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Investigation of the Effect of Nozzle Temperature in Fused Deposition Modelling on the Mechanical Properties and Degradation Behaviour of 3D-Printed PLA/PCL/HA Biocomposite Filaments

Rifky Ismail[1,3,*], Deni Fajar Fitriyana[1,2], Muhammad Dzaky Arizsa Athallah[1,3], Fariz Wisda Nugraha[3,4], Baharudin Priwintoko[1,3], Athanasius Priharyoto Bayuseno[1], Samsudin Anis[2], Januar Parlaungan Siregar[5,6], Tezara Cionita[7], Dwi Novriadi[8], Opa Fajar Muslim[8]

1 Department of Mechanical Engineering, Faculty of Engineering, Diponegoro University, Semarang 50275, Indonesia
2 Department of Mechanical Engineering, Faculty of Engineering, Universitas Negeri Semarang, Kampus Sekaran, Gunungpati, Semarang 50229, Indonesia
3 Center for Biomechanics, Biomaterial, Biomechatronics, and Biosignal Processing (CBIOM3s), Diponegoro University, Semarang 50275, Indonesia
4 Department of Mechanical Engineering, Faculty of Engineering, Universitas PGRI Semarang, Semarang 50232, Indonesia
5 Automotive Engineering Center (AEC), Universiti Malaysia Pahang Al-Sultan Abdullah (UMPSA), Pahang, Malaysia
6 Faculty of Mechanical & Automotive Engineering Technology, Universiti Malaysia Pahang Al-Sultan Abdullah, Pekan 26600, Malaysia
7 Faculty of Engineering and Quantity Surveying, INTI International University, Nilai, Malaysia
8 Research Centre for Polymers Technology, National Research and Innovation Agency (BRIN), 460 Building Puspiptek Area, South Tangerang, Banten 15314, Indonesia

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ABSTRACT

The invention of three-dimensional (3D) printing has transformed the medical field, offering sophisticated and accurate options for surgery planning, education, and individualized therapy. Although 3D printing is widely used, little is known about how the parameters of the process affect the properties of composites reinforced with hydroxyapatite (HA) that has been derived from crab shells. The present study investigates the influence of nozzle temperature in fused deposition modeling (FDM) on the physical, mechanical and degrading properties of PLA/PCL/HA biocomposite specimens, assessing their viability as biodegradable implant materials. The biocomposites were produced with a mixture of polylactic acid (PLA), polycaprolactone (PCL), and hydroxyapatite (HA) sourced from crab shells. The nozzle temperature during the printing process was adjusted between 190°C and 215°C to assess its impact on key properties, including density, flexural strength, flexural modulus, and degradation rate. The results highlight the significance of nozzle temperature in affecting the performance of the biocomposites. The specimens produced at 205°C exhibited superior mechanical properties, featuring a flexural strength of 41.09 MPa, a flexural modulus of 474.789 MPa, and a density of 1.28 g/cm³, closely resembling the mechanical and density attributes of human cortical bone. Furthermore, this specimen demonstrated the lowest degradation rate, rendering it very appropriates for biomedical applications. This study utilizes crab shell waste to create biodegradable medical implants, enhancing healthcare while reducing environmental impact. Advanced 3D printing integrates sustainable practices, aligning with Sustainable Development Goals (SDGs) like Good Health (SDG 3), Innovation (SDG 9), and Marine Sustainability (SDG 14).

* *Corresponding author.*
E-mail address: r.ismail.undip@gmail.com

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1. Introduction

Bones are one of the important organs in the human body as support for the body. However, bone performance can decrease due to congenital defects, age factors or accidents that cause fractures [1]. ORIF (Open Reduction and Internal Fixation) is a medical procedure in the form of implant surgery to realign fractured bones [2]. The implants that are widely used today are stainless steel. 316L stainless steel is one of the most common stainless steels [3]. However, stainless metal materials have several disadvantages, such as they can interfere with taking X-Ray and MRI images, disrupt tissue growth and require a second operation to remove the implant [4-6]. In addition to 3166L stainless steel, titanium and its alloys are extensively employed in medicine and dentistry due to their exceptional mechanical properties and biocompatibility. Titanium is regarded as inert and safe for human utilization, exhibiting little adverse effects within the human body. Titanium-based implants are linked to non-degradability, susceptibility to corrosion, cosmetic constraints, and the risk of peri-implantitis [7,8]. In addition, stress shielding may result from titanium and 3166L stainless steel implants, which are more rigid than natural bone. This occurs when the implant absorbs the majority of the mechanical stress [9].

