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Mechanical Properties of Biocomposite with Various Composition of $CaCO_3$ and Starch

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ABSTRACT

Calcium carbonate has the potential to be used in the development of medical materials, including biomaterials. Biocomposite is composed of $CaCO_3$ as matrix material and bioplastic from the combination of corn starch and cassava starch as reinforcement. This study aims to determine mechanical properties such as tensile strength and bending/flexural strength with varying compositions of $CaCO_3$ and bioplastic. Characterization of the biocomposite uses Scanning Electron Microscope to observe the microstructure and composition elements of their structure. This study used 4 variations in the ratio of $CaCO_3$ suspension: (Corn Starch + Cassava Starch). Each sample was characterized using specimen code A for composition 30:70 (w/w)% and specimen B for composition 40:60 (w/w)%, specimen C for composition 50:50 (w/w)%, and specimen D for composition 60:40 (w/w)%. Based on the results of shrinkage measurements on flexural strength specimens, specimen B has the lowest percentage value of 15±0.01%. The lowest tensile strength specimen is found in specimens C and D at 12±0.01%. The tensile test results also showed that specimen D had a higher ultimate strength value than the other specimens, which was 0.06±0.03 MPa. Microstructure characterization was carried out using scanning electron microscopy with energy-dispersive X-ray spectroscopy, which revealed the presence of Oxygen at approximately 48.39% mass, Carbon at approximately 30.27% mass, Nitrogen at approximately 11.77% mass, Calcium at approximately 9.57% mass, with Calcium being detected in the form of Calcium Carbonate ($CaCO_3$).

Keywords: *Bending strength, biocomposite, bioplastic, $CaCO_3$, cassava starch, tensile strength*

I. Introduction

Calcium phosphate- and $CaCO_3$–based ceramic materials have garnered significant attention in medical applications due to their similar mineral compositions and crystal structure with natural bone, excellent biocompatibility, osteoconductivity, and osteoinductivity [1]. Calcium carbonate or $CaCO_3$ has six polymorphs: vaterite, aragonite, calcite, amorphous, crystalline monohydrate, and hexahydrate. It has a typical biomineral that is abundant in both organisms and nature and has important industrial applications [2]. Calcium carbonate is a derivative material from limestone that is processed with calcinate to extract calcium content. The industry has consumed limestone for many purposes and fields such as iron and steel fluxes, manufacturing industries for glass making, papermaking, and agricultural fields as soil conditioner [3]. Calcium carbonate has the potential for development in biomedical applications [4]. Bioceramics are ceramics that are used for the

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health of the body and teeth in humans [5]. The material used in the manufacture of this bioceramic is calcium carbonate ($CaCO_3$).

Bioplastics or often called biodegradable plastics have properties that are compatible with the body. Bioplastics such as corn starch and cassava starch. Cassava starch is a natural polymer. For plasticized purposes, we can add glycerol [6], even with low mechanical properties and hydrophilic [7]. Citric acid-epoxidized soybean oil oligomers (CESO) were prepared and utilized to improve the properties of corn starch-based bioplastics [8]. The properties of cassava starch can be improved their properties and biocompatibility by using reinforcement from natural fiber and celluloses [9]. Tontowi et al. developed biocomposite from the hydroxyapatite–bioplastic material [10]. Biphasic calcium phosphate (BCP) development has been broadly performed in bone tissue engineering [11]. Also, the combination of hydroxyapatite (HA) and biphasic calcium phosphate (BCP) has the potential to develop in application bone tissue engineering [12,13]. Pure HA has poor biodegradability, which limits bone ingrowth and may lead to deformity after implantation in the long term [14]. A combination of calcium carbonate and natural bioplastics such as cassava and corn starch are an alternative to developing a biomaterial.

This study was conducted to determine the composition variation of $CaCO_3$ suspension as matrix and bioplastic from the combination of cassava starch and corn starch as reinforces that have tensile and bending strength values. They then characterized the highest bending and tensile value with Scanning Electron Microscope (SEM) to determine their microstructure.

