 1038 | 1038 | 1039 |
| \(v_1 \text{PO}_4^{3-}\) | 970\(^1\) | 966 | 966 | 965 | 965 | 965 | 965 |
| \(\text{CO}_3^{2-}\) | 1473\(^1\) | 1466 | 1467 | 1466 | 1460 | 1461 | 1460 |
| \(v_4 \text{PO}_4^{3-}\) | 568\(^1\) | 573 | 572 | 573 | 571 | 572 | 572 |
| \(v_4 \text{PO}_4^{3-}\) | 605\(^1\) | 607 | 609 | 607 | 609 | 609 | 609 |
| \(\text{HPO}_4^{2-}\) | 870\(^1\) | 876 | 877 | 874 | 875 | 875 | 874 |
| \(\text{CaO}\) | 3640\(^2\) | 3646 | 3647 | 3645 | 3644 | 3645 | 3645 |
| \(\text{OH}...\text{F}\) | 3546\(^1\) | 3539 | 3541 | 3543 | 3542 | 3547 | 3546 |

\(^1\) Sumber : Eslami \textit{et al.} 2009
\(^2\) Sumber : Nasrazadani \textit{et al.} 2008
The HPO$_4^{2-}$ function group appears at wave numbers about 870 cm$^{-1}$ in all samples. The CaO functional group appears in all samples at wavenumbers around 3645-3646 cm$^{-1}$ [16]. This justifies the data shown in XRD testing. This CaO functional group arises because it has not bonded with other compounds during the process of precipitation and sintering. In addition, it is also possible to increase the volume of CaO, so that it cannot be paired with other functional groups as expected.

Characteristics of PO$_4^{3-}$ functional groups have four different asymmetric vibration modes including $v_1$, $v_2$, $v_3$ and $v_4$. Vibration modes $v_1$ and $v_2$ are observed respectively at wavenumbers 961 and 471 cm$^{-1}$. Vibration mode $v_3$ is the main vibrational mode of the PO$_4^{3-}$ functional group which is at wavenumbers between 1000-1100 cm$^{-1}$, and finally is the vibration mode $v_4$ at wave number 560-610 cm$^{-1}$ which occupies two crystal lattice locations, 603 and 574 cm$^{-1}$ respectively [7]. The PO$_4^{3-}$ functional group found in the sample is only vibration mode $v_1$, $v_3$, and $v_4$. Vibration mode $v_1$ PO$_4^{3-}$ of all samples is around the wave numbers 966 and 965 cm$^{-1}$ [16]. For vibration mode, $v_3$ PO$_4^{3-}$ of all samples are around wave numbers 1038 to 1052 cm$^{-1}$ and vibration mode $v_4$ are at wavenumbers between 571-573 cm$^{-1}$ and 607-609 cm$^{-1}$ [16].

Wave numbers around 744-747 cm$^{-1}$ appear in all samples that are owned by hydroxyl (OH$^-$) functional groups. When this hydroxyl group is partly replaced by a fluorine ion, it will switch to a new bond to an OH $\ldots$ F bond [17]. This functional group appears in all samples around the wave number 3542-3546 cm$^{-1}$. This is a unique characteristic possessed by fluorhydroxyapatite which is not possessed by other types of calcium phosphate. Based on this, it is clear that all the samples produced were fluorhydroxyapatite.

The carbonate (CO$_3^{2-}$) functional group also appeared in all fluorhydroxyapatites samples, which were present in wavenumbers around 1460-1467 cm$^{-1}$. This indicates the presence of apatite carbonate. This carbonateapatite can arise due to absorption of fluorhydroxyapatite samples of carbon dioxide from the atmosphere [16].

3.3 Conductivity evaluation

Conductivity can occur due to ion jumps. In fluorhydroxyapatite, the conduction mechanism is related to the release of fluoride ions along the c axis from the cell unit to the lattice in the interstitial state and then back again. Fluoride ions must move to other positions by forming defects, where these defects can occur through thermal activities such as Schottky defects which require high activation energy due to the nature of the fluorhydroxyapatite material [18].

The conductivity of the sample can be seen in figure 5 and figure 6. It can be seen that the conductivity value of all samples increased with increasing frequency, in other words, the conductivity value is linearly related to frequency. This can be explained through theory, where the frequency value corresponds to the R-C (resistor-capacitor) model. The ion contained in a material is a complex conductive and capacitive state [19]. Meanwhile, the irradiation used in the process of fluorhydroxyapatite synthesis does not show any relationship with the conductivity value of fluorhydroxyapatite. It can be seen that the variation in molarity of [P]/[F] 4 and [P]/[F] 6 conductivity values are different and are not consistent with increasing frequency. Fluorhydroxyapatite with 30P of microwave irradiation at [P]/[F] 4 has the lowest conductivity among other samples, while at [P]/[F] 6 the lowest conductivity is owned by 100P of microwave radiation. This shows that the irradiation of the micro irradiation microwave used does not affect the conductivity value of fluorhydroxyapatite.
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4. Conclusion

Fluorhydroxyapatite synthesis based on chicken eggshells was carried out using precipitation method assisted by microwave irradiation, by varying the ratio of molarity and microwave irradiation used. The XRD results show that samples at 100P irradiation both in [P]/[F] 4 and 6 molarity variations, fluorhydroxyapatite has the least impurity intensity among the others and the highest fluorhydroxyapatite intensity among the others. FTIR analysis also shows that all samples have the same functional groups. The FTIR analysis also shows that fluorhydroxyapatite has formed, which is shown by the emergence of the OH...F functional group at wavenumber 3539-3544 cm⁻¹. Microwave irradiation and molarity ratio [P]/[F] showed no relationship with conductivity value of fluorhydroxyapatite.
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