MECHANICAL PROPERTIES OF $CaCO_3$ EXTRACTED FROM COCKLE SHELL WITH HIGH DENSITY POLYETHYLENE (HDPE) FOR BIOMATERIALS IN BONE SUBSTITUTE APPLICATION

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ABSTRACT: *This study was conducted to produce $CaCO_3$ powder extracted from cockle shells as bioceramic materials which later combined with high density polyethylene (HDPE) as the polymer to produce composite as the final product. For $CaCO_3$ clarification, the powder form of bioceramics was analyzed using FTIR, SEM and EDX analyses. Then, the composites produced were tested for mechanical properties via tensile and hardness tests. Firstly, the wasted cockle shells were all washed to remove dirts and soaked in regular water overnight before left to dry at room temperature. Then, they were all ground up between range 100 – 200 µm several times until the required size were obtained. The spectrum for FTIR showed identical result as previous work at reading 857.22cm-1 which represent vibrational bonds that can be attributed to the characteristics of external plane bending vibration of carbonate. After the confirmation, it was added to the melted HDPE to produce stronger composite via injection moulding method. Injection moulding process was to produce the sample into the shape of dumbbell to perform mechanical tests, tensile and hardness test with three parameters for each weight ratio. It could be concluded that pressure, velocity and temperature affecting the hardness of samples. In this research, the greatest value of Young's modulus and maximum force which are 852.2 MPa and 271.457 kN, respectively. In conclusion, cockle shell could become great biomaterial as it provide good in mechanical properties. Furthermore, the source also abundantly available and with the fully usage of this waste to something more useful, it is able to reduce contamination to the earth. Then, the combination with any polymer is able to produce strong composite that could apply in any field. For this research, the composite is focus in biomaterial usage, especially in orthopaedic field for bone implant. For instance, $CaCO_3$ are proved to be function at higher temperature, and further future works might be required to search the maximum temperature that this material could achieve.*

Keywords: Biomaterials, mechanical properties, synthetic implants, calcium carbonate

1. INTRODUCTION

Shellfish is type of seafood plentifully available in Malaysia and be a favorite to mostly Malaysian. Malaysia is expected to produce 13000 metric ton shells in the entire period of the Ninth Malaysia Plan with Selangor aims to deliver 10 years of mussels in 2010 [1]. Unfortunately, the wasted from it, which is the cockle shell could contribute to bad odor to the environment. On top of that, it also polluting the beautiful and clean environment. The shells thrown away and dumbed may cause an unpleasant smell and not show a very good scenery to the environments.

An innovation to convert this waste into something more useful to society have come forward these days. Hoque, Sheryar and Nurul Islam (2013) came out with Calcium Carbonate ($CaCO_3$) bioceramics that extracted from cockle shell [2]. In their research this material is potentially applied in multiple tissue engineering such in this work, the bioactive material that might be useful in orthopaedic application, specialty in bone implant. The problems arise from conventional techniques such as autograft and allograft. There is no 100 percent assurance that bone from donor host is healthy. To achieve the requirement, usually the bone must be cleaned, processed and tested for sterility before it is sent to doctors for surgical operation [3]. Besides the said problem from allograft, autograft claimed to be better method but unfortunately patient need to face double pain, which is from the donor and fracture site [4].

Anadara Granosa locally known as 'kerang' in Malaysia is a bivalve owned by family Arcidae [5]. It contains almost 95-99% by weight of $CaCO_3$. Cockle shell contains of $CaCO_3$ which has enabled it to be used for quite some purposes such as biomaterials for bone repair [5]. It also could be useful for industry and daily practice such as in waste water and sewage treatment, the production of glass, construction materials, agriculture and more. A previous study by Abu Bakar, Noazri and Zaleha (2004) showed that the mineral composition of cockle shells has a lot of similarities to that of coral means that the possibility of using cockle shell as an alternative biomaterials for bone substitute in managing bone defects [6]. Polymers are long chains of molecules consist of repeating units. There are many types of polymers including natural materials such as cellulose, collagen and synthetic materials [7]. On years of experiments and clinical investigation, there are few synthetic polymer which is considered as 'biocompatible' [8]. Those polymers are well known as biocompatible for human body and widely used in the medical applications: polyethylene (PE), polypropylene (PP), polyurethane (PU), polytetrafluoroethylene (PTFE), poly vinyl chloride (PVC), polyamides (PA), poly (methy1 methacrylate) (PMMA), polyacetal, polycarbonate (PC), poly (ethy1ene terephthalate) (PET), polyetheretherketone (PEEK), and polysulfone (PSU).