II. Material and Methods

1. Material

The materials used in this research are $CaCO_3$, corn starch, and cassava starch with other supporting ingredients, namely citric acid and glycerol. Biocomposites are made by mixing bioceramics and bioplastics by varying their composition. $CaCO_3$ suspension of 20% (w/v) was prepared by dispersing $CaCO_3$ powder in aquadest with 10% (w/v) citric acid. The suspension $CaCO_3$ was stirred using a hot plate magnetic stirrer to obtain a homogeneous suspension and become bioceramic. Corn starch suspension of 60% (w/v) was prepared by dispersing corn starch in aquadest with the addition of 10% (w/w) citric acid, then 40% (v/w) glycerin, as well as making suspension of cassava starch with 40% (w/v) in aquadest. Suspension of corn starch and cassava starch was converted into bioplastic by stirring at 500 RPM at 50^{o} C until homogeneous. The biocomposite paste was created by mixing bioceramics and bioplastic suspensions in a weight percent variation (w/w) ratio, as shown in Table 1.

Table 1. Composition of biocomposite variations

Code of specimen	Composition Ratio (% w/w)	
	Suspension of $CaCO_3$	Corn starch + cassava starch
A	30	70
B	40	60
C	50	50
D	60	40

2. Shrinkage

Shrinkage is done after the drying process. The shrinkage measurement aims to see the volume change in the specimen after the molding process.

3. Tensile Test

The tensile test was carried out using the Hung Ta HT – 2402 Universal Testing Machine made in China with a crosshead speed setting of 10 mm/min. Specimen standard using ASTM D 638 Type IV (116 mm x 22 mm x 4mm), as shown in Figure 1, to determine the ultimate tensile strength and Young modulus.

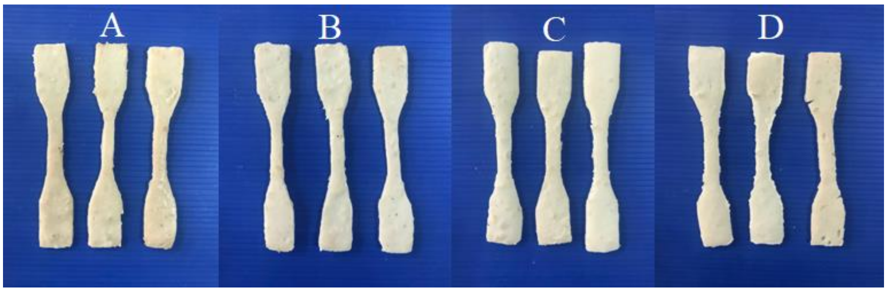

Fig. 1. Specimen σ_{UTS} ASTM D 638 type IV

4. Flexural Test

The flexural test specimen using ASTM D 790 standard (50 mm x 25 mm x 4 mm), which can be seen in Figure 2, to determine the value of flexural strength.

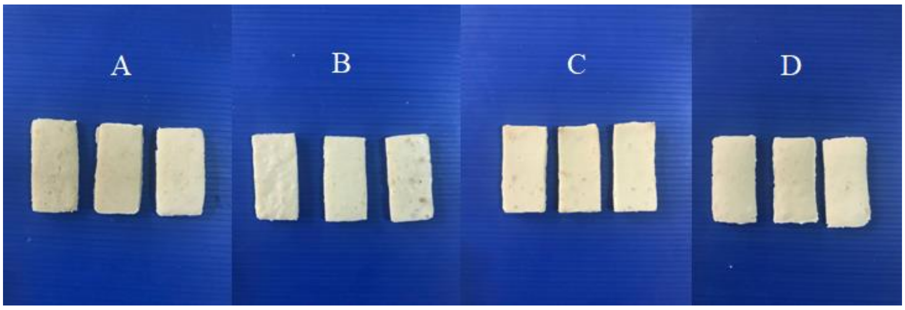

Fig. 2. Specimen σ_{FS} ASTM D 790

Microstructure Characterization using Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy (SEM-EDX)

SEM-EDX was utilized to qualitatively and quantitatively determine the surface morphology and chemical composition of the specimens elements.

III. Results and Discussions

1. Shrinkage Analysis

The average shrinkage value of the tensile test specimen is shown in Figure 3, and the average shrinkage of the bending test is shown in Figure 4.