The use of (polycaprolactone) PCL and (polylactic acid) PLA in biomaterial applications has been widely developed in the medical world. PCL and PLA can provide temporary structural support as it is absorbed by the hydrolytic degradation process. This process is utilized by natural bone for tissue regeneration [10]. Apart from that, PLA has good biocompatibility, biodegradable and hardness properties [11]. Some of the mechanical properties of PLA include density 1.252 g/cm^3, melting temperature 180-190°C, flexural strength 65 Mpa, flexural modulus 2−4 Gpa and elongation at break 2-6% [9,10]. Besides that, PLA has disadvantages, namely its brittle nature and poor thermal stability. One method that is widely used is mixing PLA with biodegradable polyester which has high flexibility such as PCL [11-13]. PCL has a glass transition temperature of around 60°C with biodegradable, bioabsorbable, non-toxic, ductile and good mechanical properties [14]. Mixing PCL with PLA will increase the ductility of PLA by sacrificing the hardness of PLA to a minimum without damaging the biocompatibility and biodegradable properties of both materials [15]. PCL and PLA have proven to be very suitable in biomedical applications [16].

Furthermore, the use of calcium phosphate bioceramics such as hydroxyapatite (HA) has been widely researched as an alternative bone replacement material. The high potential as a bioactive possessed by HA is able to mimic the structure and dimensional characteristics of potassium phosphate in human bone tissue [17]. Due to these properties, it is widely used as an implant material in bone tissue engineering (BTE), for controlled drug release, dental implants, toothpaste additives, matrices for bone cement, and so on [18]. HA has several shortcomings in some of its mechanical strengths such as flexural, tensile and compressive strengths ranging between 38-250 MPa, 38-300 MPa and 120-150 MPa so development needs to be carried out to increase them [19]. On the other hand, the development of organic-based HA is still being widely researched from cow bones. Crab shells have great opportunities because they can be used for the synthesis of hydroxyapatite with a calcium carbonate content of up to 70% [20]. Apart from that, the potential availability of crab in Indonesia has a high quantity of around 534 tons in 2020 [21]. If crab shells have a maximum total weight of 50% of the crab weight, then the crab waste obtained is around 267 tons per year [20]. Therefore, HA from crab shells has enormous potential to be developed.

Fused deposition modeling (FDM) is among the most prevalent additive manufacturing (AM) techniques in the medical field, attributed to its affordability and user-friendliness relative to alternative AM methods [22-26]. Furthermore, FDM is applicable in many biomaterial applications like medical implants, dental models, hearing aids, orthopaedics, cranial implants, surgical instruments, dental restorations, and external prosthetics [22,23,27]. The nozzle temperature is a critical variable in the 3D printing process since it directly influences material flow, density, and the mechanical qualities of the produced prototype [26,28,29]. Research by Rivera-López *et al.,* [29] indicates that printing PLA filaments via the FDM method at lower temperatures may cause inadequate material flow, resulting in diminished density and compromised structural integrity, adversely impacting the printed object's mechanical performance and quality.

Conversely, elevated nozzle temperatures, reaching up to 260°C, may result in excessive material deposition, but they do not immediately compromise mechanical qualities. An ideal nozzle temperature range of 220-240°C has been established for most applications since it guarantees enhanced mechanical qualities while preventing complications such as excessive PLA filament deposition. Further research regarding the temperature of the 3D printed FDM nozzle was carried out by Alsoufi *et al.,* [28]. This research was carried out to determine the effect of extrusion temperature on the mechanical properties of pure PLA using a temperature of 190°C-250°C with a difference in each temperature of 5°C. It was concluded that variations in density values tended to increase with increasing extrusion temperature.

Polylactic acid (PLA) is a well-studied biomaterial in the biomedical sector and has been effectively 3D printed for several purposes, including pins, screws, washers, and darts [26,30]. Alongside PLA, PMMA (polymethyl methacrylate) [31] and composites of PLA, polycaprolactone (PCL), and HA derived from green mussel shells [32] have been effectively 3D printed for medical screw applications. Previously, research regarding the PLA/PCL/HA combination was carried out and it was found that this combination had good mechanical properties and prosthesis integration [33]. Subsequently, similar research was carried out by Ismail *et al.,* [34] with a combination of PLA/PCL and HA from green mussel shells. It was found that increasing the composition of HA and PLA increased the mechanical properties of the biocomposite. However, the degree of degradation in the specimen is increasing.

Although 3D printing is widely used, little is known about how the parameters of the process affect the properties of composites reinforced with hydroxyapatite (HA) that have been derived from crab shells. Therefore, the present study aims to investigate the influence of nozzle temperature in fused deposition modelling (FDM) on the physical, mechanical and degrading properties of PLA/PCL/HA biocomposite specimens, assessing their viability as biodegradable implant materials. The biocomposites were produced with a mixture of polylactic acid (PLA), polycaprolactone (PCL), and hydroxyapatite (HA) sourced from crab shells.

This research examines the creation of novel biodegradable medical implants sourced from crab shell waste. This category of biological waste can be efficiently managed while facilitating medicinal technology. This research advocates for sustainable production by reducing ecological degradation and optimizing resource utilization with sophisticated 3D printing technology. This method is consistent with other significant Sustainable Development Goals (SDGs), including enhancing medical outcomes to foster health and well-being (SDG 3), addressing marine waste challenges within the framework of contemporary manufacturing advancements, industry, innovation, and infrastructure (SDG 9), and safeguarding marine ecosystems (SDG 14). The formulation of comprehensive plans addressing solutions to developing issues in global health and the environment can be exemplified through health technology and environmental sustainability.

