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Article

Hydroxyapatite-Polycaprolactone Coating on 316L Stainless Steel Surface Using Dip Coating Method

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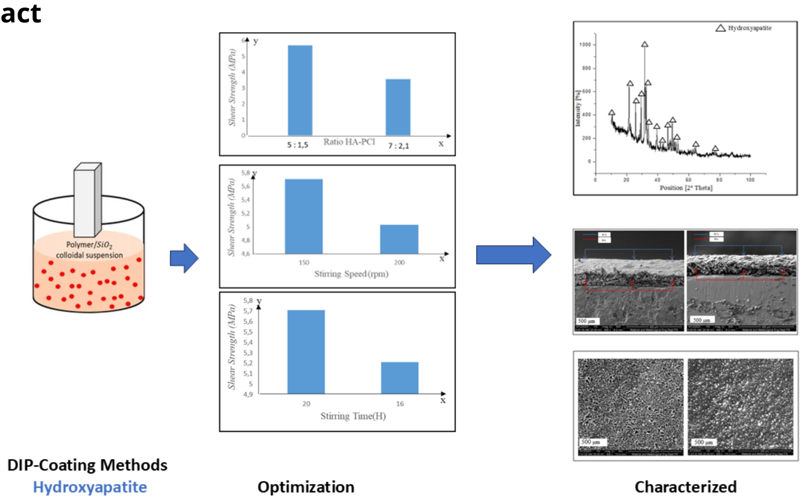
Abstract

Stainless steel 316L is a metal that can be used for bone implants but exhibits low biocompatibility. The low biocompatibility can lead to inflammation, infection, or rejection within the body's tissue system. It is coated with hydroxyapatite-polycaprolactone to enhance the biocompatibility of stainless steel 316L. This study aims to examine the effects of stirring time, stirring speed, and the appropriate hydroxyapatite-polycaprolactone ratio on the shear strength of hydroxyapatite-polycaprolactone using the dip coating method and to determine the empirical model for the resulting shear strength of the hydroxyapatite-polycaprolactone layer. Hydroxyapatite and polycaprolactone were mixed using acetone and stirred at a speed of 150 rpm for 20 hr. Then, the stainless steel 316L substrate was immersed in the suspension and dried at 56°C for 1 hr. The process conditions optimization in this study employed a 2k modeling approach. The empirical shear strength model in this research is represented as y = -216.9 + 36.42A + 1.426B + 14.43C - 0.2345AB - 2.380AC - 0.08943BC + 0.01468AB*C, with an R2 value of 0.99. The variables with the most significant influence on shear strength, ranked from largest to smallest, are the HA-PCl ratio (A), followed by the two-way interaction between the HA-PCl ratio (A) and stirring speed (B), the three-way interaction between the HA-PCl ratio (A), stirring speed (B), and stirring time (C), followed by the two-way interaction between the HA-PCl ratio (A) and stirring time (C), stirring time (C), stirring speed (B), and the two-way interaction between stirring speed (B) and stirring time (C). The highest shear strength of the hydroxyapatite layer was achieved at a HA-PCl ratio of 5:1.5, stirring speed of 150 rpm, and stirring time of 20 hours, with a value of 5.71 MPa.

Keywords: *Empirical Model, Hydroxyapatite-Polycaprolactone, Stainless Steel 316L.*

Graphical Abstract



Introduction

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Hydroxyapatite with the molecular formula ($Ca10(PO_4)_6(OH)_2$) is a crystalline substance that shares a mineral structure similar to that of bones and teeth, featuring nanoscale calcium phosphate. Hydroxyapatite can be derived from both natural and synthetic sources of calcium. Researchers have been utilizing hydroxyapatite in biomedical applications for several years due to its biocompatible, bioactive, and osteogenic properties toward bones and teeth [1]. Additionally, HA is widely used as a bioactive coating for dental and orthopedic implants. Its excellent osteoconductivity and osteoinductivity promote biological fixation between bone tissue and implants, enhancing the integration and longevity of the implants [2]. Comprising calcium and phosphorus, hydroxyapatite is highly suitable for crafting bone implants due to its compatibility with the human skeletal system. Both natural and synthetic sources of calcium can be used to produce hydroxyapatite [3].