Polyethylene (PE) is the most stand out polymers among all bio stables polymers [7]. PE is a synthetic polymer and a chemical formula (ch^2ch^2). PE is made from a material called ethylene through different process [9]. There are few types of PE in the market: low density polyethylene (LDPE), linear low density polyethylene (LLDPE), high density polyethylene (HDPE), cross-linked polyethylene (XLPE) and ultra-high molecular weight polyethylene (UHMWPE). The density of polyethylene ranges from 0.92 to 0.97 g/cm^2. HDPE and UHMWPE are both which found widely used in the medical field [9].

From mechanical point of view, artificial bone implant material should have the same strength as an original bone especially cortical bone and the stress have to match as well to prevent fracture [10]. $CaCO_3$ embedded in HDPE could produce stronger composite as an artificial bone substitute.

2. EXPERIMENTAL DETAILS

The experimental work including the production of bioceramic from cockle shell, followed with producing composite materials. The sample preparation for this study can be classified into 3 main sections, namely crushing, mixing and injection molding proses. The samples were tested for hardness, tensile and

2.1 Crushing and Grinding Process

Before the process of crushing and grinding is carried out, collected cockle shell have to be cleaned up from dirt by immersed in regular water overnight. Then, let them completely dry at room temperature to ensure that it will not stick to the blade of grinding machine. Once done, fragments of the crushed cockle shell have to undergo the same process of crunching few times to get the smallest size of it. The powder of the cockle shells was filtered with the size of 200µm. By using a rotor mills, the size is reduced to under 100µm. To obtain a uniform size powder, it was all sieved using 100 µm sieve equipment. The final product is appear in fine white powder known as Calcium Carbonate ($CaCO_3$).

2.2. Mixing Process

HDPE is mixed with $CaCO_3$ via mixing process. The process is repeated three times based on three chosen parameters, which are pressure, velocity and temperature that set up for injection moulding process. The ratio percentage of mass of the $CaCO_3$ powder to HDPE are as listed in the following: 60% $CaCO_3$ with 40% HDPE as sample 6, 50% $CaCO_3$ with 50% HDPE as sample 5, 40% $CaCO_3$ with 60% HDPE as sample 4, 30% $CaCO_3$ with 70% HDPE as sample 3, 20% $CaCO_3$ with 80% HDPE as sample 2 and 10% $CaCO_3$ with 90% HDPE as sample 1.

In this method, HDPE polymer was heated to the melting point. Then, $CaCO_3$ powder was added into melted polymer. The process was conducted by using machine hot roll mixer. Then, the mixture was left to be dried at room temperature. After that, the resulting mixture was crushed again into a fine details to ensure that injection moulding process will be easier. *2.3 Injection Moulding*

The mixture of HDPE and $CaCO_3$ were melted at different temperature, pressure and velocity. Then, shaped the melted mixture composite into dumbbell. The melting point for HDPE is 170℃. There are three parameters used for this process. Parameter 1 pressure is 60%, velocity is 60% and temperature is 210℃. Parameter 2 pressure is 65%, velocity is 65% and temperature is 215℃. Parameter 3 pressure is 70%, velocity is 70% and temperature is 220℃.

2.4 Samples Testing

The clarification of $CaCO_3$ powder were implemented using three types of analyses which are FTIR, SEM and EDX analyses. Then, all the samples were undergone through two types of testing to obtain their mechanical properties. There are tensile and hardness test. For tensile testing, all the procedures were referred to ISO 527. While for hardness test, it was referred to ISO 179 standard.

3. RESULTS AND DISCUSSION

There are three types of analyses involved to interpret $CaCO_3$ powder which are FTIR, SEM and EDX analyses. Next was evaluation of their mechanical properties through two type of testing as said.

3.1 $CaCO_3$ Analysis

3.1.1 Fourier Transform Infra-Red (FtiR) Analysis of $CaCO_3$

Figure 1(b) shows graph obtained for $CaCO_3$ by using Perkin Elmer Fourier Transform Infra-Red machine. The spectrum showed vibrational bonds at 710.07 cm^{-1} and 857.39 cm^{-1} that can be attributed to the characteristic of internal plane bending mode of aragonite and external plane bending vibration of carbonate, respectively. These readings are compared with previous works by Ihli and friends [11] that confirm the powder produced is purely $CaCO_3$ as can be seen from Figure 1 (a).