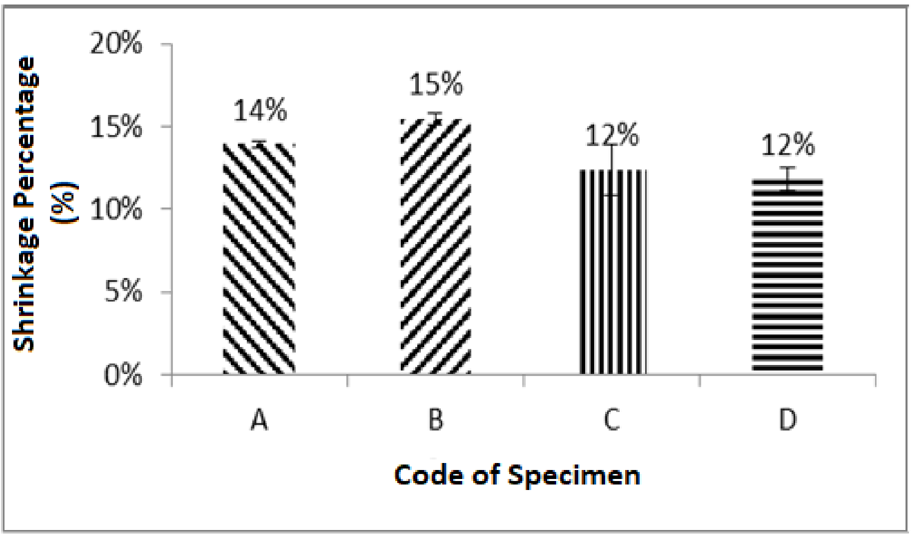

Fig. 3. Average shrinkage percentage of UTS specimen

In Figure 3, it is shown that specimen B has the highest average value of shrinkage tensile test specimen, which is 15±0.00%, compared to specimen A, 14±0.00%, and specimen C and specimen D, which has an average shrinkage value of 12±0.01%.

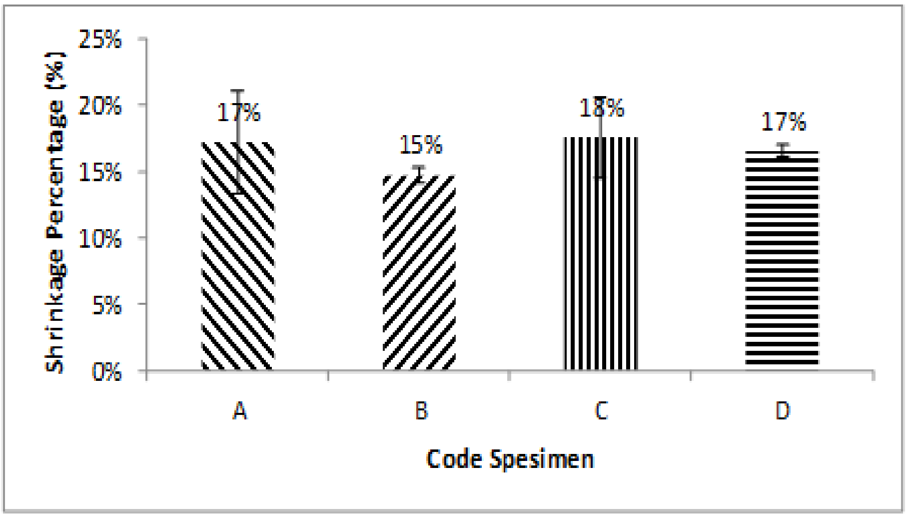

Fig. 4. Average shrinkage percentage of the flexural test specimen

Figure 4 shows that specimen B has the lowest mean value of shrinkage flexural test specimen, which is 15±0.01%, compared to specimen A, 17±0.04%, and specimen C, 18±0.03%, and specimen D which has an average shrinkage value of 17±0.00%. Biocomposite specimens undergo shrinkage due to the presence of gas molecules that cause porous. During the solidification process, porosity can inhibit solidification and affect the mechanical properties of the material. The level of porosity is influenced by the composition of the suspension of bioceramics and bioplastic. The optimum composition was found to be a suspension of 50% hydroxyapatite and 50% cassava starch (by weight), resulting in a shrinkage value of approximately 28% [15].