Hydroxyapatite serves as the foundational material to coat titanium (Ti) with the incorporation of titania (TiO_2) buffer using the sol-gel method [4]. Hydroxyapatite is widely employed to enhance the bioactivity of Ti and O_2 substrates, while a buffer layer is incorporated to prevent corrosion of the Ti substrate and strengthen the bond between hydroxyapatite and the substrate. However, numerous studies have highlighted challenges associated with non-biodegradable coating materials, particularly their potential to induce inflammation and crack propagation pressure in the human body. These issues have motivated researchers to explore biodegradable coating materials and strategies to improve bioactivity and bonding strength [5]. Hydroxyapatite has been extensively recommended for coating applications due to its biocompatibility and crystallographic and chemical properties that closely resemble those of bone tissue. Despite these advantages, hydroxyapatite is limited by its brittleness and low adhesive strength, necessitating the inclusion of additional materials to serve as load-bearing supports and to enhance cation reinforcement [6].

Polycaprolactone (PCL) is a biodegradable, biocompatible, and non-toxic aliphatic polyester. Within the realm of biodegradable polymers, polylactic acid (PLA) and PCL are particularly notable for packaging applications, attributed to their accessibility, biodegradability, and advantageous mechanical properties. PCL is distinguished by its exceptional chemical and solvent resistance, commendable toughness, and low glass transition temperature (approximately -60°C) and melting temperature (around 60°C) [7]. The polymer's high chain segment mobility and minimal intermolecular interactions contribute to these low thermal transition temperatures. Notably, PCL exhibits greater thermal stability compared to PLA and undergoes complete degradation via enzymatic activity [8]. Its inherent chain flexibility allows for synthesis across a spectrum of molecular weights, enhancing its versatility in various applications. In comparison to PLA, PCL offers higher flexibility but has relatively low strength and a low melting point of 60°C, which restricts its use in certain applications. Additionally, PCL's hydrophobic nature results in lower wettability compared to PLA, which can influence cell adhesion in biomedical applications [7]. The enzymatic degradation of PCL is influenced by factors such as molecular weight and copolymer composition. Studies have shown that an increase in molecular weight leads to a decrease in the enzymatic degradation rate, likely due to increased chain entanglement that hinders enzyme access. Furthermore, the incorporation of hydrophilic segments, such as polyethylene glycol (PEG), into PCL-based copolymers can enhance the degradation rate by increasing the material's overall hydrophilicity [9]. These characteristics render PCL a material of significant interest for applications requiring biodegradable and biocompatible polymers with tunable properties.

Despite its higher cost, polycaprolactone (PCL) is frequently selected as a biodegradable component for polymer blending due to its compatibility with various biopolymers, notably starch and lignin. This compatibility facilitates the development of composites with enhanced properties. For instance, blending PCL with starch can improve the biodegradation rate of PCL, while PCL can modulate the humidity sensitivity of starch, resulting in materials with balanced mechanical and degradation characteristics [10]. Similarly, incorporating lignin into PCL matrices has been explored to enhance thermal stability and mechanical properties, although the compatibility between PCL and lignin can vary depending on processing methods and the specific types of lignin used. Extensive research has been conducted on blending polylactic acid (PLA) with PCL to combine the advantageous properties of both polymers. Such blends aim to achieve a balance between the rigidity of PLA and the flexibility of PCL, resulting in materials with improved toughness and biodegradability. Studies have shown that the addition of PCL to PLA can enhance impact strength and elongation at break, making these blends suitable for applications requiring both strength and flexibility. The development of PLA/PCL blends has been explored for various applications, including packaging materials, medical devices, and drug delivery systems, due to their combined biodegradability and mechanical performance [11]. In this paper aims to study the influence of the hydroxyapatite-polycaprolactone ratio, stirring speed, and stirring duration on the shear strength of hydroxyapatite-polycaprolactone. This study is also aimed at determining the empirical model for the shear strength of the resulting hydroxyapatite-polycaprolactone coating.

Material and Methods

Materials and Instrumentations

The materials used in this research are hydroxyapatite (Lianyungan Kede Chemical Industry Co. Ltd, China), stainless steel 316L (Jindal Stainless, India), polycaprolactone (Juren Chemical, China), acetone (Merck, Germany), and distilled water (Brataco Chemica, Indonesia). The sample was characterized using a Scanning Electron Microscope (SEM) to examine its morphology and determine the thickness of the coating. X-Ray Diffraction (XRD) analysis was performed to identify the chemical compounds present in the sample and their respective compositions. Additionally, the shear strength of the sample was evaluated using an autograph machine

Methods

Preparation of Suspension. Hydroxyapatite was weighed in variations of 5 and 7 grams each and placed into a chemical glass. Then, 15 ml of acetone and 30% polycaprolactone/HA were added. The suspension was then stirred using a magnetic stirrer at the speeds of 150 rpm and 200 rpm for 16 and 20 hours, respectively. The suspension preparation followed the research method outlined by previous study [12].