2. Methodology

Biocomposite production was carried out using the chemical blending method which refers to previous research [34,35]. The study utilized biocomposites composed of 85 wt.% PLA and 15 wt.%

PCL, with the incorporation of 5% HA relative to the overall mixture of PLA and PCL. HA derived from crab shells was acquired from Center for Bio Mechanics Bio Material Bio Mechatronics and Bio Signal Processing (CBIOM3S) laboratory, Diponegoro University, Semarang, Indonesia. Biocomposites comprising 85 wt.% PLA and 15 wt.% PCL, reinforced with 5% HA derived from crab shells, were pulverized using a chopper machine and subsequently processed in a handmade filament extruder. The fabrication of biocomposite filaments required two temperature settings: 165°C for pre-heating and 175°C for the nozzle, as well as a motor speed of 20 rpm. The biocomposite is extruded by a screw through a nozzle with a diameter of 1.75 mm to produce a filament. The filament extrusion process is illustrated in Figure 1.

Fig. 1. Filament extrusion process

The experimental setup in this study is shown in Figure 2. The filament that has been produced through the extrusion process is then fed into the 3D printer machine via a feeder which will push the filament towards the nozzle. The specimens were printed using a rectilinear pattern with a bed temperature of 50°C and a nozzle movement speed of 60 mm/s. The feed rate was limited to 1.6 mm/s in order to prevent filament disintegration during the 3D printing process, since the filament utilized in this investigation was a custom filament with inconsistent diameter precision. The printing was conducted at multiple nozzle temperatures: 190°C, 195°C, 200°C, 205°C, 210°C, and 215°C. The specimens were fabricated according to the dimensions indicated by ASTM D790. After the specimens were printed, they were permitted to cool and stabilize to guarantee uniform temperature. This technique was essential to avert deformation during handling and to guarantee the specimens were prepared for further material characterization examinations.

This study assessed the density of the biocomposites using a Vibra Canada Inc. densitometer (DME 220 series) in accordance with ASTM 792-08. The flexural modulus and flexural strength of the biocomposites were subsequently assessed via a three-point flexure test in compliance with ASTM D790. Biodegradation tests were conducted to determine the mass of the biocomposite prior to and following immersion. Soaking was conducted using a NaCl solution comprising 8.75 grams of NaCl dissolved in 250 ml of distilled water. The biocomposite underwent biodegradability testing for durations of 2, 4, and 6 days. The application of NaCl solution in the degradation test is based on previous studies [30,32]. The bending, density, and deterioration tests were conducted three times and averaged for calculation. The final assessment was the scanning electron microscopy (SEM) analysis to evaluate the surface morphology of the biocomposite. The instrument utilized was the JSM-6510, manufactured by JEOL, Japan. The examination was conducted at a magnification of 250x. This test was conducted to assess the level of homogeneity of the biocomposite.