2. Tensile Test Analysis (σUTS)

The mean ultimate tensile strength (σ_{UTS}) value is shown in Figure 5. It shows that specimen D has the highest mean ultimate tensile strength (σ_{UTS}) of 0.06±0.03 MPa, while specimen A of 0.03±0.01 MPa, specimen B of 0.04±0.01 MPa, and specimen C of 0.04±0.03 MPa.

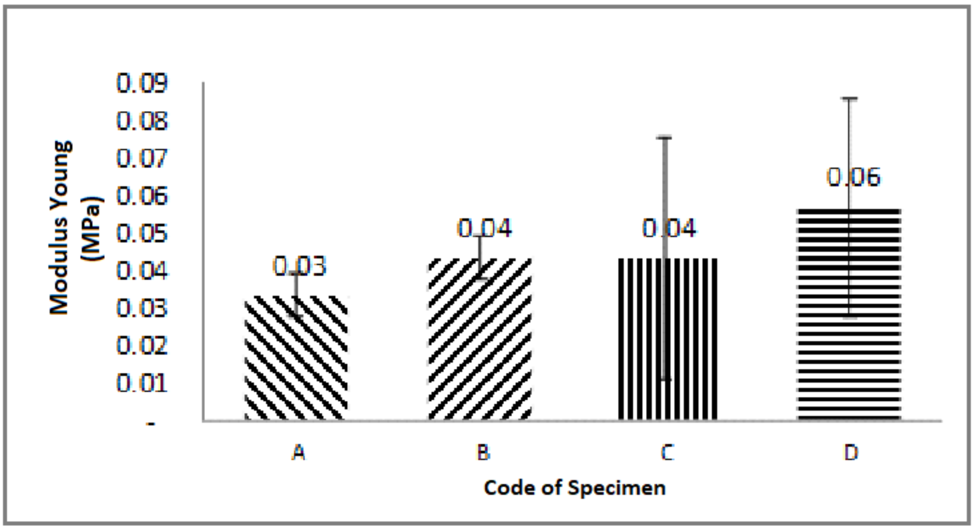

Fig. 5. Average of ultimate tensile strength

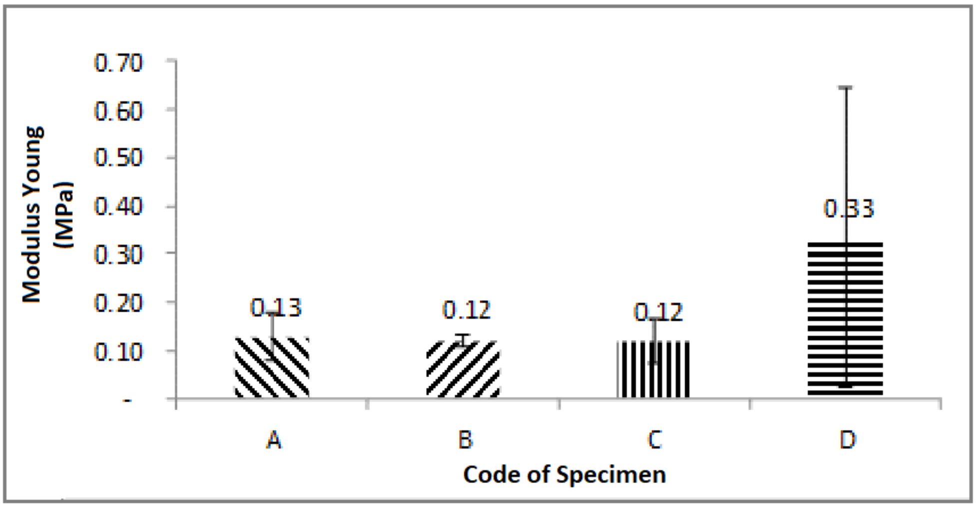

Fig. 6. Average Young's modulus

The average Young's modulus is shown in Figure 6. It is shown that specimen D has the highest Young's modulus average value of 0.33±0.031 MPa, while specimen A of 0.13±0.05 MPa, specimen B of 0.12±0.01 MPa, and specimen C of 0.12±0.04 MPa. It should also be noted that the composition of cassava starch/corn starch bioplastic as a reinforcement that functions as a binder in the specimen and its thermoplastic nature must also be considered. So, to get the maximum value of tensile strength, one must pay attention to the composition of $CaCO_3$ and cassava starch/corn starch and the effect of glycerol as a plasticizer. In research conducted by Li et al. on the composite composition with 60% corn starch content (w/w), the tensile strength can reach 10.95 MPa [16]. The value of ultimate tensile strength