Preparation of Substrat. Stainless steel 316L was cut into 2 cm x 3 cm x 0.1 cm, then polished using SiC 1200 grit sandpaper. The polished stainless steel 316L was subsequently treated by immersing it in 25% HNO_3 solution, following the research method of Kannan et al., 2004 [13], using 50 ml of 20% HNO_3 solution for 1 hour at room temperature. It was then rinsed with distilled water and dried in an oven for 30 min at a temperature of 50°C. The metal was further heated to a temperature of 600°C at a heating rate of 2°C per min for 1 hR.

Coating Process. The coating method follows the research conducted by Fadli et al., 2021 [14]. Pieces of stainless steel that have been treated were attached to a dip coating apparatus. The dipping process began by immersing the substrate into the slurry. When approximately ¾ of the substrate was submerged, the apparatus was stopped and left for 50 seconds, and then the apparatus was restarted. This results in a withdrawal process where the substrate in the suspension was pulled upward, allowing a thin layer to adhere to the substrate naturally. Subsequently, a drying process was carried out by placing the coated substrate in an oven at a temperature of 56ºC for 60 min.

Results and Discussions

The Effect of HA-PCL Ratio on Shear Strength Value

The influence of the ratio in HA-PCL on the shear strength of hydroxyapatite on stainless steel surfaces results in increased viscosity. Higher viscosity prevents the formation of interfacial layers and substrates, thus providing favorable conditions for particle adhesion to the substrate. According to Tangestani and Hadianfard (2021), a ceramic-polymer ratio of 2 g/L PCl prevents agglomeration in the layer. This PCL content is optimal for creating high adhesion between particles and the substrate. However, at a ratio of 4 g/LPCl, the layer structure contains cracks that open the way to penetrate corrosive fluids onto the exposed metal surface.

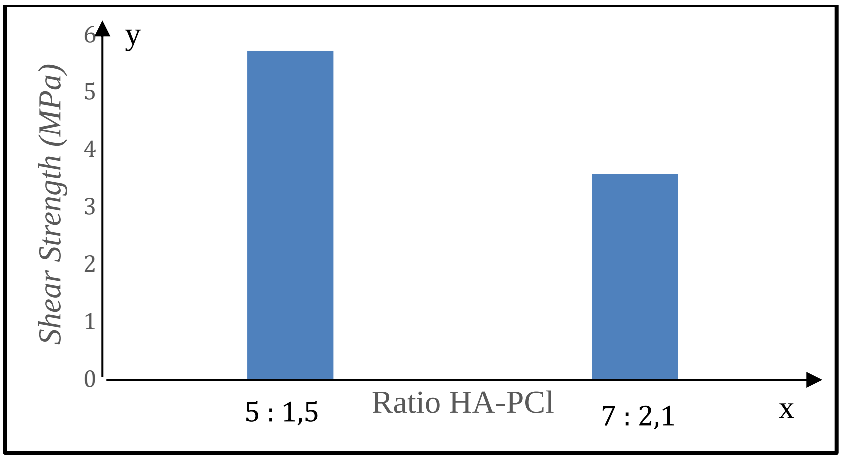

Figure 1. The Effect of Ratio on Hydroxyapatite Shear Strength

The influence of this ratio is in line with the theory proposed by previous study [15]. Optimizing the use of the HA-PCL ratio results in improved shear strength. As shown in Figure 4.1, it can be observed that the ratio affects the shear strength of the layer. The use of a HA-PCl ratio of 7:2.1 yields a lower shear strength value compared to a HA-PCl ratio of 5:1.5. This ratio is optimal for creating the best shear strength between the suspension and the substrate, with the highest value being 5.71 MPa. This is because the ratio of PCl to HA in the layer can influence shear strength. The addition of HA to PCL can enhance shear strength due to the stronger mechanical properties of HA. However, an excessive amount of HA addition can reduce the solubility of PCL in the solvent and affect the formation of a proper layer.

An increase in PCl within the suspension results in higher suspension viscosity, thereby enhancing the shear strength of the coating.Using a PCl ratio of 7:2.1 leads to agglomeration within the formed suspension, resulting in uneven deposition and surface cracks, yielding lower shear strength. Figure 1 illustrates the extent of agglomeration and deposition resulting from the use of the HA-PCl ratio.