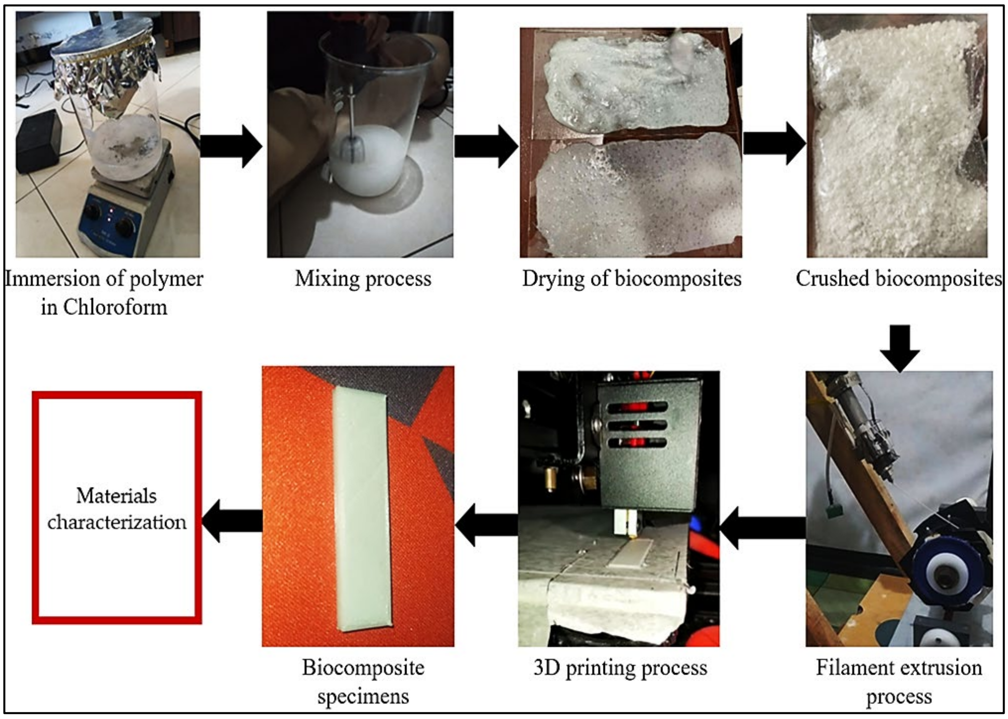

Fig. 2. Experimental setup

3. Results and Discussion

This research investigates the effect of nozzle temperature on the characteristics of PLA/PCL/HA biocomposites with varying nozzle temperatures of 190°C, 195°C, 200°C, 205°C, 210°C and 215°C. The specimens produced at a nozzle temperature of 190°C were inadequately formed, as illustrated in Figure 3. The failure resulted from under-extrusion during the printing process, characterized by inadequate filament flow. As a result, the layers were either incomplete or inadequately formed, affecting the overall quality of the print product. Research by Rivera-López *et al.,* [29] indicates that printing PLA filaments via the FDM method at lower temperatures may cause inadequate material flow, resulting in diminished density and compromised structural integrity, adversely impacting the printed object's mechanical performance and quality.

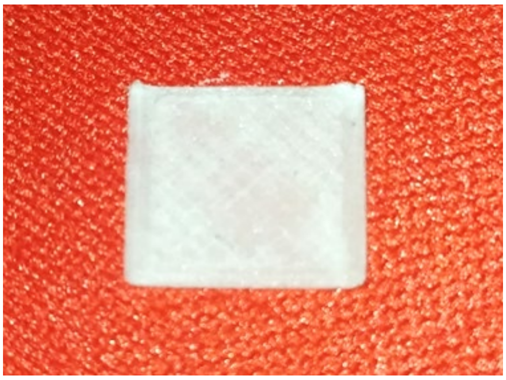

Fig. 3. Specimens printed using a nozzle temperature of 190^{o}C

The three point bending testing was carried out to determine the mechanical properties of the resulting biocomposite. The specimens in this test have gone through an immersion process for 24 hours. The testing process uses standardization according to ASTM D790. A comparison of the three point bending test results can be seen in Figures 4 and 5. Figure 4 depicts the effect of nozzle temperature in the 3D printing process on the flexural strength of the produced specimens. At 195°C, the specimen's flexural strength was 36.48 MPa. When the nozzle temperature was increased to 200 °C, the specimen's flexural strength decreased to 29.66 MPa. The specimens' flexural strength maximum was 41.09 MPa at 205 °C. Furthermore, at 210 °C, the specimens' flexural strength reduced slightly to 40.70 MPa. The material's flexural strength decreased to 34.65 MPa at 215°C. According to this evidence, the best nozzle temperature for achieving the highest flexural strength is 205 °C, while 200 °C results in the lowest flexural strength.

This study's results indicate that a nozzle temperature of 205°C in 3D printing yields excellent material performance. The material attains the best viscosity at this temperature, facilitating smooth extrusion and consistent layer deposition. Optimal melting at 205°C guarantees uninterrupted flow, eradicates flaws and preserves the structural integrity of the printed component. Conversely, reduced temperatures, specifically 195°C and 200°C, lead to insufficient material flow, incomplete melting, and suboptimal interlayer adhesion, undermining mechanical characteristics. Elevated temperatures, specifically 210°C and 215°C, may induce thermal deterioration in PLA/PCL/HA composites. This degradation disrupts the polymer chains and induces microstructural flaws, diminishing the material's strength. The stability attained at 205°C mitigates these issues, rendering it the optimal temperature for enhancing flexural strength and mechanical performance.

The results of this study followed those of Nurgesang *et al.,* [36] who found a maximum tensile strength of 32.40 MPa at a nozzle temperature of 205°C and concentric infill patterns. On the other hand, their research reported a decrease in tensile strength above 205 °C nozzle temperature, resulting from either material decomposition or inappropriate bonding, leading to poor mechanics of printed specimens. Behzadnasab and Ali [37] investigated the effects of various nozzle temperatures on the mechanical characteristics of 3D-printed PLA parts. The nozzle temperature in their investigation was established at 180°C, 200°C, 220°C, and 240°C.Their research indicated that the tensile strength of the PLA components augmented with a rise in nozzle temperature, reaching optimal strength at 240°C. Temperatures over 240°C resulted in polymer breakdown, establishing the maximum temperature threshold for 3D printing materials made of polymeric. This degradation undermines the mechanical qualities, highlighting the necessity of meticulously regulating nozzle temperatures for efficient 3D printing.

Abeykoon *et al.,* [38] studied the influence of temperature of the nozzle on the tensile modulus of PLA samples printed at four different temperatures: 200°C, 205°C, 215°C, and 230°C. The study determined that optimal tensile performance was achieved at 215°C, aligning with prior research recommendations. At temperatures of 200°C and 205°C, inadequate filament melting produces suboptimal viscosity, resulting in weak interlayer adhesion and inferior mechanical performance. This was seen in the mode of specimen failure during tensile testing. Conversely, at temperatures above 215°C, the filament's diminished viscosity results in slower cooling, adversely affecting the material's crystallinity and overall bonding. Moreover, applying layers onto warm underlying surfaces can impede adequate adhesion, jeopardizing the structural integrity of the component. Elevated temperatures also enhance the probability of material overflow, resulting in dimensional errors and instability in the printed components.