(σ_{UTS}) is directly proportional to the value of Young's modulus, which means that the greater the resulting stress against the strain in the biocomposite specimen.

3. Flexural Test Analysis (σFS)

The mean value of flexural strength (σFS) is shown in Figure 7. Figure 7 shows that specimen A has the highest mean flexural strength (σFS) value of 0.02±0.006 MPa, while specimen B has 0.013±0.006 MPa. Specimen C and specimen D has an average value of 0.02±0.006 MPa.

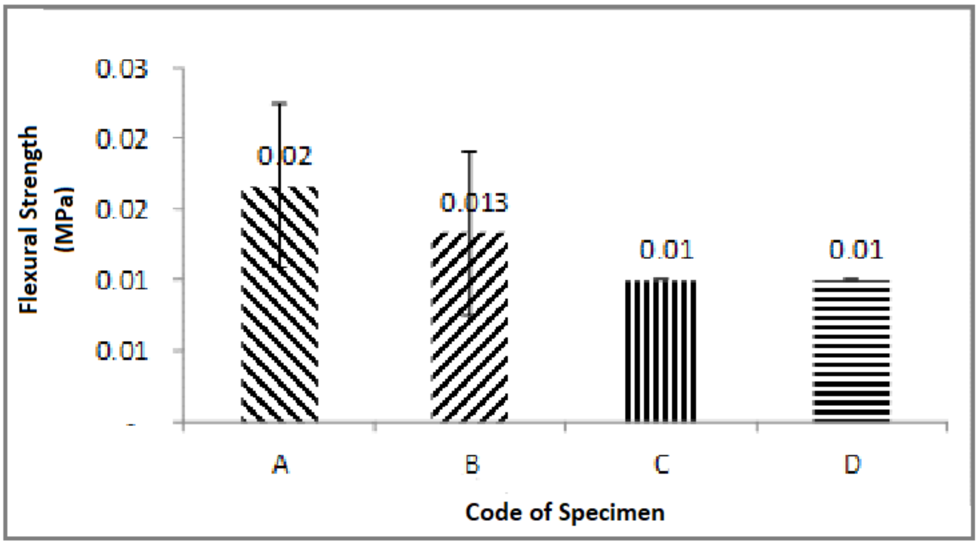

Fig. 7. Average of flexural strength

The percentage of bioplastics can have an impact on the flexural strength value of each composition, which is influenced by the level of hydrogen content in the bioplastics. During the evaporation process, which is also affected by temperature, the formation of pore sizes occurs, leading to increased porosity. The larger the porosity, the lower the density of the resulting biocomposites. The results of the low flexural test, when compared to the research conducted by Yamaguchi et al., the value of the compressive test obtained a compressive test value of 270 MPa using a sintering process with a temperature of 200ºC-250ºC for 1 hour [17].

4. Microstructure Analysis (σ_{FS})

Microstructural testing was conducted to determine the microstructure on the surface of the sample and the composition of the elements on the surface of the sample. As shown in Figures 8 (a) – 8 (d), the particles are solid and form a clump. At 5,000x magnification, as shown in Figure 8(d), the bonds in the particles become denser and form flakes. The structure formed can be affected by the sulfur content and acidity of the composite [18], and also heating temperature affects the shape. The structure formation of cellulose/$CaCO_3$ nanocomposite has been influenced by heating temperature. With the heating time of 2 hours and 4 hours, there is $CaCO_3$ aggregation and induces the formation of a porous structure in $CaCO_3$ agglomerates [19].