The Effect of Stirring Speed on Shear Strength Value

In this study, the effect of stirring speed on the shear strength of hydroxyapatite coatings applied to 316L stainless steel was examined at rotational speeds of 150 rpm and 200 rpm (Figure 2). Stirring speed is a critical parameter in mixing processes, as it influences particle collisions and interactions, leading to alterations in the solution's density and viscosity. Consequently, optimizing stirring speed is essential to achieve a homogeneous mixture. Research indicates that increasing the stirring rate during the nucleation phase can reduce hydroxyapatite nanoparticle size, suggesting that higher stirring speeds enhance homogeneity in the mixture [16].

Additionally, studies have demonstrated that higher agitation forces, achieved through increased stirring speeds, elevate the system's dissipation energy, creating significant turbulence that promotes uniform particle distribution [17]. Therefore, adjusting stirring speed is a pivotal factor in the preparation of hydroxyapatite coatings, directly affecting the mixture's homogeneity and, consequently, the coating's shear strength on stainless steel substrates.

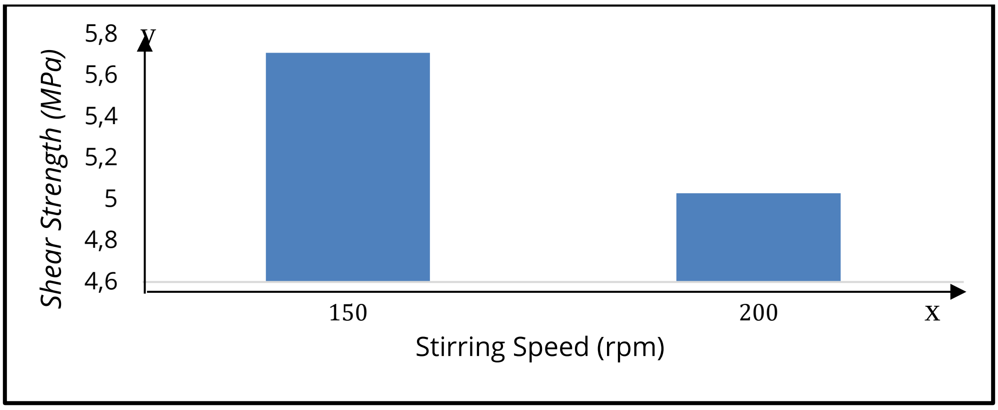

Figure 2. The Effect of Stirring Speed on Hydroxyapatite Shear Strength

An increase in stirring speed can result in a layer with higher strength. This is associated with better homogenization and dispersion effects of HA particles within the PCL matrix. High stirring speed can help break down particle clusters and evenly distribute them within the matrix, enhancing the interaction between particles and the matrix, thus increasing shear strength.However, excessively high stirring speed can potentially damage HA particles or lead to poor particle agglomeration. This can reduce shear strength due to inadequate interaction between particles and the matrix. To assess the extent of the influence of stirring speed in this study, refer to Figure 3.2, which explains that a stirring speed of 150 rpm yields a higher shear strength value compared to a stirring speed of 200 rpm. the maximum result was achieved at 150 rpm. Figure 2 shows that as stirring speed increases, shear strength values consistently decrease because faster collisions occur, resulting in HA particle damage and agglomeration within the suspension [18].

At a stirring speed of approximately 150 rpm, particle mobility within the suspension without temperature variation produces better results. With a decrease in stirring speed, particle mobility within the suspension increases, resulting in a shear strength value of 5.71 MPa. However, at a stirring speed of 200 rpm, the suspension begins to agglomerate, reducing particle mobility in the suspension, which is directly proportional to shear strength. Figure 3 depicts the optimal HA-PCL composite position with the use of stirring speed (a) 150 rpm compared to stirring speed (b) 200 rpm, which yields lower shear strength. Therefore, it is concluded that the optimum results are obtained when employing a stirring speed of 150 rpm in this comparative study of different stirring speeds.

The Effect of Stirring Time on Shear Strength Value

Stirring time has an impact on particle deposition in the solution. Longer stirring times result in smaller particles. Thus, the extended stirring time leads to optimally dispersed particles. Stirring time positively affects hydroxyapatite coating suspension as it can stabilize particle deposition and create a thicker coating. However, if the stirring time exceeds the optimum duration, it can lead to agglomeration, preventing maximal dispersion and resulting in a thinner coating [19]. In this study, the stirring time's influence on hydroxyapatite's shear strength value can be observed in Figure 3.3, which demonstrates that a stirring time of 20 hours yields a higher shear strength value compared to a stirring time of 16 hr.