Figure 5 depicts the fluctuation in flexural modulus of specimens produced at different nozzle temperatures during the 3D printing process. Specimens created with different nozzle temperatures throughout the 3D printing process had a flexural modulus of 248.87 MPa at 195°C. When the nozzle temperature is increased to 200 °C, the flexural modulus rises to 293.12 MPa. The flexural modulus reached the highest value of 474.79 MPa at 205°C. In the case of 210°C, the flexural modulus decreased to 274.21 MPa. Meanwhile, the specimen's flexural modulus decreased to 247.29 MPa at

215°C. Based on this data, the best nozzle temperature for the highest flexural modulus is 205°C, while 215°C results in the lowest flexural modulus.

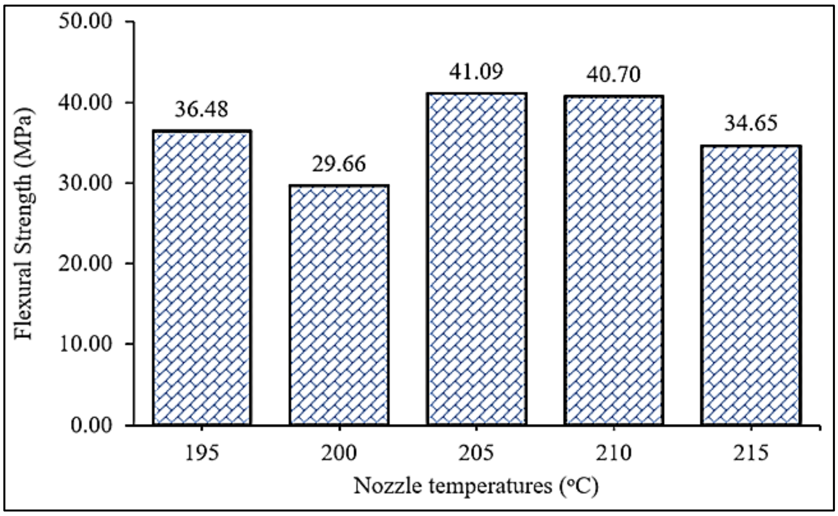

Fig. 4. Flexural strength of 3D printed biocomposites

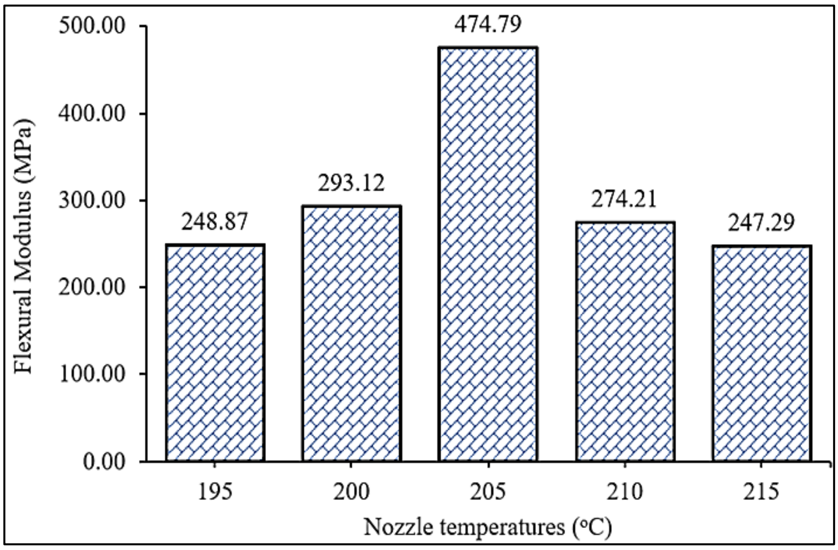

Fig. 5. 3D printed biocomposite flexural modulus

The test results show that the 3D printed specimen with nozzle temperature of 205°C has mechanical properties with a flexural strength value of 41.09 MPa and an elastic modulus value of 474.79 MPa. This investigation identified that specimens printed at a nozzle temperature of 205°C had the maximum flexural modulus and flexural strength. This indicates that this temperature is the best setting for generating materials with superior mechanical properties. At this temperature, the material attains its optimal viscosity, facilitating seamless material flow and uniform layer deposition. This combination produces a robust adhesion between layers and a more compact internal structure, enhancing the material's capacity to endure flexural loads. The findings of this study align with the research conducted by Widodo *et al.,* [39] which demonstrated that the specimen exhibiting the highest strength value also corresponded with a high modulus value. This affirms the strong correlation between the material's strength and stiffness (modulus).

This outcome correlates with the relationship between material density and the crystallinity index; hence, an increase in the crystallinity index is concomitant with an increase in material density.