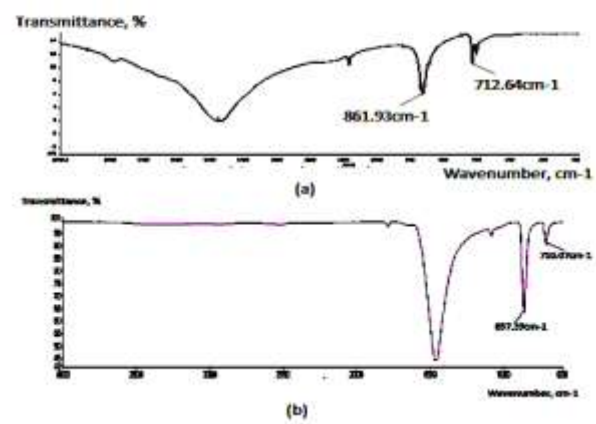

Figure 1: FTIR wavenumber for $CaCO_3$ (a) Referred to previous work [11], and (b) Done by the author

3.1.2 Energy Dispersive X-ray Spectrometry (EDX)

Figure 2 (a) shows the EDX spectrum of tests that have been carried out on the powder of Calcium Carbonate, $CaCO_3$. The purpose of this test is to identify the percentage of the elements contained in powder $CaCO_3$. The results obtained from this test has been compared with that of previous research to ensure the percentage of the elements contained in the powder $CaCO_3$ is very similar to previous studies as shown in Figure 2 (b).

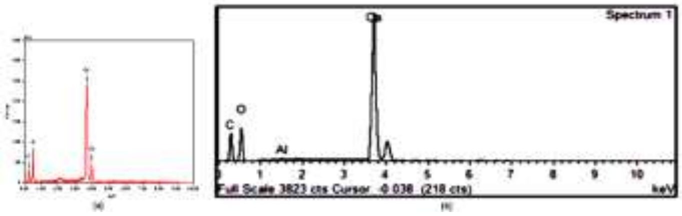

Figure 2: EDX spectra show peaks of various elements contained in $CaCO_3$ (a) Done by the author, and (b) Obtained from previous work [12]

3.1.3 Scanning Electron Microscopy (SEM) Analysis of $CaCO_3$

Figure 3 illustrates the surface morphology of $CaCO_3$ from cockle shell powder. Micron-sized solid calcite crystals as observed in commercial calcium carbonate, while the rod-like aragonite crystal powder found in cockle shells Figure 3 (a). This agrees with the results of previous studies Figure 3 (b) [12], in which the cubic-like calcite and rod-like aragonite were observed.

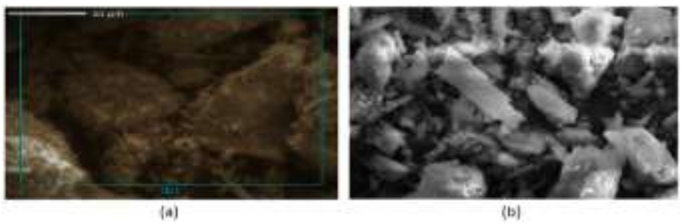

Figure 3: The surface morphology of calcium carbonate powder $CaCO_3$ (a) Analysed $CaCO_3$ extracted from cockle shell, and (b) Obtained from previous work [12]

3.2 Mechanical Test

3.2.1 Hardness Test

A strong bond between matrice and reinforcement occurs in this mixing. HDPE is a polymer that serves as a matrice while $CaCO_3$ serves as reinforcement. The existence of pores in material such as HDPE makes the materials softer. The possibility of the existence of $CaCO_3$ in the composite can fill the hole caused the composite harder.