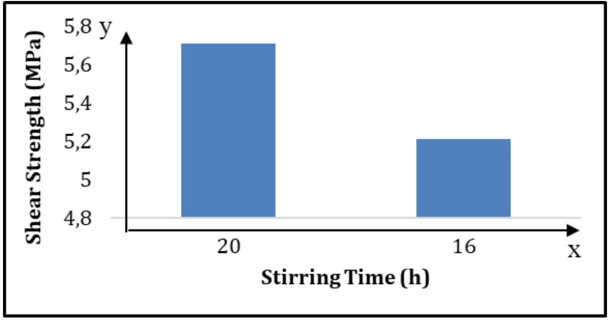

Figure 3. The Effect of Stirring Time on Hydroxyapatite Shear Strength.

Figure 3. shows that there is a significant decrease in viscosity in the suspension with one of the time variables used. For a stirring time of 16 hours, the stabilization effect has not yet reached the optimum point. Although this effect can also be achieved with slightly lower shear strength values (5.21 MPa), the achieved shear strength has a higher average value compared to a stirring time of 20 hr (5.71 MPa). This can be seen in that the shear strength values decrease with shorter stirring times and reach their maximum value at 20 hrs of stirring. This indicates that a 20-hr stirring time creates the best adhesion between HA particles and the PCl matrix.

The thickness of the layer is directly proportional to the shear strength value, increasing as the stirring time lengthens. As the layer thickness increases, the shear strength also increases. However, this condition also has an optimum time. The thickness increases, the shear strength value decreases because a thicker surface layer requires more energy to fracture, causing the interfacial shear strength of the composite to gradually decrease with increasing layer thickness [20]. A sufficiently weak surface layer has a significant positive impact on the fracture toughness of the composite. Therefore, it can be concluded that if the stirring time exceeds the optimum point, the formed of particle deposition becomes thinner, leading to lower adhesion between HA particles and polycaprolactone. Conversely, when the stirring time is at the optimum point, the layer thickness is directly proportional to the shear strength of the hydroxyapatite layer.

Scanning Electron Microscopy Characterization

Scanning Electron Microscopy (SEM) is one of the common methods for producing images of the microstructure and morphology of various materials. In this research, SEM analysis was conducted at a magnification of 500 times. The samples analyzed consisted of 2 samples to study the influence of the HA-PCL ratio on the thickness of the hydroxyapatite layer produced on the surface of stainless steel 316L. The HA-PCL concentration ratio, stirring speed, and stirring time variations for these two samples were (a) HA-PCL 5: 1.5 g, 150 rpm, 20 hours, and (b) HA-PCL 7: 2.1 g, 150 rpm, 20 hours. From the SEM analysis results, the average thickness of hydroxyapatite for both samples was calculated. For the HA-PCL ratio of 5: 1.5 g, stirring speed of 150 rpm, and stirring time of 20 hours, the average thickness of hydroxyapatite was found to be 65.27 μm, and it increased to 67.02 μm for the HA-PCL ratio of 7: 2.1 g with the same stirring speed and time. As more HA is added, the thickness increases, as shown in Figures 4 (a) and 4 (b). This is because when more HA is used, the mass of HA deposited on the substrate surface increases [21]

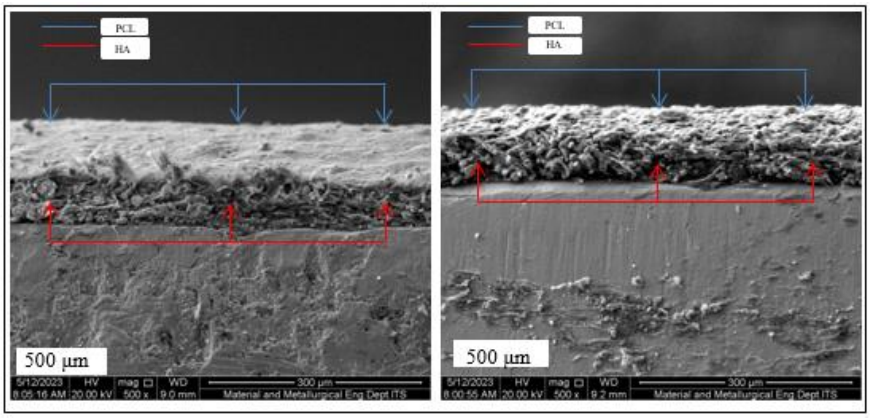

Figure 4. SEM Analysis Results of HA-PCL Layer Thickness on Stainless Steel 316L with Variable HA-PCL Ratio, Stirring Speed, and Stirring Time (a) 5:1.5, 150 rpm, 20 hr; (b) 7:2.1, 150 rpm, 20 hr.