An increase in crystallinity enhances the close packing of polymer chains, hence making the material denser and more organized. This directly influences the qualities, as materials with high density and high crystallinity exhibit superior strength, stiffness, and other mechanical characteristics [40]. In addition, the flexural strength value of the 3D printed specimen with nozzle temperature of 205°C is close to the criteria for cortical bone with a flexural strength of 51 MPa [41]. The results of biodegradable biocomposite testing can be seen in Figure 6. Furthermore, the results of observing the biodegradable level of the biocomposite can be seen from the reduction in the weight of the biocomposite after being soaked in NaCl solution. The reduction in specimen weight is calculated from the difference in the results of weighing the specimen before soaking and after soaking. Based on Figure 6, it can be confirmed that the reduction in specimen weight is directly proportional to the durations of soaking.

The specimens printed at nozzle temperatures of 195°C, 200°C, 205°C, 210°C and 215°C experienced weight loss of 0.0006 g, 0.0008 g, 0.0005 g, 0.0006 g and 0.0006 g respectively after 6 days of immersion. This study shows that the nozzle temperature affects the mass loss rate of the sample after the degradation test. A nozzle temperature of 200°C resulted in the highest weight loss, 0.0008 g. Meanwhile, a temperature of 205°C resulted in the lowest weight loss of 0.0005g, so it can be considered a better temperature for reducing mass loss. From the biodegradable test results, it can be concluded that the degradation rate value of each specimen is influenced by the density of the specimen. This can happen because the smaller the density value of the specimen, the larger the pores in each layer of the 3D printed specimen, so that contact with the NaCl solution occurs more easily in the specimen. This result is in accordance with research conducted by Akhoundi [42], where specimens with a nozzle temperature of 250°C, which is the best temperature, have a closer distance between layers than other specimens.

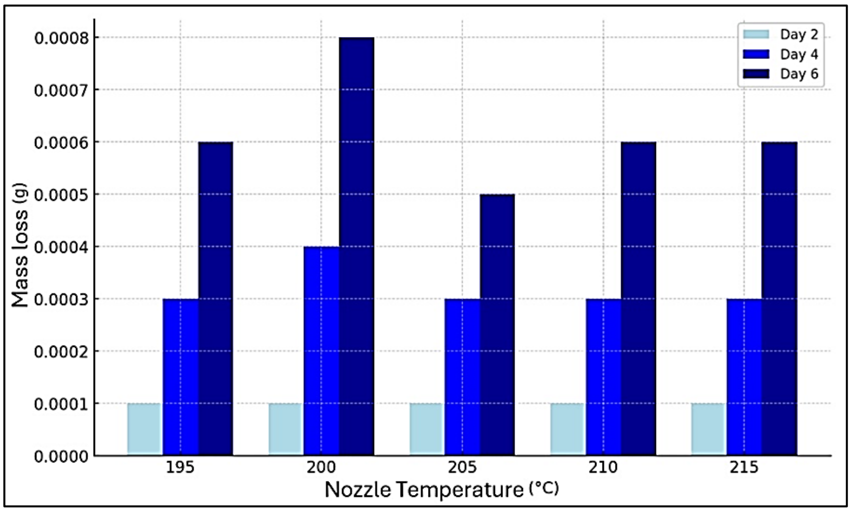

Fig. 6. Biodegradable biocomposite test results

Figure 7 displays the results of the density measurements. Density testing is typically conducted to ascertain the density of an object. This study conducted density testing to assess the impact of the 3D printing process on biocomposites composed of PLA and PCL biopolymers and HA bioceramics. PLA has a density of 1.252 g/cm^3 [13], PCL has a density of 1.15 g/cm^3 [43] and HA has a density of 3.16 g/cm3, so if the density is calculated theoretically the biocomposite density should be 1.26 g/cm3. Based on the Figure 7, it can be concluded that the heat in the 3D printing process will affect the density of the resulting biocomposite. This result is in accordance with the results of the crystallinity index calculation where each specimen is influenced by the nozzle temperature in the 3D printing process. The results of this test are in accordance with research by Alsoufi [28] which shows the results of testing the density of 3D printed specimens made from PLA filament with a nozzle temperature range of 195-250°C.