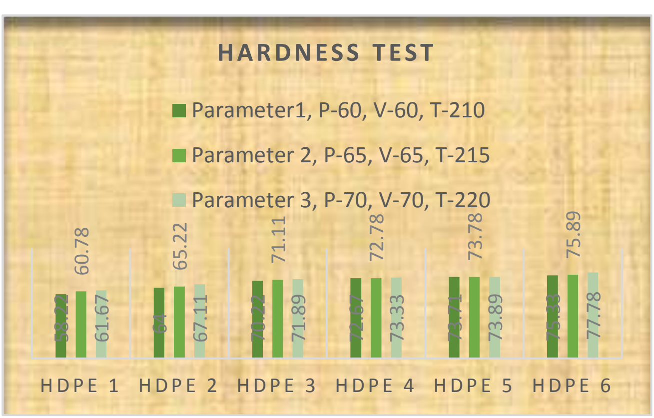

Figure 4: Hardness Test Graph for Each Weight Ratios and Parameters

From the bar graph, it can be concluded that the hardness percentage recorded highest value when the composite contains highest percentage of $CaCO_3$. HDPE 6, as referred to graph in Figure 4 shows reading at 77.78 with 60% $CaCO_3$ in the composite compared to other composite that having lower percentage of bioceramics such in HDPE 1 until HDPE 5. This also proved that if the composite material is well design and fit with some of the properties, it is able to improve its strength, hardness and heat insulation [13].

3.2.2 Tensile Test

3.2.2.2 Young's modulus

The value of Young's modulus are changing according to the percentage of $CaCO_3$ and parameters. For sample 6 parameter 2 showed the highest value Young's modulus with the value of 852.2 MPa. Meanwhile, the second value obtained from sample 6 parameter 1 with the value of 764.3 MPa and sample 6 parameter 3 is the third reading with value of 720.8 MPa.

Besides that, for sample 5 the highest value of young's modulus is 583.7 MPa for parameter 2 while the other two samples are 458.2 MPa for parameter 3 and 447.5 MPa for parameter 1, respectively. For sample 4, parameter 1 shows higher force with 529.9 MPa followed sample from parameter 2 at 484.6 MPa and lastly, parameter 3 at 409.4 MPa.

Next, for sample 3 the highest value for Young's modulus is 408.9 MPa for parameter 2. Then, parameter 1 followed with parameter 3 with value recorded at 352.3 MPa and 338.7 MPa, respectively. For sample 2 the highest value for Young's modulus is parameter 3 with the value of 195.4 MPa and parameter 2 is the second highest with the value 180.0 MPa. Parameter 1 is the least with 167.0 MPa. The lowest value of young's modulus among all sample is sample 1 with the highest value is 83.2 MPa for parameter 1, 71.9 MPa for parameter 3 and 70.7 MPa for parameter 2. Young's modulus is elastic properties that demonstrate the ability of the material returned back to its original shape after the load being applied upon it. The highest value for young's modulus recirded is from sample 6 parameter 2 with the value of 852.2 Mpa. All the results are simplified as shown Figure 5.

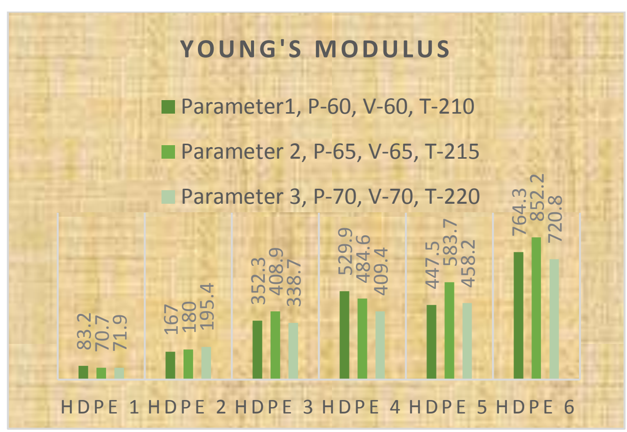

Figure 5: Young's Modulus graph for each weight ratios and parameters

4. CONCLUSIONS

$CaCO_3$ Was successfully extracted from cockle shell as proved by three analyses; FTIR, SEM and EDX via several simple steps. Based on analysis had been done on the $CaCO_3$ powder by using FTiR testing, it can be concluded that the fine powder extracted from $CaCO_3$ powder has the potential to be used as material biomaterial. This is because the elements contained in calcium carbonate $CaCO_3$ such as calcium, carbon and oxygen mentioned in this EDX and SEM analysis. When compared with previous studies [6], there are similarities in terms of the required element in the$CaCO_3$.

Next, their combination with HDPE improves the strength of the composite. As expected the highest amount of $CaCO_3$ give the highest value of the modulus Young, maximum stress and maximun force but the material becomes more brittle. The parameters of injection moulding did not reveal any significant change with the inconsistent value among the parameters.

5. ACKNOWLEDGEMENT

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