The SEM analysis data in Figure 4-5 indicates that the thickness of the hydroxyapatite layer produced supports the results of the bond strength of the hydroxyapatite layer on the surface of stainless steel. Hydroxyapatite with excessive thickness results in a low shear strength. This is due to the increase in the thickness of the hydroxyapatite layer, which can enhance the shear strength up to a certain point. When the layer thickness increases, more energy is released from plastic deformation. The process of plastic deformation in HA-PCL involves the molecular arrangement within the material. When this material is subjected to pressure or force, the intermolecular bonds in PCL can shift or break [22].

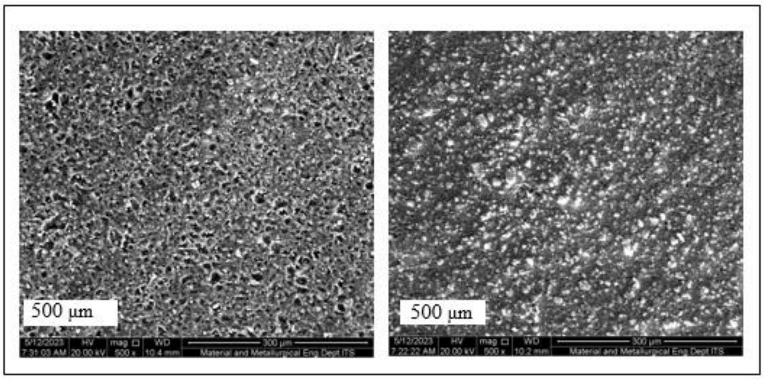

Figure 5. Surface Morphology of Stainless Steel 316L Coated with HA-PCL with Variable HA-PCL Ratio, Stirring Speed, and Stirring Time (a) 5:1.5, 150 rpm, 20 hrs; (b) 7:2.1, 150 rpm, 20 hrs.

Figure 4 shows the SEM image of the HA-PCL coating deposited on the surface of stainless steel 316L at a magnification of 500x. It can be observed in Figure 5 (a) that the surface morphology of the metal exhibits uniform apatite formation, covering the metal surface with small crystal-like structures. Meanwhile, in Figure 3.5 (b), HA particles tend to form agglomerates or distribute non-uniformly within the PCL matrix. This is due to the high concentration of particles in the solution or suspension, which can increase the likelihood of agglomeration. When the particle concentration exceeds a certain limit, particles tend to come into contact and interact more intensely, leading to agglomeration. Additionally, non-uniform particle distribution can also cause particles to be close to each other and form clusters [15].

X-ray Diffraction (XRD) Analysis

X-ray Diffraction (XRD) Analysis is a characterization technique that can be used to determine the phases, structure, and crystallinity of crystalline materials [23]. In this study, X-ray diffraction (XRD) analysis was performed to determine the crystallinity of the layers formed on the surface of stainless steel 316L. Figure 6 shows the diffractogram of the hydroxyapatite layer on the surface of Stainless Steel 316L. It can be observed that the product formed is hydroxyapatite (HA). Overall, the hydroxyapatite peaks after coating in Figure 3.6 have hkl values similar to the characteristic pattern of standard hydroxyapatite XRD analysis data from ICDD with No. 01-072-1243, which are (200), (210), (211), and (300) with 2θ angles of 21.743°, 28.896°, 31.741°, and 32.868°. The main peaks of hydroxyapatite after coating at 2θ angles of 21.5619°, 29.2687°, 31.5470°, and 32.6697° confirm the presence of hydroxyapatite content in the coating layer.

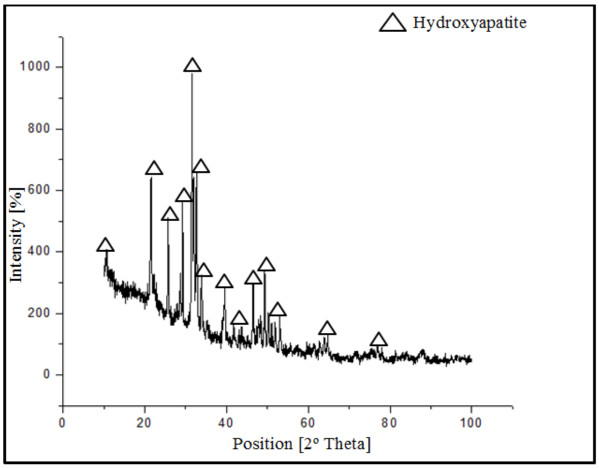

Figure 6. XRD Diffractogram of Stainless Steel 316L Substrate After Coating Using HA-PCL with

HA-PCL Ratio of 5:1.5, Stirring Speed of 150 rpm, and Stirring Time of 16 hr.