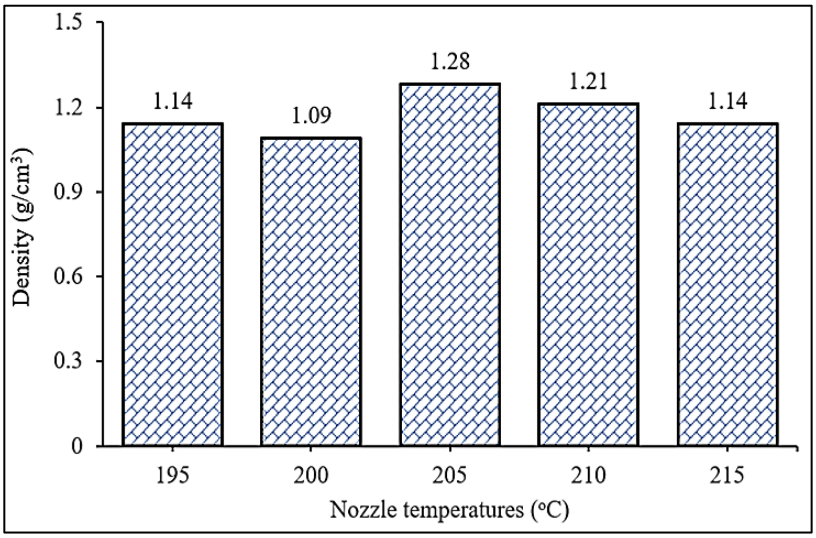

Fig. 7. 3D printed biocomposite density test results

There are differences in density values for each specimen produced, this is due to the optimal temperature for carrying out the process. 3D print using PLA material. The optimal nozzle temperature for the 3D print process for PLA material in research conducted by Alsoufi [28] is in the temperature range of 205-225°C, specimens extruded at temperatures below 205°C are still too hard because they have high viscosity values and low fluidity. It is important to know that the optimal nozzle temperature range for biocomposites made from PLA, PCL and HA crab shells is 195-215°C, where under extrusion occurs at 190°C and over extrusion occurs at 220°C, this occurs because of the PCL content in biocomposites which has a melting point at 60°C. Based on the density test results, it can be concluded that the 3D printed specimen with nozzle temperature of 205°C has the highest density (1.28 g/cm^3). In other hand, the 3D printed specimen with nozzle temperature of 200°C has the lowest density with a value of 1.09 g/cm^3.

Kroemer *et al.,* [44] found that cortical bone had a density of 1.1-1.3 g/cm^3. As a result, the findings of this study demonstrate that specimen's 3D printed at temperatures of 195°C, 205°C, 210°C, and 215°C create densities comparable to cortical bone density. However, the specimen 3D printed at 200oC has a density that is not comparable to the requirements for cortical bone. So, it can be concluded that increasing the nozzle temperature can increase the density of the specimen because the higher the nozzle temperature it will reduce the viscosity value of the material and increase the fluidity value of the material so that each layer can be printed more densely, however, an excessive increase in temperature can cause thermal degradation which will affect the mechanical properties of the specimen [45].

Figure 8 presents the SEM results of a 3D-printed biocomputer at a magnification of 250x. Scanning Electron Microscope (SEM) analysis is required to assess the impact of the 3D printing process on the morphology and homogeneity of the resultant biocomposite. It is essential to ascertain whether the thermal conditions during the 3D printing process will influence the uniformity of the PLA and PCL blend and the dispersion of HA. This can be accomplished by contrasting the SEM results of the five 3D-printed specimens with the raw material. The SEM test findings suggest that the morphologies of PLA and PCL are no longer discernible, signifying the effective mixing of the two polymers. The formation of a surface that tends to be rough indicates the presence of hydroxyapatite mineral content in accordance with the SEM results of biocomposite filaments made from

PLA/PCL/HA in Akerlund's research [46]. The results of this test are also in accordance with research conducted by Pitjamit *et al.,* [41] who mixed PLA/PCL/5% HA and PLA/PCL/15% HA to make 3D printing filament.

Subsequently, SEM test findings at 1000x magnification reveal several small, luminous particles uniformly scattered across the filament's surface. This signifies that the distribution of HA in the specimen is uniform. Furthermore, a comparison of the SEM results of the five specimens with the raw material reveals no morphological differences between the materials before and after the 3D printing process, indicating that the heat generated during 3D printing does not impact the homogeneity of the PLA, PCL, and HA mixture. The SEM data of the five specimens exhibit commonalities in hydroxyapatite distribution. This transpires as the hydroxyapatite within the specimen deposits at the surface's base and is subsequently enveloped by a polymer layer. In the mixing process, the polymer predominantly remains atop the hydroxyapatite, whereas the hydroxyapatite predominantly accumulates in the lower layer of the specimen. This transpires due to the density of hydroxyapatite exceeding that of PLAl and PCL [47].