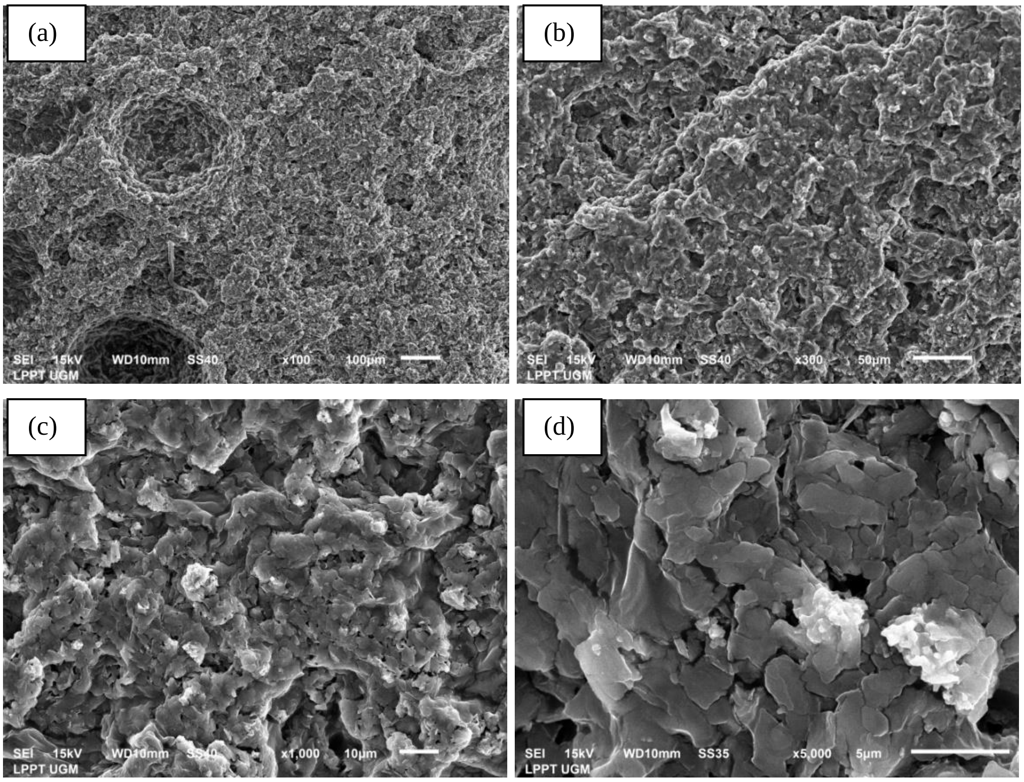

Fig. 8. Microstructures at magnification; (a) 100x, (b) 300x, (c) 1,000x, (d) 5,000x

Table 2. EDX data results

Element	Mass (%)	Atom (%)
C K	30.27	38.04
N K	11.77	12.69
O K	48.39	45.66
Ca K	9.57	3.61
Total	100.00	100.0

Table 2 shows the elemental content in the biocomposite specimen on SEM – EDX observations at 5,000x magnification. The element in the biocomposite analysis reveals that Carbon (C) is the dominant element, accounting for approximately 30.275% of the mass in the K atom-shell. Nitrogen (N) accounts for about 11.77% mass in the K atom shell, while Oxygen (O) accounts for approximately 48.39% mass in the K atom-shell. Calcium (Ca) is detected in the K atom shell with approximately 9.57% mass. The study also shows that both Carbon and Oxygen are present in significant amounts in the biocomposite. In a previous study by Siriprom et al., C-O bonds were detected in both $CaCO_3$ and cellulose [20]. Balzera et al. conducted a comparative study of the mineral element $CaCO_3$ contained in shellfish, oysters, and artificial $CaCO_3$ [21].

IV. Conclusions

Biocomposite ($CaCO_3$ suspension: bioplastic corn starch + cassava starch) has the potential to develop as soft material, regarding mechanical properties such as ultimate tensile strength (σ_{UTS}) and flexural strength (σ_{FS}). The highest tensile strength and the lowest flexural strength are 0.06±0.03 MPa and 0.01±0.00 MPa, respectively. Increasing the density of the material by considering the amount of aquades and the heating temperature can lead to an improvement in its mechanical properties. The microstructure of the material consists mainly of flake forms, with Carbon and Oxygen being the dominant elements present.

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