Based on the XRD analysis results presented in Figure 6, it is evident that the high intensity and narrow peak width of the diffractogram confirm that the majority of hydroxyapatite particles crystallize on the surface of the stainless steel 316L substrate. The degree of crystallinity in the hydroxyapatite-coated on stainless steel 316L is approximately 63.47%. The crystallinity value of the hydroxyapatite layer obtained in this study meets the allowed range of hydroxyapatite layer crystallinity, which is 60-90%. A high degree of crystallinity can enhance the adhesion of the hydroxyapatite layer [24]

The absence of polycaprolactone (PCL) peaks in X-ray diffraction (XRD) analysis can be attributed to its semi-crystalline nature, comprising both crystalline and amorphous regions. When PCL is heated above its melting point (approximately 55–60°C), its crystalline regions transition into a molten state. Rapid cooling from this state can hinder the reformation of crystalline structures, resulting in an amorphous configuration. In this amorphous state, PCL lacks the long-range order necessary to produce distinct diffraction peaks in XRD analysis, leading to its non-detection. The mechanical properties of PCL are significantly influenced by its degree of crystallinity. Amorphous PCL exhibits a random molecular arrangement, imparting greater elasticity and flexibility. In contrast, semi-crystalline PCL, with its ordered crystalline regions, tends to be more rigid and exhibits higher mechanical strength. This distinction is crucial for tailoring PCL's properties for specific applications, such as in biomedical devices where flexibility or rigidity may be desired. Studies have demonstrated that the crystallinity of PCL can be manipulated through various processing techniques. For instance, the incorporation of nanoparticles has been shown to influence the crystallization behavior of PCL, thereby affecting its mechanical properties. Additionally, the rate of cooling during processing plays a pivotal role; rapid quenching can lead to amorphous structures, while controlled cooling may promote crystallinity [5]. Furthermore, the presence of other polymers can impact the crystallinity of PCL. Blending PCL with amorphous polymers, such as polyurethane (PU), can alter its crystalline structure. XRD patterns of PCL/PU blends have shown that the semi-crystalline nature of PCL can be modified by the amorphous characteristics of PU, resulting in changes to the overall crystallinity and, consequently, the mechanical properties of the blend [6]. Understanding the relationship between processing conditions, crystallinity, and mechanical properties of PCL is essential for optimizing its performance in various applications. By controlling factors such as cooling rates and blending with other polymers, it is possible to tailor the material properties of PCL to meet specific requirements.

Fourier Transform Infrared Spectroscopy (FTIR) Analysis.

Fourier Transform Infrared Spectroscopy (FTIR) Analysis is a method used to identify chemical compounds based on the pattern of infrared spectra it produces. This method is based on the interaction between molecules and infrared radiation. The FTIR testing process begins by directing infrared light onto the sample to be analyzed. Infrared light consists of various frequencies covering the infrared wavelength range. As the infrared light passes through the sample, the molecules within the sample will absorb energy at specific frequencies. This process is referred to as infrared absorption. The FTIR testing process begins by directing infrared light onto the sample to be analyzed. Infrared light consists of various frequencies covering the infrared wavelength range. As the infrared light passes through the sample, the molecules within the sample will absorb energy at specific frequencies. This process is referred to as infrared absorption.FTIR spectrum analysis is performed to confirm the functional group information of the compounds $Ca_{10}(PO_4)_2(OH)_2$ and $C_6H_{10}O_2$ that are produced.