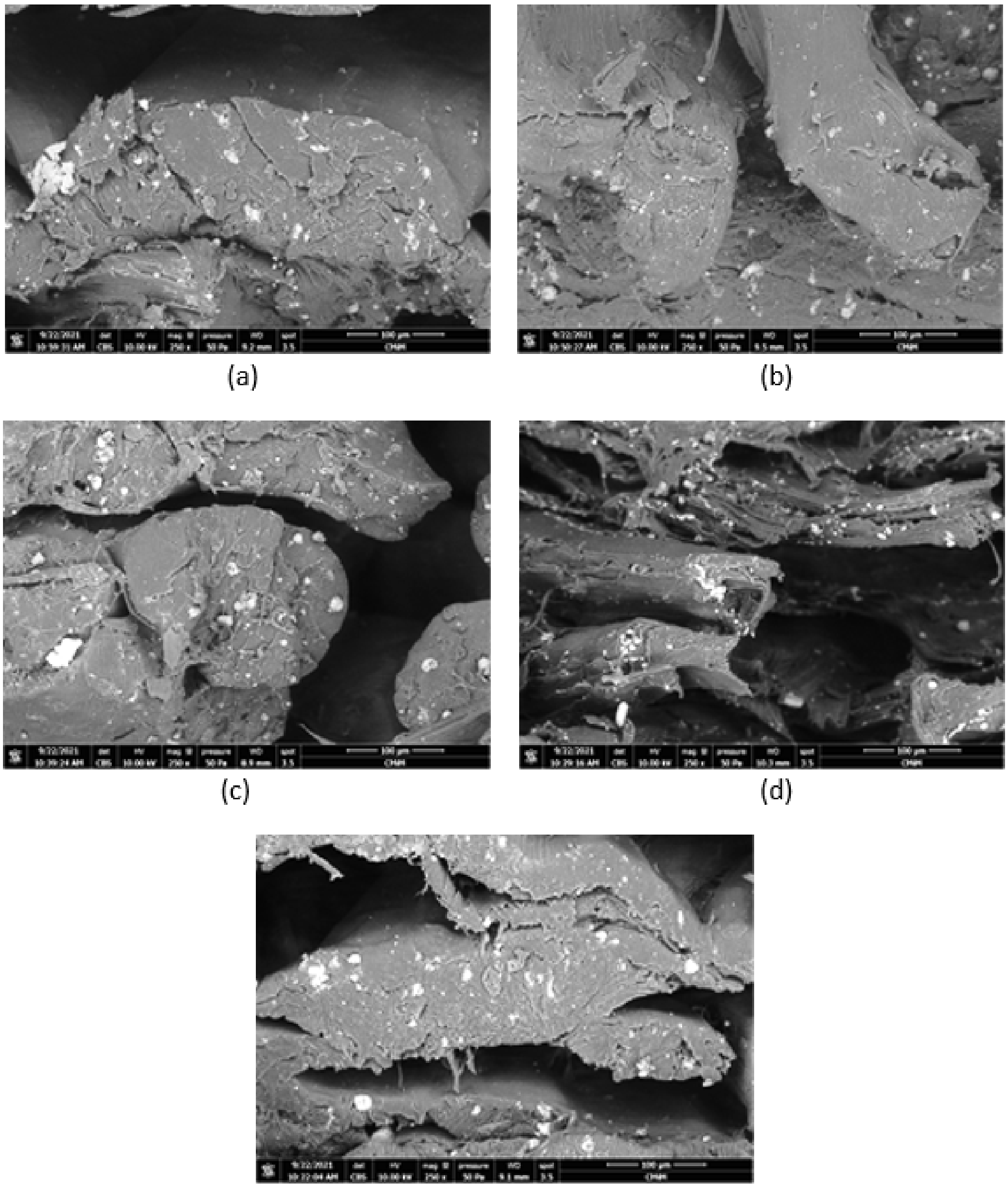

Fig. 8. SEM images of 3D printed biocomposites with nozzle temperatures (a) 195°C (b) 200°C (c) 205°C (d) 210°C (e) 215°C (f) Raw material

4. Conclusions

The recent development of the technology for 3D printing has greatly enhanced the production of biodegradable bone implant materials, particularly through the efficiency of process parameters to attain improved mechanical properties and appropriate biodegradation behavior. This study evaluated the impact of nozzle temperature in the Fused Deposition Modelling (FDM) procedure on the properties of PLA/PCL/HA biocomposites. The findings indicate that nozzle temperature significantly affects the biocomposite material's mechanical properties, density, degradation rate, and morphology. The nozzle temperature of 205°C yielded optimal results, achieving a flexural strength of 41.09 MPa, a flexural modulus of 474.79 MPa, and a 1.28 g/cm^3 density. These values were superior to those of other specimens and closely aligned with the properties of human cortical bone.

Nozzle temperatures below 205°C, specifically 195°C and 200°C, lead to increased material viscosity, hinder material flow, and result in inadequate interlayer adhesion, reducing mechanical strength and elevating material porosity. Nozzle temperatures exceeding 205°C, specifically at 210°C and 215°C, lead to thermal degradation, resulting in the breakdown of polymer chains, the formation of microstructural defects, and a reduction in the mechanical properties of the biocomposite. The degradation test results indicated that specimens printed at a nozzle temperature of 205°C exhibited the minimal mass loss of 0.0005 g following 6 days of immersion. This phenomenon arises due to the specimen's high density, which effectively slows the penetration of NaCl solution and mitigates material degradation. Density analysis indicated that reduced nozzle temperatures result in less dense coatings characterized by increased porosity. The 205°C nozzle temperature results in a denser coating, enhancing mechanical stability and reducing biodegradation rates.

Morphological analysis using Scanning Electron Microscope (SEM) revealed a homogeneous distribution of hydroxyapatite (HA) within the material, with surface structures demonstrating effective fusion of PLA, PCL, and HA. No significant difference was observed in the morphology of the material pre- and post-printing, suggesting that the heat applied during the printing process did not impact the homogeneity of the material mixture. This biocomposite, derived from processed crab shell waste into hydroxyapatite, contributes to sustainability objectives, specifically enhancing health (SDG 3), fostering industrial innovation (SDG 9), and promoting the sustainability of marine ecosystems (SDG 14).

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