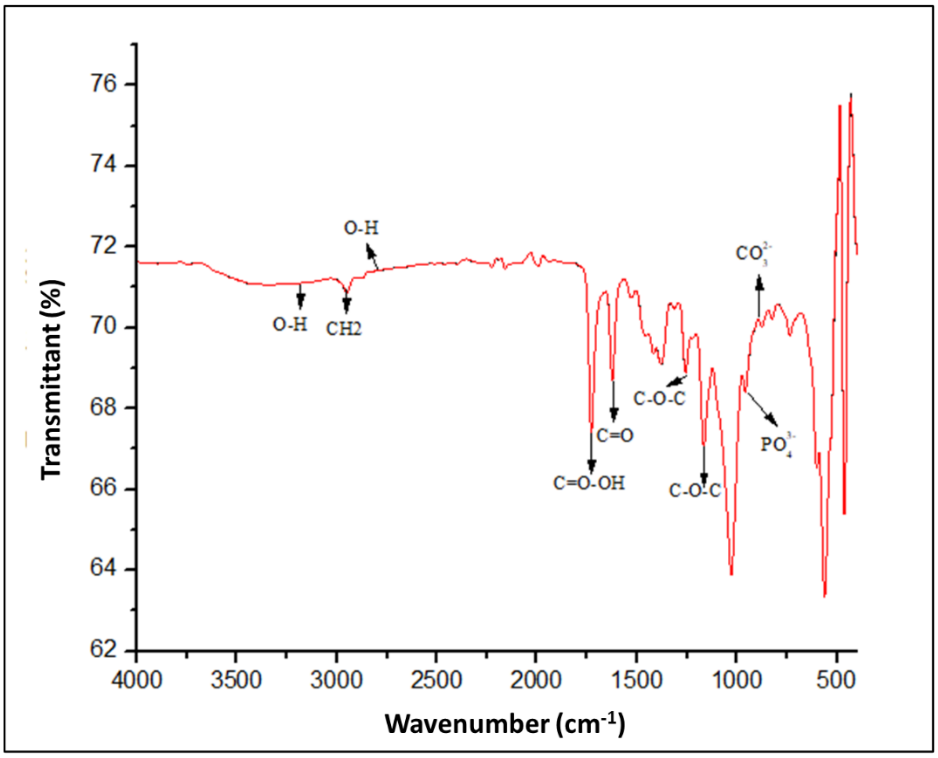

Figure 6. FTIR Analysis of the Bond Strength of the HA-PCL Layer on Stainless Steel 316L with HA-PCL Ratio of 5:1.5, Stirring Speed of 150 rpm, and Stirring Time of 20 hours.

The FTIR spectrum of the synthesized HA can be seen in 6. The spectrum of HA shows absorption at a wavelength of 958.18 cm^{-1}, which corresponds to the vibration of the PO_4^3 group. The wavenumber for the vibration of the PO_4^{3-} group obtained aligns with the research findings reported by Yusoff et al., 2014 [21] where it appears in the wavenumber range around 1000-960 cm-1. The presence of OH- group vibration is indicated by the absorption at wavenumbers of 3361 and 2951 cm^{-1}. OH- groups appear in the wavenumber range of 3570-630 cm^{-1}. The weak peak, which is the vibration of the CO32 group, is indicated by the absorption at a wavenumber group, which is indicated by the absorption at a wavelength of 875.69 cm^{-1}. The vibration of the CO_3^{2-} group is a weak spectrum, indicating the presence of CO_3^{2-} groups at a wavenumber of 875.69 cm^{-1} as a result of CO_2 absorption from the atmosphere on the surface of the HA particles.

Meanwhile, the spectrum analysis of PCL shows absorption at a wavenumber of 1725 cm-1, which corresponds to the vibration of the carbonyl group C=O. Additionally, there is a vibration of the C-O-C ester group, as indicated by absorption at wavenumbers of 1165.69 and 1256.76 cm^{-1} Yusoff et al., 2014 [21], reported their research findings that the C-O-C group appears in the wavenumber range of approximately 1300-1150 cm^{-1}. Vibration at a wavenumber of 2951 cm^{-1} is observed in the methylene CH_2 group. The carbonyl acid C=O-OH group shows vibration at a wavenumber of 1727 cm^{-1}.

Conclusion

The highest shear strength of hydroxyapatite-polycaprolactone on stainless steel 316L is 5.71 MPa with an HA-PCL ratio of 5:1.5, stirring speed of 150 rpm, stirring time of 20 hours, and a layer thickness of 67.02 μm. The empirical model for the shear strength of hydroxyapatite on stainless steel 316L is given as $y = -216.9 + 36.42A + 1.426B + 14.43C - 0.2345AB - 2.380AC - 0.08943BC + 0.01468AB*C$, where (A) is the HA-PCL ratio, (B) is the stirring speed, and (C) is the stirring time, with an R2 of 0.99.

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Author Contributions

Conceptualization, AH and MR.; Methodology, AH and MR; Software, AH and MF.; Validation: AF and SH., ST., MT; Formal Analysis, Abdul Hariz and MR.; Investigation, AH and MR.; Resources, Abdul Hariz and MR.; Data Curation, AH and MR.; Writing – Original Draft Preparation, AH, MR, ; Writing – Review & Editing, AH, MR, AF, SH; Visualization: AH and MR.; Supervision, AF and SH; Project Administration, AF.

Conflic of Interest

The authors declare no conflict of interest

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